

12-2013

Friction and Wear of Polytetrafluoroethylene/ Graphene Oxide Composite Thin Films

Justin Kyle Carter

University of Arkansas, Fayetteville

Follow this and additional works at: <http://scholarworks.uark.edu/etd>

 Part of the [Nanoscience and Nanotechnology Commons](#), and the [Polymer and Organic Materials Commons](#)

Recommended Citation

Carter, Justin Kyle, "Friction and Wear of Polytetrafluoroethylene/Graphene Oxide Composite Thin Films" (2013). *Theses and Dissertations*. 930.

<http://scholarworks.uark.edu/etd/930>

This Thesis is brought to you for free and open access by ScholarWorks@UARK. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of ScholarWorks@UARK. For more information, please contact scholar@uark.edu, ccmiddle@uark.edu.

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

December 2013
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.

ACKNOWLEDGEMENTS

Many well-deserved thanks and acknowledgements come to mind for making this thesis possible. First and foremost, I'd like to thank Dr. Min Zou for her continual support, advice, and encouragement. Without her, this opportunity and thesis would have never materialized into reality. I would also like to thank my thesis committee consisting of Dr. Douglas E. Spearot and Dr. Rick J. Couvillion. Next, I would like to thank and acknowledge my fellow lab-mates, Sam Beckford, Drew Fleming and Corey Thompson, for their help, support, and training during my time at the University of Arkansas.

Finally, I would like to thank and acknowledge my friends and family who provided support and love during my time at the University of Arkansas. I owe a lifetime of thanks and gratitude to my grandparents, Roger and Jeanie Carter, who made my all of my dreams come true to attend my undergraduate and graduate career at the University of Arkansas. Much thanks and appreciation also goes to Sally Carder for her determination and help to attain scholarships from the University of Arkansas to continue my collegiate career. I am also thankful for the unconditional love and support from my parents, Roger and Tammy Carter. Ben Thomas, Daniel Stovall, Cory Smith, Neil Royston, and many other close friends dear to me made my time at the University of Arkansas unforgettable. I will cherish and treasure the memories made with them for the rest of my life. I would also like to thank the entire staff of the Mechanical Engineering Department at the University of Arkansas for their help and support during my academic career.

TABLE OF CONTENTS

INTRODUCTION	1
1.1 Tribology and Solid Lubrication	1
1.2 PTFE Structure and Use as a Solid Lubricant.....	2
1.2.1 PTFE Composites: Adding Fillers to Reduce the Wear of PTFE.....	4
1.2.2 Graphene Oxide	5
1.2.3 Addressing Adhesion Issues of PTFE Films to Substrates.....	7
1.2.4 Polydopamine	8
1.3 Thesis Goal and Objectives	9
1.4 Organization of Thesis	9
LITERATURE REVIEW	11
2.1 Friction and Wear of Bulk PTFE	11
2.2 Addition of Micro-fillers and Nano-fillers to Bulk PTFE	12
2.3 Thin PTFE Films.....	17
2.4 Addition of Various Fillers to PTFE Films	19
2.5 Increasing Adherence of PTFE Films to Substrates	24
EXPERIMENTAL DETAILS	28
3.1 Materials and Properties	28

3.1.1 Stainless Steel Substrate	28
3.1.2 Materials Used for PTFE and PDA films	28
3.1.3 GO Filler Material.....	29
3.2 Sample Types	30
3.3 Sample Fabrication	30
3.3.1 Sample Fabrication Equipment.....	30
3.4 Friction and Wear Testing	37
3.5 Sample Characterization	38
3.5.1 Thickness and Wear Track Cross Section Measurements	38
3.5.2 Optical Imaging of Wear Tracks and Counterfaces.....	40
3.5.3 Atomic Force Microscopy	40
RESULTS AND DISCUSSION	42
4.1 Summary of Experiments	42
4.2 Characterization Prior to Experiments.....	42
4.2.1 Coating Thicknesses	42
4.2.2 AFM of Coating and Counterface Surfaces.....	44
4.3 Durability Testing	46
4.3.1 Single Coating Durability	46
4.3.2 Dual Coating Durability.....	48
4.4 Cycle Studies	49

4.4.1 Single Coating 100 Cycle Study	50
4.4.2 Dual Coating 2000 Cycle Study	55
4.4.3 Single Coating vs. Dual Coating: Importance of PDA Adhesive Layer.....	59
4.5 Investigation of Counterfaces for Transfer Film Formation.....	63
CONCLUSIONS AND FUTURE DIRECTION OF RESEARCH.....	67
5.1 Conclusions.....	67
5.2 Future Research Direction	70
REFERENCES	71
APPENDIX.....	76

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].

Solid Lubricant Materials	
Category	Example
Carbon-based materials	Graphite and diamond-like carbon
Metal dichalcogenide compounds	MoS ₂ and WS ₂
Soft metals	Silver, Tin, Indium, Gold
Polymers	PTFE, Polyimide, Nylon

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, $(-\text{CF}_2-\text{CF}_2)_n$. 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_7 helix structure. The 15_7 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 13_6 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 CF_2 groups.

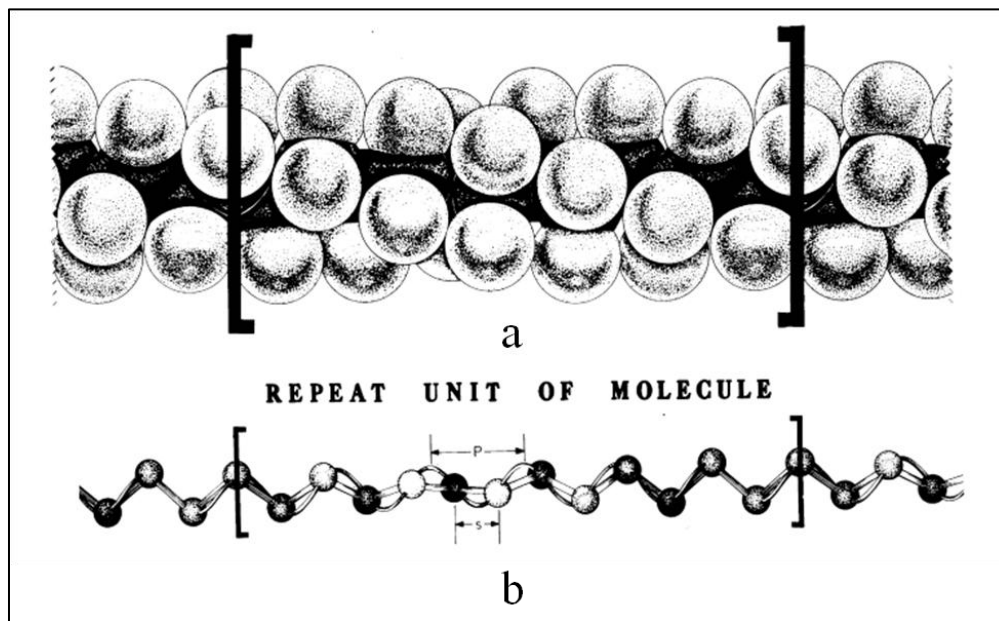


Figure 1.1 (a) Smallest repeat unit of a 13_6 helical arrangement of PTFE; (b) helix configuration of carbon backbone [5]. Reprinted with permission from Elsevier.

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.

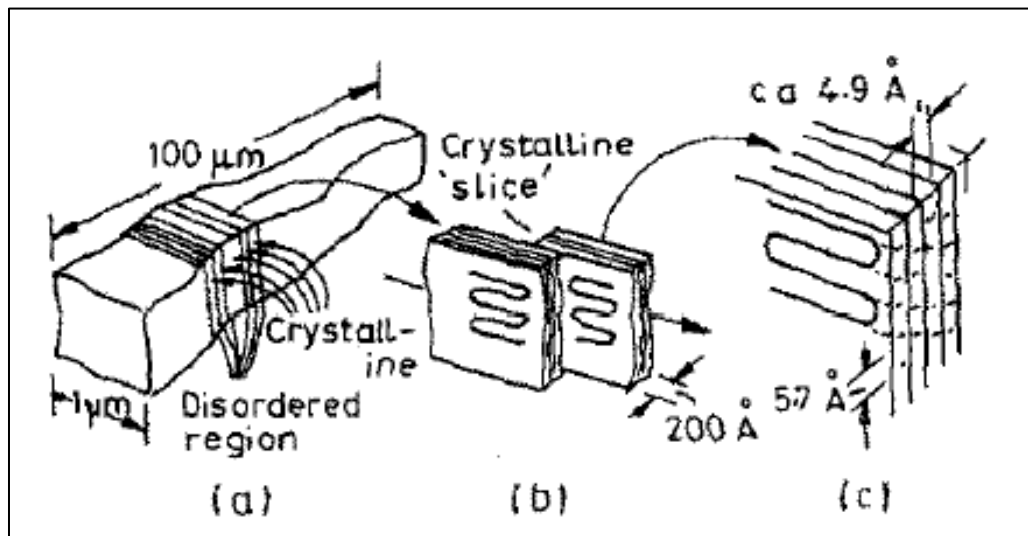


Figure 1.2 Banded Structure of PTFE: (a) semi-crystalline block of crystalline slices and amorphous regions of PTFE chains; (b) crystalline slices of PTFE chains during sliding; (c) dimensions of PTFE molecular chains [4]. Reprinted with permission from Elsevier.

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 sp^2 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. Kandamur 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].

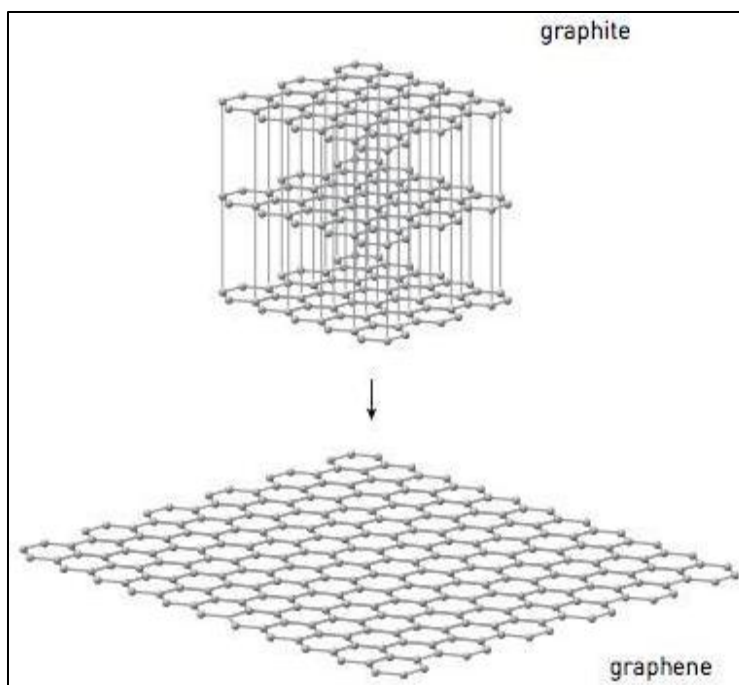


Figure 1.3 Structure of graphite and graphene. Graphene sheets are the building blocks that make up the structure of graphite [15]. © Airi Iliste/Royal Swedish Academy of Sciences

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].

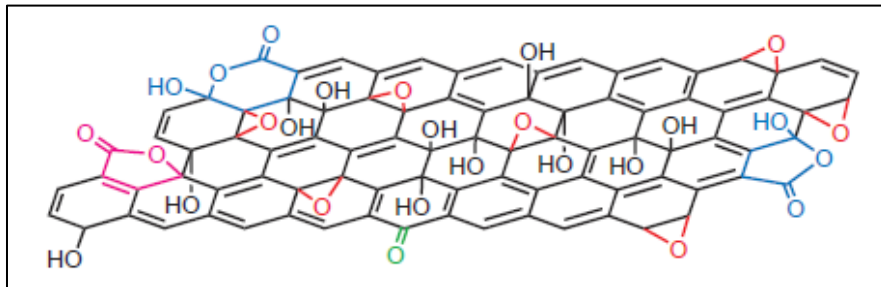


Figure 1.4 Typical structure of a GO sheet containing various oxygen functionalities along the basal plane and edges. Reprinted by permission from Macmillan Publishers Ltd: Nature Chemistry [17], copyright 2009. www.nature.com/nchem.

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 ($C_9H_{11}NO_4$), and lysine, $HO_2CCH(NH_2)(CH_2)_4NH_2$, 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 (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].

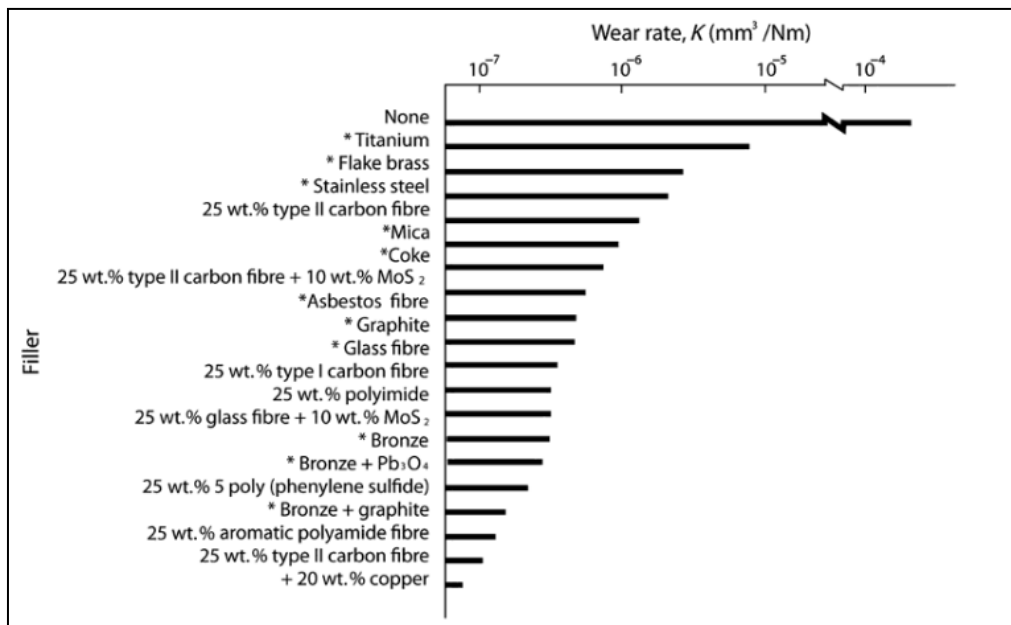


Figure 2.1 Various micro-filled PTFE composite wear rates [31]. Crown copyright.

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 (Al_2O_3) particles between 0.1 wt% and 50 wt% to bulk PTFE. At a 20 wt% filler concentration, the PTFE/ Al_2O_3 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 Al_2O_3 particle size on the wear resistance and COF of bulk PTFE composites. Two Al_2O_3 nano-filler sizes, 40 nm and 80 nm, and four Al_2O_3 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% Al_2O_3 filler. From Figure 2.2, steady state wear rates for micro-sized and nano-sized Al_2O_3 fillers tended to be 2 and 4 orders of magnitude, respectively, less than unfilled PTFE. Both micro-fillers and nano-fillers of Al_2O_3 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 Al_2O_3 nanoparticles were less abrasive than composites using Al_2O_3 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].

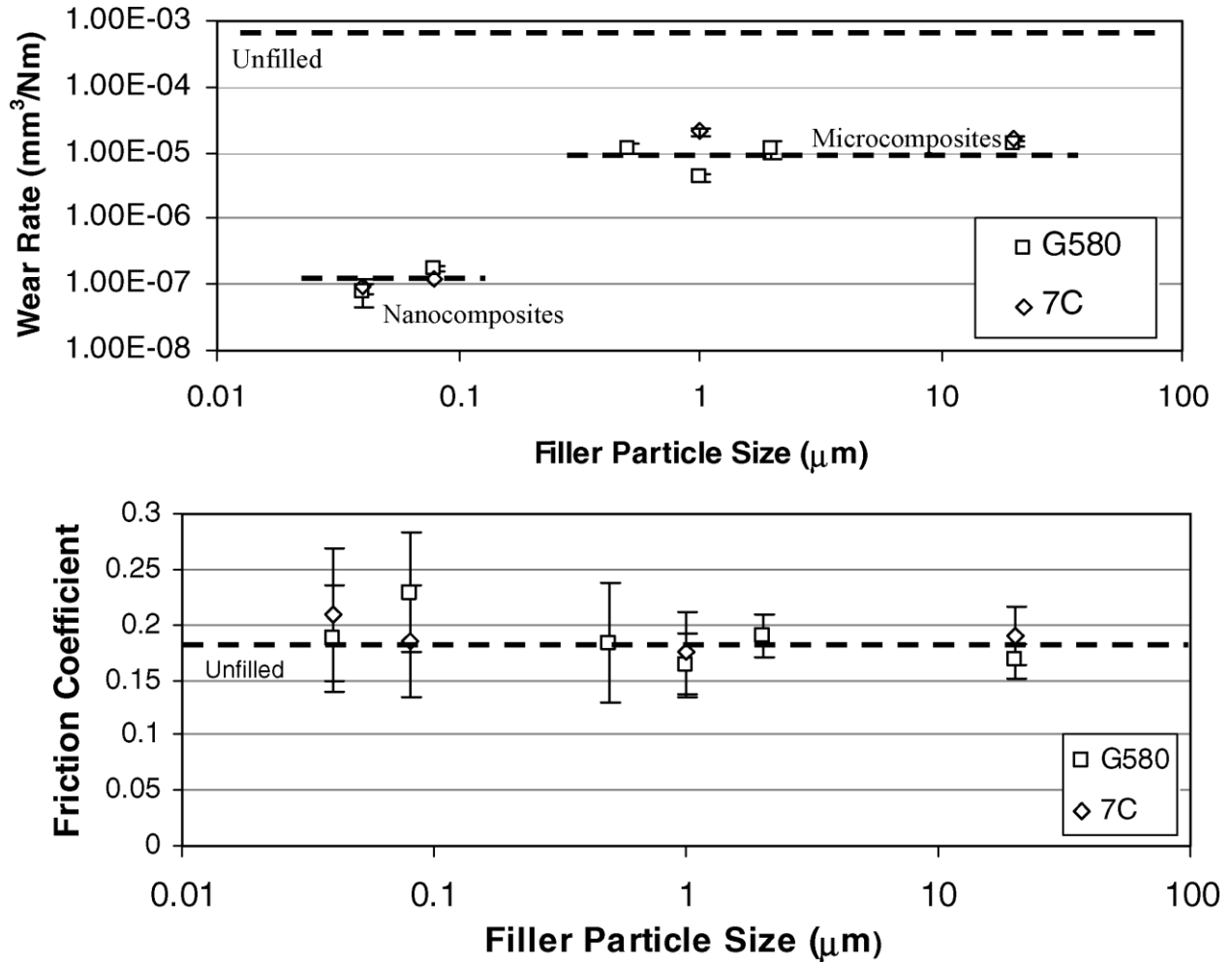


Figure 2.2 Steady state wear rate (top) and COF (bottom) for various Al_2O_3 filler particle sizes for PTFE/ Al_2O_3 composites vs. unfilled PTFE for G580 and 7C PTFE resins [38].

Reprinted with permission from STLE in Tribology Transactions, www.stle.org.

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]. Burriss 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 Al_2O_3 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].

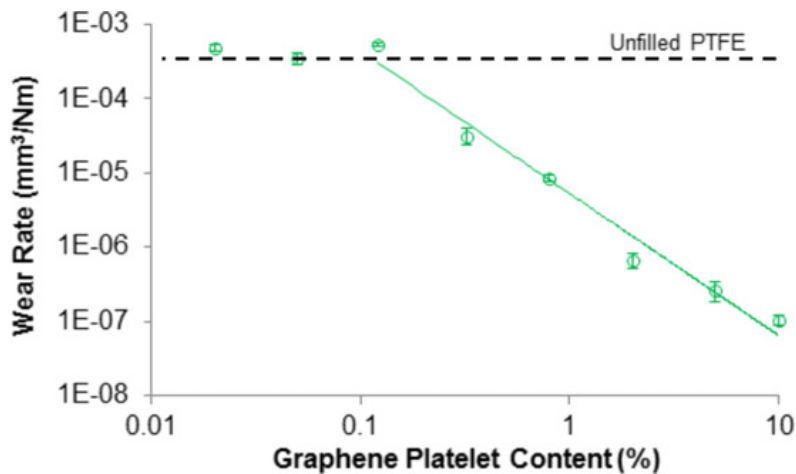


Figure 2.3 Steady state wear rate of unfilled PTFE vs. graphene platelet filled PTFE composite at various graphene platelet wt% contents [14].

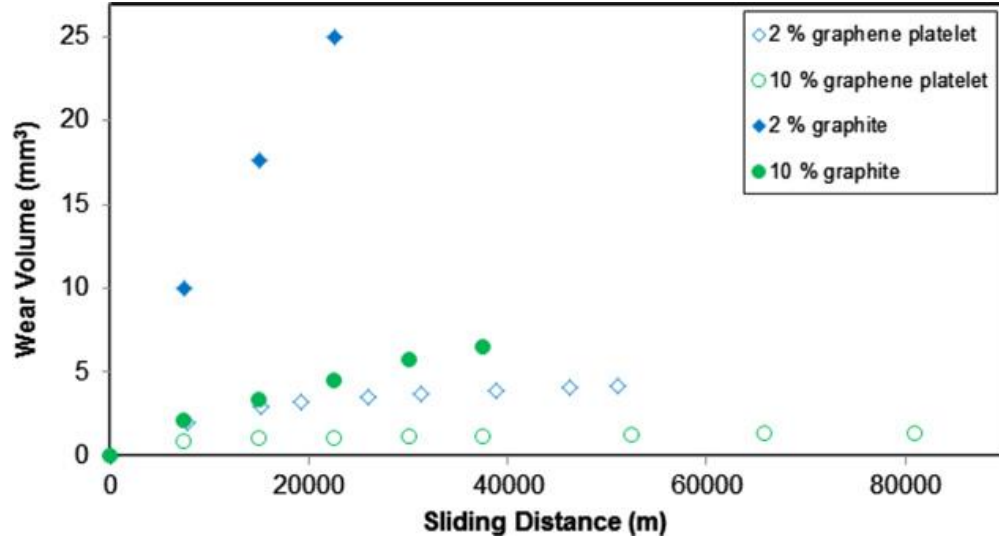


Figure 2.4 Wear volume vs. sliding distance between 2 wt% and 10 wt% graphene platelet and graphite fillers in bulk PTFE [14].

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 μm 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.

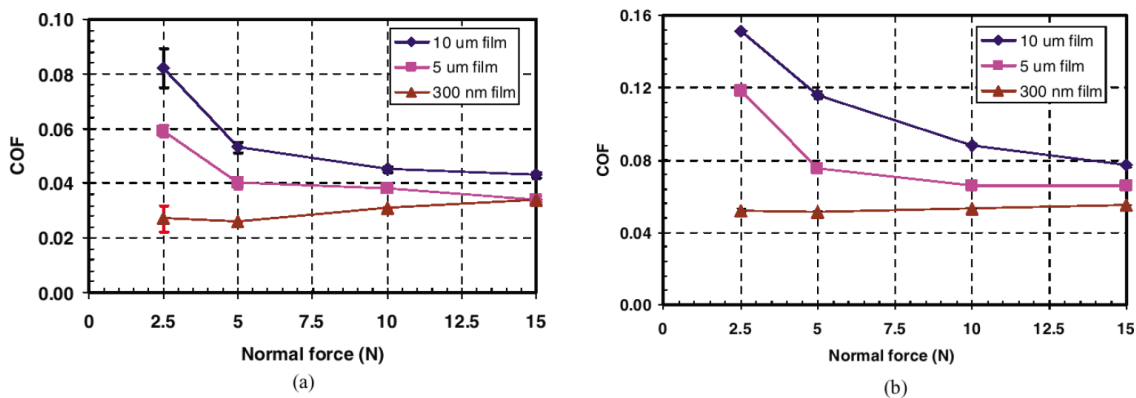


Figure 2.5 COF of 300 nm, 5 μm , and 10 μm PTFE films deposited on glass by HFCVD at different loads and sliding speeds of (a) 0.014 mm/s and (b) 1.4 mm/s [42].

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], SiO₂ nanoparticles [45], Au nanoparticles [46], and Al₂O₃ [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 SiO₂ 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% SiO₂ filled PTFE/SiO₂ 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].

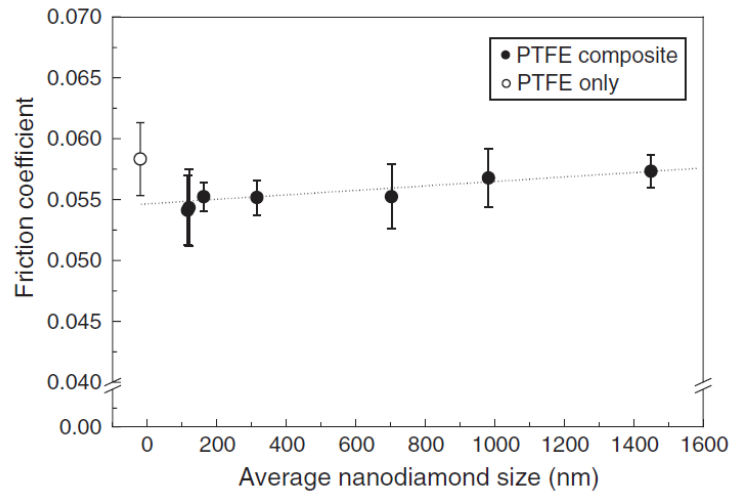


Figure 2.6 COF for unfilled PTFE and PTFE/ND composite coatings for different average ND sizes [43].

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.

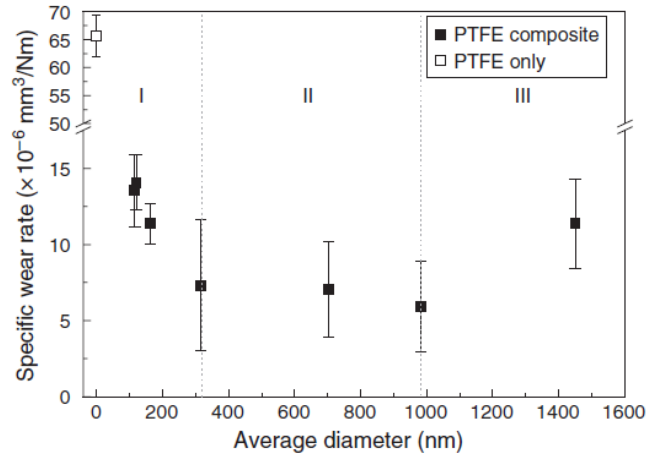


Figure 2.7 Wear rates for unfilled PTFE and PTFE/ND composite coatings for different average ND sizes. Three different wear rate regimes are present [43].

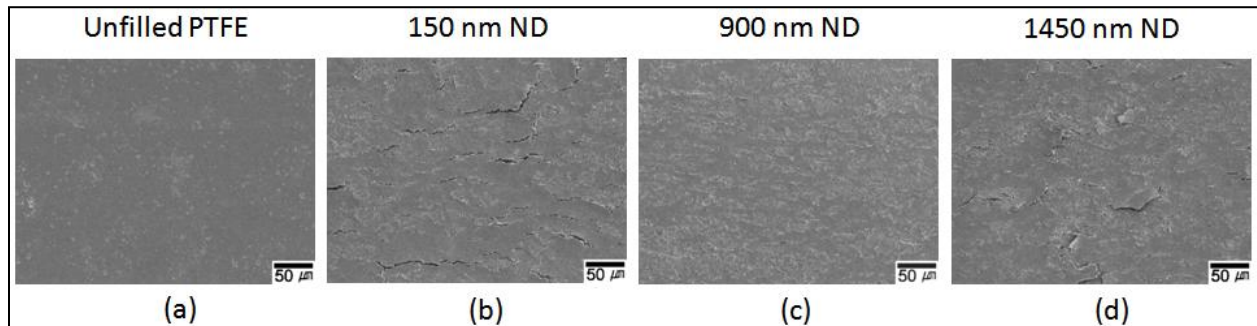


Figure 2.8 Wear surface of unfilled PTFE and PTFE/ND composite from each wear regime. Wear surface of wear regimes I, II, and III, from Figure 2.7, are (b), (c), and (d), respectively [43].

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

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].

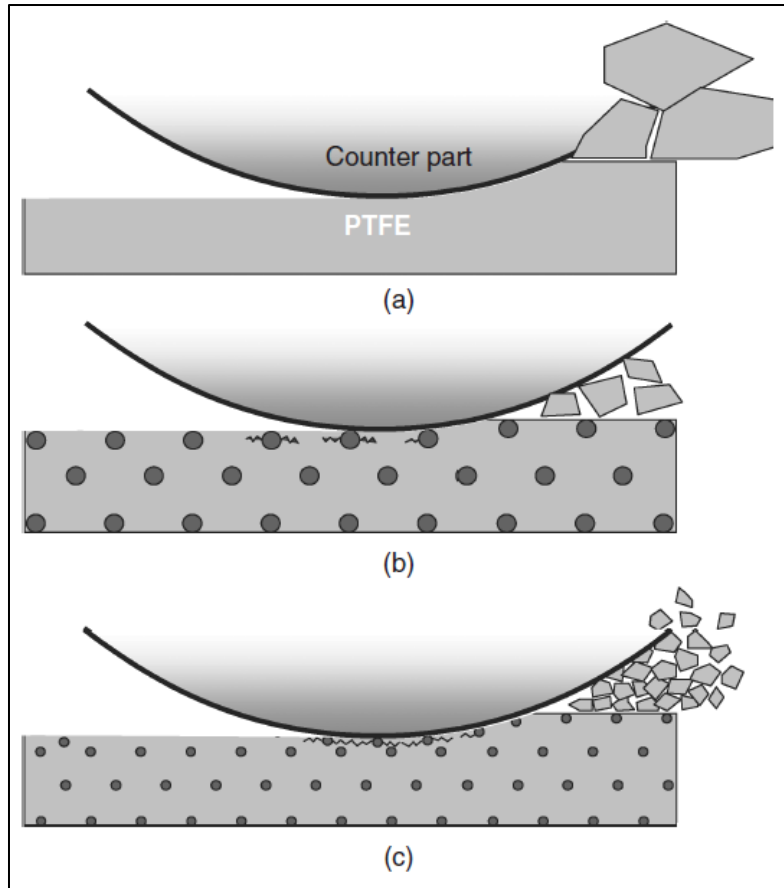


Figure 2.9 Wear behavior of (a) unfilled PTFE and PTFE/ND composite with (b) larger ND particles and (c) smaller ND particles [43].

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.

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/ZrO₂ 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/ZrO₂, a film thickness around 100 nm was achieved. When compared to homogenous films of ZrO₂, the aforementioned PDA/ZrO₂ 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/ZrO₂ films when compared to monolayer ZrO₂ 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/ZrO₂ 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-perfluorodecyltrichlorosilane (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.

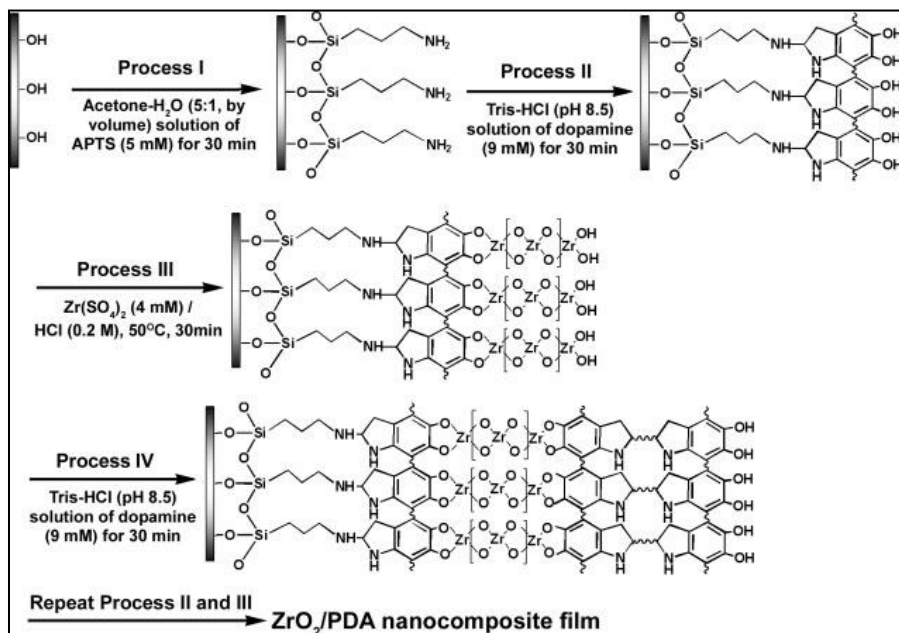


Figure 2.10 Overall procedure used to create PDA/ZrO₂ multilayered films on silicon substrates [54]. Reprinted with permission by John Wiley and Sons.

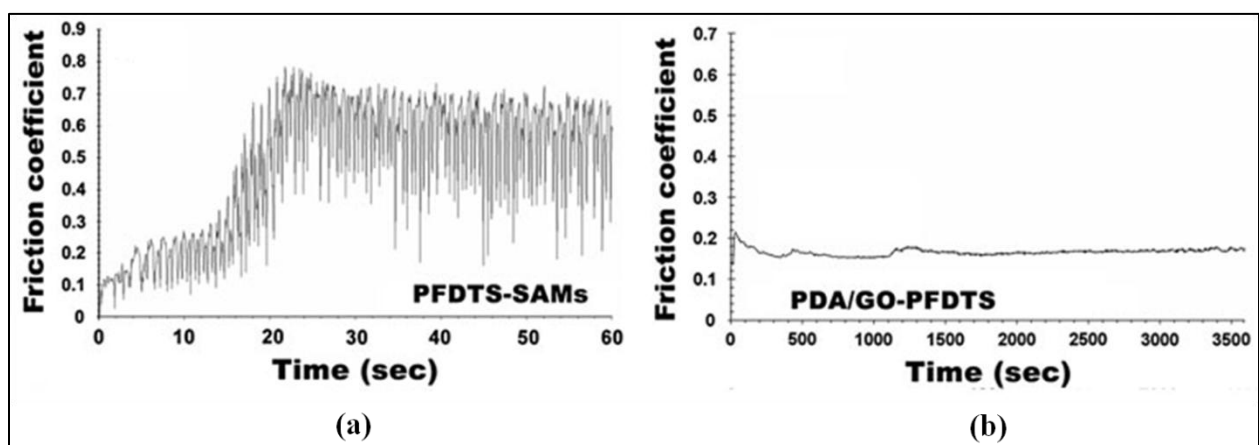


Figure 2.11 COF vs. time plots for (a) self-assembled monolayers of PFDTs on silicon and (b) PDA/GO-PFDTs coating on silicon [56]. Reprinted with permission from Springer Science and Business Media.

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.

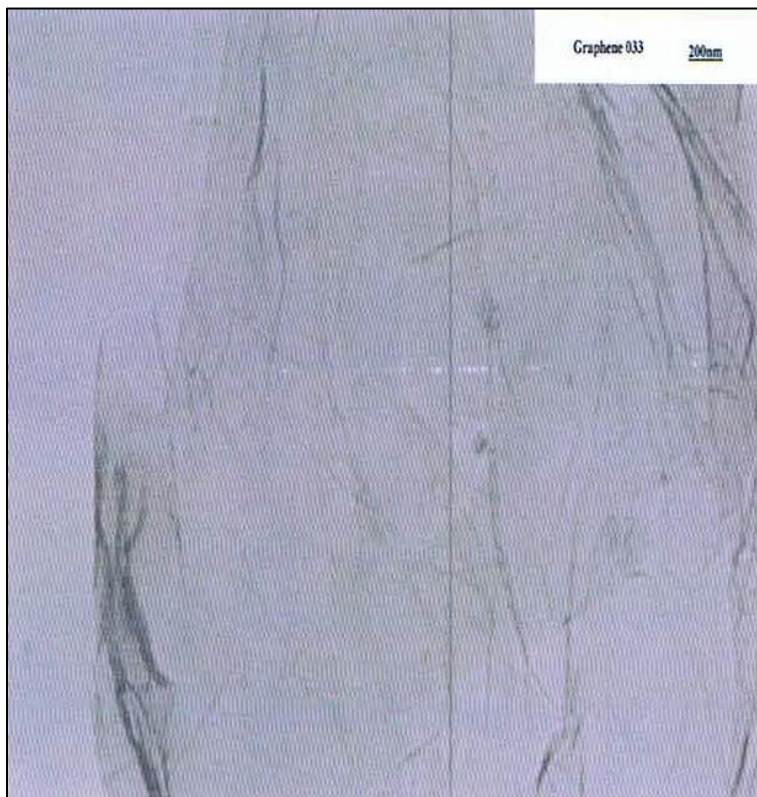


Figure 3.1 TEM image of GO sheets [60].

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 3.1 Sample types for each set of samples created for testing.

Samples		
Set	Type	Description
1	PTFE	Single coating of PTFE
	PFLGO2	Single coating of PTFE + 0.2 wt% GO dispersion (2:1 volume ratio of PTFE:GO dispersions)
	PFLGO5	Single coating of PTFE + 0.5 wt% GO dispersion (2:1 volume ratio of PTFE:GO dispersions)
2	PDA/PTFE	Dual coating of PDA and PTFE (Top coat: PTFE)
	PDA/PFLGO2	Dual coating of PDA and PFLGO2 (Top coat: PFLGO2)

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.



(a)



(b)

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.

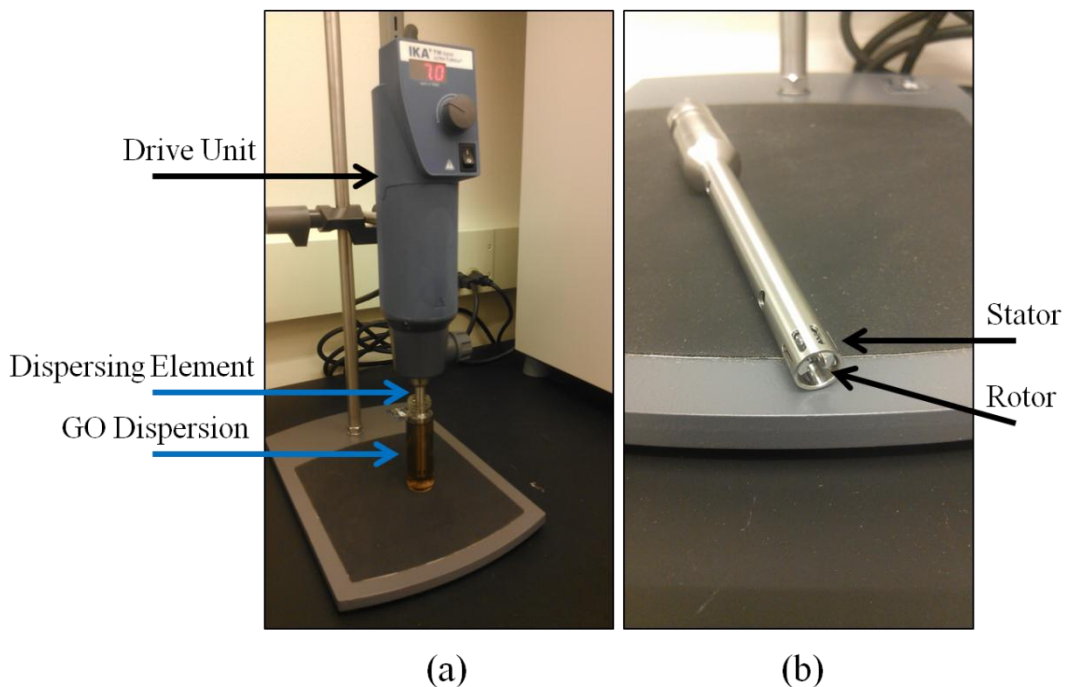


Figure 3.3 Photograph of (a) IKA® T 18 digital ULTRA-TURRAX® disperser and (b) S18N-10G dispersing element.

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 diluted 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.

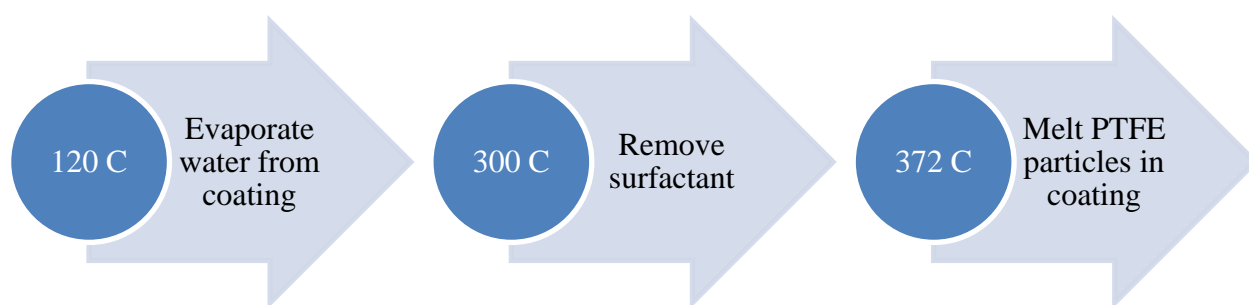


Figure 3.4 DuPont’s recommended heating procedure for PTFE TE-3859 aqueous dispersion [57].

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.

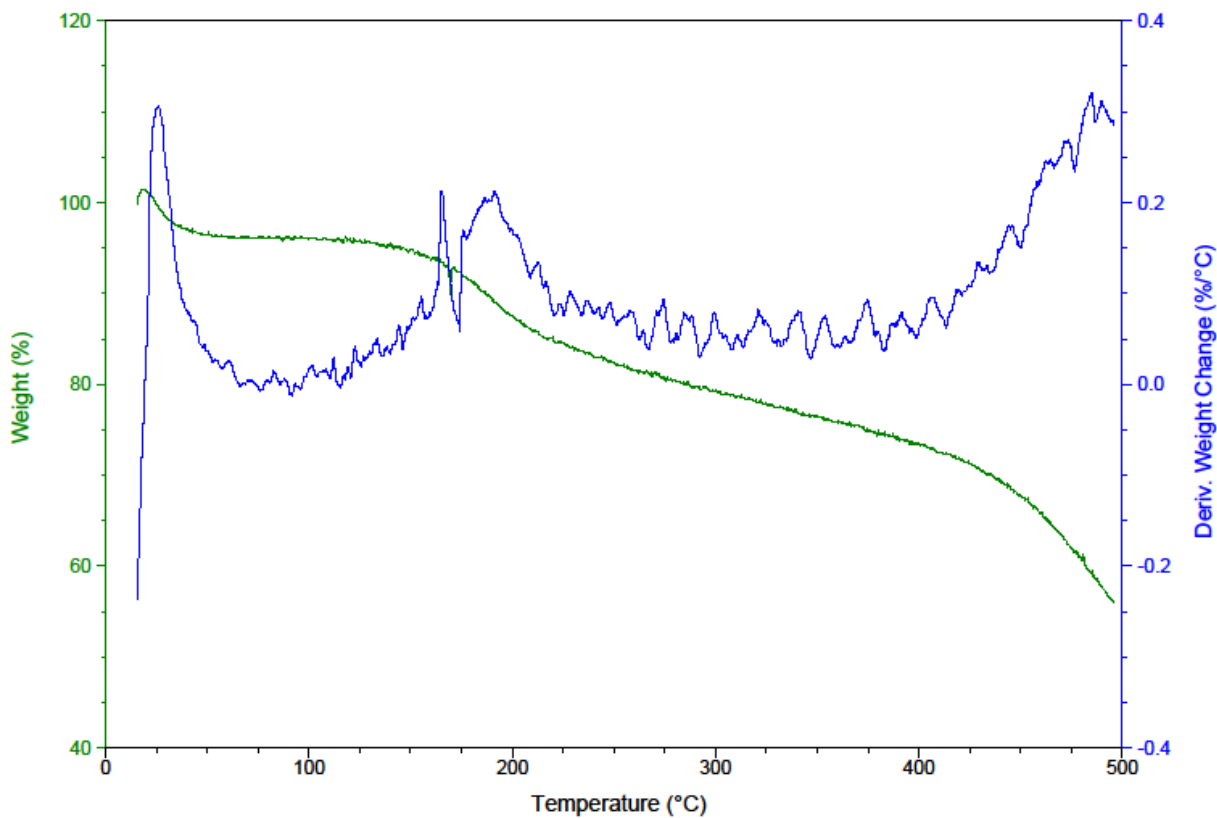


Figure 3.5 TGA of dopamine hydrochloride [61].

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.

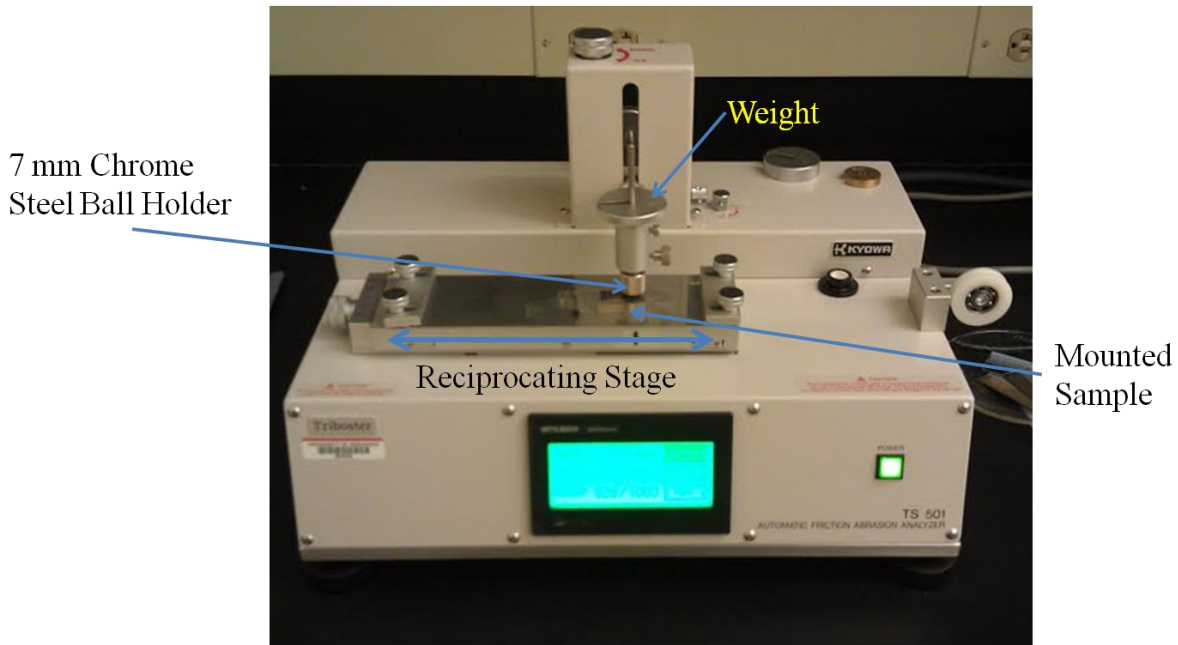


Figure 3.6 Picture of Tribometer during friction and wear testing.

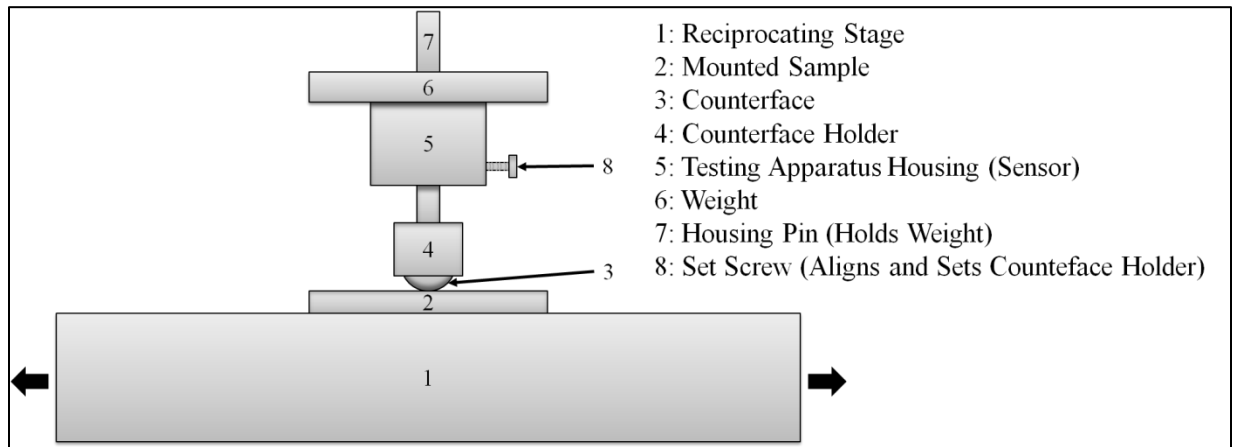


Figure 3.7 Schematic of friction and wear testing setup for Tribometer.

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 scribe 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.

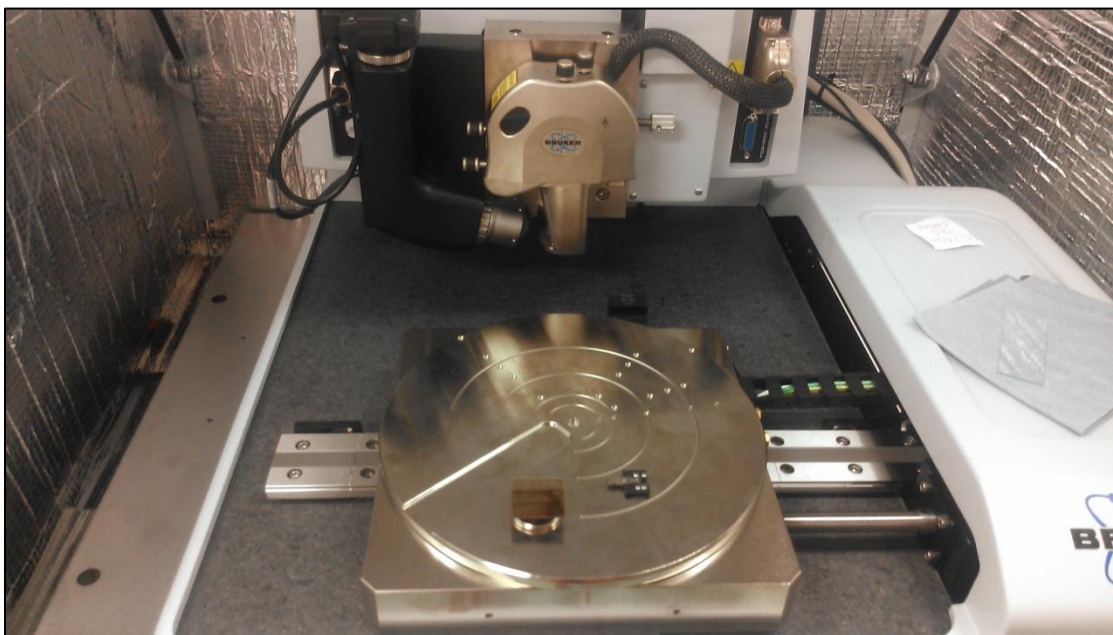


Figure 3.9 Picture of Bruker Dimension Icon AFM. A mounted stainless steel sample and probe holder are on the AFM stage.

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.

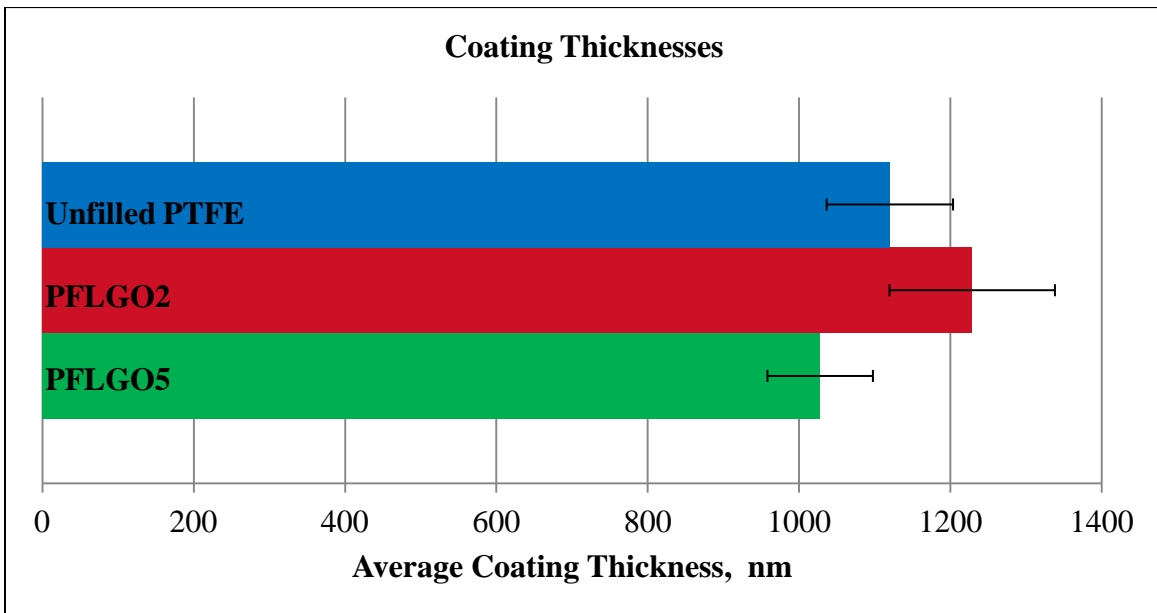


Figure 4.1 Average Thickness of PTFE, PFLGO2, and PFLGO5 coatings. Error bars represent one standard deviation.

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.

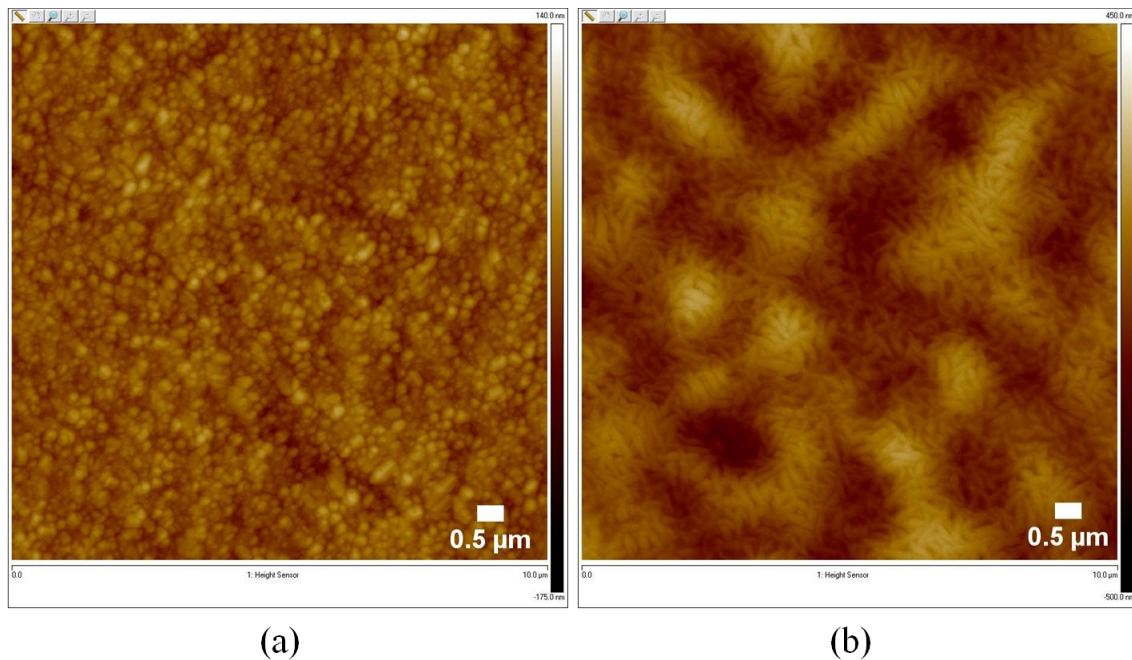


Figure 4.2 AFM images of single coated (a) unmelted PTFE particles and (b) melted PTFE particles processed using the suggested DuPont heating procedure. Scan sizes are 10 μm .

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.

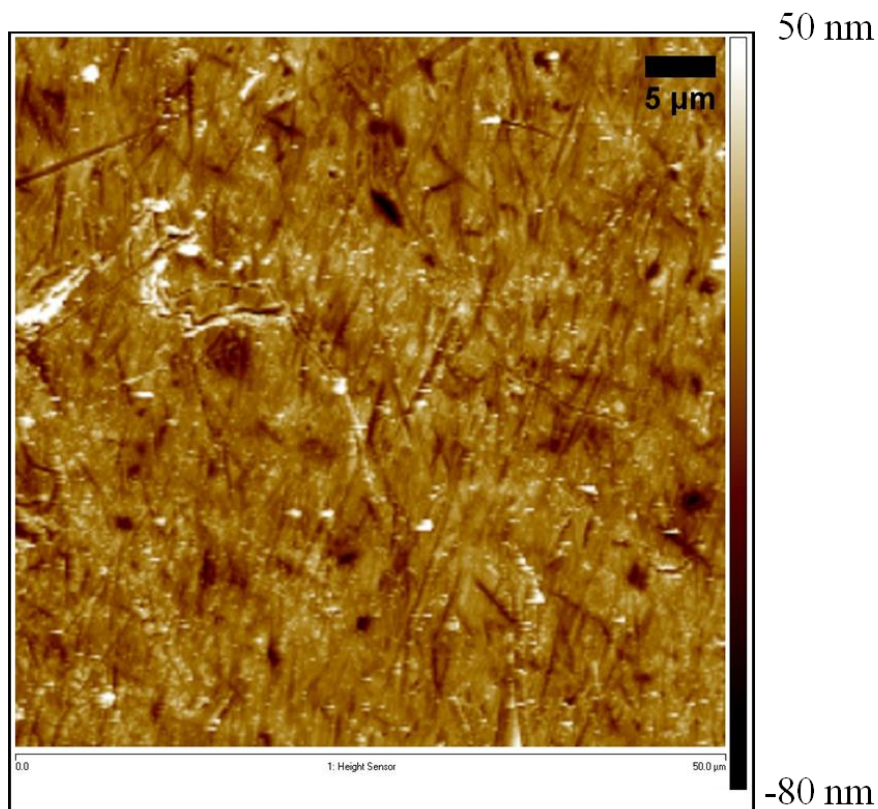


Figure 4.3 AFM tapping mode image of clean chrome steel ball counterface. Scan size is 50 μm .

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.

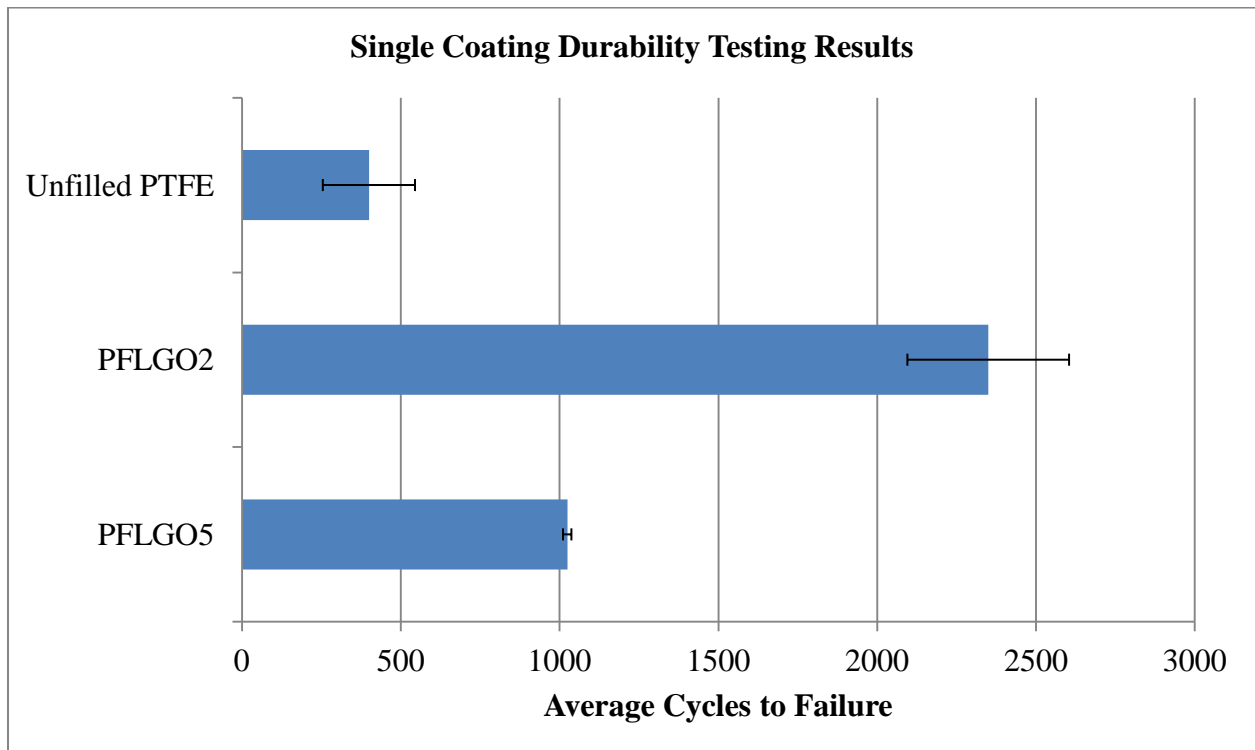


Figure 4.4 Durability results for single layer coatings of unfilled PTFE, PFLGO2, and PFLGO5. Error bars represent one standard deviation.

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.

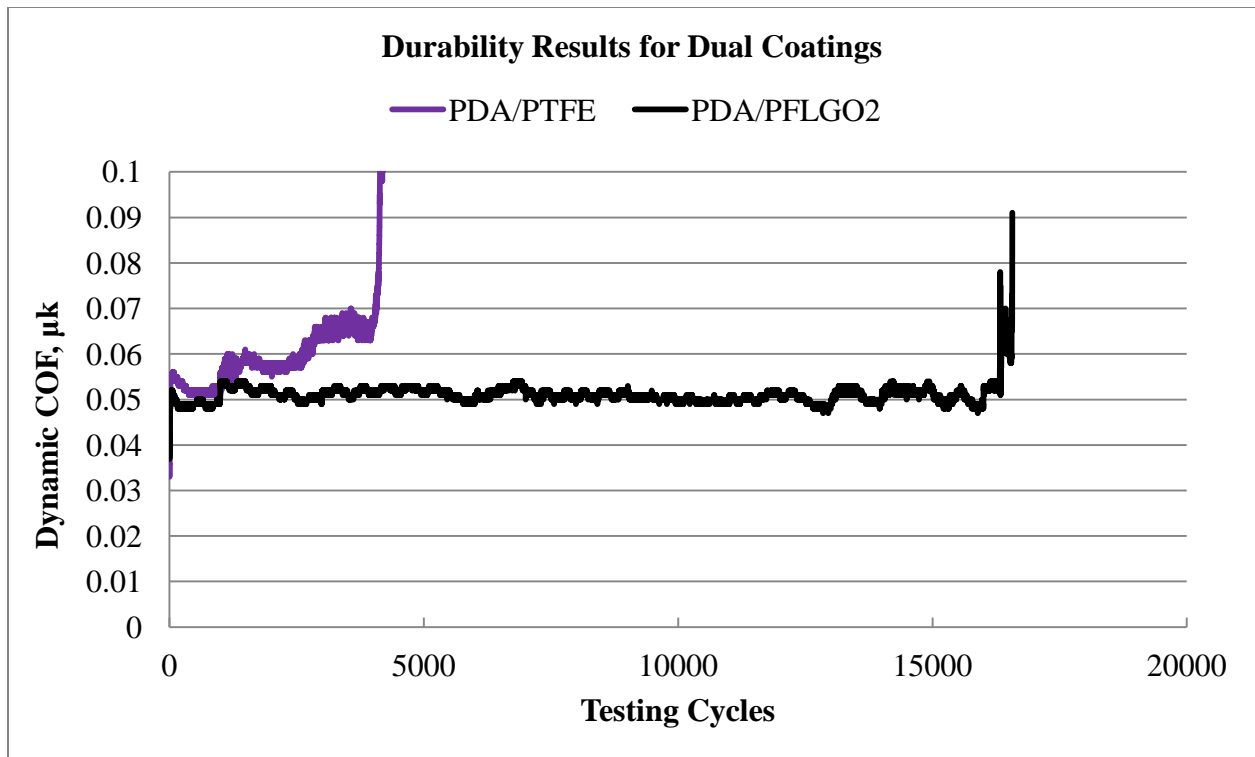


Figure 4.5 Durability results for dual coatings of PDA/PTFE and PDA/PFLGO2.

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_2O_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_2O_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.

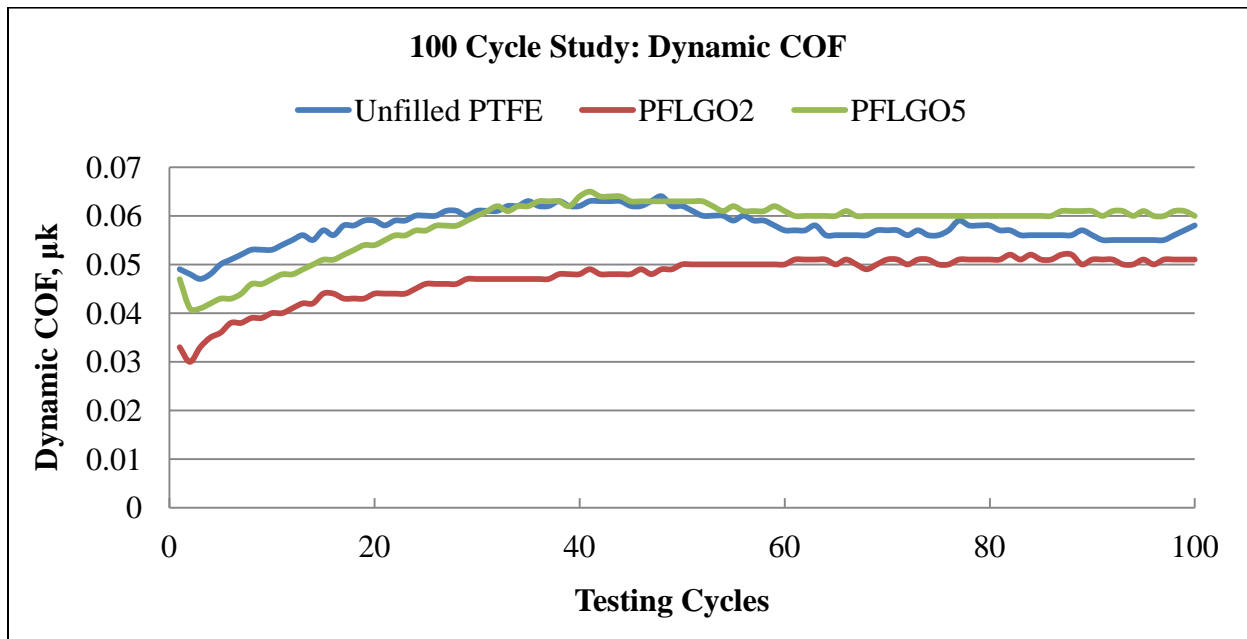


Figure 4.6 Dynamic COF curves from 100 cycle study for unfilled PTFE, PFLGO2, and PFLGO5.

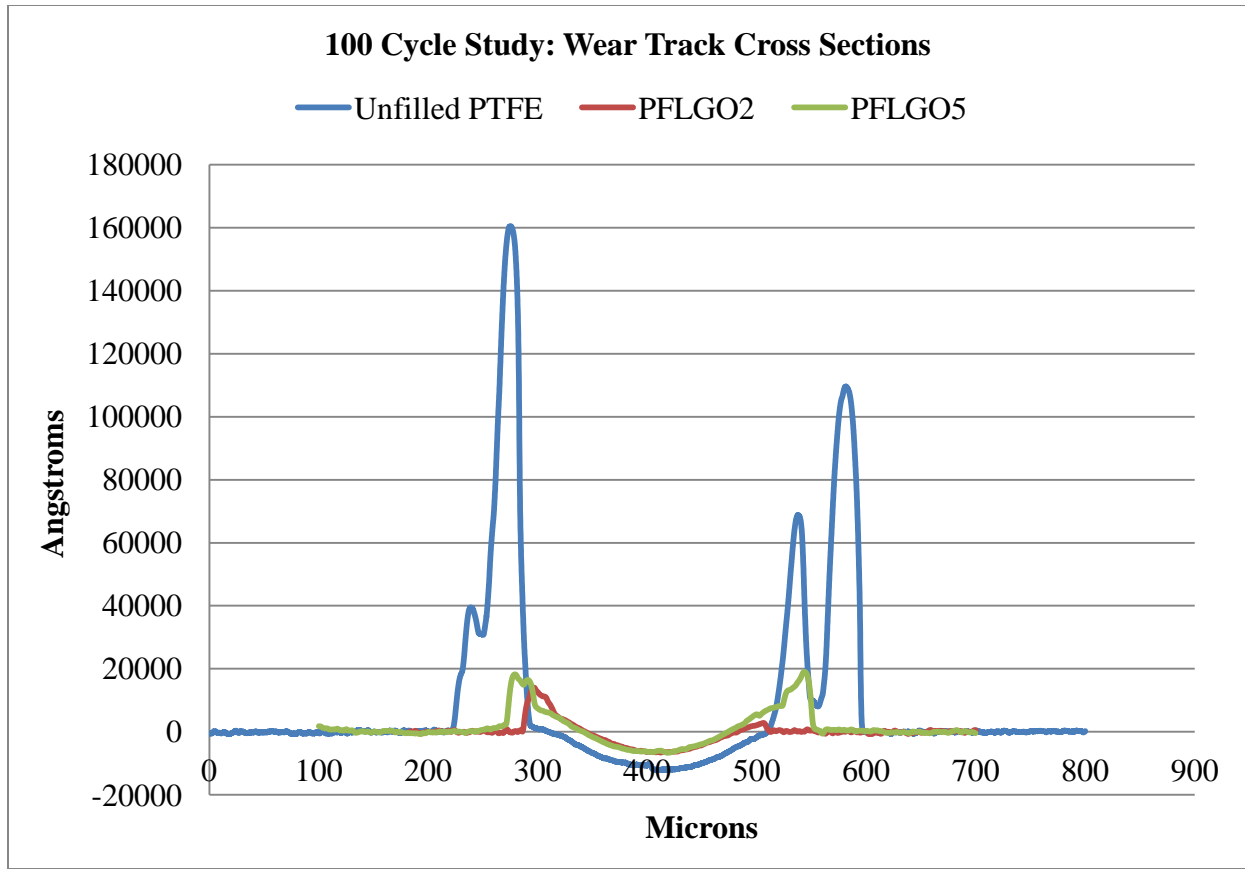


Figure 4.7 Wear track cross sections of unfilled PTFE, PFLGO2, and PFLGO5 samples tested at 100 cycles.

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

Sample Type	Wear Depth, nm		Wear Width, μm		Wear Volume, mm^3	
	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
Unfilled PTFE	1079	52.8	207	0.436	2.50E-03	6.76E-05
PFLGO2	673	66.9	137.9	6.45	8.90E-04	1.212E-04
PFLGO5	709	37.6	141.6	2.24	1.000E-03	7.40E-05

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.

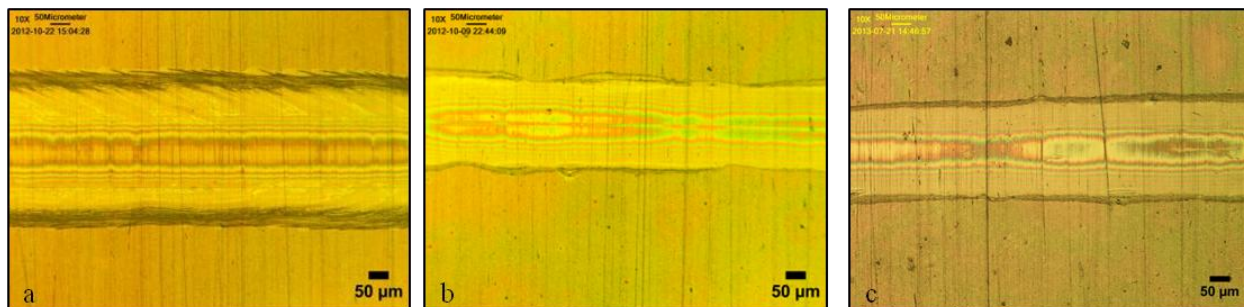


Figure 4.8 Optical images of wear tracks of 100 cycle tested samples of (a) unfilled PTFE, (b) PFLGO2, (c) PFLGO5.

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.

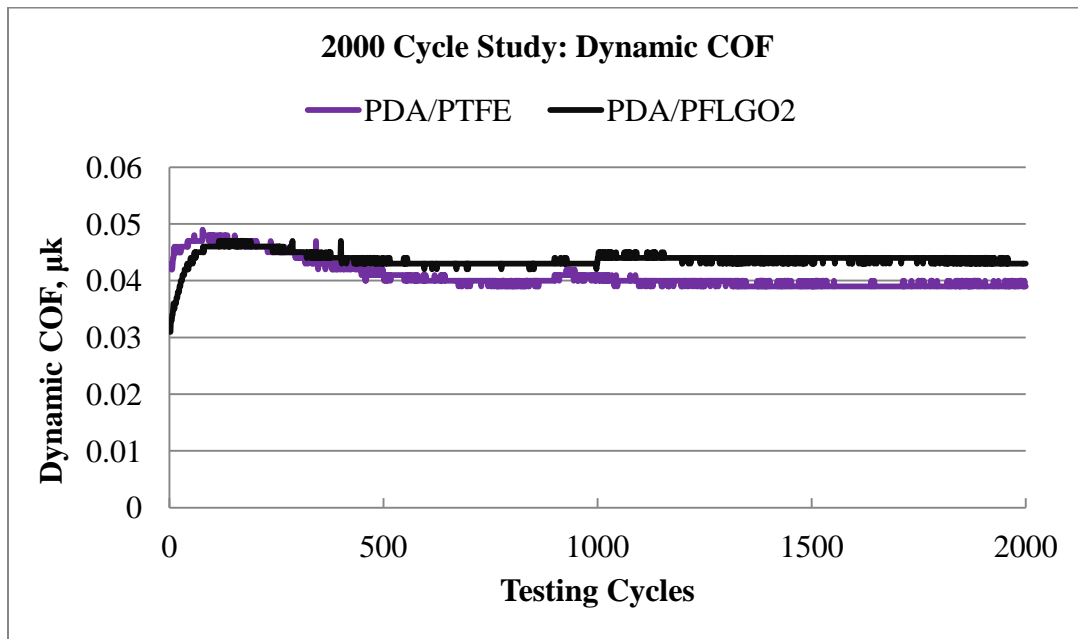


Figure 4.9 Dynamic COF for 2000 cycle tested PDA/PTFE and PDA/PFLGO2.

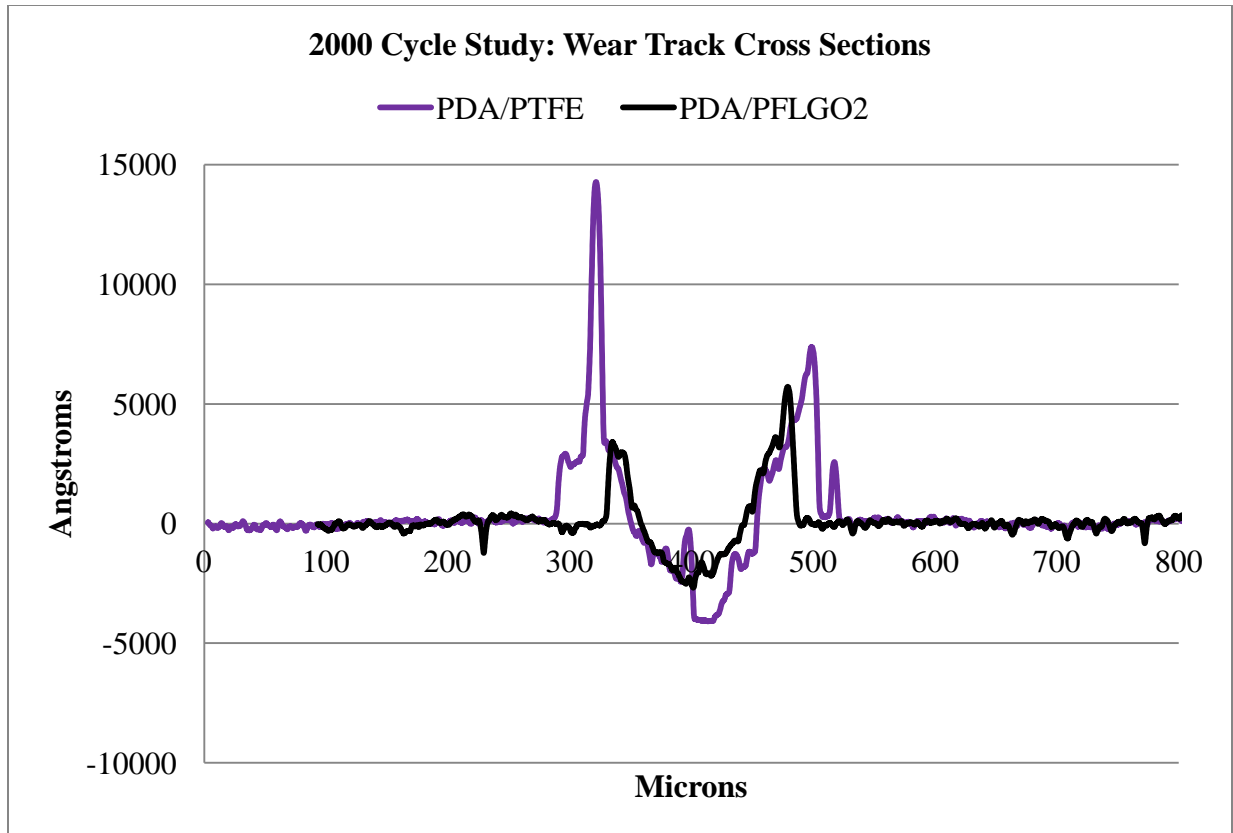


Figure 4.10 Wear tracks of PDA/PTFE and PDA/PFLGO2 after 2000 testing cycles.

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

Sample	Average Wear Volume, mm ³	Standard Deviation, mm ³
PDA/PTFE	3.55E-04	3.77E-05
PDA/PFLGO2	2.65E-04	6.24E-05

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.

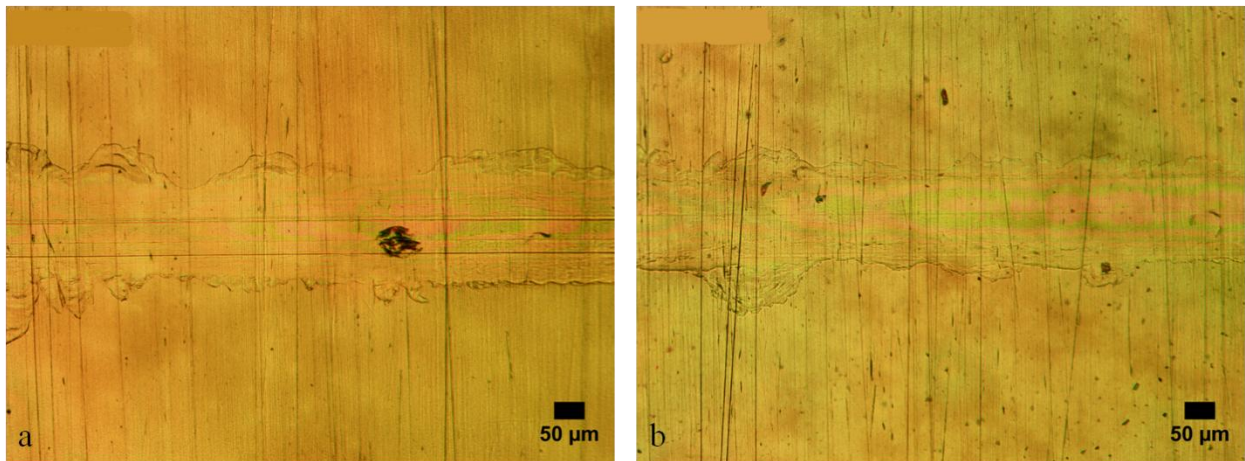


Figure 4.11 Wear tracks of 2000 cycle tested (a) PDA/PTFE and (b) PDA/PFLGO2.

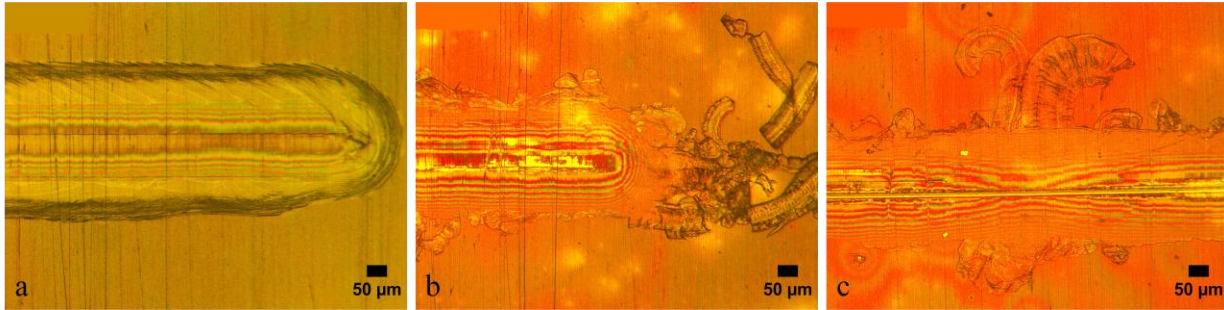


Figure 4.12 Wear tracks of (a) 100 cycle tested single coating of PTFE and (b,c) durability tested dual coating of PDA/PTFE (4278 cycles).

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.

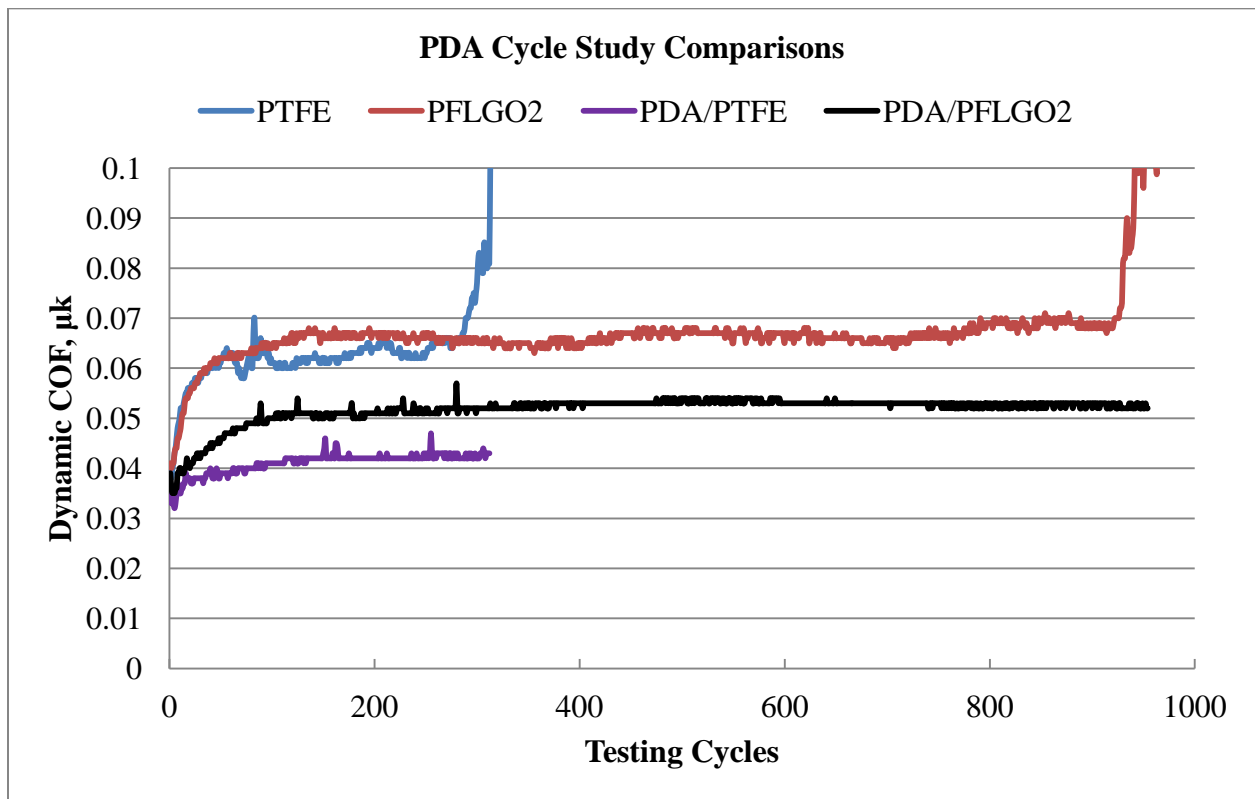


Figure 4.13 COF of single and dual coatings of PTFE and PFLGO2 after 312 and 954 testing cycles, respectively.

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.

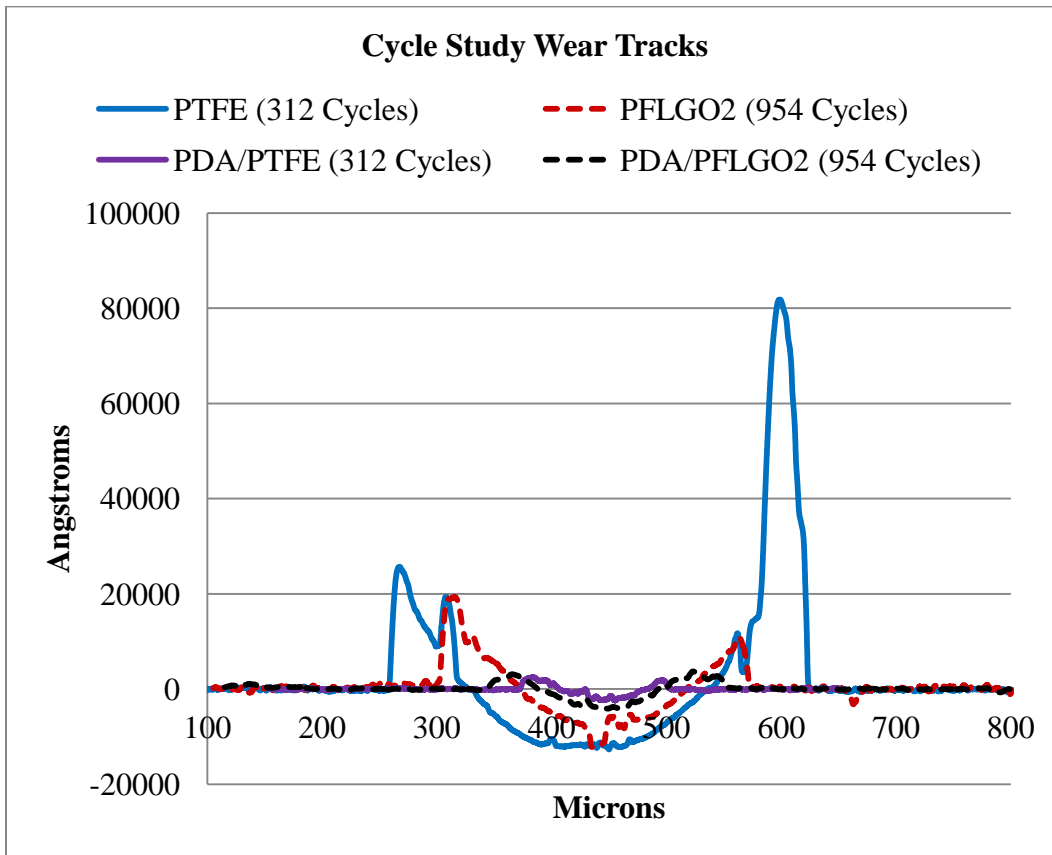


Figure 4.14 Wear track comparisons between single and dual coatings of PTFE vs. PDA/PTFE (312 cycles) and PFLGO2 vs. PDA/PFLGO2 (954 cycles).

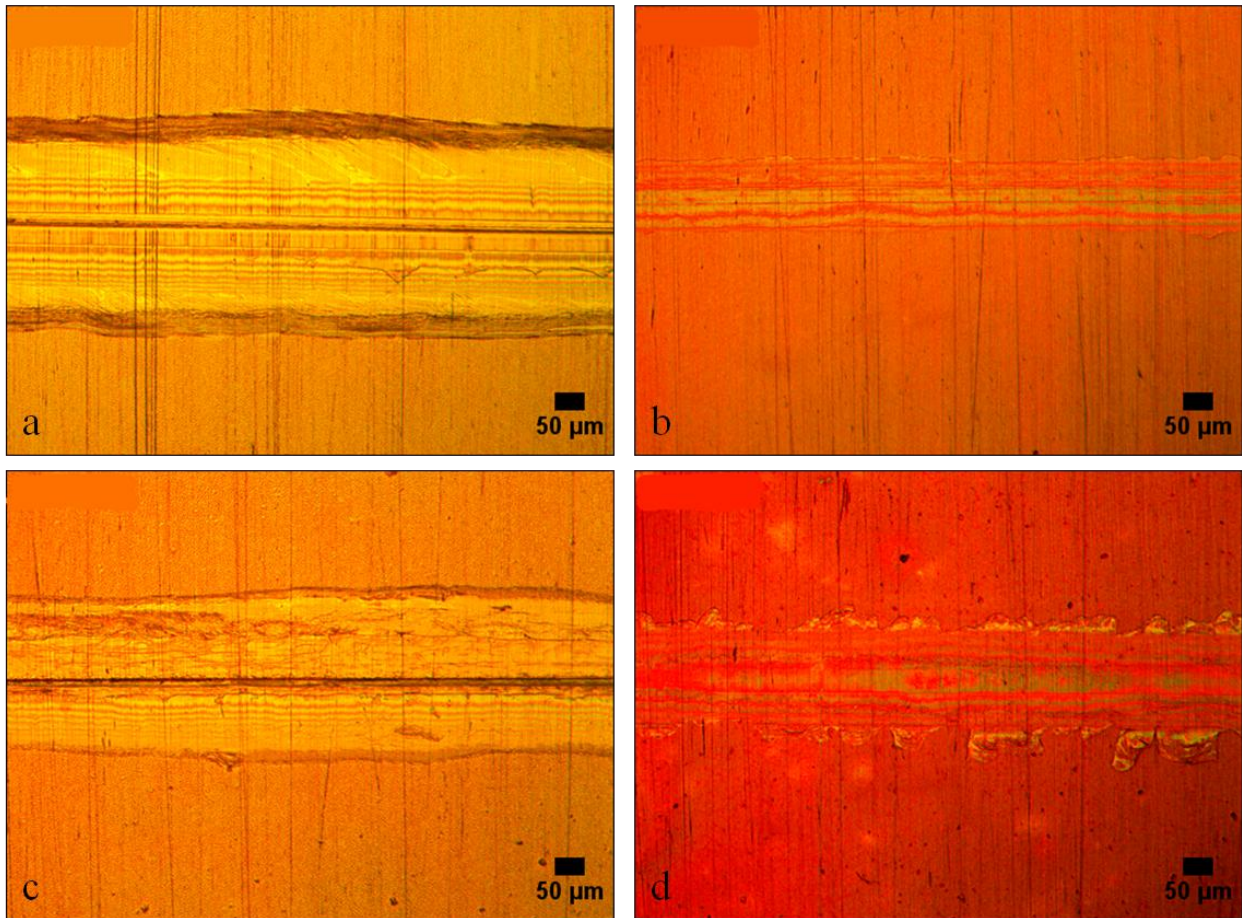


Figure 4.15 Single coatings vs. dual coatings tested at same number of cycles: PTFE (a) vs. PDA/PTFE (b) run at 312 cycles and PFLGO2 (c) vs. PDA/PFLGO2 (d) run at 954 cycles.

4.5 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.

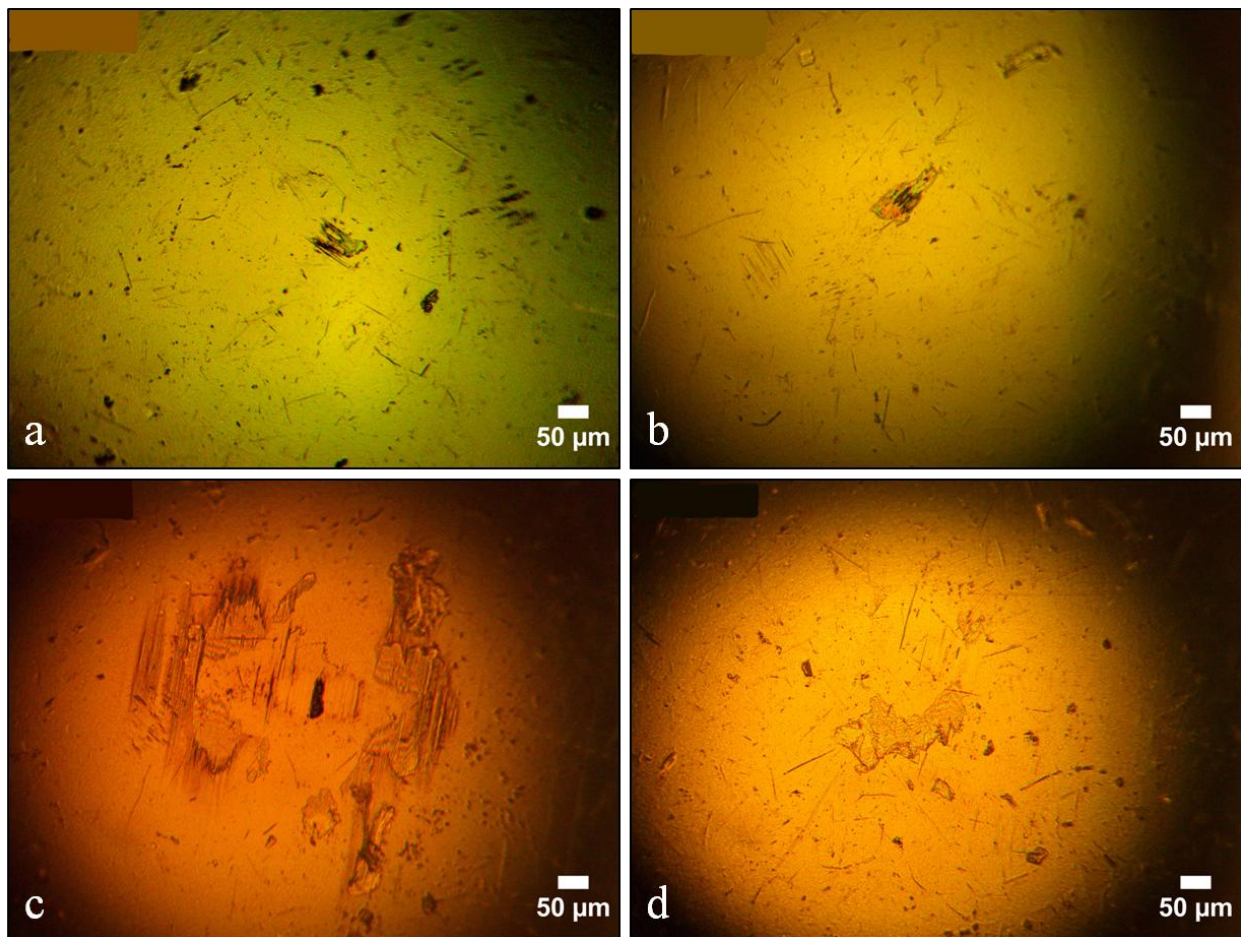


Figure 4.16 Counterface optical images of (a) PTFE, (b) PFLGO2, (c) PDA/PTFE, and (d) PDA/PFLGO2.

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 Al_2O_3 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.

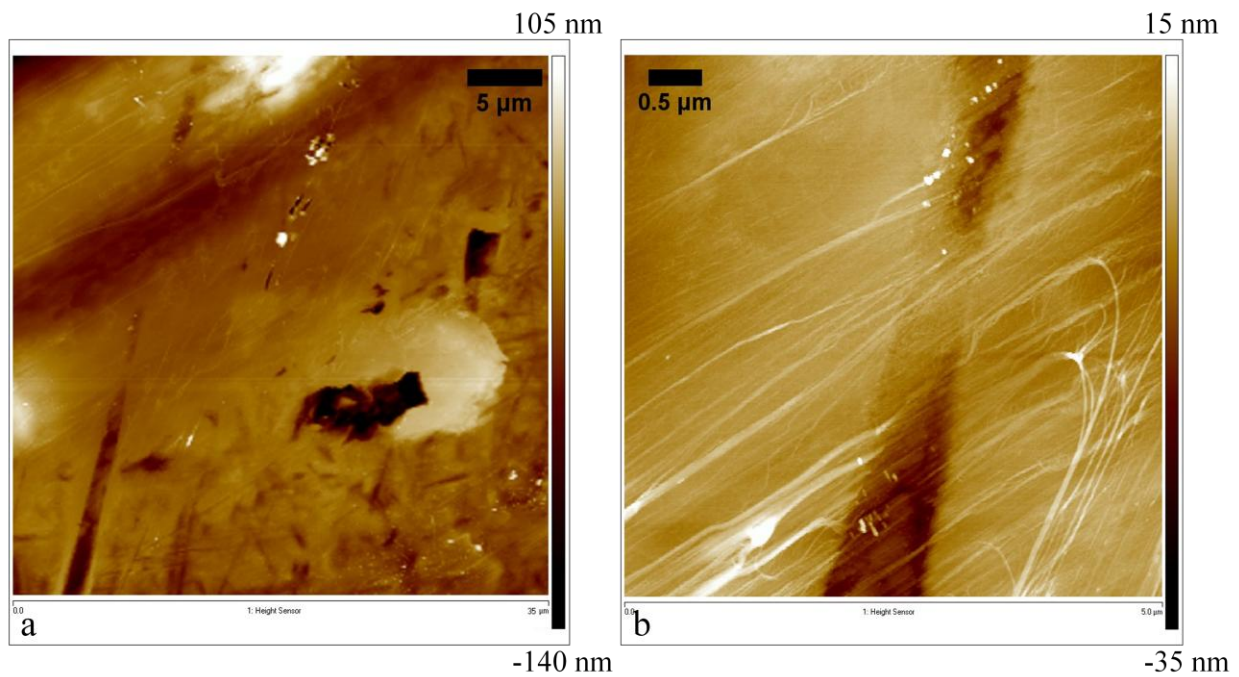


Figure 4.17 AFM images of tested counterface for a PFLGO2 coating. (a) 35 μm scan of edge of transfer film area. (b) 5 μm scan of transfer film filling in counterface scar.

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

- [1] Campbell, M.E., Loser, J.B., and Sneegas, E., 1966, "Solid lubricants," National Aeronautics and Space Administration (NASA).
- [2] Scharf, T. W., and Prasad, S. V., 2013, "Solid Lubricants: A Review," *Journal of Materials Science*, **48**(2) pp. 511-531.
- [3] Donnet, C., and Erdemir, A., 2004, "Solid Lubricant Coatings: Recent Developments and Future Trends," *Tribology Letters*, **17**(3) pp. 389-397.
- [4] Biswas, S. K., and Vijayan, K., 1992, "Friction and Wear of PTFE-a Review," *Wear*, **158**(1-2) pp. 193-211.
- [5] Clark, E. S., 1999, "The Molecular Conformations of Polytetrafluoroethylene: Forms II and IV," *Polymer*, **40**(16) pp. 4659-4665.
- [6] Bahadur, S., and Tabor, D., 1984, "The Wear of Filled Polytetrafluoroethylene," *Wear*, **98** pp. 1-13.
- [7] Makinson, K. R., and Tabor, D., 1964, "Friction and Transfer of Polytetrafluoroethylene," *Nature*, **201** pp. 464-466.
- [8] Pooley, C. M., and Tabor, D., 1972, "Friction and Molecular Structure: The Behaviour of some Thermoplastics," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, **329**(1578) pp. 251-274.
- [9] Burris, D. L., and Sawyer, W. G., 2006, "Improved Wear Resistance in Alumina-PTFE Nanocomposites with Irregular Shaped Nanoparticles," *Wear*, **260**(7) pp. 915-918.
- [10] Lee, J., and Lim, D., 2004, "Tribological Behavior of PTFE Film with Nanodiamond," *Surface and Coatings Technology*, **188-189**(1-3) pp. 534-538.
- [11] Novoselov, K. S., Geim, A. K., Morozov, S. V., 2004, "Electric Field in Atomically Thin Carbon Films," *Science*, **306**(5696) pp. 666-669.
- [12] Lehman, K., 2011, "Reviews of Science for Science Librarians: Graphene," *Science and Technology Libraries*, **30**(2) pp. 132-142.
- [13] Jang, B. Z., and Zhamu, A., 2008, "Processing of Nanographene Platelets (NGPs) and NGP Nanocomposites: A Review," *Journal of Materials Science*, **43**(15) pp. 5092-5101.
- [14] Kandanur, S. S., Rafiee, M. A., Yavari, F., 2012, "Suppression of Wear in Graphene Polymer Composites," *Carbon*, **50**(9) pp. 3178-3183. Reprints through permission of Elsevier.

- [15] Nobel Foundation, 2010, "Nobel Prize in Physics 2010 for Graphene -- 'Two-Dimensional' Material," [Online]. 2013 (08/13). Available: <http://www.sciencedaily.com/releases/2010/10/101005085507.htm>.
- [16] Xu, Y., Hong, W., Bai, H., 2009, "Strong and Ductile Poly(Vinyl Alcohol)/Graphene Oxide Composite Films with a Layered Structure," *Carbon*, **47**(15) pp. 3538-3543.
- [17] Gao, W., Alemany, L. B., Ci, L., 2009, "New Insights into the Structure and Reduction of Graphite Oxide," *Nat Chem*, **1**(5) pp. 403-408.
- [18] Dreyer, D. R., Park, S., Bielawski, C. W., 2010, "The Chemistry of Graphene Oxide," *Chemical Society Reviews*, **39**(1) pp. 228-240.
- [19] Goncalves, G., Marques, P. A. A. P., Barros-Timmons, A., 2010, "Graphene Oxide Modified with PMMA Via ATRP as a Reinforcement Filler," *Journal of Materials Chemistry*, **20**(44) pp. 9927-34.
- [20] Jen-Yu Wang, Shin-Yi Yang, Yuan-Li Huang, 2011, "Preparation and Properties of Graphene Oxide/Polyimide Composite Films with Low Dielectric Constant and Ultrahigh Strength Via in Situ Polymerization," *Journal of Materials Chemistry*, **21**(35) pp. 13569-75.
- [21] Lee, H., Dellatore, S. M., Miller, W. M., 2007, "Mussel-Inspired Surface Chemistry for Multifunctional Coatings," *Science*, **318**(5849) pp. 426-30.
- [22] Herbert Waite, J., 2008, "Surface Chemistry: Mussel Power," *Nature Materials*, **7**(1) pp. 8-9.
- [23] Ball, V., Del Frari, D., Michel, M., 2012, "Deposition Mechanism and Properties of Thin Polydopamine Films for High Added Value Applications in Surface Science at the Nanoscale," *BioNanoScience*, **2**(1) pp. 16-34.
- [24] Ball, V., Frari, D. D., Toniazzo, V., 2012, "Kinetics of Polydopamine Film Deposition as a Function of pH and Dopamine Concentration: Insights in the Polydopamine Deposition Mechanism," *Journal of Colloid and Interface Science*, **386**(1) pp. 366-372.
- [25] Briscoe, B. J., and Tabor, D., 1978, "FRICTION AND WEAR OF POLYMERS: THE ROLE OF MECHANICAL PROPERTIES," *The British Polymer Journal*, **10**(1) pp. 74-78.
- [26] Shooter, K. V., and Tabor, D., 1952, "The Frictional Properties of Plastics," *Proceedings of the Physical Society. Section B.*, **65** pp. 661-671.
- [27] Tanaka, K., Uchiyama, Y., and Toyooka, S., 1973, "The Mechanism of Wear of Polytetrafluoroethylene," *Wear*, **23**(1) pp. 153-72.
- [28] Myshkin, N. K., Petrokovets, M. I., and Kovalev, A. V., 2005, "Tribology of Polymers: Adhesion, Friction, Wear, and Mass-Transfer," *Tribology International*, **38**(11-12) pp. 910-921.

- [29] Bahadur, S., 2000, "The development of transfer layers and their role in polymer tribology," International Symposium on Genesis and Role of Transfer Layer/Mechanically Mixed Layer in Wear of Materials, Anonymous Elsevier, Netherlands, **245** pp. 92-9.
- [30] Yang, E. -, Hirvonen, J. -, and Toivanen, R. O., 1991, "Effect of Temperature on the Transfer Film Formation in Sliding Contact of PTFE with Stainless Steel," *Wear*, **146**(2) pp. 367-76.
- [31] Holmberg, K., and Matthews, A., 2009, "Coatings Tribology: Properties, Mechanisms, Techniques and Applications in Surface Engineering," Elsevier Science.
- [32] Tanaka, K., and Kawakami, S., 1982, "Effect of various Fillers on the Friction and Wear of Polytetrafluoroethylene-Based Composites," *Wear*, **79**(2) pp. 221-34.
- [33] Jones, R. F., 1998, "Fluoropolymer composite industry," Part 3 (of 3), April 26, 1998 - April 30, Anonymous Soc Plast Eng, Atlanta, GA, USA, **3**, pp. 2763-2768.
- [34] Blanchet, T. A., and Kennedy, F. E., 1992, "Sliding Wear Mechanism of Polytetrafluoroethylene (PTFE) and PTFE Composites," *Wear*, **153**(1) pp. 229-243.
- [35] Sawyer, W. G., Freudenberg, K. D., Bhimaraj, P., 2003, "A Study on the Friction and Wear Behavior of PTFE Filled with Alumina Nanoparticles," *Wear*, **254**(5-6) pp. 573-580.
- [36] Li, F., Hu, K., Li, J., 2001, "The Friction and Wear Characteristics of Nanometer ZnO Filled Polytetrafluoroethylene," *Wear*, **249**(10-11) pp. 877-882.
- [37] Chen, W. X., Li, F., Han, G., 2003, "Tribological Behavior of Carbon-Nanotube-Filled PTFE Composites," *Tribology Letters*, **15**(3) pp. 275-278.
- [38] McElwain, S. E., Blanchet, T. A., Schadler, L. S., 2008, "Effect of Particle Size on the Wear Resistance of Alumina-Filled PTFE Micro- and Nanocomposites," *Tribology Transactions*, **51**(3) pp. 247-253.
- [39] Nishimura, M., Miyakawa, Y., Furukawa, H., 1984, "SEM BUILT-IN FRICTION TESTER AND ITS APPLICATION TO OBSERVING THE WEAR PROCESS OF SOLID LUBRICANT FILMS." ASLE Proceedings - 3rd International Conference on Solid Lubrication 1984. Anonymous ASLE, Denver, CO, USA, pp. 50-65.
- [40] Nishimura, M., Watanabe, M., and Yoshimura, R., 1989, "Friction and Wear of Sputtered PTFE Films," *Tribochemistry: International Symposium: Papers*, Anonymous pp. 213-222.
- [41] Nishimura, M., et al, 1982, "Effect of atmosphere on the friction and wear of sputtered PTFE films," Anonymous JSLE, Tohoku, Japan, pp. 85-85-89.
- [42] Karnath, M. A., Sheng, Q., White, A. J., 2011, "Frictional Characteristics of Ultra-Thin Polytetrafluoroethylene (PTFE) Films Deposited by Hot Filament-Chemical Vapor Deposition

(HFCVD)," Tribology Transactions, **54**(1) pp. 36-43. Reprint permission through Taylor & Francis.

[43] Lim, D. P., Lee, J. Y., Lim, D. S., 2009, "Effect of Reinforcement Particle Size on the Tribological Properties of Nano-Diamond Filled Polytetrafluoroethylene Based Coating," Journal of Nanoscience and Nanotechnology, **9**(7) pp. 4197-201.

[44] McCook, N. L., Burris, D. L., Bourne, G. R., 2005, "Wear Resistant Solid Lubricant Coating made from PTFE and Epoxy," Tribology Letters, **18**(1) pp. 119-24.

[45] Beckford, S., Wang, Y. A., and Zou, M., 2011, "Wear-Resistant PTFE/SiO₂ Nanoparticle Composite Films," Tribology Transactions, **54**(6) pp. 849-858.

[46] Beckford, S., Osborn, L., Zou, M., 2011, "Tribological study of PTFE/Au nanoparticle composite thin films," ASME/STLE 2011 International Joint Tribology Conference, IJTC 2011, October 24, 2011 - October 26, 2011, Anonymous American Society of Mechanical Engineers, Los Angeles, CA, United states, pp. 1-3.

[47] Gao, W., 2008, "Modification of Surface Tribology Characteristic of PTFE," Zhongguo Youse Jinshu Xuebao/Chinese Journal of Nonferrous Metals, **18**(6) pp. 1129-1134.

[48] Allen, G., 2002, "Adhesive Bond Tool having Improved Release Coating for Advanced Composite and Metallic Components and Method," **09/159,133**(U.S. Patent 6,365,232 B1) .

[49] Tannenbaum, H., 1993, "Non-Stick Coating System with PTFE-PFA for Concentration Gradient," U.S. Patent **762,068**(5,240,775) .

[50] Tannenbaum, H., 1992, "Non-Stick Coating System with Thin Undercoat of Polyamide Imide," U.S. Patent **396,590**(5,079,073) .

[51] Dadalas, M., Hintzer, K., Loehr, G., 2008, "Primer Coating of PTFE for Metal Substrates," **11/172,345**(U.S. Patent 7,462,667 B2) .

[52] Tannenbaum, H., 1993, "Non-Stick Coating System with PTFE-FEP for Concentration Gradient," U.S. Patent **626,491**(5,230,961) .

[53] Ou, J., Wang, J., Liu, S., 2009, "Self-Assembly and Tribological Property of a Novel 3-Layer Organic Film on Silicon Wafer with Polydopamine Coating as the Interlayer," Journal of Physical Chemistry C, **113**(47) pp. 20429-20434.

[54] Ou, J., Wang, J., Qiu, Y., 2011, "Mechanical Property and Corrosion Resistance of Zirconia/Polydopamine Nanocomposite Multilayer Films Fabricated Via a Novel Non-Electrostatic Layer-by-Layer Assembly Technique," Surface and Interface Analysis, **43**(4) pp. 803-8.

- [55] Mi, Y., Wang, Z., Liu, X., 2012, "A Simple and Feasible in-Situ Reduction Route for Preparation of Graphene Lubricant Films Applied to a Variety of Substrates," *Journal of Materials Chemistry*, **22**(16) pp. 8036-42.
- [56] Ou, J., Liu, L., Wang, J., 2012, "Fabrication and Tribological Investigation of a Novel Hydrophobic Polydopamine/Graphene Oxide Multilayer Film," *Tribology Letters*, **48**(3) pp. 407-415.
- [57] DuPont, 2006, "DuPont™ Teflon® PTFE TE-3859 Aqueous Fluoropolymers made with Echelon™ Dispersion Technology," [Online]. **2013**(08/02) pp. 4. Available: http://www2.dupont.com/Teflon_Industrial/en_US/assets/downloads/k10918.pdf
- [58] Li, D., Mueller, M. B., Gilje, S., 2008, "Processable Aqueous Dispersions of Graphene Nanosheets," *Nature Nanotechnology*, **3**(2) pp. 101-105.
- [59] Park, S., and Ruoff, R. S., 2010, "Chemical Methods for the Production of Graphenes," *Nature Nanotechnology*, **5**(4) pp. 309-309.
- [60] Cheap Tubes Inc., 2012, "TEM Image of Few Layered Graphene Oxide Sheets," (Unpublished laboratory data) Brattleboro, VT .
- [61] Taylor, E., 2012, "TGA Data for Dopamine Hydrochloride," (Unpublished laboratory data) University of Arkansas, Fayetteville .
- [62] Mc Gee, R. L., and Collier, J. R., 1986, "SOLID STATE EXTRUSION OF POLYTETRAFLUOROETHYLENE FIBERS," *Polymer Engineering and Science*, **26**(3) pp. 239-242.
- [63] Sawai, D., Watanabe, D., Morooka, N., 2006, "Superdrawing of Polytetrafluoroethylene Nascent Powder by Solid-State Coextrusion," *Journal of Polymer Science, Part B (Polymer Physics)*, **44**(23) pp. 3369-77.
- [64] Endo, R., Jounai, K., Uehara, H., 1998, "Uniaxial Drawing of Polytetrafluoroethylene Virgin Powder by Extrusion Plus Cold Tensile Draw," *Journal of Polymer Science, Part B (Polymer Physics)*, **36**(14) pp. 2551-62.

APPENDIX

Permissions to use copyrighted material:

Figure 1.1

ELSEVIER LICENSE TERMS AND CONDITIONS

Aug 19, 2013

This is a License Agreement between Justin K Carter ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Justin K Carter
Customer address	2988 W Glenmeadow Dr. FAYETTEVILLE, AR 72704
License number	3206680494233
License date	Aug 12, 2013
Licensed content publisher	Elsevier
Licensed content publication	Polymer
Licensed content title	The molecular conformations of polytetrafluoroethylene: forms II and IV
Licensed content author	E.S. Clark
Licensed content date	July 1999
Licensed content volume number	40
Licensed content issue number	16
Number of pages	7
Start Page	4659
End Page	4665
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No

Will you be translating?	No
Order reference number	
Title of your thesis/dissertation	FRICITION AND WEAR OF POLYTETRAFLUOROETHYLENE/GRAPHENE OXIDE THIN FILMS
Expected completion date	Sep 2013
Estimated size (number of pages)	67
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.0 USD / 0.0 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

 "Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. **Reservation of Rights:** Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. **License Contingent Upon Payment:** While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.
10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. **Website:** The following terms and conditions apply to electronic reserve and author websites:
Electronic reserve: If licensed material is to be posted to website, the web site is to be password-protected and made available only to bona fide students registered on a relevant course if:

This license was made in connection with a course,

This permission is granted for 1 year only. You may obtain a license for future website posting. All content posted to the web site must maintain the copyright information line on the bottom of each image,

A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>, and

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

17. **Author website** for journals with the following additional clauses:

All content posted to the web site must maintain the copyright information line on the bottom of each image, and the permission granted is limited to the personal version of your paper. You are not allowed to download and post the published electronic version of your article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx>. As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier's online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article's Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

18. **Author website** for books with the following additional clauses:

Authors are permitted to place a brief summary of their work online only.

A hyper-text must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

19. **Website** (regular and for author): A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx>. or for books to the Elsevier homepage at <http://www.elsevier.com>

20. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

21. **Other Conditions**:

v1.6

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501088599. Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

**Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006**

For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

Figure 1.2

**ELSEVIER LICENSE
TERMS AND CONDITIONS**

Aug 19, 2013

This is a License Agreement between Justin K Carter ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard,Langford Lane Kidlington,Oxford,OX5 1GB,UK
Registered Company Number	1982084
Customer name	Justin K Carter
Customer address	2988 W Glenmeadow Dr. FAYETTEVILLE, AR 72704
License number	3206680809565
License date	Aug 12, 2013
Licensed content publisher	Elsevier
Licensed content publication	Wear
Licensed content title	Friction and wear of PTFE — a review
Licensed content author	S.K. Biswas,Kalyani Vijayan
Licensed content date	15 October 1992
Licensed content volume number	158
Licensed content issue number	1-2
Number of pages	19
Start Page	193
End Page	211
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this	No

Elsevier article?
 Will you be translating? No
 Order reference number
 Title of your thesis/dissertation FRICTION AND WEAR OF POLYTETRAFLUOROETHYLENE/GRAPHENE OXIDE THIN FILMS
 Expected completion date Sep 2013
 Estimated size (number of pages) 67
 Elsevier VAT number GB 494 6272 12
 Permissions price 0.00 USD
 VAT/Local Sales Tax 0.0 USD / 0.0 GBP
 Total 0.00 USD
 Terms and Conditions

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

“Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER].” Also Lancet special credit - “Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier.”

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. **Reservation of Rights:** Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. **License Contingent Upon Payment:** While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.
10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to

Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. **Website:** The following terms and conditions apply to electronic reserve and author websites:
Electronic reserve: If licensed material is to be posted to website, the web site is to be password-protected and made available only to bona fide students registered on a relevant course if:

This license was made in connection with a course,

This permission is granted for 1 year only. You may obtain a license for future website posting,

All content posted to the web site must maintain the copyright information line on the bottom of each image,

A hyper-text must be included to the Homepage of the journal from which you are licensing at

<http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at

<http://www.elsevier.com> , and

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

17. **Author website** for journals with the following additional clauses:

All content posted to the web site must maintain the copyright information line on the bottom of each image, and the permission granted is limited to the personal version of your paper. You are not allowed to download and post the published electronic version of your article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version.

A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> . As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier's online service

ScienceDirect (www.sciencedirect.com). That e-mail will include the article's Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

18. **Author website** for books with the following additional clauses:

Authors are permitted to place a brief summary of their work online only.

A hyper-text must be included to the Elsevier homepage at <http://www.elsevier.com> . All content

posted to the web site must maintain the copyright information line on the bottom of each image. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

19. **Website** (regular and for author): A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or for books to the Elsevier homepage at <http://www.elsevier.com>

20. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

21. **Other Conditions**:

v1.6

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501088602. Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

**Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006**

For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

Figure 1.3



Justin Carter <justinkc3788@gmail.com>

SV: Permission to use image in thesis

All, Fredrik <fredrik@kva.se>

Mon, Aug 19, 2013 at 2:25 AM

To: "justinkc3788@gmail.com" <justinkc3788@gmail.com>

Dear Justin Carter,

You may use the attached image in your thesis. Please be sure to add the credits © *Airi Iliste/The Royal Swedish Academy of Sciences*

A high resolution version is available at <http://kva.se/en/pressroom/Press-releases-2010/The-Nobel-Prize-in-Physics-2010/> (column to the right).

Best regards,

FREDRIK ALL

Kommunikationsansvarig/Head of Communications

Tel +46 8 673 95 63

Mobil +46 70 673 95 63

KUNGL. VETENSKAPSAKADEMIEN

THE ROYAL SWEDISH ACADEMY OF SCIENCES

Box 50005, SE-104 05 Stockholm, Sweden

Besök/Visit Lilla Frescativägen 4 A,
SE-114 18 Stockholm, Sweden

Reception +46 8 673 95 00

Fax +46 8 15 56 70

Web <http://kva.se>

Kungl. Vetenskapsakademien har till uppgift att främja vetenskaperna och stärka deras inflytande i samhället.

The Royal Swedish Academy of Sciences has as its aim to promote the sciences and strengthen their influence in society.

This e-mail message including attachments, if any, is intended for the person to whom or the entity to which it is addressed and may contain information that is privileged, confidential or exempt from disclosure under applicable law. If you are not the intended recipient, please be notified that any use, disclosure, dissemination,



Justin Carter <justinkc3788@gmail.com>

Permission Request to use Image in Thesis

airi iliste <a@airi.se>

Thu, Aug 15, 2013 at 7:27 AM

To: Justin Carter <justinkc3788@gmail.com>

Justin, thank you for asking, it's ok to use the illustration in you thesis. Good luck!
Best regards
/Airi

14 aug 2013 kl. 22:27 skrev Justin Carter <justinkc3788@gmail.com>:

Airi,

I would like to request permission to reuse an image you illustrated. I found it on the following website:

<http://www.sciencedaily.com/releases/2010/10/101005085507.htm>

I would like to put it in my thesis. My thesis it titled, "Friction and Wear of Polytetrafluoroethylene/ Graphene Oxide Composite Thin Films." This thesis will be completed at the University of Arkansas for my Master's degree in mechanical engineering. I also contacted the Royal Swedish Academy of Sciences for permission. Let me know if you have any more questions.

Kind Regards,
Justin Carter

<http://www.airi.se> | [airi iliste](http://airi.iliste.se) | [ILLUSTRA ILISTE](http://www.illustra.iliste.se) | tel 08-604 16 06 | mobil 0768-722 162

Figure 1.4

**NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS**

Aug 19, 2013

This is a License Agreement between Justin K Carter ("You") and Nature Publishing Group ("Nature Publishing Group") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Nature Publishing Group, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	3206680994626
License date	Aug 12, 2013
Licensed content publisher	Nature Publishing Group
Licensed content publication	Nature Chemistry
Licensed content title	New insights into the structure and reduction of graphite oxide
Licensed content author	Wei Gao, Lawrence B. Alemany, Lijie Ci and Pulickel M. Ajayan
Licensed content date	Jul 5, 2009
Volume number	1
Issue number	5
Type of Use	reuse in a thesis/dissertation
Requestor type	academic/educational
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
High-res required	no
Figures	Figure 1c: Model of graphene oxide
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	FRICITION AND WEAR OF POLYTETRAFLUOROETHYLENE/GRAPHENE OXIDE THIN FILMS
Expected completion date	Sep 2013
Estimated size (number of pages)	67
Total	0.00 USD
Terms and Conditions	Terms and Conditions for Permissions

Nature Publishing Group hereby grants you a non-exclusive license to reproduce this material for this purpose, and for no other use, subject to the conditions below:

1. NPG warrants that it has, to the best of its knowledge, the rights to license reuse of this material. However, you should ensure that the material you are requesting is original to Nature Publishing Group and does not carry the copyright of another entity (as credited in the published version). If the credit line on any part of the material you have requested indicates that it was reprinted or adapted by NPG with permission from another source, then you should also seek permission from that source to reuse the material.
2. Permission granted free of charge for material in print is also usually granted for any electronic version of that work, provided that the material is incidental to the work as a whole and that the electronic version is essentially equivalent to, or substitutes for, the print version. Where print permission has been granted for a fee, separate permission must be obtained for any additional, electronic re-use (unless, as in the case of a full paper, this has already been accounted for during your initial request in the calculation of a print run). NB: In all cases, web-based use of full-text articles must be authorized separately through the 'Use on a Web Site' option when requesting permission.
3. Permission granted for a first edition does not apply to second and subsequent editions and for editions in other languages (except for signatories to the STM Permissions Guidelines, or where the first edition permission was granted for free).
4. Nature Publishing Group's permission must be acknowledged next to the figure, table or abstract in print. In electronic form, this acknowledgement must be visible at the same time as the figure/table/abstract, and must be hyperlinked to the journal's homepage.
5. The credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)
For AOP papers, the credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].XXXXX)

Note: For republication from the *British Journal of Cancer*, the following credit lines apply.

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication) For AOP papers, the credit line should read:

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj. [JOURNAL ACRONYM].XXXXX)

6. Adaptations of single figures do not require NPG approval. However, the adaptation should be credited as follows:

Adapted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)

Note: For adaptation from the *British Journal of Cancer*, the following credit line applies.

Adapted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)

7. Translations of 401 words up to a whole article require NPG approval. Please visit <http://www.macmillanmedicalcommunications.com> for more information. Translations of up to a 400 words do not require NPG approval. The translation should be credited as follows:

Translated by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication).

Note: For translation from the *British Journal of Cancer*, the following credit line applies.

Translated by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)

We are certain that all parties will benefit from this agreement and wish you the best in the use of this material. Thank you.

Special Terms:

vl.1

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501088607. Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

**Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006**

For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

Figure 1.5

**NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS**

Aug 19, 2013

This is a License Agreement between Justin K Carter ("You") and Nature Publishing Group ("Nature Publishing Group") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Nature Publishing Group, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	3212630443722
License date	Aug 19, 2013
Licensed content publisher	Nature Publishing Group
Licensed content publication	Nature Materials
Licensed content title	Surface chemistry: Mussel power
Licensed content author	J. Herbert Waite
Licensed content date	Jan 1, 2008
Volume number	7
Issue number	1
Type of Use	reuse in a thesis/dissertation
Requestor type	academic/educational
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
High-res required	no
Figures	Figure 1 Dopamine is a small-molecule mimic of the adhesive proteins found in the 'footprints' of mussels. a, In their natural environment, mussels show strong adhesion to marine surfaces. b, Dopamine has a chemical structure comprising both alkylamine (yellow, lysine-like) and catechol (blue, DOPA-like) functionalities.
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	FRICITION AND WEAR OF POLYTETRAFLUOROETHYLENE/GRAPHENE OXIDE THIN FILMS
Expected completion date	Sep 2013
Estimated size (number of pages)	67

Total 0.00 USD

Terms and Conditions

Terms and Conditions for Permissions

Nature Publishing Group hereby grants you a non-exclusive license to reproduce this material for this purpose, and for no other use, subject to the conditions below:

1. NPG warrants that it has, to the best of its knowledge, the rights to license reuse of this material. However, you should ensure that the material you are requesting is original to Nature Publishing Group and does not carry the copyright of another entity (as credited in the published version). If the credit line on any part of the material you have requested indicates that it was reprinted or adapted by NPG with permission from another source, then you should also seek permission from that source to reuse the material.
2. Permission granted free of charge for material in print is also usually granted for any electronic version of that work, provided that the material is incidental to the work as a whole and that the electronic version is essentially equivalent to, or substitutes for, the print version. Where print permission has been granted for a fee, separate permission must be obtained for any additional, electronic re-use (unless, as in the case of a full paper, this has already been accounted for during your initial request in the calculation of a print run). NB: In all cases, web-based use of full-text articles must be authorized separately through the 'Use on a Web Site' option when requesting permission.
3. Permission granted for a first edition does not apply to second and subsequent editions and for editions in other languages (except for signatories to the STM Permissions Guidelines, or where the first edition permission was granted for free).
4. Nature Publishing Group's permission must be acknowledged next to the figure, table or abstract in print. In electronic form, this acknowledgement must be visible at the same time as the figure/table/abstract, and must be hyperlinked to the journal's homepage.
5. The credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)
For AOP papers, the credit line should read:
Reprinted by permission from Macmillan Publishers Ltd: [JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.[JOURNAL ACRONYM].XXXXXX)

Note: For republication from the *British Journal of Cancer*, the following credit lines apply.

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication) For AOP papers, the credit line should read:

Reprinted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK:

[JOURNAL NAME], advance online publication, day month year (doi: 10.1038/sj.
[JOURNAL ACRONYM].XXXXX)

6. Adaptations of single figures do not require NPG approval. However, the adaptation should be credited as follows:

Adapted by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication)

Note: For adaptation from the *British Journal of Cancer*, the following credit line applies.

Adapted by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)

7. Translations of 401 words up to a whole article require NPG approval. Please visit <http://www.macmillanmedicalcommunications.com> for more information. Translations of up to a 400 words do not require NPG approval. The translation should be credited as follows:

Translated by permission from Macmillan Publishers Ltd: [JOURNAL NAME] (reference citation), copyright (year of publication).

Note: For translation from the *British Journal of Cancer*, the following credit line applies.

Translated by permission from Macmillan Publishers Ltd on behalf of Cancer Research UK: [JOURNAL NAME] (reference citation), copyright (year of publication)

We are certain that all parties will benefit from this agreement and wish you the best in the use of this material. Thank you.

Special Terms:

v1.1

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501093541. Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

**Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006**

For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable

license for your reference. No payment is required.

Figure 2.1



Justin Carter <justinkc3788@gmail.com>

FW: Open Government Licence.htm [UNCLASSIFIED]

1 message

Alexander, Hugh <Hugh.Alexander@nationalarchives.gsi.gov.uk>
To: "justinkc3788@gmail.com" <justinkc3788@gmail.com>

Wed, Aug 21, 2013 at 9:45 AM

This is what you need to clear this item, Justin.

Regards

Hugh

Hugh Alexander

Image Library Deputy Manager

The National Archives

Kew Richmond

Surrey TW9 4DU

t: +44 (0)20 8392 5225

F: +44(0)20 8487 1974

M:+44 07956 134076

E: image-library@nationalarchives.gov.uk

www.nationalarchives.gov.uk



Open Government Licence
for public sector information

delivered by
A The National Archives

[Back to The National Archives](#)

You are encouraged to use and re-use the Information that is available under this licence, the Open Government Licence, freely and flexibly, with only a few conditions.

Using information under this licence

Use of copyright and database right material expressly made available under this licence (the "Information") indicates your acceptance of the terms and conditions below.

The Licensor grants you a worldwide, royalty-free, perpetual, non-exclusive licence to use the Information subject to the conditions below.

This licence does not affect your freedom under fair dealing or fair use or any other copyright or database right exceptions and limitations.

You are free to:

- copy, publish, distribute and transmit the Information;
- adapt the Information;
- exploit the Information commercially for example, by combining it with other Information, or by including it in your own product or application.

You must, where you do any of the above:

- acknowledge the source of the Information by including any attribution statement specified by the Information Provider(s) and, where possible, provide a link to this licence;

If the Information Provider does not provide a specific attribution statement, or if you are using Information from several Information Providers and multiple attributions are not practical in your product or application, you may consider using the following:

Contains public sector information licensed under the Open Government Licence v1.0.

- ensure that you do not use the Information in a way that suggests any official status or that the Information Provider endorses you or your use of the Information;
- ensure that you do not mislead others or misrepresent the Information or its source;
- ensure that your use of the Information does not breach the Data Protection Act 1998 or the Privacy and Electronic Communications (EC Directive) Regulations 2003.

These are important conditions of this licence and if you fail to comply with them the rights granted to you under this licence, or any similar licence granted by the Licensor, will end automatically.

! Exemptions

This licence does not cover the use of:

- personal data in the Information;
- Information that has neither been published nor disclosed under information access legislation (including the Freedom of Information Acts for the UK and Scotland) by or with the consent of the Information Provider;
- departmental or public sector organisation logos, crests and the Royal Arms except where they form an integral part of a document or dataset;

- military insignia;
- third party rights the Information Provider is not authorised to license;
- Information subject to other intellectual property rights, including patents, trademarks, and design rights; and
- identity documents such as the British Passport.

No warranty

The Information is licensed "as is" and the Information Provider excludes all representations, warranties, obligations and liabilities in relation to the Information to the maximum extent permitted by law.

The Information Provider is not liable for any errors or omissions in the Information and shall not be liable for any loss, injury or damage of any kind caused by its use. The Information Provider does not guarantee the continued supply of the Information.

Governing Law

This licence is governed by the laws of the jurisdiction in which the Information Provider has its principal place of business, unless otherwise specified by the Information Provider.

Definitions

In this licence, the terms below have the following meanings:

Information

means information protected by copyright or by database right (for example, literary and artistic works, content, data and source code) offered for use under the terms of this licence.

Information Provider

means the person or organisation providing the Information under this licence.

Licensors

means any Information Provider which has the authority to offer Information under the terms of this licence or the Controller of Her Majesty's Stationery Office, who has the authority to offer Information subject to Crown copyright and Crown database rights and Information subject to copyright and database right that has been assigned to or acquired by the Crown, under the terms of this licence.

Use

as a verb, means doing any act which is restricted by copyright or database right, whether in the original medium or in any other medium, and includes without limitation distributing, copying, adapting, modifying as may be technically necessary to use it in a different mode or format.

You

means the natural or legal person, or body of persons corporate or incorporate, acquiring rights under this licence.

About the Open Government Licence

The Controller of Her Majesty's Stationery Office (HMSO) has developed this licence as a tool to enable Information Providers in the public sector to license the use and re-use of their Information under a common open licence. The Controller invites public sector bodies owning their own copyright and database rights to permit the use of their Information under this licence.

The Controller of HMSO has authority to license Information subject to copyright and database right owned by the Crown. The extent of the Controller's offer to license this Information under the terms of this licence is set out in the UK Government Licensing Framework.

This is version 1.0 of the Open Government Licence. The Controller of HMSO may, from time to time, issue new versions of the Open Government Licence. However, you may continue to use Information licensed under this version should you wish to do so.

These terms have been aligned to be interoperable with any Creative Commons Attribution Licence, which covers copyright, and Open Data Commons Attribution License, which covers database rights and applicable copyrights.

Further context, best practice and guidance can be found in the UK Government Licensing Framework section on The National Archives website.

Please don't print this e-mail unless you really need to.

National Archives Disclaimer

This email and any files transmitted with it are intended solely for the use of the individual(s) to whom they are addressed. If you are not the intended recipient and have received this email in error, please notify the sender and delete the email. Opinions, conclusions and other information in this message and attachments that do not relate to the official business of The National Archives are neither given nor endorsed by it.

Information in this email including any attachments may be privileged, confidential and is intended exclusively for the addressee. The views expressed may not be official policy, but the personal views of the originator. If you have received it in error, please notify the sender by return e-mail and delete it from your system. You should not reproduce, distribute, store, retransmit, use or disclose its contents to anyone. Please note we reserve the right to monitor all e-mail communication through our internal and external networks. SKY and the SKY marks are trade marks of British Sky Broadcasting Group plc and are used under licence. British Sky Broadcasting Limited (Registration No. 2906991), Sky Interactive Limited (Registration No. 3554332), Sky-In-Home Service Limited (Registration No. 2067075) and Sky Subscribers Services Limited (Registration No. 2340150) are direct or indirect subsidiaries of British Sky Broadcasting Group plc (Registration No. 2247735). All of the companies mentioned in this paragraph are incorporated in England and Wales and share the same registered office at Grant Way, Isleworth, Middlesex TW7 5QD.

This email was received from the INTERNET and scanned by the Government Secure Intranet anti-virus service supplied by Vodafone in partnership with Symantec. (CCTM Certificate Number 2009/09/0052.) In case of problems, please call your organisation's IT Helpdesk. Communications via the GSI may be automatically logged, monitored and/or recorded for legal purposes.

Please don't print this e-mail unless you really need to.

National Archives Disclaimer

This email and any files transmitted with it are intended solely for the use of the individual(s) to whom they are addressed. If you are not the intended recipient and have received this email in error, please notify the sender and delete the email. Opinions, conclusions and other information in this message and attachments that do not relate to the official business of The National Archives are neither given nor endorsed by it.

Figure 2.2



Justin Carter <justinkc3788@gmail.com>

Requesting permission to use image from paper published in tribology transactions

Karl Phipps <kphipps@stle.org>
To: Justin Carter <justinkc3788@gmail.com>

Wed, Aug 14, 2013 at 12:24 PM

Hi Justin,

Thanks for contacting STLE. That shouldn't be a problem, and you have STLE's permission to use the following figure in your thesis paper. We would just ask if you could please provide the following acknowledgment to STLE:

Reprinted with permission in *Tribology Transactions*, the bi-monthly peer-review journal published by the Society of Tribologists and Lubrication Engineers, a not-for-profit professional society headquartered in Park Ridge, Ill., www.stle.org.

If you need anything else, please let me know.

Thanks, Justin, and good luck!

Best regards,

Karl

Karl Phipps
Associate Director of Communications

STLE
840 Busse Highway
Park Ridge, Illinois 60068 (USA)
1.847.825.5536 ext. 203 (phone)
1.847.825.1456 (fax)

khipps@stle.org

www.stle.org

From: Justin Carter [mailto:justinkc3788@gmail.com]
Sent: Monday, August 12, 2013 4:14 PM
To: Karl Phipps
Subject: Requesting permission to use image from paper published in tribology transactions

Mr. Phipps,

I would like to request permission to use an image in my thesis from a paper published by STLE in Tribology Transactions. The title of the paper is: Effect of Particle Size on the Wear Resistance of Alumina-Filled PTFE Micro- and Nanocomposite by Steven McElwain. Figure 3 is the figure I'd like to use.

Here is an excerpt at the top of the paper that I'm talking about:

Tribology Transactions, 51: 247-253, 2008

Copyright © Society of Tribologists and Lubrication Engineers

ISSN: 1040-2004 print / 1547-357X online

DOI: 10.1080/10402000701730494

If it helps, I am a member of STLE and attended the recent conference in Detroit.

Thanks,

Justin Carter

Figure 2.3 and Figure 2.4

ELSEVIER LICENSE TERMS AND CONDITIONS

Aug 19, 2013

This is a License Agreement between Justin K Carter ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Justin K Carter
Customer address	2988 W Glenmeadow Dr. FAYETTEVILLE, AR 72704
License number	3206691149473
License date	Aug 12, 2013
Licensed content publisher	Elsevier
Licensed content publication	Carbon
Licensed content title	Suppression of wear in graphene polymer composites
Licensed content author	Sashi S. Kandamur, Mohammad A. Rafiee, Fazel Yavari, Michael Schrameyer, Zhong-Zhen Yu, Thierry A. Blanchet, Nikhil Koratkar
Licensed content date	August 2012
Licensed content volume number	50
Licensed content issue number	9
Number of pages	6
Start Page	3178
End Page	3183
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
Format	both print and electronic

Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Title of your thesis/dissertation	FRICTION AND WEAR OF POLYTETRAFLUOROETHYLENE/GRAPHENE OXIDE THIN FILMS
Expected completion date	Sep 2013
Estimated size (number of pages)	67
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.0 USD / 0.0 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

“Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER].” Also Lancet special credit - “Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier.”

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. **Reservation of Rights:** Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. **License Contingent Upon Payment:** While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.
10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to

Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. Translation: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. Website: The following terms and conditions apply to electronic reserve and author websites:
Electronic reserve: If licensed material is to be posted to website, the web site is to be password-protected and made available only to bona fide students registered on a relevant course if

This license was made in connection with a course,

This permission is granted for 1 year only. You may obtain a license for future website posting. All content posted to the web site must maintain the copyright information line on the bottom of each image,

A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>, and

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

17. Author website for journals with the following additional clauses:

All content posted to the web site must maintain the copyright information line on the bottom of each image, and the permission granted is limited to the personal version of your paper. You are not allowed to download and post the published electronic version of your article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx>. As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier's online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article's Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

18. Author website for books with the following additional clauses:

Authors are permitted to place a brief summary of their work online only.

A hyper-text must be included to the Elsevier homepage at <http://www.elsevier.com>. All content

posted to the web site must maintain the copyright information line on the bottom of each image. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

19. **Website** (regular and for author): A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or for books to the Elsevier homepage at <http://www.elsevier.com>

20. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

21. **Other Conditions**:

v1.6

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501088623. Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

**Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006**

For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

Figure 2.5



Permissions

8/19/2013

T & F Reference Number: P081913-06

Justin Carter
justinkc3788@gmail.com

Dear Mr. Carter:

We are in receipt of your request to reproduce the image of the article

"Frictional Characteristics of Ultra-Thin Polytetrafluoroethylene (PTFE) Films Deposited by Hot Filament-Chemical Vapor Deposition (HFCVD)", MICHAEL A. KARNATH, QIAN SHENG, ALEKSANDR J. WHITE et al , 2010, *Tribology Transactions*, Volume 54, Issue 1, pp. 36-43 .

to be included in the publication of your dissertation

This permission is all for editions, both print and electronic.

We will be pleased to grant you permission free of charge on the condition that:

This permission is limited to non-exclusive world rights for this usage only.

This permission does not cover any third party copyrighted work which may appear in the material requested.

Full acknowledgement must be included showing article title, author, and full Journal title, reprinted by permission of Taylor & Francis (<http://www.tandfonline.com>).

Thank you very much for your interest in Taylor & Francis publications. Should you have any questions or require further assistance, please feel free to contact me directly.

Sincerely,

Mary Ann Muller
Permissions Coordinator
Telephone: 215.606.4334
E-mail: maryann.muller@taylorandfrancis.com

Figure 2.6, Figure 2.7, Figure 2.8, and Figure 2.9



Justin Carter <justinkc3788@gmail.com>

Re: Request for reuse of an image in thesis from Journal of Nanoscience and Nanotechnology

nalwa@mindspring.com <nalwa@mindspring.com>
Reply-To: nalwa@mindspring.com
To: Justin Carter <justinkc3788@gmail.com>

Tue, Aug 13, 2013 at 3:55 PM

Dear Justin:

American Scientific Publishers grants permission to use Figure 4, 5, 6 and 8 from D. P. Lim, J. Y. Lee, D. S. Lim, S. G. Ahn, and I. W. Lyo, Effect of Reinforcement Particle Size on the Tribological Properties of Nano-Diamond Filled Polytetrafluoroethylene Based Coating, *Journal of Nanoscience and Nanotechnology*, vol.9, pp. 4197–4201 (2009) in the forthcoming PhD thesis entitled "Friction and Wear of Polytetrafluoroethylene/Graphene Oxide Composite Thin Films" to be submitted to the University of Arkansas in Fayetteville. The permission is granted for print and online editions in English medium only. A proper credit by citing full reference should be given in figure captions.

H. S. Nalwa

American Scientific Publishers

www.aspbs.com

—Original Message—

From: Justin Carter
Sent: Aug 13, 2013 10:42 AM
To: nalwa@mindspring.com
Subject: Re: Request for reuse of an image in thesis from Journal of Nanoscience and Nanotechnology

Dr. Nalwa,

Attached is the research paper I'm wanting to reuse images from. It is titled: Effect of Reinforcement Particle Size on the Tribological Properties of Nano-Diamond Filled Polytetrafluoroethylene Based Coating. The journal is *Journal of Nanoscience and Nanotechnology* Vol.9, 4197–4201, 2009. My thesis title is *Friction and Wear of Polytetrafluoroethylene/Graphene Oxide Composite Thin Films*. I'd like to request permission to use Figure 4, Figure 5, Figure 6, and Figure 8 in my thesis. My university is the University of Arkansas in Fayetteville. Let me know if you need anymore information.

Thanks,
Justin Carter

On Mon, Aug 12, 2013 at 5:36 PM, wrote:

> Please give details of research paper from which you want to reuse an
> image and title of your PhD thesis and university, etc.

>
>
,

Figure 2.10

**JOHN WILEY AND SONS LICENSE
TERMS AND CONDITIONS**

Aug 19, 2013

This is a License Agreement between Justin K Carter ("You") and John Wiley and Sons ("John Wiley and Sons") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by John Wiley and Sons, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	3206710601022
License date	Aug 12, 2013
Licensed content publisher	John Wiley and Sons
Licensed content publication	Surface & Interface Analysis
Licensed content title	Mechanical property and corrosion resistance of zirconia/polydopamine nanocomposite multilayer films fabricated via a novel non-electrostatic layer-by-layer assembly technique
Licensed copyright line	Copyright © 2010 John Wiley & Sons, Ltd.
Licensed content author	Junfei Ou, Jinqing Wang, Yinong Qiu, Lanzhong Liu, Shengrong Yang
Licensed content date	Jun 22, 2010
Start page	803
End page	808
Type of use	Dissertation/Thesis
Requestor type	University/Academic
Format	Print and electronic
Portion	Figure/table
Number of figures/tables	1
Original Wiley figure/table number(s)	Figure 1. A schematic view for constructing ZrO ₂ /PDA nanocomposite multilayer films.
Will you be translating?	No
Total	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or a society for whom a Wiley Company has exclusive publishing rights in relation to a particular journal (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms

and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

1. The materials you have requested permission to reproduce (the "Materials") are protected by copyright.
2. You are hereby granted a personal, non-exclusive, non-sublicensable, non-transferable, worldwide, limited license to reproduce the Materials for the purpose specified in the licensing process. This license is for a one-time use only with a maximum distribution equal to the number that you identified in the licensing process. Any form of republication granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before may be distributed thereafter). The Materials shall not be used in any other manner or for any other purpose. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Material. Any third party material is expressly excluded from this permission.
3. With respect to the Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Materials without the prior permission of the respective copyright owner. You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Materials, or any of the rights granted to you hereunder to any other person.
4. The Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc or one of its related companies (WILEY) or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto.
5. NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS,

INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.

6. WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.

7. You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.

8. IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.

9. Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.

10. The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.

11. This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

12. Any fee required for this permission shall be non-refundable after thirty (30) days from receipt

13. These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in

writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

14. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.

15. WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

16. This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

17. This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

Wiley Open Access Terms and Conditions

Wiley publishes Open Access articles in both its Wiley Open Access Journals program [<http://www.wileyopenaccess.com/view/index.html>] and as Online Open articles in its subscription journals. The majority of Wiley Open Access Journals have adopted the Creative Commons Attribution License (CC BY) which permits the unrestricted use, distribution, reproduction, adaptation and commercial exploitation of the article in any medium. No permission is required to use the article in this way provided that the article is properly cited and other license terms are observed. A small number of Wiley Open Access journals have retained the Creative Commons Attribution Non Commercial License (CC BY-NC), which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

Online Open articles - Authors selecting Online Open are, unless particular exceptions apply, offered a choice of Creative Commons licenses. They may therefore select from the CC BY, the CC BY-NC and the Attribution-NoDerivatives (CC BY-NC-ND). The CC BY-NC-ND is more restrictive than the CC BY-NC as it does not permit adaptations or modifications without rights holder consent.

Wiley Open Access articles are protected by copyright and are posted to repositories and websites in accordance with the terms of the applicable Creative Commons license referenced on the article. At the time of deposit, Wiley Open Access articles include all changes made during peer review, copyediting, and publishing. Repositories and websites that host the article are responsible for incorporating any publisher-supplied amendments or retractions issued subsequently. Wiley Open Access articles are also available without charge on Wiley's publishing platform,

Wiley Online Library or any successor sites.

Conditions applicable to all Wiley Open Access articles:

- The authors' moral rights must not be compromised. These rights include the right of "paternity" (also known as "attribution" - the right for the author to be identified as such) and "integrity" (the right for the author not to have the work altered in such a way that the author's reputation or integrity may be damaged).
- Where content in the article is identified as belonging to a third party, it is the obligation of the user to ensure that any reuse complies with the copyright policies of the owner of that content.
- If article content is copied, downloaded or otherwise reused for research and other purposes as permitted, a link to the appropriate bibliographic citation (authors, journal, article title, volume, issue, page numbers, DOI and the link to the definitive published version on Wiley Online Library) should be maintained. Copyright notices and disclaimers must not be deleted.
 - Creative Commons licenses are copyright licenses and do not confer any other rights, including but not limited to trademark or patent rights.
- Any translations, for which a prior translation agreement with Wiley has not been agreed, must prominently display the statement: "This is an unofficial translation of an article that appeared in a Wiley publication. The publisher has not endorsed this translation."

Conditions applicable to non-commercial licenses (CC BY-NC and CC BY-NC-ND)

For non-commercial and non-promotional purposes individual non-commercial users may access, download, copy, display and redistribute to colleagues Wiley Open Access articles. In addition, articles adopting the CC BY-NC may be adapted, translated, and text- and data-mined subject to the conditions above.

Use by commercial "for-profit" organizations

Use of non-commercial Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee. Commercial purposes include:

- Copying or downloading of articles, or linking to such articles for further redistribution, sale or licensing;
- Copying, downloading or posting by a site or service that incorporates advertising with such content;
- The inclusion or incorporation of article content in other works or services (other than

normal quotations with an appropriate citation) that is then available for sale or licensing, for a fee (for example, a compilation produced for marketing purposes, inclusion in a sales pack)

- Use of article content (other than normal quotations with appropriate citation) by for-profit organizations for promotional purposes
- Linking to article content in e-mails redistributed for promotional, marketing or educational purposes;
- Use for the purposes of monetary reward by means of sale, resale, license, loan, transfer or other form of commercial exploitation such as marketing products
- Print reprints of Wiley Open Access articles can be purchased from: corporatesales@wiley.com

The modification or adaptation for any purpose of an article referencing the CC BY-NC-ND License requires consent which can be requested from RightsLink@wiley.com.

Other Terms and Conditions:

BY CLICKING ON THE "I AGREE..." BOX, YOU ACKNOWLEDGE THAT YOU HAVE READ AND FULLY UNDERSTAND EACH OF THE SECTIONS OF AND PROVISIONS SET FORTH IN THIS AGREEMENT AND THAT YOU ARE IN AGREEMENT WITH AND ARE WILLING TO ACCEPT ALL OF YOUR OBLIGATIONS AS SET FORTH IN THIS AGREEMENT.

v1.8

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501088644. Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

**Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006**

For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

Figure 2.11

**SPRINGER LICENSE
TERMS AND CONDITIONS**

Aug 19, 2013

This is a License Agreement between Justin K Carter ("You") and Springer ("Springer") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Springer, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	3206710690375
License date	Aug 12, 2013
Licensed content publisher	Springer
Licensed content publication	Tribology Letters
Licensed content title	Fabrication and Tribological Investigation of a Novel Hydrophobic Polydopamine/Graphene Oxide Multilayer Film
Licensed content author	Junfei Ou
Licensed content date	Jan 1, 2012
Volume number	48
Issue number	3
Type of Use	Thesis/Dissertation
Portion	Figures
Author of this Springer article	No
Order reference number	
Title of your thesis / dissertation	FRICITION AND WEAR OF POLYTETRAFLUOROETHYLENE/GRAPHENE OXIDE THIN FILMS
Expected completion date	Sep 2013
Estimated size(pages)	67
Total	0.00 USD

Terms and Conditions

Introduction

The publisher for this copyrighted material is Springer Science + Business Media. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

Limited License

With reference to your request to reprint in your thesis material on which Springer Science and Business Media control the copyright, permission is granted, free of charge, for the use indicated in your enquiry.

Licenses are for one-time use only with a maximum distribution equal to the number that you identified in the licensing process.

This License includes use in an electronic form, provided its password protected or on the university's intranet or repository, including UMI (according to the definition at the Sherpa website: <http://www.sherpa.ac.uk/romeo/>). For any other electronic use, please contact Springer at (permissions.dordrecht@springer.com or permissions.heidelberg@springer.com).

The material can only be used for the purpose of defending your thesis, and with a maximum of 100 extra copies in paper.

Although Springer holds copyright to the material and is entitled to negotiate on rights, this license is only valid, subject to a courtesy information to the author (address is given with the article/chapter) and provided it concerns original material which does not carry references to other sources (if material in question appears with credit to another source, authorization from that source is required as well).

Permission free of charge on this occasion does not prejudice any rights we might have to charge for reproduction of our copyrighted material in the future.

Altering/Modifying Material: Not Permitted

You may not alter or modify the material in any manner. Abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of the author(s) and/or Springer Science + Business Media. (Please contact Springer at (permissions.dordrecht@springer.com or permissions.heidelberg@springer.com))

Reservation of Rights

Springer Science + Business Media reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

Copyright Notice:Disclaimer

You must include the following copyright and permission notice in connection with any reproduction of the licensed material: "Springer and the original publisher /journal title, volume, year of publication, page, chapter/article title, name(s) of author(s), figure number(s), original copyright notice) is given to the publication in which the material was originally published, by adding: with kind permission from Springer Science and Business Media"

Warranties: None

Example 1: Springer Science + Business Media makes no representations or warranties with respect to the licensed material.

Example 2: Springer Science + Business Media makes no representations or warranties with respect to the licensed material and adopts on its own behalf the limitations and disclaimers established by CCC on its behalf in its Billing and Payment terms and conditions for this licensing transaction.

Indemnity

You hereby indemnify and agree to hold harmless Springer Science + Business Media and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

No Transfer of License

This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without Springer Science + Business Media's written permission.

No Amendment Except in Writing

This license may not be amended except in a writing signed by both parties (or, in the case of Springer Science + Business Media, by CCC on Springer Science + Business Media's behalf).

Objection to Contrary Terms

Springer Science + Business Media hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and Springer Science + Business Media (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

Jurisdiction

All disputes that may arise in connection with this present License, or the breach thereof, shall be settled exclusively by arbitration, to be held in The Netherlands, in accordance with Dutch law, and to be conducted under the Rules of the 'Netherlands Arbitrage Instituut' (Netherlands Institute of Arbitration). **OR:**

All disputes that may arise in connection with this present License, or the breach thereof, shall be settled exclusively by arbitration, to be held in the Federal Republic of Germany, in accordance with German law.

Other terms and conditions:

v1.3

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501088645. Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

**Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006**

**For suggestions or comments regarding this order, contact RightsLink Customer Support:
customer care@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.**

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.
