Adhesion and Deformation Mechanisms of Polydopamine and Polytetrafluoroethylene: A Multiscale Computational Study

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Adhesion and Deformation Mechanisms of Polydopamine and Polytetrafluoroethylene: A Multiscale Computational Study

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering, with a concentration in Mechanical Engineering

by

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Brigham Young University – Idaho
Bachelor of Science in Physics, 2015

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This dissertation is approved for recommendation to the Graduate Council.

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Abstract

Polytetrafluoroethylene (PTFE) has an exceptionally low coefficient of friction, but a high wear rate. Polydopamine (PDA) has been shown to bond via covalent bonding, van der Waals forces, and hydrogen bonding and is known to adhere strongly to almost any material. The application of PDA between a substrate and a PTFE surface coating has resulted in low friction and a greatly reduced wear rate. Previous research probing the capabilities and limitations of PDA/PTFE films have studied the wear and mechanical properties of the film, but the overall adhesive and deformation mechanisms remain unclear.

In this research, we investigate the tribological properties of PDA and PTFE molecules and composites from the atomic to the microscale using computational modeling. Molecular dynamics is used to investigate the mechanical properties of individual PTFE chains. The elastic moduli of varying lengths of PTFE molecules are tested in vacuum and in water and at varying temperatures, showing how the chain length and the surrounding environment affect the elastic strength of PTFE molecules. The deformation mechanisms of a nanoscale PTFE film are observed during an indentation and scratch test, and various scratch angles are used during the scratch tests to elucidate the deformation mechanisms of individual PTFE chains within a film. Based on molecular dynamics simulations, a coarse-grained model of PTFE is developed which allows modeling of PTFE particles and films up to the microscale. Micrometer sized PTFE particles are then modeled which show that frictional values of PTFE are dependent on the surface topography.

Individual properties of PDA and PTFE molecules are investigated with density functional theory and molecular dynamics simulations. The adhesive properties of each molecule are tested as well as the deformation mechanisms. The primary source of adhesion between the PDA and PTFE molecules was observed to be van der Waals interactions, although, hydrogen bonding was also
observed between PDA-PDA interactions. A PDA/PTFE thin film composite is studied, and an indentation and scratch test are performed to uncover deformation mechanisms. During scratch tests of the PDA/PTFE composite, a tenacious layer of PTFE is observed to adhere to the PDA substrate similar to experimental observations of PDA/PTFE composite films. Due to PTFE molecules penetrating the PDA substrate, and the unique deformation mechanisms of PDA oligomers, peeling is highly unlikely at the PDA/PTFE interface which increases wear resistance of the film.

To continue the investigation of PTFE films and particles, the coarse-grained model was used to investigate PTFE films annealed for 0-, 4- and 8-minutes. PTFE films were created using images of experimental PTFE films taken by atomic force microscopy. The properties of PTFE films are investigated to understand how the chain length and film density affect the formation of the film, and the coefficient of friction. A machine learning algorithm is developed and used to evaluate whether the numerous models created can affectively predict the coefficient of friction prior to testing. Friction was seen to be dependent on the internal fiber orientation of the films and not just the surface topography.
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Table of Contents

Chapter 1: Introduction ........................................................................................................... 1

1.1. Motivation ......................................................................................................................... 1

1.1.1. Polytetrafluoroethylene .............................................................................................. 1

1.1.2. Polydopamine ................................................................................................................. 3

1.1.3. PDA/PTFE Composites ............................................................................................... 4

1.2. Objectives .......................................................................................................................... 5

1.3. Dissertation layout ............................................................................................................. 9

1.4. References .......................................................................................................................... 9

Chapter 2: Deformation Mechanisms of Polytetrafluoroethylene at the Nano and Microscales ................................................................................................................................. 13

Abstract ..................................................................................................................................... 13

2.1. Introduction ......................................................................................................................... 14

2.2. Methods ............................................................................................................................... 16

2.2.1. Atomistic Modeling ........................................................................................................ 16

2.2.2. Coarse-grained Modeling ............................................................................................. 18

2.3. Results and Discussion ...................................................................................................... 27

2.3.1. Single Chain PTFE Simulations .................................................................................... 27

2.3.2. Elastic Modulus .............................................................................................................. 27

2.3.3. The Effects of Initial Chain Length on Maximum Stress .............................................. 29

2.3.4. The Effect of Water and Vacuum Environments on Maximum Stress ......................... 31

2.3.5. The Effect of Temperature Variation .............................................................................. 32

2.3.6. Single Chain Study Summary ....................................................................................... 33

2.4. Nanoscale Indentation and Scratch Simulations ................................................................ 33

2.4.1. Molecular Dynamics Indentation Results ..................................................................... 33
2.4.2. Nanoscale Scratch Test ................................................................. 35
2.4.3. Summary of MD Indentation and Scratch Studies ......................... 37
2.5. Coarse-grained Model Indentation and Scratch ................................ 38
  2.5.1. Indentation of Coarse-grained PTFE Particles ................................ 38
  2.5.2. Scratch Test of Coarse-grained Models ........................................ 40
  2.5.3. Summary of coarse-grained simulations ....................................... 43
2.6. Conclusions ....................................................................................... 43
2.7. Acknowledgements ............................................................................ 45
2.8. References .......................................................................................... 45

Chapter 3: Adhesion and interface properties of polydopamine and
polytetrafluoroethylene thin films ................................................................ 50

Abstract ..................................................................................................... 50
3.1. Introduction ......................................................................................... 50
3.2. Methods .............................................................................................. 53
  3.2.1. Density Functional Theory ............................................................. 53
  3.2.2. Molecular Dynamics .................................................................... 56
3.3. Results and Discussion ....................................................................... 58
  3.3.1. Adhesion between PTFE and PDA ............................................... 58
  3.3.2. Adsorption Energy ...................................................................... 60
  3.3.3. Shear, Peel and Rotation Tests ...................................................... 61
  3.3.4. PTFE and PDA Thin Film ............................................................. 63
  3.3.5. Indentation .................................................................................... 64
  3.3.6. Scratch ........................................................................................ 66
3.4. Conclusions ......................................................................................... 68
3.5. Acknowledgements .............................................................................. 70
Chapter 4: The effect of density and surface topography on the coefficient of friction of polytetrafluoroethylene films

Abstract

4.1. Introduction

4.2. Methods

4.3. Results and discussion

4.4. Conclusions

4.5. Acknowledgments

4.6. References

4.7. Supplementary Materials

4.7.1. Convolutional neural network (CNN) architecture and validation

4.7.2. Chain length and the effect on image resolution

4.7.3. Indenter radius results and discussion

4.7.4. Comparison of 3 nm and 30 nm scratch length

4.7.5. Characterization of film dataset

4.7.6. Internal fiber orientation image creation

4.7.7. Internal fiber orientation simulations

4.7.8. References

Chapter 5: Conclusions

5.1. Investigating the effects of environmental conditions on mechanical properties of PTFE chains

5.1.1. The wear and mechanical properties of PTFE chains

5.1.2. The wear and mechanical properties of PTFE nano-film

5.1.3. Investigate PTFE topography change due to annealing

5.2. Investigating adhesion and interfacial properties of PDA/PTFE composites
5.2.1. The adhesion of polydopamine oligomers ......................................................... 100
5.2.2. PDA and PTFE film deformation mechanisms ................................................. 101
5.3. Using coarse-grained modeling techniques to investigate friction and wear on microscale particles and films ................................................................. 103
5.3.1. Coarse-grained modeling to examine deformation of PTFE on experimental scales ........................................................................................................ 103
5.3.2. Investigate friction of realistic PTFE models .................................................. 103
5.3.3. Confirming experimental observations of released PTFE fibers ..................... 105
5.3.4. Adhesion between microscale PTFE particles ................................................. 105
5.4. Future Work ........................................................................................................ 106
5.5. References .......................................................................................................... 107

Chapter 6: Supplementary Material ........................................................................ 108

6.1. The effects of annealing conditions on the wear of PDA/PTFE coatings .......... 108
6.1.1. Introduction ...................................................................................................... 108
6.1.2. Methods .......................................................................................................... 109
6.1.3. Results ............................................................................................................ 109
6.1.4. Conclusions .................................................................................................... 112
6.1.5. References ..................................................................................................... 113
6.2. Rapid deposition of uniform polydopamine coatings on nanoparticle surfaces with controllable thickness ................................................................................. 114
6.2.1. Introduction ..................................................................................................... 114
6.2.2. Methods .......................................................................................................... 115
6.2.3. Results ............................................................................................................ 115
6.2.4. Conclusions .................................................................................................... 119
6.2.5. References ..................................................................................................... 119
List of Published Papers

Chapter 2

Chapter 3

Chapter 4

Supplementary Material – Section 6.1

Supplementary Material – Section 6.2
Chapter 1: Introduction

1.1. Motivation

1.1.1. Polytetrafluoroethylene

Polytetrafluoroethylene (PTFE) was accidentally discovered in 1938\(^1\) and has since been investigated for many applications in the biomedical field\(^2^3\), energy systems\(^4\), microfluidic systems\(^5\), and as a surface coating. PTFE is chemically inert, heat resistant, and hydrophobic, which in part contributes to its wide use and study.\(^5^7\) PTFE is a polymer with a carbon backbone surrounded by fluorine atoms and contains a 15/7 helical conformation (Figure 1.1).\(^8^10\) Due to its rigid, rod-like molecular profile it has an exceptionally low coefficient of friction.\(^8\)

![Figure 1.1 PTFE chain at equilibrium showing carbon backbone and helical structure. A) Orthographic view showing the entire length of the chain. B) Close up view showing the helical structure of the chain.](image)

Reducing the friction between surfaces has been a driving motivator for PTFE research and has contributed to a thorough investigation of the material. When PTFE is in contact with another surface, a transfer film is formed which helps reduce the coefficient of friction between PTFE and the countersurface.\(^11^13\) The coefficient of friction of PTFE has been observed to be dependent on
the sliding orientation.\textsuperscript{14} As the sliding orientation changes, the coefficient of friction increases. However, as the rubbing distance increases and film transfer occurs, the coefficient of friction again decreases.\textsuperscript{8, 15} The low coefficient of friction is partially attributed to the structure of the individual chains, allowing a smooth sliding between aligned PTFE chains during rubbing.\textsuperscript{8, 12}

Properties of individual molecules of PTFE can be investigated with the use of molecular dynamics simulations. Multiple simulations involving PTFE chains oriented perpendicular and parallel to each other have been considered in previous literature.\textsuperscript{14, 16-18} PTFE chains are broken during rubbing of the surface, these chains undergo large deformation during the rubbing test.\textsuperscript{17-18} These simulations also showed that as rubbing direction changes, PTFE chains will reorient themselves parallel to rubbing direction.\textsuperscript{18} The lowest coefficient of friction of PTFE sliding on PTFE was reported to occur when PTFE chains are oriented parallel to the rubbing direction.\textsuperscript{18} Through these simulations, it is apparent that the macroscale properties of PTFE, such as the coefficient of friction, are affected by nanoscale behavior of individual PTFE chains. Few studies of PTFE have incorporated nanoscale phenomena to explain effects of macroscale PTFE properties.

While the coefficient of friction of PTFE is impressive, the wear rate is not. Delamination, debris formation and chain scission all contribute to wear in PTFE films.\textsuperscript{14, 19-20} The wear rate of macroscale PTFE increases with sliding distance.\textsuperscript{21} While observing sliding on the atomistic scale, carbon-carbon bonds are broken in individual PTFE chains during frictional heating, and a thin layer of PTFE is observed to adhere to the counterface. One experimental study reported that broken PTFE chains adhere to a metal counter surface allowing buildup on the counter surface film.\textsuperscript{13} This thin layer of PTFE increases in thickness as the number of rubbing cycles increases.\textsuperscript{12} While it appears the wear of PTFE may help in reducing the coefficient of friction, being able to
discover a way to prevent wear of the PTFE substrate while also keeping the coefficient of friction low would be ideal.

Because chain scission has been reported during testing of PTFE films, the mechanical properties of PTFE may help explain failure mechanisms of PTFE films. The elastic properties of PTFE have been calculated using force field calculations and density functional theory. A study by D’Amore et al investigating the effects of temperature on the physical structure of PTFE showed that at temperatures above 30 ºC, the uniformity of the helical structure diminishes, and takes on a disordered conformation. The helical structure has also been observed to reverse the spiral direction at high temperatures. The effect of the length of the PTFE chain was shown to alter the bond length, angle, and dihedral angles between atoms, but how this affects the mechanical properties of the chain has not yet been addressed. Rudimentary simulations were performed on PTFE molecules which predicted that PTFE chains without a 15/7 helix would soften compared to chains with the helix present.

PTFE composites have been created and tested in an effort to reduce wear rate, and some studies even reported a reduced coefficient of friction. An ultra-low wear PTFE film was created using a PTFE/alumina composite and reported that PTFE chains chelated to the stainless steel substrate. PTFE composites offer increased durability and strength to the PTFE while still providing low coefficients of friction, desirable for mechanical applications.

1.1.2. Polydopamine

Another PTFE composite which has greatly improved the materials wear rate was the introduction of polydopamine (PDA) as a substrate. Based on the adhesive properties of mussels, PDA is a bioinspired material which has been used as a surface coating, in drug administration, and
microfluidic systems and shows promise as an additive to many materials.\textsuperscript{31-33} PDA has the ability to adhere to virtually any surface and is therefore an ideal candidate for creating low friction low wear PTFE composites.\textsuperscript{32}

PDA films consist of multiple dopamine oligomers (Figure 1.2A) which polymerize and self-assemble to form polydopamine. The dopamine molecule oxidizes to form the 5,6-dihydroxyindole (DHI) molecule (Figure 1.2B) which then forms higher order oligomers, such as dimers and trimers (Figure 1.2C).\textsuperscript{34-35} There are two possible polydopamine polymerization pathways which can occur. One through covalent bonding with the DHI molecule, and another via self-assembly of the dopamine molecules.\textsuperscript{35} Regardless of polymerization pathway, the adhesive properties of the oligomers within the PDA film are contributed to charge transfer, pi-stacking, and hydrogen bonding.\textsuperscript{35-36} It is believed that the adhesiveness of this material comes from the catechol group at the end of the dopamine benzene ring.\textsuperscript{32}

![Figure 1.2](image.png)

\textbf{Figure 1.2} A) Dopamine molecule before polymerization. B) 5,6-dihydroxyindole (DHI) used to create oligomers of larger size. C) PDA trimer comprised of three DHI molecules.

\subsection*{1.1.3. PDA/PTFE Composites}

PDA has been used as an intermittent layer between stainless steel and PTFE and has proven to lower the wear rate of the PTFE film substantially. PDA/PTFE composites have shown an
increased wear resistance and sometimes a reduced coefficient of friction.\textsuperscript{29, 37-38} During scratch, a thin layer of PTFE strongly adheres to the PDA interface allowing for a small layer of PTFE to adhere after scratch tests are performed. This tenacious layer of PTFE is believed to be the reason the coefficient of friction remains low for the duration of the experiment.\textsuperscript{29, 37-38} While experimental observations of PDA/PTFE composites have shown incredible wear life, computational models have yet to be used to understand how PTFE adheres to the PDA film. Understanding the adhesive mechanisms of PDA and PTFE may encourage the development of better adhesive PTFE films with greater wear resistance.

The exact adhesive mechanisms between PDA and PTFE have yet to be studied, however, van der Waals forces, hydrogen bonding, and pi-stacking have been observed as adhesive mechanisms of PDA to other materials.\textsuperscript{34, 36} PTFE contains the element fluorine, which has been reported to form halogen bonds with other negatively charged particles.\textsuperscript{39} The complex interactions between the atoms in PDA and PTFE may hold key information in unlocking the mystery of why PTFE adheres so well to PDA. By using multiscale computational modeling techniques, we can gain a better understanding of the adhesive and mechanical properties of PDA/PTFE composites.

1.2. Objectives

The objective of this dissertation is to gain insight into PDA/PTFE composites and their low friction low wear properties. Multiple computational methods are used spanning from the nanoscale to the microscale to conduct a full investigation of PTFE and PDA. We use density functional theory (DFT) to investigate the atomic interactions between PDA and PTFE, and molecular dynamics (MD) to study the friction and wear of the two materials at room temperature.
during indentation and scratch tests. A coarse-grained modeling technique is developed which allows for dynamic simulation of PTFE films on the microscale.

Using these simulation techniques, we study both materials independently to understand mechanical behavior in isolation and compare this with the behavior of the materials when combined in a composite. We also study the mechanical properties of PTFE on multiple length scales, and the adhesive properties of PDA with PTFE. The purpose of this dissertation can be broken down into three main goals with subobjectives:

1. Investigating the effects of environmental conditions on mechanical properties of PTFE chains.
   a. Study the wear and mechanical properties of PTFE chains. Molecular dynamics is used to investigate PTFE chain deformation mechanisms during rubbing tests. Tensile tests are conducted to investigate how the chain length, the presence of water, and the temperature affect the elastic modulus.
   b. Investigate wear and mechanical properties of PTFE nano-film. Nano indentation and scratch tests are performed using molecular dynamics on a pure PTFE substrate. Deformation mechanisms are observed, and the indentation forces recorded. Comparisons between the individual chain tensile tests and the nano-indentation can be drawn to understand how deformation of individual chains affect the deformation of a bulk nanoscale PTFE substrate.
   c. Investigate PTFE topography change due to annealing. Using molecular dynamics, large bundles of PTFE chains are equilibrated at varying temperatures to observe physical changes in the particle shape during annealing.

2. Investigating adhesion and interfacial properties of PDA/PTFE composites.
a. Study the adhesion of PDA oligomers. Using molecular dynamics, we investigate
the adhesion of PDA and the formation of hydrogen bonds in an aqueous solution.
It is believed that by mixing a dopamine aqueous solution, the hydrogen formation
bond increases, thus increasing the deposition rate and uniformity of a
polydopamine coating.

b. Investigate PDA and PTFE composite deformation mechanisms. Density
functional theory is used to investigate the adhesion mechanisms between PTFE
and PDA. Molecular dynamics is used to predict adsorption energy between PTFE
and PDA, as well as displace PTFE molecules from PDA to observe deformation
mechanisms and forces. Nanoscale indentation and scratch are performed on a
PDA/PTFE composite film to understand how the tenacious layer of PTFE adheres
to PDA, even after rubbing cycles are complete.

3. Using coarse-grained modeling techniques to investigate friction and wear on microscale
particles and films.

   a. Use coarse-grained modeling to examine the deformation of PTFE on experimental
scales. Microscale sized PTFE particles are created in various shapes and densities.
Indentation and scratch are performed and compared to experimental PTFE, and
previous nanoscale simulations.

   b. Investigate friction of microscale PTFE models. Numerous PTFE films are created
to investigate how the topography of PTFE affects the coefficient of friction. A
machine learning algorithm is developed and used to assess what properties of
PTFE films affect the value of the coefficient of friction.
c. Reproducing experimental observations of released PTFE fibers. After experimental scratch tests on PTFE films, running lines are observed in the wear track and are believed to be released PTFE fibers due to the rubbing process. Steered molecular dynamics simulations are performed to mimic AFM probes on a PTFE particle and used to investigate the process of creating loose fibers in a PTFE film.

d. Study the adhesion between microscale PTFE particles. Using two different types of micrometer sized PTFE particles, coarse-grained simulations are performed to predict how the surface area and shape of PTFE particles affects the adhesive properties between them.

While the objectives of this research are many, they can be summarized into three purposes which stand out as novel objectives. The first is the development and use of a coarse-grained model of PTFE which increases modeling capabilities of PTFE up to the microscale. This coarse-grained model directly shows how characteristics of PTFE on the nanoscale effect the microscale behavior of the material. The second novel outcome of this dissertation is the development and implementation of a convolutional neural network which predicts the coefficient of friction of PTFE films based solely on topography images. Although improvement in the machine learning program can be made, it is the first attempt at predicting the coefficient of friction of a film prior to testing the surface. The third novel objective in this dissertation is the investigation of the adhesive and deformation mechanisms of PDA and PTFE. The observations made in Chapter 3 are the first ever observations of simulated PDA and PTFE using molecular dynamics that we are aware of. All objectives of this dissertation are steppingstones to these novel accomplishments.
1.3. Dissertation layout

This dissertation is organized into six chapters. Chapter 2 investigates the wear and mechanical properties of PTFE on multiple length scales. Chapter 3 uses molecular dynamics simulations to investigate the adhesion, wear and mechanical properties of PDA and PTFE. Chapter 4 uses a coarse-grained model of PTFE, developed in Chapter 2, to investigate deformation mechanisms of PTFE films, including the effects of altering nanoscale properties of PTFE such as chain length or density. Chapter 5 contains the conclusion of the dissertation and addresses the objectives listed in section 1.2 above. Chapter 6: contains two coauthored papers which, due to the regulations of the dissertation formatting, cannot be held in the body of the dissertation. Section 6.1 contains the summary of a paper which discusses the adhesion of PDA oligomers. In this paper a method of depositing uniform layers of PDA coatings on nanoparticles was developed. My contributions include developing models of PDA aqueous solution on a metallic nanoparticle and investigating the deposition process. Section 6.2 contains a summary from another paper that investigates the wear of PDA/PTFE film coatings and the affects annealing has on PTFE particle structure. Simulations of PTFE were used to investigate the effects of annealing on a bundle of PTFE chains, and observe wear mechanisms on microscale PTFE particles. The adhesion between two various shaped microscale PTFE particles was also investigated.

1.4. References


Chapter 2: Deformation Mechanisms of Polytetrafluoroethylene at the Nano and Microscales

Abstract

Polytetrafluoroethylene (PTFE) has a low coefficient of friction but also a high wear rate. Numerous studies investigating the possibility of reducing wear and the mechanisms of deformation have been conducted using experimental and computational studies. In this paper the deformation and mechanical failure of single chains, and bulk PTFE are investigated using molecular dynamics (MD). Due to the length scale limitations of the model that MD simulations can investigate, a coarse-grained model is developed and PTFE particles of varying densities are generated to investigate the mechanical properties at the microscale. The coarse-grained potential parameters and coarse-grained model of PTFE are derived from first principle based ReaxFF forcefield simulations and are then used to investigate the microscale mechanical properties of PTFE. The MD study indicate that temperature has a pronounced effect on the maximum strength of a single chain, the elastic modulus is dependent on chain length, and chains shorter than 100 Å have an increase in maximum strength. During indentation and scratch the frictional coefficient of bulk PTFE is dependent on the direction of the scratch on the PTFE substrate. The coarse-grained PTFE simulations show that indentation force is dependent on the density of PTFE, and the smoother the surface roughness of the particle the lower the coefficient of friction. The coarse-grained model that connects the atomic and macroscales of PTFE will lead to direct comparison with experimental PTFE thin films.
2.1. Introduction

Polytetrafluoroethylene (PTFE) is used in various fields as sealant material\(^1\), applications in biological implants\(^2\), and protective surface films and coatings.\(^3-4\) PTFE has excellent thermal and chemical properties and exhibits hydrophobic behavior.\(^5\) However, since its discovery in 1938\(^6\) PTFE has been of great interest for its particularly low coefficient of friction.\(^7-9\) Atomic force microscopy reveals that PTFE, once heated, coalesces into a fiber-like cohesive coating.\(^10\) The pulling of the macroscale PTFE orients the fibers in the pulling direction. When tested, the coefficient of friction depends on the direction of the oriented PTFE fibers.\(^11\)

Despite its unique and useful properties, PTFE has the disadvantage of low wear resistance and loading capacity.\(^9,12-13\) The longevity of PTFE can be improved by increasing crystallinity, or adding filler particles into the polymer matrix.\(^14\) To improve wear rate, micrometer sized filler particles were introduced into the polymer which increased wear rate by one to two orders of magnitude.\(^12-13,15-18\) The fillers were also able to increase crystallinity and ultimate strength of the PTFE sample.\(^19\) Nanometer sized particles were also investigated and proven to be effective at reducing wear rate.\(^20-21\) Copper nanoparticle fillers with a polydopamine coating were found to decrease wear rate even further without increasing the coefficient of friction.\(^10,22-23\) PTFE particles on the microscale have approximately a spherical shape, but when heated to 372 \(^\circ\)C, they form a needle shape.\(^10\) Why the shape changes during heating is unknown and investigating the properties of the shapes of PTFE particles will illuminate failure mechanisms within thin film PTFE.

Investigations involving thin film PTFE and imbedded alumina nanoparticles led to the discovery of the formation of an ultralow wear thin film deposited on a counterface.\(^24\) This deposition occurs within the first cycle of sliding on a substrate and creates a robust tribofilm on both sliding surfaces\(^3,25-26\) which protects and increases wear rate to hundreds of thousands of rubbing cycles.\(^4\)
While some believe the counter-surface effect is purely mechanical\textsuperscript{27}, others have proposed the effects are more structural\textsuperscript{28-29}, or even chemical.\textsuperscript{4} Ultralow wear PTFE composites show exceptional promise for materials of the future.\textsuperscript{20, 26, 30}

Molecular dynamics simulations have been performed in multiple studies to investigate the effects of filler particles, surface topology, and durability and wear on PTFE at the nanoscale. Studies involving the investigation of the wetting behavior of PTFE\textsuperscript{31}, the effects of sliding orientation of polyethylene\textsuperscript{32}, and the effects of temperature of friction and wear are a few relevant studies conducted using molecular dynamics.\textsuperscript{33} Herbold et al. investigated the effects of metallic particles in a PTFE-W-Al composite, they suggested that the filler particles create force chains which help distribute and support any load on the PTFE matrix, increasing its wear resistance and load capacity.\textsuperscript{34}

Multiscale models can be used to increase the length scale under investigation from nanometers to micrometers. Multiscale methods involving PTFE have been studied before to investigate various properties of perfluorosulfonic acid (PFSA) membranes, which consist of PTFE backbone and a perfluorinated ether side chain but never has a coarse-grained model of pure PTFE been investigated for its mechanical properties.\textsuperscript{35-37} The concept of creating a coarse-grained model has been used to investigate the self-folding mechanics of carbon nanotubes\textsuperscript{38}, mechanics of twisting carbon nanotube yarns\textsuperscript{39}, and the aforementioned study investigating PFSA membranes.\textsuperscript{36}

Recent experimental studies show a continuing promise for PTFE as a thin film, particularly with the use of a polydopamine substrate or alumina particles.\textsuperscript{10, 22-23, 25} Molecular dynamics simulations have been used to investigate the rubbing of PTFE on a metallic substrate as well as PTFE - PTFE interactions.\textsuperscript{4, 33} Further improving our understanding of deformation mechanisms on the nanoscale and how those mechanisms affect the microscale particles will allow the design of more
durable thin films. In this work, molecular dynamics simulations are used to study solvated, and unsolvated individual PTFE chain response to tensile stress under different temperatures. Indentation and scratch tests are performed on bulk PTFE using MD, and a coarse-grained model of PTFE is developed which increases the length scale of feasible models from nanometers to micrometers. Indentation and scratch tests are then performed on the coarse-grained models that mimic PTFE particles at the macroscale to compare deformation mechanisms between the coarse-grained microscale PTFE and the atomic scale models.

2.2. Methods

We develop atomistic scale models of individual PTFE chains to study the effect of length and temperature on the chain strength. To study the frictional properties of PTFE particles of varying shape, we develop a coarse-grained model from the atomistic model.

2.2.1. Atomistic Modeling

Molecular dynamics method is used to simulate tensile tests on single chain PTFE (Figure 2.1A). The chain lengths investigated range from approximately 3 Å to 1000 Å, and only chains longer than 25 Å are studied further due to their stabilized elastic modulus during preliminary testing. 100 Å long chains (Figure 2.1B) are stacked parallel in a square lattice to create a bulk PTFE (Figure 2.1C). Nanoindentation and scratch tests are performed on the bulk PTFE model to study the effect that chain orientation has on the resistance to scratch. All MD simulations are performed using the ReaxFF force field due to the near quantum mechanical level accuracy and it is especially suited to model fluorinated graphene. The ReaxFF force field is also capable of performing the chemical reactions between PTFE and water molecules. All simulations are performed using Large-scale
Atomic/Molecular Massively Parallel Simulator (LAMMPS)\textsuperscript{42} and visualized in Visual Molecular Dynamics (VMD).\textsuperscript{43}

**Figure 2.1** (A) A Single Chain of PTFE comprising of a backbone of carbon atoms bonded to fluorine atoms. (B) Selection of a single PTFE chain used to develop (C) the bulk PTFE model. Each chain was 107.7 Å long after equilibration, placed parallel to the Z axis and approximately 5 Å apart to create the bulk PTFE model.

Understanding atomic scale single chain PTFE and its reaction to stress and strain, temperature, and water will provide insight to nanoscale deformation mechanisms. Measuring the tensile strength of PTFE chains will provide an explanation of failure mechanisms at the nanoscale. Tensile tests are performed on single PTFE chains of varying length, temperature, and water content. Chain lengths (Figure 2.1A) vary from \( l = 25, 50, 100, 200, 600 \) and 1000 Å, where each chain contains 20, 40, 80, 160, 450, and 755 carbon atoms respectively. Chains are tested at 300 K in 57.5 wt\% water and in vacuum. A chain length of 100 Å is chosen to test the effects of
temperature and chemical environment. Temperature variation ranged from 300 K to 600 K incremented by 50 K.

In each tensile test simulation, PTFE chains are minimized for 2 ps. To prevent the chain from curling, the carbon atoms at either end of the chain are prevented from moving in the Y and Z direction, restricting their movement parallel to the chain orientation. After equilibration, one end carbon atom is held fixed, while the other is stretched until 20% strain is achieved. This process is carried out for all chain lengths and will determine the tensile strength of individual chain lengths.

To create the bulk PTFE model, chains are oriented in a square lattice, parallel to the Z axis (Figure 2.1B). The PTFE block dimensions are 99 x 55 x 108 Å (Figure 2.1C) after equilibration. The X and Z dimensions are periodic, and the bottom two layers of PTFE chains (10 Å) are held fixed after equilibration is finished, the rest of the atoms are free to move in any dimension while the indentation and scratch tests are performed. To investigate how the chain orientation affects the coefficient of friction, a spherical indenter with radius of 25 Å is indented 10 Å into the surface of the PTFE sample, then scratched at angles 0, 45, and 90 degrees measured from the Z axis, for scratch length of 10 Å.

### 2.2.2. Coarse-grained Modeling

Experimental observations show PTFE forms different sized and shaped particles during the annealing process. By developing a coarse-grained force field and model, larger length scales can be achieved than would be possible simply using molecular dynamics. Spanning larger simulation length scale allows for the investigation of micrometer-sized particles as seen in experimental work and how different shapes of these particles change the coefficient of friction.
To develop the coarse-grained force field, multiple PTFE chains are configured to generate a bundle with dimensions 28.18 x 17.75 x 17.41 Å (Figure 2.2A&B). Bundle dimensions are chosen to include the twist in PTFE chains (that is inherent to PTFE chain longer than 25 Å) and also considering the ReaxFF force field, which is computationally expensive using molecular dynamics. In this study, PTFE chains are placed in an ideal crystalline alignment. Each bundle is equilibrated at 300 K to allow the bundle to reach a minimum energy and orientation. The relaxed coarse-grained fibers are visually similar to experimentally observed microscale fibers. An amorphous phase can lead to change in our coarse-grained parameters especially bending test parameters listed in Table 2.1.

Molecular dynamics is used to perform mechanical tests in order to calculate coarse-grained parameters from fitted energy curves. Three tests are run using the PTFE bundle model, a tensile test, three-point bending test and equilibrium distance test. Each simulation is performed using the ReaxFF force field. The purpose of the tests is to approximate the 1088 atoms in the bundle as three coarse-grained beads (Figure 2.2C&D), to increase length scale capabilities by allowing multiple beads to create a fiber (Figure 2.2E). A coarse-grained potential is developed to describe the bond and angle interactions between the three beads, and the interactions of multiple fibers via van der Waals forces. Multiple PTFE beads are used to create a PTFE fiber (Figure 2.2E). Multiple fibers coalesce to form a micrometer sized particle (Figure 2.2F) after equilibration at 300 K.
Figure 2.2 (A) PTFE bundle comprising of parallel PTFE chains. (B) Side view of the PTFE bundle. (C) A silhouette (purple) of Figure 2.2B where three yellow beads are placed showing the scale between molecular dynamics and the coarse-grained beads. (D) Close view of three coarse-grained beads separated by distance $r$, and forming angle $\theta$, parameters obtained from molecular dynamics bundle simulations. (E) A selection of a PTFE fiber from the coarse-grained model showing the three distinct PTFE Beads. (F) A PTFE particle measuring 0.1 µm across.

The coarse-grained parameters that describe bonding are derived from the energies of the MD simulation of a bundle under tensile stress. During the simulation, the end carbon atoms are held fixed in the Y and Z dimensions to restrict movement of the chain. The fixed carbon atoms are then pulled at a strain rate of 0.05 ps$^{-1}$ until 13% strain. The length and energy of the bundle was recorded for parameter extraction. The strain, and energy of the simulation was plotted and an energy curve was fit to equation (2.1).

\[
E = K_T (r - r_0)^2
\]  

(2.1)

The variable $r$ is the length of the bundle, $r_0$ is the equilibrium length, $K_T$ is the tensile energy constant and $E$ is the energy of the system. The necessary parameters for describing the bonding parameters of the coarse-grained beads are equilibrium length ($r_0$) and tensile energy constant
Because three beads are placed in the coarse-grained model to represent the bundle, one bead at each end and one in the middle, the values used in the potential file for the equilibrium bead length \( r_0 \) is 13.60 Å. The energy constant is then set to 481.07 Kcal/mol-Å\(^2\), to ensure a correct correlation between the molecular dynamics and coarse-grained simulations.

**Figure 2.3** (A) Plot of MD bundle data (blue dots) and the energy fit (red line) used to create coarse-grained model parameters. The energy fit curve is fit to equation 1 and the parameters \( r_0 \) and \( K_T \) are calculated. (B) Images of PTFE bundle at equilibrium length \( l = 27.1876 \) Å (i) and at 11\% strain \( l + \Delta l = 30.40 \) Å (ii).

A three-point bend test is used to describe the dihedral angles between coarse-grained beads. The end carbon atoms are held fixed in all dimensions, the center carbon atoms were also fixed and displaced in the Y dimension at a strain rate of 0.05 ps\(^{-1}\). The angle of the bundle and the energy are measured and plotted, and an energy curve is fit to equation (2.2).

\[
E = K_B (\theta - \theta_0)^2
\]  

(2.2)

The bending energy constant \( (K_B) \) and the equilibrium bend angle \( (\theta_0) \) are used in the coarse-grained potential, while the energy \( (E) \) and the bend angle \( (\theta) \) of the bundle are measured during the simulation.
Figure 2.4 (A) Plot of MD Bundle data (blue) during bending test and the energy fit (red) used to create coarse-grained model parameters. (B) Images of PTFE bundle before and during the bending test.

The van der Waals interactions in the coarse-grained model are determined by the attractive or repulsive forces from the MD simulations. The equilibrium test uses two separate completely fixed bundles parallel to one another, which are brought closer together as the simulation progresses. The distance and energy of the system is measured and plotted, and an energy curve is fit to the potential energy of the two bundles using the Lennard-Jones 12:6 curve (equation (2.3)).

\[ E = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]  

(2.3)

The energy well depth at equilibrium (\(\epsilon\)), and the distance parameter (\(\sigma\)) are calculated via the curve fit. The distance between PTFE bundles (\(r\)) and the energy (\(E\)) of the bundle are measured during the simulation. The parameters necessary to model the coarse-grained force field are the energy well depth at equilibrium (\(\epsilon\)), and the distance parameter (\(\sigma\)).
Figure 2.5 (A) Plot comparing two molecular dynamics equilibrium distance data points to the Lennard Jones curve. Images show the bundle at distances of 23.1 Å (B) and 35 Å (C).

The parameters gathered from the equilibrium distance test are those that create the best Lennard Jones fit to the data. The energy cutoff distance $r_{cut}$ was chosen to be 45.65 Å, when the energy of two interacting bundles was zero. The values for the energy well depth, and the zero-crossing distance were chosen to ensure the equilibrium distance and the equilibrium energy matched the bundle simulation. Due to the thermal fluctuations in the data used to fit the Lennard Jones curve, the coarse-grained force field may cause variation in the forces predicted. By conducting parametric studies, we have quantified the variation in forces to be up to 5 nN. The necessary parameters to model PTFE are summarized in Table 2.1.
Table 2.1 List of Coarse-grained Parameters

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Parameter Description</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Test</td>
<td>Energy Parameter ($K_T$)</td>
<td>481.07</td>
<td>$Kcal/mol\ Å^2$</td>
</tr>
<tr>
<td></td>
<td>Equilibrium Bond Distance ($r_0$)</td>
<td>13.60</td>
<td>Å</td>
</tr>
<tr>
<td>Three Point Bend Test</td>
<td>Energy Parameter ($K_B$)</td>
<td>1330.82</td>
<td>$Kcal/mol\ rad^2$</td>
</tr>
<tr>
<td></td>
<td>Equilibrium Angle ($\theta_0$)</td>
<td>177.31</td>
<td>Degrees</td>
</tr>
<tr>
<td>Equilibrium Distance Test</td>
<td>Energy Well Depth ($\epsilon$)</td>
<td>30.60</td>
<td>$Kcal/mol$</td>
</tr>
<tr>
<td></td>
<td>Zero-crossing Distance ($\sigma$)</td>
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<td>Å</td>
</tr>
<tr>
<td></td>
<td>Energy Cutoff ($r_{cut}$)</td>
<td>50</td>
<td>Å</td>
</tr>
</tbody>
</table>

Table 2.1 The list of parameters extracted from the molecular dynamics simulations on PTFE bundles. Three tests are performed: tensile, three point bend, and equilibrium distance tests. These parameters are used to define the bonding, angle, and van der Waals forces between PTFE beads in the coarse-grained potential.

A three-bead model is generated to test the coarse-grained parameters against the bundle simulations. Tensile, three point bend, and equilibrium distance tests are performed using the new coarse-grained model and potential. Results from the coarse-grained simulations recreate the MD simulation energies in the coarse-grained potential.

Using the coarse-grained equilibrium distances, PTFE beads are placed into 10,000 PTFE fibers. To create the model, 500 Å long fibers are positioned and oriented randomly. The model was set to equilibrate at 300 K for 15.6 ns. The PTFE fibers coalesce into a porous interwoven mesh which gradually condense to a particle.

The resultant nanoparticle with an approximate spherical shape is referred here as the porous nanoparticle (Porous) (Figure 2.6A&B). A flattened particle (Figure 2.6C&D) with lower porosity
(Flat) was also generated using LAMMPS which is half the original height of the porous nanoparticle. Finally, a high density needle shaped (Needle) particle (Figure 2.6E&F) was also generated with a similar length to width ratio (3.26) as fibers found in experimental works (2.6-3.77).\textsuperscript{10} The radial distribution of atoms in each model is measured and indicates that the models are indeed different sizes and shapes of the same material with different densities (Figure 2.6F). Various shapes of PTFE particles are observed in experimental literature and our particles were modeled after the shape and size of these particles.\textsuperscript{10,47} In our studies the porous model replicates the particles observed in experiments at room temperatures before annealing. We compress the porous model to different densities to generate the flat and needle particle models. The density of the porous, flat, and needle model are 0.7376, 0.8420 and 1.0120 g/cm\textsuperscript{3} respectively which are similar to the density of PTFE powder ranging from 0.5 to 2.0 g/cm\textsuperscript{3}.\textsuperscript{47}

Fibers of equilibrated coarse-grained models were measured \~{} 10 nm in diameter. AFM images from experimental studies show PTFE fibers ranging from 400 nm to 10 nm in diameter and forming an entangled web-like structure, which is also observed in the equilibrated coarse-grained particles.\textsuperscript{46, 48} Although bundle simulations use an ideal structure of PTFE to approximate the coarse-grained parameters, the coarse-grained particles contain a similar density and shape to particles observed experimentally.\textsuperscript{10,47}

Indentation is performed at the same location for all particles. A purely repulsive spherical LAMMPS indenter with a diameter of 50 nm is used to indent each nanoparticle. The indentation speed was held constant at 5 m/s for each indenter, and an indentation depth of 10 nm was studied.
Figure 2.6 (A) The porous particle (Porous) is generated by equilibrating random PTFE fibers for 15.6 nanoseconds. (B) Side view of porous particle. (C) The flattened particle (Flat) is generated by indenting the porous particle in the Y dimension until the particle is half the original size. (D) Side view of flattened particle. (E) We generate the needle particle (Needle) by varying the density of the PTFE fibers. (F) Side view of needle particle. (G) Radial distribution function showing that each particle contains the proper peaks where PTFE coarse-grained beads rest, but each has a difference in density.
2.3. Results and Discussion

2.3.1. Single Chain PTFE Simulations

Molecular dynamics simulations on single PTFE chains study how the initial chain length affects the maximum tensile stress before the chain fails. The chains are studied in vacuum and in a water environment, at 300 K. Results from the length studies show the chains shorter than 100 Å withstand a slightly higher stress than the others, for this reason the 100 Å long chain was selected for the temperature study. The pulling velocity is investigated and found to have a negligible effect on the mechanical properties of atomistic PTFE chains.

2.3.2. Elastic Modulus

To explore the effects of chain length on elastic modulus, and also to compare results with previous studies, the length of chains investigated ranged from 3 Å to 1000 Å. Values for elastic modulus of PTFE have been reported at 160 GPa using force field calculations and 221 and 247 GPa using DFT.\textsuperscript{49-51} In order to compare our MD model results to density functional theory (DFT) calculations. We use the smallest chain of PTFE to recreate the simulation conditions of DFT; the elastic modulus at 1 K is calculated to be 248.1 GPA agreeing with previously reported data. We observed an increase in the elastic modulus of the PTFE chains as the chain length increases at 300 K (Figure 2.7A). Using the linear elastic region (from 0 to 2.5 % strain) of the stress strain curve (see Figure 2.8A and B), the elastic modulus is calculated to be 525 GPa for the 100 Å chain at 300 K in vacuum and 524.8 GPa in water.
Figure 2.7 (A) Graph of elastic modulus vs chain length of PTFE at 300 K. The dotted line separates small chains (< 25 Å) from longer chains (≥ 25 Å). Once the chain length reaches 25 Å, a twist in the backbone of the chain is observed at equilibrium. When under tensile load, the chain stretches by unraveling the twist, any chain that does not have a twist has a significantly lower elastic modulus. (B) 21.3 Å long chain at equilibrium showing straight chain without a dihedral twist. (C) 25 Å long chain at equilibrium showing a single dihedral twist. (D) Close up view of the twist in the 25 Å long chain.

PTFE is known to have a torsion angle of approximately 162.5 degrees.\textsuperscript{52-53} At equilibrium, the carbon backbone of PTFE gradually rotates under the torsion angle, however, we observe at a length of 21.3 Å (with 20 carbon atoms) a twist occurring in the chain. Chains with more than 20 carbon atoms all are observed to have at least one twist at equilibrium. During the tensile test dihedral angles slowly unravel, bond angles increase, and bond lengths stretch. Failure ultimately occurs when the bond between carbon atoms stretches too far. Chains with a twist are observed to have an extra phase where the twist is unraveled before bond lengths or bond angles increase. Once the twist has straightened, the dihedrals, bond angle, and bond lengths increase simultaneously just as observed in the chains without the twist. This explains the variation of modulus values.
2.3.3. The Effects of Initial Chain Length on Maximum Stress

When hydrated, the initial stress of the chain increases, as well as the maximum stress the chain can withstand. In every simulation, the chain with water surpasses the strength of the chain without water. Nanoscale tensile tests in vacuum (Figure 2.8A) show only a small change in maximum stress as chain length increases. Chain lengths investigated range from 25 Å to 1000 Å. The 25 and 50 Å chain lengths both in water and vacuum exhibit a slightly larger maximum stress than the longer chains. The increase in strength is due to the decreased initial stress in the shorter PTFE chains prior to the tensile test. To prevent the curling of the chains during equilibration, the ends of the chain are prevented from moving in any direction except the direction parallel to the chain orientation (X direction), leaving the chain in a state of stress visualized in Figure 2.8C, and graphically by the non-zero stress at zero strain in Figure 2.8A. The residual stress in the chains increase as the length of the chain increases, resulting in lower maximum stress values for the longer chains.
The maximum stress for longer chains decreases as the length of the chain increases, but appears to plateau at a length of 100 Å. A similar phenomenon was observed in polyyne carbyne where the smaller length chains were also reported to have a higher strength.\textsuperscript{54-55} The dependency the maximum strength of the chain has on length can be explained by the high axial strain energy for shorter chains, as well as the increase in probability that longer chains will break due to the increased number of bonds.

\textbf{Figure 2.8} (A) Stress strain plot for PTFE in vacuum and (B) in water. (C) PTFE 100 Å long after equilibration and (D) after break. (E) PTFE 100 Å long in water environment after equilibration and (F) after break.
2.3.4. The Effect of Water and Vacuum Environments on Maximum Stress

The addition of water to the PTFE chains increases the maximum tensile stress before the chain breaks (Figure 2.9A). The models which have been hydrated can withstand 4-8% more stress than their vacuum counterparts. Interestingly, the shorter chain lengths appear to benefit less from the water than the longer chain lengths. There was no covalent bonding, healing, or altering of the PTFE chain physical attributes during the simulations.

Water has been observed to increase the maximum strength of polyynes, but through a very different mechanism. In PTFE, water is able to prevent the chain from excessive movement in the Y or Z directions. The chain with water, being hindered in two dimensions, is able to withstand a greater stress because the shape of the chain is more unified in the direction of the tensile load. An illustration of a chain under tensile load with water can be seen in Figure 2.9B, the stabilizing effects are apparent when compared to the chain without water. While in both illustrations the calculated engineering strain is the same, the actual length between individual carbon bonds is greater in the chain without water, and therefore has a larger stress. This increase in bond distance is what ultimately causes the chain to fail.
Figure 2.9 (A) Initial PTFE chain length vs maximum tensile stress before chain breaks, showing that the maximum tensile stress experienced by PTFE chains can be increased by adding water to stabilize the chain. It is observed that the maximum tensile stress is decreased as the length of the chain increases, but this effect diminishes as the chain length increases. (B) An illustration of a single PTFE chain under tensile stress with water. The water acts as a stabilizer and prevents redundant movements. Illustration of a PTFE chain without the water stabilizing effect. (C) Initial length of PTFE chain vs strain at break. The strain at break decreases as the length of the chain increases, but again plateaus similar to the max tensile stress. (D) Temperature of chain vs the maximum tensile stress. As temperature increases, we observe that the maximum stress of the PTFE chains decreases.

2.3.5. The Effect of Temperature Variation

We study the effect of temperature on PTFE chain by varying the temperature from 300 K to 600 K incrementing by 50 K and performing a tensile test. The temperature of the PTFE chain drastically affects the strength of the polymer (Figure 2.9D). The maximum stress before the chain breaks has a negative correlation with the temperature of the chain. With the increase in kinetic
energy of the atoms, it becomes easier to break the bonds of the chain. Similar results have been recorded on macroscale PTFE in tension, the higher the temperature, the lower the yield stress. During a scratch test on PTFE film, chains are observed to break and radicals are formed. With the increase in rubbing cycles, more chains are broken and radicals are formed. It has been observed that higher temperatures cause a decrease in the coefficient of friction as well as a reduction in the adhesive forces between PTFE chains. High temperatures that occur during rubbing of a PTFE film can be attributed with the failure of the film, and the increase of radicals.

2.3.6. Single Chain Study Summary

The shorter PTFE chains are observed to have up to 9% higher ultimate stress which decreases as the length of the chain increases. This decrease in strength is due to the high axial strain energy for longer chains, and the increased probability of a broken bond as the chains get longer. Water stabilizes the chains by limiting movement to the strain direction. PTFE chains exhibit lower strength as temperature raises from 300 K to 600 K. The calculated Young’s Modulus for a 100 Å long PTFE chain at 300 K in vacuum is 525 GPa.

2.4. Nanoscale Indentation and Scratch Simulations

In order to predict the frictional properties, a bulk PTFE model is indented 10 Å by an indenter with a radius of 25 Å. After indentation, scratch tests are performed at three different scratch angles: 0 degrees, 45 degrees, and 90 degrees parallel to the chain orientation (Z axis).

2.4.1. Molecular Dynamics Indentation Results

The indentation force and the indentation depth are measured during this simulation (Figure 2.10A). Under the compressive load, when the indentation force reach 400 nN (Figure 2.10i) a chain is then displaced from the PTFE surface by the force of the indenter (Figure 2.10ii). As the
indenter continues through the PTFE, the indentation force continues to rise and more chains are displaced from the surface (Figure 2.10iii).

![Graph and images](image)

**Figure 2.10** (A) Indentation Force vs Indentation Depth. Drops in the indentation force occur as chains are ejected from the surface of the PTFE. (i) Image of PTFE surface during indentation at the first peak in the force displacement plot before any chains are ejected. (ii) Image showing a PTFE chain protruding from the surface causing a drop in the force displacement plot. (iii) After 10 Å of indentation, multiple chains have been ejected from their original positions and are now protruding from the surface.

No chains are observed to break during indentation and the chain displacement phenomena occurred on both the first and second layers of PTFE. The maximum tensile stress a single chain of PTFE can withstand is approximately 80 GPa (Figure 2.8A), we see the maximum force sustained by the bulk PTFE model is 400 nN before chains protrude from the surface of the PTFE. Dividing the maximum force before deformation by the approximate contact area of the indenter \( (\pi r^2) \), the contact pressure on the bulk PTFE is 20.37 GPa. The chains slip around the indenter at the same pressure as they would break under tensile stress. Because PTFE chains have an intrinsically low adhesion to each other, it is easy to separate the chains during indentation without significant damage to the PTFE surface.\(^8\) This allows for the chains to separate without breaking and to deform away from the indenter.
The elastic modulus of the bulk PTFE was found by computing stress by dividing the normal force by the contact area of the indenter, and a strain by computing the compressive strain on the center of the PTFE sample. The elastic modulus during indentation is 80.23 GPa for the first 5% strain. Experimental studies on thin film PTFE have been conducted investigating the thickness effect of PTFE on the elastic modulus, showing that decreasing film size greatly increases the elastic modulus of the film. While no direct comparison is available, the smallest PTFE film tested by Wang et al had a thickness of 48.1 nm and an elastic modulus of 12 GPa, where our film thickness is 5.5 nm and has an elastic modulus of 80.23 GPa.\textsuperscript{57}

2.4.2. Nanoscale Scratch Test

Once an indentation depth of 10 Å is reached, a scratch test is performed on the surface for 10 Å. A scratch angle of 0 degrees (parallel to the chain orientation in the Z axis) shows a zipper like deformation during the scratch. The 0 degree scratch shows the ability of PTFE to deform without damaging the surface. The sections of chains in front of the indenter are displaced out of the indenter path, while the sections behind the indenter return to their original positions. This is because the PTFE chains have a relatively low adhesion force to one another. The van der Waals forces that attract the chains are easily separated by the indenter resulting in the parting of chains while the chains fall naturally back to their original positions due to the attraction forces from the neighboring chains.

A scratch angle of 90 degrees (perpendicular to the chain orientation) shows major deformation of the chains. Pile-up occurs (Figure 2.10iii) as the indenter moves through the surface of the PTFE, and the chains behind the indenter remain relatively motionless. During the scratch test, the sections of chain in the path of the indenter cause pile-up. While the chains are forced out of their initial positions, the ends of the chains cannot remain connected to the neighboring chains. The
ends of the chains slip past the neighboring fluorine atoms causing the drop in the force displacement graph (Figure 2.11A), and coefficient of friction graph (Figure 2.11B). The large drop occurring around 6 Å occurs when a chain is displaced from the surface of the PTFE, seen as the top chain in Figure 2.11E.

**Figure 2.11** (A) Indentation force vs scratch distance for scratch angles of 0, 45, and 90 degrees. (B) Coefficient of friction computed from scratch tests at 0, 45, and 90 degree scratch angles. (C) Scratch distance of 10 Å for 0 degree scratch angle showing an arrow illustrating the scratch path. Chains have been displaced during the indentation but the scratch does not create more ejected chains. The indenter acts like a zipper, opening the PTFE surface by separating the individual chains. (D) Scratch distance of 10 Å for 45 degree scratch angle showing an arrow illustrating the scratch path. The chains ejected during the indentation are deformed slightly, but no new chains have been ejected from the surface. (E) Scratch distance of 10 Å for the 90 degree scratch angle. This image shows the pile-up of debris as the indenter displaces individual chains from the surface.

The results for scratch angle of 45 degrees shows a mixture between the 0 and 90 degree scratch angles. Chains in front of the indenter path have a low resistance to indentation and will deform to allow the indenter to pass over them, but are eventually displaced similar to the 90 degree scratch.
Pile-up was not observed for the length of the scratch at 45 degrees. Similar to the 90 degree scratch, sudden decrease in the force displacement graphs are caused by the slipping of chains past neighboring chains. Unlike the 90 degree scratch angle, the chains are never displaced far enough to cause a chain to completely detach from the surface.

From the observations of these results, we can conclude that the polymer orientation during scratch is much less resistant when the chains are oriented in the same direction as the indenter direction. This result is supported by Barry et al who investigated sliding directions of PTFE sheets. The PTFE sheets were observed to break and some chains reoriented based off of sliding direction. Frictional forces reported by Barry et al range from 2.1 to 10.7 nN, well within the values found in this work.

Coefficient of friction values for the 90 degree scratch average to 0.15. The 45 degree scratch shows values of 0.1 while the 0 degree scratch averages to 0.05. Previously reported values of the coefficient of friction for PTFE fall between 0.1 and 0.16 during initial sliding of PTFE. The coefficient of friction reported in this work support the values found in experimental work of bulk PTFE during the initial sliding of a scratch test. During scratch, experimental studies observe a decrease in the coefficient of friction, after the initial scratch has begun which may be result of chains reorienting to the scratch direction.

2.4.3. Summary of MD Indentation and Scratch Studies

Indentation on PTFE shows some self-repairing characteristics due to the weak secondary bonds of PTFE chains. Chains begin to be ejected from the surface of the film at 400 nN of force. After 10 Å of indentation, multiple chains have been ejected from the PTFE film surface. Scratching parallel to chain orientation shows a COF of 0.05, scratching at a 45 degree angle to the chain
orientation shows a COF of approximately 0.1, and the 90 degree scratch angle shows a COF of 0.15.

2.5. **Coarse-grained Model Indentation and Scratch**

We preform indentation and scratch studies on coarse-grained particles (flat, needle and porous) to predict their frictional properties. These are the common geometries of PTFE found at the microscale and can affect the frictional properties of PTFE coating.

2.5.1. **Indentation of Coarse-grained PTFE Particles**

During indentation of the coarse-grained particles (Figure 2.12A), the porous particle required the least force for the indenter to penetrate the particle. Because of the low density of the particle, most of the indentation depth is used to compress the fibers the indenter encounters. The porous particle compacts, and shears slightly in the positive Z direction, which is most likely due to the internal structure of the particle. The inside structure of the particle has column like supports created from high density tangled fibers, oriented in random directions. The largest support near the indenter extends in the positive Z direction, so when it is compressed, the support causes shear in the entire particle in the Z direction.
Figure 2.12 (A) Plot of indentation distance vs indentation force showing the denser a particle is, the greater the force is needed to indent the same indentation depth. (B) Coefficient of friction during the scratch in the X direction. The flat particle has a low initial coefficient of friction value which increases due to increasing resistance from the shearing surface. Since the surface of all particles is uneven, the indenter experiences increasing or decreasing frictional forces depending on the amount of material obstructing the indentation motion.

The flat particle shows a much greater resistance to the indenter than the porous particle. As the indenter begins to penetrate the surface of the flat particle, the compression of the fibers begins immediately. Due to the high density, the fibers cannot compress much farther and the force begins to rise. Sudden drops in the force displacement graph occur when support columns or groups of fibers slip past other support columns or fibers. The flattened particle undergoes a shearing similar to the porous model, unlike the porous particle, most of the flat particle support columns are oriented horizontally due to the compression used to create the flat surface. The lower half of the particle is more porous than the top half, and is mainly responsible for the shear visible in the particle during the scratch.

The force measured during the indentation of the needle particle was larger in magnitude than the force measured on any of the other particles. The indenter contacts the particle surface on top of a raised segment of the particle. Drops in the force displacement plot again correspond to slipping of support columns past other columns in the model (Figure 2.12F). Because the density of the
needle particle is slightly higher than the flat particle, the drops in force are not high, as the support columns have less space to slip into.

2.5.2. **Scratch Test of Coarse-grained Models**

Scratch test on the porous particle had little resistance to the indenter (Figure 2.12B), similar to the results from the indentation studies. As the indenter scratches the surface of the porous particle the indenter remains at the initial indentation depth of 100 Å. The frictional coefficient gradually increases throughout the simulation due to the slope of the surface topography, and continually shearing PTFE fibers, which is seen during the scratch test of all particles. While the normal and frictional forces measured during the scratch test are low, the coefficient of friction is high due to the large amount of resistance from the topography of the particle. The density of summits ($S_{ds}$) of the particle is calculated by counting the peaks and dividing by the surface area of the particle (Figure 2.13A), the density of summits of the porous particle is $2.242 \times 10^{-3}$ nm$^{-2}$. The deviation of summit heights ($S_{dv}$) is also calculated (Figure 2.13B) and the porous particle has a summit height deviation of 31.56 nm.
Figure 2.13 A) Density of summits vs coefficient of friction showing the higher the density of summits on the particle, the lower the coefficient of friction. B) Deviation of summit heights vs coefficient of friction showing the lower the deviation the lower the coefficient of friction. C) Flat particle surface topography which has more peaks at a constant height. D) Needle particle surface topography showing a few peaks at varying heights. E) Porous particle showing greatest peak height and peak height variation.

The coefficient of friction of the flat particle steadily increases from 0.03 to 0.20 (Figure 2.12B). Small fluctuations in the coefficient of friction are seen at 40 Å scratch distance which are caused by shear deformation in the particle. Three more scratch tests were performed at 10 Å intervals where coefficient of friction values ranged from 0.05 to 0.2. The additional scratch tests provide evidence that the coefficient of friction varies depending on the surface topography. The density of summits for the flat particle is $9.903 \times 10^{-3}$ nm$^{-2}$ and the deviation of summit heights is 11.17 nm. The flat particle has the highest density of summits and the lowest deviation of summit heights. These localized peaks help reduce friction, as less material is able to come in contact with the indenter during the scratch test.
The needle particle has a high coefficient of friction similar to the porous particle. Three additional scratch tests were performed at 10 Å intervals. Coefficient of friction values ranged from 0.35 to 0.5 during the additional scratch tests. The density of summits for the needle particle is $8.325 \times 10^{-5}$ nm$^{-2}$ and deviation of summit height of 16.16 nm.

The coefficient of friction calculated and plotted in Figure 2.12B is calculated by running one scratch down the center of the particles. To estimate an error of these values, three more tests were performed on the flat and needle particles, scratching horizontal to the first scratch at intervals of 10 Å. The average coefficient of friction for the flat, needle, and porous particles are 0.1324, 0.4351, and 0.6392 respectively. Reported coefficient of friction values for PTFE film during micrometer length scratch tests range from 0.15 to 0.20 which are slightly higher than the coefficient of friction values for the flattened particle.$^{59}$ The attributes of the particles that govern the coefficient of friction values are the density of summits, and the deviation of summit heights. As seen in Figure 2.13A, the higher the density of summits, the lower the coefficient of friction. The summit deviation also plays a big role in lowering the coefficient of friction (Figure 2.13B), as the deviation of summit height decreases, the coefficient of friction also decreases.

The porous particle had the lowest summit density and highest deviation of summit height. The porous particle is modeled after the spherical particles seen before annealing a PTFE film. The porous particle takes a rather spherical shape, which allows the PTFE fibers to stay as straight as possible and bend the least number of times. The needle particle has a much higher density than the porous particle, causing the PTFE fibers to bend to fit more particles in a smaller area. The bending and buckling of fibers cause an increase in summit density, and a decrease in the deviation of summit height. The compression of the porous particle increases the density of summits by forcing the relatively straight PTFE fibers to form a dense straight edge on the surface of the flat
particle. This dense edge of the flat particle is compressed to the same height therefore decreasing the deviation of summit heights.

2.5.3. **Summary of coarse-grained simulations**

A coarse-grained model is obtained from the results of fully atomistic molecular dynamics simulations which allows for the investigation of much larger length scales. Equilibration of the coarse-grained models show that PTFE chains would prefer to remain straight, but due to the sheer number and length of chains, will form an amorphous particle. Indentation on porous, flat, and needle shaped particles show that the particles with higher density will require a higher force to indent. Scratch tests reveal that a particle with higher summit density and lower deviation of summit height will have a lower coefficient of friction. Coefficient of friction values of the coarse-grained particles fall within the values calculated during the MD simulations, and the coefficient of friction value for the flattened particle agrees with experimental studies.

2.6. **Conclusions**

We have investigated single PTFE chain strength and found that the length of the chain does not affect the strength of the PTFE chain except for very short chains. Adding water strengthens the PTFE chain, while the pulling rate does not affect the maximum stress of the chain. Increasing the temperature of the chain decreases the tensile strength of the PTFE chain.

We also studied nanoindentation of compact PTFE on the nanoscale using molecular dynamics. We observed that PTFE chains slip around the indenter after 5 Å of indentation depth, which is equal to the depth of one layer of PTFE chains, or 400 nN of force. PTFE chains resisted scratch much greater when the scratch direction was perpendicular to the chain orientation resulting in deformation of the PTFE surface.
We generated a bundle of PTFE chains to derive the coarse-grained potential for microscale PTFE. Three different particle shapes were investigated, the porous, flattened, and the needle, modeled after experimental observations of PTFE particles. We observed that PTFE tends to form relatively straight fibers which gather to create a porous interwoven mesh. The maximum strength of PTFE particles tested using the coarse-grained force field was 60 nN before severe deformation occurred, approximately 6 times weaker than results of PTFE on the nanoscale using the ReaxFF force field.

Indentation on the porous nanoparticle using the coarse-grained model showed least resistance to indentation, while the flattened particle showed a greater resistance, and the needle particle showed the greatest resistance to indentation. Each model had slightly greater density than the last, suggesting the greater the density of the particle the more resistant to indentation the particle will be. The deformation of each of these particles was similar, showing that the deformation of an individual particle is based on the internal structure of the particle, not just the surface topography or the shape.

Scratch tests performed on the three micrometer sized particles show how the surface topography, shape, and density of a particle will affect the coefficient of friction. The value of the coefficient of friction is affected mainly by the density and height deviation of peaks in the particle. The coefficient of friction is highest when the particle has a low density of summits, and a high deviation of summit height. The coefficient of friction values for the coarse-grained models ranged from 0.13 to 0.64 while reported values for experimental coefficient of friction values range from 0.1 to 0.3\textsuperscript{7,8,21} and accepted numerical simulations at the nanoscale range from 0.1 to 0.6\textsuperscript{4,33}.

The generation of the coarse-grained model and potential allows for the modeling of PTFE on a microscale reaching length scales that have not previously been possible. The results from indentation and scratch tests performed on the coarse-grained PTFE model show that high density
and even surface roughness create the PTFE particle with the lowest coefficient of friction. Further investigations of micrometer sized PTFE particles can illuminate phenomena seen in PTFE thin films, such as adhesion mechanisms, interaction with filler particles, and the effects of fiber length, thus paving the path for modeling of more realistic PTFE surfaces. The studies outlined here will enhance the possibilities of PTFE for multi-disciplinary applications.

2.7. Acknowledgements

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2.8. References


5. DEBIES, L. M. T.; TAKACS, G., Adhesion of copper to poly (tetrafluoroethylene) surfaces modified with vacuum UV radiation downstream from He and Ar microwave plasmas. Polymer Surface Modification: Relevance to Adhesion 2004, 3, 139.


Chapter 3: Adhesion and interface properties of polydopamine and polytetrafluoroethylene thin films

Abstract

Polytetrafluoroethylene (PTFE) has been studied as a low friction surface coating since its discovery. The high wear rate of PTFE reduces the usefulness of the polymer for mechanical purposes, however, combining PTFE with polydopamine (PDA) has been shown to greatly reduce the film wear rate. During rubbing tests involving PDA/PTFE thin films, a tenacious layer of PTFE remains intact after substantial testing even though pure PTFE film layers are destroyed quickly. Understanding the interface mechanics that allow PTFE and PDA to adhere so well during experimental rubbing tests is necessary to improve the wear rate of PDA/PTFE thin films. In this study, we use density functional theory and molecular dynamics simulations to investigate the adhesive properties and interface deformation mechanisms between PDA and PTFE molecules. Steered molecular dynamics is then performed on isolated pairs of PDA and PTFE molecules to investigate different modes of deformation from equilibrium. PDA trimer oligomers were identified as the most adhesive to PTFE and selected to use in a PDA/PTFE thin film, where nanoindentation and scratch tests are performed. Our results indicate that a combination of the unique deformation mechanisms of PDA molecules and the penetration of PTFE molecules into the PDA substrate provide the PTFE/PDA interface with its wear resistance.

3.1. Introduction

Polytetrafluoroethylene (PTFE) is a fluoropolymer known for its low coefficient of friction and high wear rate. PTFE has many applications due to its tribological properties, superhydrophobicity, and chemical inertness which have made it a topic of investigation for the last few
decades. The tribological properties of PTFE make it an ideal material for solid lubricants and has been investigated for its use as a surface coating on mechanical devices including spacecraft parts. The tribological properties of PTFE have been studied in an effort to improve the adhesion and reduce wear; ultimately searching for a long lasting low friction solid lubricant.

The mechanical properties of PTFE vary depending on the force applied, and the rubbing speed on the film, where higher normal loads, or faster rubbing velocities drastically increase the coefficient of friction and are accompanied with massive material deformation of the PTFE film. PTFE films are easily sheered during rubbing and transfer material is deposited on the counterface, which is responsible for the low coefficient of friction seen in experiments. If the sliding direction is changed, the orientation of molecules changes to align parallel with sliding direction.

The low surface energy and chemical inertness of PTFE are in part obstacles to overcome in creating a PTFE sample to adhere to a substrate. Macroscale PTFE wears by sheering layers of material off during rubbing, while microscale PTFE films wear through three stages: run in, transition, and steady state. Ultra-low wear in PTFE films have been observed and is regarded to be caused by PTFE radicals which chelate to a substrate. To further investigate the wear properties of PTFE, many computational studies investigating the friction and wear of PTFE molecules have been performed. Simulations of sliding on PTFE have observed chain scission and reorientation of chain segments after a prolonged sliding.

Reducing the wear of PTFE coatings is desirable because pure PTFE has an extremely high wear rate. Various types of composites and filler particles have been used, including carbon nanotubes and alumina nanocomposites, to improve thermal conductivity, diffusivity, wear resistance, and even reducing the coefficient of friction.
The application of a polydopamine (PDA) substrate has shown incredible adhesion and promise as a modifier to PTFE films.²³ PDA is a bio-inspired material based on the adhesive proteins secreted by mussels.²⁴ PDA can adhere to almost any surface and can be applied by a simple aqueous solution for dip coating. PDA is biocompatible and has been used in a variety of applications such as an in vivo surface coating, energy, and environmental applications.²⁵-²⁶

During synthesis of polydopamine, the dopamine monomer oxidizes and forms 5,6-dihydroxyindole (DHI). The DHI molecule self-assembles into dimers, trimers and larger oligomers.²⁷ After the PDA has synthesized and a film is formed, traces of the original dopamine monomer, DHI, and higher order oligomers are observed in the PDA film, but the exact concentration of each oligomer is unknown.²⁷-²⁸

A close investigation of the PDA film reveals that dopamine monomers form stacked structures with an interspatial distance resembling pi-stacked materials.²⁹ The entire PDA film is believed to adhere by charge transfer, pi-stacking and hydrogen bonding. Various PDA configurations were studied using ab initio methods to investigate the formation of early polymerized PDA oligomers.³⁰ It was concluded that PDA films are composed of nearly planar oligomers forming graphite-like layered aggregates, biased towards smaller oligomers, as the larger PDA oligomers were found less likely to form.

By including a layer of PDA in between the PTFE coating and substrate, Beckford and Zou were able to greatly improve the wear resistance of PTFE films.²³,³¹-³² Rubbing tests were performed on the PDA/PTFE composite and a decreased wear was observed with a tenacious layer of PTFE strongly adhered to the surface after the tests had concluded.²³
Combining PDA with PTFE results in a remarkable reduction in wear but also increases the complexity of the system, which warrants the investigation of PDA/PTFE interface properties and adhesive mechanisms between them. The fluorine atoms in the PTFE molecule may introduce the possibility of weak halogen bonding into the PDA/PTFE system.\textsuperscript{33-34} Investigating whether or not ionic, covalent or long range bonding occurs, or if interactions between PTFE and PDA are governed by van der Waals or Coulombic forces instead will provide a clear understanding of the adhesion and mechanisms which cause PTFE films to adhere so well to PDA coated surfaces.

In this study, the adhesion and interface mechanics of individual PDA and PTFE molecules and PDA/PTFE thin films are investigated using \textit{ab initio} methods. Density functional theory (DFT) is used to observe and predict the bonding between PDA and PTFE, specifically investigating the occurrence of hydrogen and halogen bonding and the adsorption energy. Molecular dynamics (MD) is then used to study the adhesive force of each molecule and to investigate how molecules adhere and deform in the presence of external forces. Finally, nano-indentation and scratch tests are performed on a PDA/PTFE thin film to investigate deformation mechanisms at the interface. The results from this study reveal unique adhesive and mechanical properties of PDA/PTFE films, thus explaining experimental observations which show a tenacious layer of PTFE that adheres to PDA after wear studies.\textsuperscript{23}

3.2. Methods

3.2.1. Density Functional Theory

Density functional theory (DFT) is capable of calculating the charges and distribution of electrons in a molecule.\textsuperscript{35} In DFT, bonds between atoms are represented by a distribution of electrons around the nucleus. DFT solves for the ground state energy of the molecule.\textsuperscript{35-36} By finding the equilibrium
state of PDA and PTFE molecules in DFT, we can observe the electron density, and thus determine the type of bonding i.e. hydrogen, halogen or other bonding that may occur between the molecules.

We use the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation \(^{37}\) with the DFT-D dispersion-correction \(^{38}\) to compute the ground state energy for each sample. This approach has previously been used to correct for the long range forces of molecules, and found to be in better agreement with experiments than uncorrected DFT.\(^{21}\) In each DFT simulation, the dispersion energy is converged to \(10^{-6}\) Ry, and a Gaussian spreading is used with a coefficient of 0.015. The kinetic energy cutoff was selected to be 32 Ry with an augmented electron density cutoff set to 200 Ry. We use \(1 \times 2 \times 2 k\) points and a supercell of \(40 \times 30 \times 30\) Å in each simulation. Parametric tests are then performed on the selected cutoff values to verify convergence. All DFT simulations are carried out in Quantum Espresso\(^{39}\) and visualized in Vesta\(^{40}\).

DFT samples each consist of two superimposed molecules, or one single PDA or PTFE molecule. Four molecules of dopamine were selected, the basic dopamine molecule (DPA), the oxygenated dopamine molecule 5,6-dihydroxyindole (DHI), a dimer (DI), and trimer (TRI) (Figure 3.1A-D). Each molecule was selected due to previous studies showing promising adhesive properties.\(^{18, 20, 26, 29}\) The fifth molecule investigated is PTFE (Figure 3.1E).
Figure 3.1 A) Dopamine molecule (DPA) which oxidizes into (B) 5,6-dihydroxyindole molecule (DHI). Atom sites are labeled for convenience in referencing throughout this paper. C) The polydopamine dimer molecule (DI) which consists of two joined DHI molecules bonded through the 2-2 bond site. D) Polydopamine trimer molecule (TRI) which consists of three DHI molecule joined by the 2-8, 5-2 bond sites. E) PTFE molecule viewed along chain backbone showing the helical structure and the side view for the PTFE molecule.

Each DFT sample of superimposed molecules was created by placing one equilibrated molecule centered and 5 Å above the other equilibrated molecule. Each sample was previously equilibrated using MD using the ReaxFF\textsuperscript{19} force field at 0.1 K in order to reduce the number of DFT computations required to find equilibrium positions. The DFT results are then compared with the MD equilibration samples to show differences in predicted hydrogen bonding or minimum energy states. Bader analysis is then used to calculate the charge on each atom, to quantify hydrogen or halogen bonds between the equilibrated molecules.\textsuperscript{41}
3.2.2. Molecular Dynamics

We use molecular dynamics (MD) to investigate PDA/PTFE adhesive forces and their interface mechanical properties. Three distinct tests are performed using MD to investigate the adhesive and interface properties of PDA and PTFE. Adsorption energy is calculated for each molecule pair system to compare with DFT results. Peeling, shearing, and rotational tests of two molecule systems are performed (see Figure 3.2) to investigate the individual PDA oligomers adhesive capabilities. Once the basic mechanisms of adhesion are understood, we perform an indentation and scratch tests on a PDA/PTFE composite thin film to observe PDA and PTFE interface adhesion and deformation.

We first equilibrate individual PDA and PTFE molecules and then study all possible combinations of the aforementioned PDA oligomers and PTFE molecules, which are equilibrated in pairs of two (DPA-DPA, DPA-DHI, DPA-DI, DPA-TRI, DPA-PTFE, DHI-DPA, DHI-DHI, DHI-DI, DHI-TRI, DHI-PTFE, DI-DPA, DI-DHI, DI-DI, DI-TRI, DI-PTFE, TRI-DPA, TRI-DHI, TRI-DI, TRI-TRI, TRI-PTFE, PTFE-DPA, PTFE-DHI, PTFE-DI, PTFE-TRI, PTFE-PTFE). The equilibration tests are performed at 0.1 K using a Nose-Hoover thermostat and allow for a comparison to be drawn between DFT and MD equilibrated states.

Steered Molecular Dynamics (SMD) simulations are useful for drawing similarities between computational studies and atomic force microscopy (AFM) experiments. SMD is used in this work to investigate how PDA molecules are affected by external forces. An external force is applied to one molecule to perform shearing, peeling and rotational tests to observe the adhesive force between each molecule in three directions. The shearing tests apply a force in the X-dimension (Figure 3.2A), the peeling tests apply a force in the Y-dimension (Figure 3.2B), and the rotational tests apply a force in the Z-dimension (Figure 3.2C).
In each test, atoms located on the 2, 6, and 9 atom sites (as shown in Figure 3.1B) are held fixed to prevent any movement. One atom at a time is selected to attach to a spring for the SMD test, using each atom labeled 1-9, and the oxygen atom bonded to the carbon in the 6 position. A total of ten simulations per sample are performed to enable statistical averaging of the results. Parametric studies are conducted to select the appropriate spring stiffness constant, as well as the pulling velocity. The spring constant in this study is chosen as 5.0 Kcal·mol⁻¹Å⁻¹, the pulling velocity is 5 m/s and the temperature 0.1 K to prevent thermal fluctuations.

Figure 3.2 A) TRI-TRI sample visualized using VMD, showing the progress of a shearing test. An arrow indicates where the spring force is applied: on the top molecule on the carbon atom in the 6 position on the right third of the molecule. B) Peel test on the TRI-TRI sample. C) Rotational test on the TRI-TRI sample.

A PDA/PTFE thin film is then created using the molecule which requires the highest force to displace from equilibrium. To create the thin film sample, a PDA film is created by equilibrating TRI molecules for 200 ps. Separately, PTFE molecules with a length of 10 nm are equilibrated for 50 ps. The equilibrated PDA and PTFE samples are then combined and equilibrated again using an NPT ensemble at 300 K for an additional 300 ps. At the end of the equilibration of the PDA/PTFE film, the root mean squared deviation in atom position is calculated to be less than 1 Å, indicating the sample had equilibrated. The density of the composite film is 1.23 g/cm³, the PTFE atoms have a density of 1.24 g/cm³, and the PDA density is 1.28 g/cm³, falling within appropriate ranges of previously reported densities of PDA and PTFE. The PDA/PTFE composite thin
film is periodic in the X and Z dimensions and has a free surface along the Y direction to perform mechanical testing.

Using the equilibrated PDA/PTFE sample, nano-indentation and scratch tests are performed to observe deformation mechanisms between the PDA and PTFE interface. The PDA/PTFE sample is indented and scratched with a spherical diamond indenter with a radius of 2 nm, and a flat diamond indenter. The spherical indenter is used to mimic an AFM tip, while the flat indenter prevents debris formation and allows for more clear observations of the PDA/PTFE interface. Forced based indentation was used to indent the PDA/PTFE samples 1, 2, and 3 nm below the PTFE free surface, using a constant indentation force method. Scratch tests are then performed by sliding the indenter in the X dimension with a constant velocity of 5 m/s, while maintaining a constant normal load. All simulations are performed using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) and visualized using Visual Molecular Dynamics (VMD). All molecular dynamics simulations are performed using a ReaxFF potential, which we compared and verified with two ReaxFF potentials previously used to study PDA and PTFE separately.

3.3. Results and Discussion

3.3.1. Adhesion between PTFE and PDA

After preforming equilibration of the PTFE and PDA molecules using DFT and computing charge distribution in each molecule, we did not observe hydrogen or halogen bonding between PTFE and PDA molecules. An abundance of hydrogen bonding was observed between the PDA - PDA molecules. Figure 3.3A shows the TRI-TRI system which contained four hydrogen bonds, three intramolecular hydrogen bonds and one intermolecular hydrogen bond (see online version). Figure
3.3B visualizes an inset of the electron density around the four oxygen atoms in Figure 3.3A. The hydrogen bonds are shown in green indicating that there is shared charge with the neighboring oxygen atom. Intramolecular hydrogen bonds were observed in the DPA-DPA, DPA-DI, DHI-DHI, DHI-DI, DHI-TRI, and TRI-TRI systems.

The longer molecules such as DI and TRI do not form as many hydrogen bonds when stacked due to less accessible hydrogen atoms as a result of the rigidity of the molecule and the spacing of the hydrogen atoms. An example of this would be the formation of intermolecular hydrogen bonds between the TRI-TRI and not the TRI-DI systems. The TRI has two accessible hydrogen atoms in the center of the molecule, while the DI does not. When another TRI molecule is stacked on top of the original TRI, both middle hydrogens can form hydrogen bonds, however, the DI-DI and the DI-TRI cannot form hydrogen bonds because the nearest accessible hydrogen atoms are on the end of the molecule, making hydrogen bonding more difficult between two longer mismatched PDA oligomers.

Bader analysis was used to quantify the charge per atom in each system. The average charge on the hydrogen atoms bonded to oxygen was found to be zero, indicating that the oxygen atoms are accepting all of the charge from the hydrogen atoms. Figure 3.3C shows the average charge in a hydrogen atom in the DPA-DPA, DHI-DHI, DI-DI, and TRI-TRI systems. Comparing the charges of the hydrogen atoms to the nitrogen atoms (Figure 3.3D) reveals that the nitrogen atoms are accepting neighboring charge. The average charges of the atoms of all systems studied were: Hydrogen, 0.5536; Carbon, 3.6412; Nitrogen 7.3606; Oxygen, 7.7925. The low hydrogen and carbon charges are seen throughout the molecule and is due to the nitrogen atoms accepting neighboring charge.
Figure 3.3 A) TRI-TRI sample showing intermolecular (vertical dotted lines) and intramolecular (horizontal dotted lines) hydrogen bonds forming. B) An inset of the electron charge density verifying the formation of hydrogen bonds observed in the sample. C) The average charge of the hydrogen atoms in same molecule pair studies shows a low hydrogen charge. D) The average charge in nitrogen atoms in the same molecule pair studies shows that the nitrogen atoms are attempting to accept charge from neighboring atoms, thus reducing total carbon and hydrogen charge.

3.3.2. Adsorption Energy

The adsorption energy of each system was calculated to quantify the which PTFE molecules adhered strongest to others. The adsorption energy was calculated using the following equation:

\[ E_{\text{Adsorption}} = E_{AB} - (E_A + E_B) \]  

(1)

where \( E_{\text{Adsorption}} \) is the calculated absorption energy, \( E_A \) is the energy of molecule \( A \), \( E_B \) is the energy of molecule \( B \), and \( E_{AB} \) is the energy of the system of combined molecules \( A \) and \( B \). The adsorption energy can show which molecules are more energetically favorable to combine, and thus, which molecules would be more difficult to remove from each other.
The adsorption energy was calculated using DFT and again in MD using the same atomic configurations. After structural relaxation, the change in the atomic positions of the MD and DFT simulations was negligible. The TRI-TRI molecule pair had the highest adsorption energy in both the DFT and the MD simulations and is used to normalize the rest of the data for better comparisons, though the results of the TRI-TRI simulation are not visualized. A material that has a higher normalized adsorption energy finds the combination of those molecules more energetically favorable.

The adsorption energy to PTFE for all PDA molecules is shown in Figure 3.4A and Figure 3.4B for DFT and MD simulations respectively. We observe a similar trend in adsorption energy for DFT and MD results for all molecules, thus revealing that the TRI molecule has the greatest adsorption energy to the PTFE molecule.

![Figure 3.4 A) The normalized adsorption energies of tested molecules to PTFE performed in DFT. B) The normalized adsorption energies of tested molecules to PTFE performed in MD. The trend in DFT is reflected in MD as well, indicating agreement between the modeling methods.](image)

3.3.3. Shear, Peel and Rotation Tests

To understand the adhesive force of each molecule pair system, shear, peel, and rotational tests are performed using MD which allow observation of deformation of each molecule in different directions. These simulations, as shown in Figure 3.2, demonstrate a correlation between the
molecule size and the maximum force required to displace the molecule from equilibrium. In Figure 3.5A, the results of the SMD simulations are visualized as averages with error bars. The DPA and DHI molecules have comparably low values, while the DI molecule has higher force values, and the TRI molecule has the maximum force values of all molecule pair systems. This is consistent with the observed adsorption energy of the molecules as discussed in section 3.3.2. It can be concluded that the TRI oligomer would require the highest amount of force to move from a PDA system made entirely of other TRI molecules. In Figure 3.5B, the results of the PDA-PTFE systems are shown. In this case, the DI and TRI molecules require the highest forces to separate from PTFE chains. Because the TRI molecule was observed to have high adsorption to both PDA and PTFE, the interface strength would be higher when the PDA/PTFE interface was entirely PDA trimers.

We also observed the straightening of the PTFE molecules during equilibration of the PDA-PTFE samples. Each PDA molecule caused a decrease in the dihedral angles of the PTFE chain. We believe this change in the dihedral angle is due to the repulsive forces between negatively charged F in PTFE and negatively charged atoms in the PDA molecule. The longer the PDA molecule, the longer the affected region in the PTFE chain. We observe that dihedral angle of PTFE straightens when near the benzene rings of the polydopamine oligomer. In Figure 3.5C the PTFE chain dihedral angle is plotted with respect to the chain length. We observe a decrease in dihedral angle corresponding to the location of the PDA trimer, visualized in Figure 3.5D. All PDA molecules showed similar straightening regions of the PTFE chain corresponding to the length of the PDA molecule and continued this pattern even at 300K. Previous studies of the mechanical properties of PTFE chains indicate that a PTFE chain favors the helical structure over planar structure, and
the straightening of the chain may soften the molecule by reducing the modulus of elasticity.\textsuperscript{22} The elastic modulus of PTFE chains has also been shown to be dependent on chain length.\textsuperscript{55}

**Figure 3.5** A) A plot of the maximum force in the oligomer pair system and the SMD test performed. In general, the larger the oligomer, the higher the force needed to move that oligomer from equilibrium position. B) Plot of the maximum force in the oligomer-PTFE system. The highest adhering oligomer was the DI, followed closely by the TRI, and the lowest was the DPA molecule. C) A plot of the dihedral angle of the PTFE chain vs the length in the PTFE chain. We observe that dihedral angle of PTFE straightens when near the benzene rings of the polydopamine oligomer. D) PTFE chain and PDA trimer showing the straightening of the PTFE chain dihedral angles at the location of the trimer.

Comparing the results, the trimer molecule was selected as the molecule to create a PDA/PTFE thin film composite. The trimer molecule had the highest adsorption energy both to itself and to PTFE, and it required higher forces to displace it from equilibrium when placed on other TRI or PTFE molecules. A film made solely from the TRI molecule could be expected to have a higher adhesion to PTFE and less susceptible to wear.

### 3.3.4. PTFE and PDA Thin Film

The PDA/PTFE thin film was created by separately equilibrating PDA trimer molecules and PTFE molecules, combining the PDA and PTFE parts to a composite, and equilibrating once more. After the equilibration of the PDA/PTFE thin film, PTFE chains were observed to penetrate the adjacent
PDA layer (Figure 3.6A&B). The PTFE adhered to the substrate by grasping the PDA with the ends of the PTFE chains, which increased the roughness of the PDA/PTFE interface (Figure 3.6C&D). The increased roughness increased the number of PTFE chains which were touching PDA which may help in reducing wear at the interface by increasing the contact area between PDA and PTFE surfaces. The PTFE molecules were observed to have a straight helical pattern with many defects and random angles mixed throughout the chains, similar to observations in the individual simulations of PDA and PTFE molecules.

3.3.5. Indentation

To study deformation mechanisms of PDA/PTFE, a spherical indenter with a radius of 2 nm and a flat indenter (Figure 3.6E&F), both made of diamond, are used to indent the PDA/PTFE thin film. Indentation depths of 1, 2, and 3 nm were indented using a constant normal force on the indenter. During the indentation using the spherical indenter, we observe PTFE chains were compressed and bent around the indenter, creating a film which wrapped around the indenter. There were some PTFE chains which did not adhere to the indenter or the PDA, which are easily removed from the film. This observation agrees with our previous simulations which showed that the lowest adsorption energy is of PTFE to PTFE. The PTFE molecules are thus easily removed when neighboring other PTFE molecules, and large deformation is observed.

During indentation with the flat indenter, chains were compressed and thus lay flat on the indenter or flat on the PDA substrate. Some segments of PTFE chains were oriented perpendicular to the PDA substrate. However, since every chain in this sample was either touching the PDA or the flat indenter, all chains eventually were oriented parallel to the substrate and indenter. The cylindrical shape of the PTFE molecules along with the nearly uniform chain orientation allowed the PTFE
layer to deform easily. The rigid PDA trimer molecules oriented randomly in the substrate however resisted deformation more during indentation.

Figure 3.6 A) TRI/PTFE thin film after equilibration, an inset showing the modeled section of PDA/PTFE. B) Combined model of PDA/PTFE during equilibration showing the formation of root like structures and the roughening of the PDA/PTFE interface. C) Isolated visualization of PTFE from (B). D) Isolated visualization of PDA from (B). E) PDA/PTFE film indented 2 nm with diamond spherical indenter. We observe that some PTFE chain adheres to the indenter. F) PDA/PTFE film indented 2 nm with flat diamond indenter.
3.3.6. Scratch

After indentation, a scratch test was performed using each indenter for a total length of 1 nm. The spherical indenter caused severe damage to the PTFE substrate in the form of debris. The flat indenter, however, prevented chains from leaving the surface and thus serves a greater purpose as a qualitative study. Due to the constant normal load applied throughout the scratch, the indenter height continued to decrease throughout the scratch. Three normal loading cycles were applied to the thin film to investigate how the film performed under scratch at varying distances from the interface. However, the indenter in every simulation continued to compress the material until the film density was 1.96 g/cm³.

PTFE chains which were near the surface of the film adhered to both the flat and spherical indenter and formed a transfer film (flat indenter visualized in Figure 3.7A). These molecules moved with the indenter as the scratch progressed. PTFE chains in an intermediate layer (Figure 3.7B) were seen to deform, however, they never left the vicinity of the neighboring PDA oligomers, most likely caused by the PTFE chains penetrating the PDA layer. PTFE molecules which were near the PDA/PTFE interface (Figure 3.7C) had a large number of adhering PDA oligomers. These molecules remained close to the PDA substrate and moved only as the PDA oligomers deformed.

The PDA oligomers formed pi stacking structures with hydrogen bonding between them as reported in previous studies of PDA substrates, and in the single molecule observations in this study.¹⁸ As the indenter penetrated the film, the oligomers were observed to deform via shearing and sliding. Delamination at the PTFE and PDA interface would require PDA molecules to deform via peeling, which was observed to require the highest force in the single molecule study, and not observed at all during the indentation or scratch. PDA trimers were observed instead to rotate and shear and fill any voids present in the PDA matrix (Figure 3.7D).
Figure 3.7 A) Top layer of PTFE after equilibration, indentation, and scratch. The PDA layer is outlined on bottom (green color, see online version), the PTFE layer is outlined on top (purple color, see online version), and the overlap between the PDA and PTFE is clearly visible. The diamond flat indenter is seen above the PTFE layer and a PTFE chain inside the silhouette of the PTFE layer. The PTFE chain adheres to the diamond indenter and remains there through the simulations. B) An intermediate PTFE chain which adheres to a few PDA oligomers. Throughout the indentation and scratch, the relative positions of the PDA oligomers and the PTFE chain remain relatively unchanged. C) Interfacial layer of PTFE and the neighboring PDA oligomers. D) PDA oligomers (orange color, see online version) shear past local surrounding PDA oligomers (blue color, see online version) during indentation and scratch. Shearing of PDA oligomers only occurs when during sliding and results in filling voids in lower layers of the PDA substrate.
PDA oligomers are observed to shear and rotate past each other as indentation and scratch occurs, ultimately favoring an orientation normal or parallel to the scratch direction. The scratch force reached as high as 500 nN before dropping, only to raise again to approximately the same value. The constant fluctuation in the forces is caused by the constant shifting of molecules in the substrate. The alignment of PDA molecules in the film was observed to change during scratch, changing orientation that aligns with the scratch direction. The movement of PDA in the film occurred through shearing and rotating of PDA oligomers. Peeling was not observed to occur, and we believe it would cause separation in the PDA substrate and ultimately lead to tearing or large deformation.

3.4. Conclusions

Simulations performed in DFT show that the main adhesive force between PDA and PTFE is van der Waals forces and inter and intra molecule hydrogen bonding is observed between PDA molecules. Adsorption energies were calculated between each molecule studied and the PDA trimer molecule was seen to have the highest adsorption energy to other molecules investigated.

Shearing, peeling and rotation tests were conducted using SMD to investigate deformation of PDA/PTFE molecules, and confirmed the PDA trimer (TRI) to be resilient to perturbations from equilibrium. Peeling of PDA oligomers from PTFE or PDA molecules required the highest force compared to shearing. All PDA oligomers were observed to prevent PTFE molecules from forming the typically observed spiral helix near the region of the PDA oligomer during isolated tests, which is known to lower the elastic modulus of PTFE molecules. However, due to the random orientations of PTFE molecules on a PDA substrate, the spiral helix is not lost on a large PDA/PTFE thin film, but consist of straight, spiral, and reversed spiral segments.
A PDA/PTFE thin film made of PDA trimers and PTFE was indented and scratched to observe interface deformation mechanisms. Some PTFE molecules were observed to penetrate the PDA substrate, which reduced the deformation seen during indentation and scratch. PTFE molecules adhering to the PDA layer deformed less than other PTFE molecules. The primary mode of deformation in the PDA layer was a combination of shearing and rotating of the PDA molecules. It is expected that delamination occurs when PDA oligomers peel from either the PTFE or PDA substrate, which did not occur in the thin film. PDA molecules were observed to orient in a manner that is conducive to peeling, however, they would deform through shearing or rotating before peeling could begin.

Interfacial PTFE chains within interaction range of multiple PDA oligomers were observed to deform less than chains not near PDA. Experimental PDA/PTFE films report a drastically decreased wear rate when compared to pure PTFE. The decreased wear rate of PDA/PTFE films is in part due to the penetration of PTFE into the PDA layer, as well as the unique deformation mechanisms of PDA which prevent tearing or major delamination from occurring.

The deformation cycle of PTFE can be explained, as well as the tenacious layer of PTFE that adheres to PDA by the deformation mechanisms seen in this paper. PTFE has a low adsorption energy to itself when compared to PDA. The top layers of PTFE are easily removed during scratch because they adhere either to the indenter or are removed from the PTFE bulk during the wearing process. The PDA surface is penetrated by PTFE chains during their first encounter of the PDA substrate. The rough surface area allows PTFE chains to adhere to PDA molecules, which decreases deformation during indentation and scratch. During the scratch of PDA/PTFE thin films, the PTFE molecules which do not adhere to PDA may be removed as debris or pileup. PTFE molecules adhering to PDA deform as the PDA molecules deform. PDA molecules are observed
to shear and rotate and prefer not to peel. By shearing and rotating, the PDA molecules slide and align parallel or perpendicular to scratch direction.

Due to the lack of deformation via peeling in the PDA molecules, and the low deformation of PTFE chains when adhering to PDA, we believe the lowest wear in PDA/PTFE films would occur when every PTFE molecule is in contact with PDA molecules. Increasing the interacting surface area between PDA and PTFE can further increase the adhesion between PDA/PTFE interface.

3.5. Acknowledgements

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3.6. References


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Chapter 4: The effect of density and surface topography on the coefficient of friction of polytetrafluoroethylene films

Abstract

Polytetrafluoroethylene (PTFE) film is observed to increase surface roughness during annealing. Longer annealing times leads to greater surface roughness. The coefficient of friction of PTFE film is affected by the shape of microscale sized particles on the film surface. In this study, we investigate the coefficient of friction of PTFE films using a coarse-grained molecular dynamics model based on experimental observations. We observe how the variation in PTFE chain length and film density affect the topography of PTFE films. We also investigate how these properties of PTFE, and the indenter radius affect the coefficient of friction observed during surface scratch. We find that short PTFE chain lengths create a dense film with greater particle spacing, but longer chains form a mesh structure which reduces the density and creates overlapping portions of particles in the film. We develop a convolutional neural network to classify PTFE film surface and predict the coefficient of friction of a modeled film based solely on the equilibrated film topography. The accuracy of the network was seen to increase when the density and images of internal fiber orientation were added as input features. These results indicate that the coefficient of friction of PTFE films in part is governed by the internal structure of the film.

4.1. Introduction

Polytetrafluoroethylene (PTFE) has been widely investigated for its low coefficient of friction.\textsuperscript{1-4} Experiments have improved wear of PTFE by incorporating filler particles, intermediate surface coatings, and forming other PTFE composites, making PTFE a more viable solution for some mechanical applications.\textsuperscript{4-7} More recent research on PTFE films showed that during annealing,
PTFE film surface topography changes and begins to form spindle shaped particles, and the wear of the films also changes.\textsuperscript{8}

Molecular dynamics and density functional theory have been previously used to investigate nanoscale properties of PTFE films.\textsuperscript{9-11} Using a recently developed coarse-grained (CG) model of PTFE, experimental length scales can be modeled and mechanical properties can be predicted based on PTFE particle shapes.\textsuperscript{12} Using coarse-grained models, PTFE film properties can be studied from nanoscale to microscale. Observing how microscale properties of PTFE are affected by nanoscale changes in the film and microscale PTFE structures is an ongoing research of PTFE films.

In our previous work, coarse-grained models of PTFE particles of various shapes were indented and scratched. We observed that the density of the particle, as well as the surface topography directly affected the friction coefficient.\textsuperscript{12} During the annealing of PTFE films, the particle shape, as well as the surface topography change from spherical particles and a relatively flat surface, to needle particles with a higher surface roughness.\textsuperscript{8, 13-14} Since the annealing of PTFE causes a physical change in the film topography and internal structure, we believe it is possible to predict the coefficient of friction of PTFE films by observing the surface topography.

Machine learning algorithms have been recently applied in the field of material science for classification and regression analysis.\textsuperscript{15-17} A convolutional neural network is a type of machine learning algorithm that uses images as inputs. If the coefficient of friction of PTFE particles can be predicted solely from images of the surface topography, a CNN would be useful in predicting, and eventually optimizing the surface topography of PTFE films.
In this study, coarse-grained models of PTFE particles are used to investigate how various nanoscale parameters affect the microscale properties of PTFE films. We investigate how the PTFE chain length, film density, and the indenter radius affect the coefficient of friction (COF) and topography of PTFE films. The number of images which can be produced using experimental methods is limited, we therefore develop a machine learning code using a convolutional neural network on images produced from molecular dynamics simulations. We attempt to predict the coefficient of friction based solely on the surface topography and density of the PTFE films. Multiple datasets are used to compare the reliability of results as well as compare to experimental PTFE films.

4.2. Methods

To mimic experimental film surface topography with different annealing times of 0, 4 and 8 minutes, height maps are extracted from small selections of AFM images (see Figure 4.1). Models are created using a coarse-grained (CG) potential utilizing ReaxFF force field. In the CG potential, there is no cross-linking between molecules and interactions between fibers are due to van der Waals forces. Further details of the potential are described in our previous study. Each model is created by generating PTFE chains with random orientations within a defined height map. Since our focus is to determine the effect of topography of the PTFE film and considering the computational limitations, the AFM image selections are reduced by a factor of 10 and used as height maps to create the CG models. The gradient of the peaks and valleys of the film surface remain the same for the scaled model. Multiple models are then created that span the entire AFM image to capture variation in surface topography and this enables the simulation of the entire AFM image area. All CG models are then equilibrated and converted into images to be used for the machine learning code (Figure 4.1).
**Figure 4.1** (Column A) Images of PTFE films taken through atomic force microscopy (reused here with the permission from the publisher).\(^8,18\) (Column B) Selections from the AFM images show a magnified view of the film which are used to create the CG models (Column C) CG models are created from the selections, equilibrated and visualized in VMD (Column D) CG models are turned back into images to compare with the original AFM selection image. Models are based on PTFE films which were annealed for 0 (Row E), 4 (Row F), or 8 (Row G) minutes.

PTFE films are each generated with periodic X and Z dimensions measuring 92 nm each and 25 nm in the Y dimension. Parametric tests were performed on PTFE chain length, film density, and indenter radius, holding all variables constant except one. The PTFE chain length is varied from 54, 81, and 108 Å, the film density is varied from 0.58, 0.71, 1.06 and 1.42 g/cm\(^3\), and a repulsive indenter with a radius varied from 8, 12, 16, 24 and 32 nm is used. Film densities are selected based on experimental reports of PTFE\(^{19}\) and the indenter size is selected to allow the CNN to better observe the local film topography and is based on previous experimental investigations of PTFE films.\(^8\) CG models are equilibrated at 300 K for 50 ps using an NVT ensemble before
indentation and scratch are performed to determine the COF. After preliminary studies, indentation and scratch velocities are selected as 10 m/s using a constant displacement repulsive indenter, at a constant indentation depth of 12 nm and scratch length of 3 nm. All simulations are performed in LAMMPS\textsuperscript{20} and results are visualized in VMD\textsuperscript{18}.

204 models based on AFM images of PTFE films are created (Figure 4.1B-D). After equilibration, indentation, and scratch, the density and maximum coefficient of friction of the model are recorded. All 204 images, the densities, and the COF values are used in a convolutional neural network to attempt to recognize patterns in the PTFE film surface which may lead to an understanding of the relationship between PTFE film topography and COF. A detailed description of the neural network architecture and validation can be found in the supplementary material.

4.3. Results and discussion

To investigate how PTFE films are affected by individual particle characteristics, we performed simulations where the PTFE chain length, film density and indenter radius are the varied parameters. Indentation and scratch tests were performed and the coefficient of friction was computed. During simulations investigating the effects of chain length on the properties of PTFE films, a topographical change was observed in the particles. The shorter PTFE chains are capable of falling into cavities in between particles (Figure 4.2A) whereas longer chains form particles with a greater inter-particle spacing (Figure 4.2B). When chains are greater than 100 Å long, they overlap particles and begin to create mesh like structures (Figure 4.2C). The density of the films decreased, and the film surface roughness increased as the chain length increased. The behavior reported is mainly due to the Lennard-Jones term in the potential describing the PTFE chains. While the bond length between coarse-grained beads remains relatively constant, the angle of
PTFE chains varies to maximize contact with neighboring chains, reducing the total energy of the system.

Figure 4.2 PTFE films created with 54 Å (A) 81 Å (B) and 108 Å (C) long chains. The 54 Å chains form closely spaced particles as opposed to the 81 Å long chains. The 108 Å long chains form particles which are separated from each other but the length of the chains begins to overlap the particle gap.

Due to the differences in surface topography, each model exhibited different COF profiles during scratch test. Each model showed an initial negative COF (see Figure 4.3), a phenomenon observed in other molecular dynamic simulations investigating friction at the nanoscale\textsuperscript{21} and is primarily due to slipping of chains during indentation and scratch, or the local surface topography in our simulations.
The normal load on the PTFE film is dependent on the film topography and indentation depth. The horizontal load shows a stick slip behavior is occurring between layers of PTFE chains in the film. Combining the forces by calculating the COF shows both the dependence on topography and stick slip behavior (Figure 4.3A).

The densities are also seen to decrease as the chain length increases (Figure 4.3B). PTFE chains are known for their ability to slide past one another easily.\textsuperscript{22-23} We observe PTFE chains sliding over each other during the scratch, and when a void is present the chains move freely and coalesce between particles. The longer chains are more likely to tangle with others and form a more porous mesh than the compact particles observed in the 54 Å long chains.

We select the 54 Å chain length for further studies, because it showed a higher density and would allow for a higher resolution surface topography images when attempting to compare to the AFM images. We then performed a single scratch test using a 12 nm radius indenter and scratched for 30 nm (parametric study for indenter size is discussed in the supplementary material). We observed that after approximately 2 nm of scratch distance, the COF profile started to reflect the patterns in surface topography, and there were no negative values for the remaining scratch distance, hence a 3 nm scratch distance is used to capture COF values.
Figure 4.3 A) Plot of the maximum COF vs scratch distance on the PTFE films of varying chain length. B) Plot of density of the PTFE film vs chain length. The visible silhouette of the indented region of the PTFE film is shown for the 54 Å (C), 81 Å (D) and 108 Å (E) long chains. Due to the valley seen in the 81, and 108 Å long chain models, the COF drops due to chains deforming into the gap region.

We next investigate how PTFE film density affects the topography and COF values. There was a change in the COF value as the indenter moves from one particle to another, however, as the film density increased, this drastic change became more gradual (Figure 4.4A). The COF of the films decreased as the density increased, agreeing with other studies of PTFE particles and films (Figure 4.4D). For further studies in this paper, we select a density of 1 g/cm$^3$ and PTFE chain length of 54 Å.
Figure 4.4 A) Plot of the coefficient of friction vs the scratch distance for the different film densities. B) Plot of COF vs film density. C) 0.58 g/cm$^3$ density film. D) 0.71 g/cm$^3$ density film. E) 1.06 g/cm$^3$ density film. F) 1.42 g/cm$^3$ density film.

Additional simulations are then performed using 54 Å long chains, with a minimum density of 1 g/cm$^3$, and an indenter radius of 12 nm. Images of 0, 4, and 8-minute annealed PTFE films are separated into 68 equal sections. Each section is used to create 204 CG models. Identical indentation and scratch tests are performed on the CG models and the density and surface topography are recorded as inputs for a convolutional neural network, while the COF is used as labels. Here we attempt to use a neural network to predict frictional property of PTFE films. Our purpose is to understand if it is possible, and if so, what factors need to be accounted for when attempting to predict the COF of PTFE films.

In previous models of PTFE films it was hypothesized that the density and surface topography were the major contributors to the COF of PTFE. In Figure 4.5 the results of the scratch tests on CG models are plotted for visualization of the dataset. Some data never resulted in positive COF values due to the negative sloping topography of the small selection of the film. We also observed a higher number of negative COF values for the lower density regions, and the longer annealed films (Figure 4.5A). Because the films which were annealed longer have a greater difference
between the peaks and valleys of the film, they are also observed to have a greater span between the maximum and minimum COF values.

**Figure 4.5** A) COF of each model vs Density. Clustering of the data shows that the models based on longer annealing times have a greater number of negative COF values. This is due to the greater number of peaks and valleys in these models B) Box plots of the density of each annealing time. C) Box plots of the COF of each annealing time model.

Isolating the density of each model shows that there appears to be a distinguishable difference between the 0-minute density values and the others, but differentiating between 4 and 8-minute models appears to be more difficult (Figure 4.5B). The resultant COF values were difficult to differentiate between all models (Figure 4.5C). Using the 12 nm indenter, COF values ranged between -0.39 and 0.30, comparable with experimental results which range between 0.1-0.3.\(^4\)

Using the CNN, we attempt to accomplish the arduous task of predicting the COF based purely from an image of the modeled PTFE film. Four separate networks were created to train all data using the same design except for the number of inputs (Figure 4.6A). As an input into the CNN, each network used the topography of the CG models. As inputs, Net 1 uses only the topography of the CG models; Net 2 includes the density of the models; Net 3 includes internal slices of the film (see supplementary material); and Net 4 includes the density, and internal slices of the film. By using these four similar networks we can identify what factors into the COF of PTFE films.
Our training data reached its peak accuracy within a couple thousand iterations (Figure 4.6A). After training and testing, Net 1, which included only the topography of the film, was able to predict the COF correct 31% of the time (Figure 4.6B). The low percent of correct predictions partially reflects the observations made on the dataset prior to training and testing. The network is learning what one annealing time COF values look like (the 0-minute) and guessing at the other two.

Net 2, which used the topography and density of the film performs the best of all the networks. This indicates that the density of the PTFE film greatly affects the COF of the models, as it almost doubles the accuracy from the original network. Including the internal images of the film, as seen in Net 3, also increases the number of correctly predicted values, but not more than Net 2, indicating that the internal structure of the film, or internal fiber orientation, does affect the COF. The difference between the number of correctly predicted COF values of Net 3 and Net 4 is negligible, indicating that knowing the density of the film and the internal structure does not increase the information we have about the film.
The inability for the networks to predict a higher number of correct COF values is due to CG model. Each model was used to copy the topography of real PTFE films but not the internal structure. It has been shown in experimental studies that there is a physical change which occurs in PTFE films during annealing which causes films to increase their surface roughness. This is not originally considered in our models because it is unclear how this process takes place.

A second dataset was created to consider the annealing process by varying the internal fiber density as annealing time increased. Using an identical CNN to Net 1, the accuracy of the predicted COF of this dataset was 57%. It is apparent by these results that if the internal structure of PTFE films changes during annealing, as is believed, a CNN could be developed for experimental films to predict the COF, and ultimately optimize the film topography to reduce the COF.

4.4. Conclusions

We investigated PTFE coarse-grained models based on the topography of PTFE film during different annealing times. We studied the effects of PTFE chain length, density, and indenter radius on PTFE coefficient of friction. We found that as the PTFE chain length increases, the surface topography changes from isolated particles to a mesh like structure. We also observed a decrease in the film density as the chain length increases.

We also concluded that as the density of PTFE increases, the coefficient of friction decreases. The lower the density, the more porous the film. A higher porosity of PTFE results in weak support as the indenter scratches through the film substrate ultimately lowering the COF.

A convolutional neural network was used to assess the topography of PTFE film models and to predict the COF based on the surface topography. We found that our data based on the 0-minute annealing time of experimental PTFE films exhibited different characteristics than those models
based on 4 or 8-minute annealing times. Our network when including the density of the film was able to predict to 1 decimal place the COF up to a 59% accuracy.

The low accuracy of our network is caused by the similarities between the internal fiber structure of the CG models. All models were based on selections of a larger topography, yet did not capture the difference between the 4- and 8-minute experimental films. When images of the internal fiber orientation were used as input to the CNN, the accuracy increased from 31% to 54%, indicating that the density, and the internal structure of PTFE affect the COF of the film. A second dataset was created which altered the internal structure of the films based on annealing time and had a base accuracy of 57%. Based on these results, we believe better accuracy could be achieved by understanding more about the internal fiber structure of PTFE films or using experimental COF results. We also believe a CNN trained on experimental COF values could be created which could predict an optimized surface topography for reducing the COF. To better understand the COF of PTFE films, the internal structure of PTFE must be investigated and how PTFE chains form particles, and change during annealing may shed further light on the internal fiber orientation of PTFE films and how the nanoscale structure of PTFE affects macroscale friction.

4.5. Acknowledgments

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4.6. References


4.7. Supplementary Materials

4.7.1. Convolutional neural network (CNN) architecture and validation

The convolutional neural network is written in Python\(^1\) using the Pytorch\(^2\) package and is described in Figure 4.7.1. Each convolutional layer uses a 2x2 filter size, a stride of 1, and a ReLu activation function. Max pooling layers have a pooling size of 2x2 and stride of 1. After the layers have been flattened, the density of the film is added to the flattened 128 filters to create 129 nodes, which are all fully connected to one single output (see Figure 4.7.1). The single output is compared to the coefficient of friction calculated during molecular dynamics tests to find the loss of the network.

Parametric tests were performed on preliminary data to optimize network performance.

![Convolutional neural network architecture](image)

**Figure 4.7.1** Convolutional neural network architecture. Notice that density (\(\rho\)) is added onto the fully connected layer once the filters are flattened.

A validation of the network was conducted by training and testing on the CIFAR-10 dataset\(^3\), using the same network architecture except the number of outputs. A secondary network validation was performed on the AFM images classifying which annealing category the image belonged. The percent of correctly predicted images for the CIFAR-10 and AFM images were 64.41% and
91.53% respectively. The network presented throughout the rest of this work uses only one output, intended to predict the coefficient of friction of the input image.

### 4.7.2. Chain length and the effect on image resolution

Because we are attempting to use a CNN to predict the coefficient of friction of PTFE films, we need to design the type of images used as inputs. The size of the image was selected to be 28x28 pixels, which span a 92 nm square film. Because the number of pixels was selected to match a specific area of the film, the image input into the network have a limited resolution. Each pixel represents 3.28 nm of the model. When PTFE chain lengths of 54 Å are used, we reduce the number of pixels an individual PTFE chain spans, increasing the definition of the images. A PTFE chain with a length of 108 Å could span up to 4 pixels (180 ÷ 32.8 = 3.29), which would reduce the definition and decrease the networks ability to distinguish features on the surface of the film.

### 4.7.3. Indenter radius results and discussion

To compare with other studies, we investigate how the variation in indenter radius affects the COF. PTFE chains of 54 Å are used to create films with a density of approximately 1 g/cm³. Indenter radius varied from 8, 12, 16, 24, and 32 nm in diameter. Due to indentation on the film as well as stick slip between PTFE layers, the initial COF value was negative, however, after 20 Å each indenter had scratched past the initial indentation point and into more stable COF values (Figure 4.7.2A). The COF values at 3 nm are averaged and the standard deviation taken to plot the results in Figure 4.7.2B.
**Figure 4.7.2** A) Plot of COF vs scratch distance. B) Plot of the COF vs indenter radius. C) Image of the center of the PTFE film before indentation and scratch. D) Topography map of the center of the PTFE film before indentation and scratch, showing the peaks and valleys each indenter would contact during indentation. E) Image of 8 nm indenter showing the indenter sitting within the peaks and F) 16 nm indenter sitting on top of the peaks.

The 8 nm indenter experienced a change in the COF at the midpoint of the scratch due to the topography of this particular model (Figure 4.7.2 C&D). The 8 nm indenter sits inside the valley
surrounded by the peaks of the PTFE film (Figure 4.7.2 E), but the indenter sits on top of all the valleys when it is as large as 16 nm (Figure 4.7.2 F) To capture how the COF changes with topography in further simulations, we selected the 12 nm indenter radius because it was small enough to observe the COF changes due to topography height, but not too small to result in major spikes of COF values.

To ensure our models were accurately representing PTFE films, a spherical indenter with a radius of 120 nm was used to calculate the COF of films and compare to experimental results. The maximum COF calculated from our simulations with a larger indenter tip was 0.064, within the range of experimental films created similarly to the ones used to form our CG models, which report COF values between 0.06-0.1.\textsuperscript{4}

4.7.4. **Comparison of 3 nm and 30 nm scratch length**

Because we are attempting to simulate data to use in a machine learning program, the amount of time each simulation can run must be kept short. By decreasing the time to perform simulations, we can create more data which is necessary in a CNN. Additional scratch tests were performed to investigate the differences between a 3 and 30 nm scratch length. During these scratch tests we observed the transient regime to be within the first 2 nm. The last 1 nm which we present in the manuscript contains the beginning of the saturated values of the COF. For the duration of the 30 nm scratch, the COF closely follows the surface topography, as seen in Figure 4.7.3A.
Figure 4.7.3 A) Plot of the coefficient of friction of a 54 Å chain model scratched for 300 Å (blue). The results for the first 30 Å are used in the CNN. After the first 20 Å, the COF exhibits behavior particular to the topography of the film. i) The initial PTFE film surface with a red circle surrounding the asperity which causes the increased COF observed from the 30-200 Å scratch distances. ii) The topography of the PTFE film after 30 Å. iii) The asperity has begun to be flattened under the indenter, and the coefficient of friction climbs. iv) The asperity is completely flattened, and the coefficient of friction has decreased to what it once was in the first 30 Å of scratch.

4.7.5. Characterization of film dataset

Characterization on the coarse-grained models was accomplished to better understand the relationship between the coefficient of friction and the film topography. In each model we performed a characterization in the same line where the indentation and scratch were performed (Figure 4.7.4A). A film profile is shown in Figure 4.7.4B, and the center-line average, the variance, and the skewness are shown for all models (Figure 4.7.4 C-D). Our results show a significant difference in the center line average and variance between the 0-minute annealed models and the others, however, the 4- and 8-minute models are very similar.
Figure 4.7.4 A) Image of a coarse-grained model based on a 0-minute annealed PTFE film. A line is drawn through the film where the scratch on the film is performed. B) Film characterization showing the profile at the point where the scratch is performed. C) Statistics of the center-line average of the entire dataset. D) Statistics of the variance of the entire dataset. E) Statistics showing the skewness of the entire dataset.

4.7.6. Internal fiber orientation image creation

The atom coordinates of each model are used to create images as input into the CNN. An image is initialized in Python using 0 as the default image color. The atom coordinates of each model are imported and looped through to find the maximum height of the model in each pixel of the initialized image. The resulting image is normalized to the total maximum height from all models and used as input into the CNN.

To create the images of the internal fiber orientation of each model, the model height is divided into quarters and the maximum atom height which can contribute to the image height is capped at each quarter interval, resulting in four separate images. The four images represent the topography
of the particle and the internal structure of the particle at three different heights. This allows the
network to view the internal fiber orientation of the models and results in a better percent of correct
COF predictions after training and testing.

4.7.7. Internal fiber orientation simulations
Based on the results in the manuscript, we investigate how internal fiber orientation affects the
COF of films with identical topographies. We used a single 0-minute annealed model and removed
the bottom 10 nm of PTFE chains, and replace them with a PTFE film where all chains are oriented
in the same direction. One film with parallel and one with perpendicular chains to scratch direction,
are both equilibrated and scratched as described in the manuscript. The results of the COF values
from these films varies depending on the internal chain orientation. The COF values where internal
chains are oriented parallel to the scratch direction have a lower COF than a random orientation,
which is lower than a perpendicular orientation. Results are represented graphically in Figure
4.7.5A, showing the trends in the COF values. Figure 4.7.5 B-D show the random, parallel, and
perpendicular internal fiber orientation of the area where scratch is performed in the film.
**Figure 4.7.5** A) Plot of the coefficient of three identical film topographies with varying internal fiber structure. B) Image of the random internal fiber orientation in the area where scratch is performed. C) Image of the parallel fiber orientation. D) Image of the perpendicular fiber orientation.

4.7.8. References

Chapter 5: Conclusions

Since the discovery of PTFE, studies have attempted to improve the durability of the low friction material. The addition of PDA has increased durability dramatically as well as reduced the coefficient of friction. In this work we have studied both PDA and PTFE and gained valuable insight to the adhesive mechanisms, mechanical properties and behavior of PDA and PTFE molecules and films.

5.1. Investigating the effects of environmental conditions on mechanical properties of PTFE chains.

5.1.1. The wear and mechanical properties of PTFE chains

PTFE chains ranging from a 3 Å to 1000 Å are investigated using tensile tests performed using molecular dynamics. It was observed that PTFE chains under 25 Å did not contain the typical spiral associated with PTFE molecules. Chains under 25 Å in length also had a lower elastic modulus than chains above 25 Å. The decrease in the elastic modulus is caused by the lack of a spiral formation in the carbon backbone of the PTFE chain. The spiral in the chain allows for a higher stress to be applied before breaking. The elastic modulus of PTFE chains stabilized at a value of 524.8 GPa.

Tensile tests were performed on PTFE chains in vacuum and water. The molecules in vacuum all exhibited slightly lower maximum stress before breaking. Water acts as a stabilizer and prevents bending in the PTFE chain which allows a slightly higher strain to be achieved compared to chains in vacuum. Raising the temperature of PTFE chains from 300 K to 600 K resulted in a linear decrease in the maximum stress the chain could withstand. At 300 K the 100 Å PTFE chain could withstand 74 GPa of tensile stress where the chain at 600 K could only withstand 60 GPa.
5.1.2. The wear and mechanical properties of PTFE nano-film

The largest obstacle to overcome in PTFE films is the high wear rate. To understand how wear affects PTFE chains, indentation and scratch tests were performed on nanoscale PTFE film. The film consisted of aligned PTFE chains each 107.7 Å in length using a LAMMPS repulsive indenter. The force necessary to penetrate through one layer of PTFE chains was 400 nN. No chains were broken during indentation or scratch, and the contact pressure of the indenter was calculated to be 20 GPa, much lower than the 80 GPa of tension the chain can withstand.

A scratch test was performed at angles 0, 45, and 90 degrees measured parallel to the PTFE chain. When the scratch orientation was parallel to chain orientation, the chains opened and closed like a zipper, allowing the indenter to slide through the material with little resistance. The coefficient of friction of the 0-degree scratch (parallel to chain orientation) was as low as 0.05. When the scratch direction was 90 degrees (perpendicular to chain orientation), a much larger deformation in the substrate was observed, showing buildup of PTFE in front of the indenter, and a higher coefficient friction averaging around 0.15. The 45-degree scratch showed a mixture of the two deformation mechanisms, with some slight buildup. However, PTFE chains moved out of the scratch path more in the 45-degree scratch than those in the 90-degree scratch. COF values for the 45-degree scratch fell in between the 0- and 90-degree scratch, averaging around 0.1.

5.1.3. Investigate PTFE topography change due to annealing

To conclude the investigation of individual PTFE molecules, simulations were performed to investigate how PTFE particles may react to annealing. PTFE particles were created and equilibrated at 26.85 °C, 226.85 °C, and 326.85 °C. As the temperature of the PTFE chains increased, the curvature of the particle also increased. It was concluded that during the annealing
process, PTFE particles undergo a structural change which leads to an uneven surface topography in the PTFE film (see Supplementary Materials section 6.1 for further details).

5.2. Investigating adhesion and interfacial properties of PDA/PTFE composites.

5.2.1. The adhesion of polydopamine oligomers

Molecular dynamics was used to investigate PDA monomers and trimers in an aqueous solution on a metal substrate. The number of hydrogen bonds was found to increase as the water percent of the solution was increased. When greater amounts of water were added into the samples, PDA monomers and trimers equilibrated with a slightly larger gap between molecules. This allowed for more water to form hydrogen bonds with other dopamine molecules.

The hydrogen bonding also increased as the film thickness increased. Naturally, with a greater number of oxygen atoms, there is greater probability of hydrogen bonds (O-H) forming. When the type of dopamine molecule was changed, however, the number of hydrogen bonds also changed. The trimers were seen to form more hydrogen bonds than the monomers, and a mixed solution containing both monomers and trimers showed even more hydrogen bonds.

The dopamine trimers often formed layers of stacked molecules and showed pi-pi stacking. The monomers formed either pi-pi stacking or a pinwheel formation. When these oligomers are mixed, the space between molecules was increased due to the inability to form stacked molecules. The increased number of hydrogen bonds in the mixed solution can be attributed to the randomness of the film, and the space between dopamine oligomers. The increased water content, dopamine layer thickness, and dopamine oligomer mixed solutions confirmed the theory that mixing a dopamine solution increased hydrogen bond formation, and thus increased the deposition rate. (See Supplementary Materials section 6.2 for further details)
5.2.2. PDA and PTFE film deformation mechanisms

Having a basic understanding of the mechanical properties of PTFE and some adhesive properties of PDA, we next studied the two materials together. Density functional theory was implemented to investigate the possibility of hydrogen or halogen bonding that may occur between PDA and PTFE. While hydrogen bonds were previously observed in PDA films, we found that the formation of hydrogen bonds was dependent on the PDA oligomer and its surrounding neighbors. Some PDA oligomers, such as the trimer, have available hydrogen bonding cites all along the molecule edges, but other oligomers, such as the dimer do not. When two dimers are near each other, they can form hydrogen bonds because their available cites align, however, when a dimer and trimer are next to each other there is a misalignment in the available hydrogen bond cites and available hydrogen. This leaves some oligomers forming less hydrogen bonds based on their molecular structure and their surroundings. In every DFT simulation performed we observed no halogen bonding.

The adsorption energy of PDA and PTFE molecules was calculated using both MD and DFT simulations. The PDA trimer was observed in DFT and MD to have the highest adsorption energy to other PDA oligomers and to PTFE. Steered molecular dynamics simulations were then performed on pairs of molecules investigating the force required to perturb molecules from equilibrium. It was found that, again, the PDA trimer required the most force to move from other PDA oligomers and from the PTFE molecules, leading to the conclusion that a film created solely of trimer molecules would exhibit the best adhesion properties.

Interestingly, we observed a physical change in individual PTFE chains when near the PDA molecules. The PTFE chain segment nearest the benzene ring of PDA molecules would straighten and locally lose the helical formation. When the PTFE molecule was pulled past the PDA molecule, the section that previously lost the spiral formation would regain it, and the new portion
of PTFE that was near the PDA oligomer would lose the spiral. This was due to the repulsion between the negatively charged fluorine atoms in PTFE and the net negative charge on the surrounding atoms of the PDA oligomers. This phenomenon, however, was not as clearly observed in PDA/PTFE thin film simulations. PTFE chains in general had a straight helical pattern, but also contained many random angles and helix defects due to their surroundings.

A single PDA/PTFE composite film was created using the strongest adhering PDA oligomer (trimer). PTFE was observed to penetrate the PDA trimer substrate during equilibration which increased the contact area between PTFE and PDA. A nanoscale diamond indenter with a radius of 2 nm was then used to indent the PDA/PTFE film. Major delamination and debris formation occurred during indentation and scratch of the PDA/PTFE film. Any PTFE chains which were not adhering to the PDA substrate, either adhered to the diamond indenter, or were lost from the substrate. No hydrogen bonds formed between PDA and PTFE, and no extra bonds were seen during DFT simulations, leading to the conclusion that van der Waals forces were responsible for the strong adhesion between PTFE and PDA. The root like structure which formed at the PTFE and PDA interface may also help increase the adhesion between the substrates.

A second, flat diamond indenter was used to indent and scratch the PDA/PTFE thin film. This flat indenter prevented debris formation because of its size. PTFE molecules which were near the indenter adhered to it and did not move relative to the indenter for the duration of the scratch. The PTFE molecules which adhered to the PDA substrate were deformed only as the PDA substrate was. Sliding occurred between the PTFE molecules adhering to the indenter and the bulk PTFE molecules. Experimental observations, such as a thin film residing on PDA after scratch, and a counter film of PTFE on the indenter are observed in these simulations.1-3 The tenacious adhesion between PDA and PTFE can be attributed to the penetration of PTFE chains into the PDA
substrate, and the unique deformation mechanisms of PDA oligomers which prevent peeling of the PDA substrate. Further reduction of wear may be possible if an increased number of PTFE molecules adhered to PDA molecules, increasing contact area between the PDA and PTFE substrate.

5.3. Using coarse-grained modeling techniques to investigate friction and wear on microscale particles and films.

5.3.1. Coarse-grained modeling to examine deformation of PTFE on experimental scales

Coarse-grained models enable the simulation of materials on a much larger length scale than molecular dynamics simulations can perform. A coarse-grained model of PTFE was developed using the ReaxFF potential to parameterize atomic interactions. Details about the potential development can be found in Chapter 2.

Using the coarse-grained model, the shape, density and surface roughness of PTFE particles and their effect on wear and frictional properties was investigated. Indentation and scratch tests were performed to measure the particle strength as well as the coefficient of friction. Each particle created was based on the shapes and sizes of microscale PTFE particles observed in experimental films. The coefficient of friction was not dependent on the shape or size of particle, but the density of the particle, the density of summits on the particle, and the deviation of the summit height.

5.3.2. Investigate friction of realistic PTFE models

Microscale coarse-grained PTFE films were created using AFM images of 0-, 4-, and 8-minute annealed PTFE films. The internal structure of PTFE films was studied by varying the fiber length and density of coarse-grained films. Films were modeled with varying PTFE chain lengths from 50 Å to 100 Å, and found that as the chain length increased, the density of the film decreased. The
chain length was held fixed and the density of the film was then altered. As the density increased, the coefficient of friction decreased. Below a density of 1 g/cm$^3$, the PTFE film appeared more like a grouping of particles, and less like a film, leading to the conclusion that using this coarse-grained model, a density of at least 1 g/cm$^3$ should be used when modeling PTFE films with a length of 50 Å.

To investigate the friction of microscale PTFE films, coarse-grained models were created using AFM images as a template. Indentation and scratch tests were performed on each film and the coefficient of friction was recorded. The paper presented in Chapter 4 attempted to predict the coefficient of friction of PTFE films based solely on the topography of the film. By using a convolutional neural network, the topography features of each model were used to predict the coefficient of friction. We observed that the network had a difficult time differentiating between the PTFE film models which were created to mimic the 4- and 8-minute annealed PTFE films. The number of correctly predicted friction values to one decimal place increased when the density, or images of the internal fiber orientation were used as input variables. The increase in network accuracy is due to the additional information of the internal structure of the PTFE film. While the topography of each model was created based on height maps of AFM images, resulting in distinct and recognizable surface topographies, the friction values are also dependent on the internal fiber structure of the film, which is not well understood. Because the frictional properties of PTFE films are affected by the internal fiber orientation, additional research on the formation of PTFE particles would bring further enlightenment to how the nanoscale properties of PTFE affect the macroscale.

Improvements to this research could be made by varying the amount of data available to train the network. While we conducted a small study on the fiber orientation, the network may benefit from a larger dataset with more variation in fiber orientation. The data created for this paper was
generated similarly, with randomly oriented fibers condensing into a film. The topography was changed, but the internal structure of each film does not vary as drastically as the topography. By changing the various properties of the internal fibers of the film (length, density, orientation etc.), the neural network will contain a wider variety of data and may be able to make more accurate predictions. An application of this network would be to predict friction values of real PTFE films. By training and testing on data from experimental PTFE films, a comparison could also be drawn to gauge the performance of the coarse-grained model and our current understanding of the friction of PTFE films.

5.3.3. Confirming experimental observations of released PTFE fibers

A brief investigation of coarse-grained PTFE particles simulated the effects of an AFM tip on the deformation of micrometer sized particles (see Supplementary Materials section 6.2). Using steered molecular dynamics, PTFE fibers were removed from the surface of a particle and the force vs displacement of the fiber measured. We observed a low force distributed throughout the PTFE particle, indicating that the force distribution in the micrometer sized PTFE particle is quite localized. The fibers were pulled out of the particle with ease and with little deformation to the rest of the coarse-grained particle. These results help to explain experimental observations of residual PTFE lines running through wear tracks. During experimental rubbing tests, individual PTFE fibers are removed from the film and left in the debris track of the PTFE film.

5.3.4. Adhesion between microscale PTFE particles

Lastly, a coarse-grained model involving two micrometer sized particles of different shape were simulated side by side to investigate adhesion of different particle shapes (see Supplementary Materials section 6.2). It was observed that the adhesiveness of these particles is based on the number of interacting fibers touching the other particle. It was concluded that the adhesion of
particles is dependent on the contact area of each particle. Spindle shaped particles had more contact surface area when placed perpendicularly, and less when placed parallel to each other. The columnar particles had a moderate amount of interacting surface area. The results from these simulations show that each particle would have unique adhesive properties based on the shape and size of the particle. It was proven that the spindle shaped particles showed a lower adhesion when parallel to each other, which explains why experiments see PTFE particles aligned parallel after scratch takes place. The parallellly aligned particles allow the indenter to scratch through without much resistance. Experimental results showed that as the annealing time in the PDA/PTFE film was increased, there were also an increase in the number of spindle particles and an increased wear rate. Because the annealing causes a greater number of spindle particles, the adhesion between the particles on the surface of the film decreases and causes a greater wear rate, as seen in experimental results.

5.4. Future Work

There are many possibilities for future work or improvement to the research accomplished in this dissertation. The simulations presented in Chapter 2 and 4 perform indentation and scratch tests on PTFE films in a vacuum. In real applications of PTFE, there is an atmosphere, or humid environment which may affect the results observed. By performing simulations of PDA/PTFE films involving oxygen or water in the simulation cell, a humid environment can be replicated and compared more directly to experiments, as well as the simulations in this work, showing the effects of water and oxygen on the wear of PTFE films.

The exact oligomer content of PDA films are not known; however, we simulate our films with no more than two different oligomers at a time. Expanding these simulations to include multiple
oligomers, or by calculating the oligomer content of PDA films could further increase our understanding of adhesion in PDA films. We also observed that PTFE chains penetrate the PDA surface during equilibration of a PDA/PTFE film. It would be interesting to observe if this penetration behavior is increased during annealing, and whether it is possible to quantify the amount.

Regarding the coarse-grained model of PTFE, it will be useful if PDA-PTFE interactions can also be incorporated. By furthering the coarse-grained model to incorporate more materials, it could add further knowledge on deformation of PDA/PTFE films at the microscale.

Lastly, the convolutional neural network presented in Chapter 4 has a lot of room for improvement. There was a high variation in the coefficient of friction in the data reported, and the lack of understanding of the internal fiber structure of PTFE films makes modeling annealing difficult. To progress this area of research, a thorough investigation of the internal fiber structure in PTFE films needs to be performed, this will enable better modeling of these films. The conclusion of Chapter 4 also indicates that using experimental AFM images and coefficient of friction values would most likely result in a more accurate and useful network, capable of predicting an optimized PTFE film topography.

5.5. References


Chapter 6: Supplementary Material

Coauthored paper 1:

6.1. The effects of annealing conditions on the wear of PDA/PTFE coatings

The following portion of the supplementary material was part of a collaborative study which was published in the journal Applied Surface Science titled “The effects of annealing conditions on the wear of PDA/PTFE coatings”.

Coauthors:

Jiang, Yan; Choudhury, Dipankar; Brownell, Matthew; Nair, Arun; Goss, Josue A; Zou, Min

6.1.1. Introduction

Experiments involving the deposition of dopamine on Ag nanoparticles was able to find an optimum concentration of dopamine which could be used to increase dopamine deposition rate and decrease free dopamine particles (Figure 6.1.1). It was hypothesized that mixing the dopamine solution increased the deposition rate by increasing the number of hydrogen bonds formed in the solution. As a collaboration with experimentalists, numerical simulations were used to investigate the mixing of polydopamine oligomers and the effects the film thickness, water content, and dopamine concentration played on the number of hydrogen bonds observed in dopamine films.
6.1.2. Methods

To study the behavior of PDA oligomers in a self-assembled film, computational models of dopamine monomers, trimers, and a mixed ratio of 1:1 monomers and trimers are created and equilibrated. Multiple film thicknesses are investigated to observe how hydrogen bonding and the assembly of the film changes with film height. The dopamine trimer film thickness after equilibration was 5.5, 11.3, 19.2, and 21.5 Å. The monomer thicknesses ranged from 11.6, 13.6, and 15.9 Å, and the mixed model thicknesses ranged from 10.3, 14.0, 21.1, and 24.2 Å. The water content was then varied from 0%, 4%, 7%, 9%, 12%, and 14% weight of the sample for the pure trimer model with a 21.5 Å thickness. Each model was created by depositing the monomers and trimers on a metal substrate and equilibrating at 300 K for 100 ps using the ReaxFF\textsuperscript{5} potential and LAMMPS\textsuperscript{6} to perform the simulations. Results are visualized in VMD.\textsuperscript{7}

6.1.3. Results

In each model a thin layer of water formed on the metal surface. Hydrogen bonds connected the water layer to the dopamine oligomers and other water molecules in the solution. As each model thickness increased, so did the number of hydrogen bonds. Dopamine oligomers were observed to
form hydrogen bonds with the oxygen atoms of other dopamine oligomers, and other water molecules (Figure 6.1.2).

**Figure 6.1.2** (A) 15.8 Å thick dopamine monomer film deposited on a face-centered cubic (fcc) metal substrate. (B) Dopamine trimer film measuring 19.2 Å thick. (C) Mixed dopamine monomer and trimer film measuring 14.0 Å. (D) A selection from the mixed dopamine monomer film measuring 14.0 Å showing hydrogen bonds forming between water and a dopamine trimer.

The water content of the trimer model with a film thickness of 21.5 Å was varied from 0% to 14%. As the water content increased the number of hydrogen bonds on dopamine trimers also increased (Figure 6.1.3A). At higher water weight percent, the water molecules created more separation between the dopamine trimers, thus allowing for a greater number of hydrogen bonds to form (Figure 6.1.3B).

All results from the simulations are presented in Figure 6.1.3C. The mixed monomer and trimer models consistently showed higher number of hydrogen bonds than the trimer or monomer models. The models with higher water content also showed a higher number of hydrogen bonds than those
with less water. Models with a higher film thickness were observed to generally have a higher number of hydrogen bonds. In general, the higher number of hydrogen bonds is a result of greater space between dopamine oligomers.

Figure 6.1.3 (A) Plot of the water weight percent in dopamine trimer films vs the number of hydrogen bonds observed. (B) Images of the trimer models with 4% (i) and 14% (ii) water weight. The stacking of trimers is more closely packed in the models with less water. (C) Plot of dopamine coating thickness vs the number of hydrogen bonds. The percent water weight and the dopamine content are labeled by colors and shapes in the scatter plot. (D) Selected images of equilibrated films showing the mixed (a) trimer (b) monomer (c) models with 12% water weight, and the monomer model with 9% water weight (d).

All dopamine oligomers in the film were observed to form pi-pi interactions. The dopamine monomers are not a flat molecule, and therefore, also formed a pinwheel pi-pi interaction (Figure 6.1.4A). Hydrogen bonding in the dopamine oligomers only occurs between hydrogen and oxygen atoms. The oxygen atoms are bonded to the benzene rings of the dopamine oligomers. The space necessary to form hydrogen bonds to the oxygen atoms does not exist in many dopamine monomer formations because they form pinwheel pi-pi interactions instead. The dopamine trimers, however,
form more hydrogen bonds because the molecule is flat and stacks neatly. The trimer also has more available oxygen atoms surrounding the molecule. When trimers and monomers are mixed (Figure 6.1.4B) the monomers break up the uniformity of the trimers, and create more space in between each molecule. With more space between molecules, there is more room for water and other dopamine oligomers to form hydrogen bonds with the dopamine oligomers, thus increasing the number of hydrogen bonds in the film.

**Figure 6.1.4** (A) Image of dopamine monomers forming a pinwheel pi-pi interaction in the 15.9 Å thick monomer film. (B) The 10.3, 13.1, and 21.1 Å thick mixed films, with a selection from the 21.1 Å film showing how dopamine monomers break up the stacking formation of the dopamine trimers.

### 6.1.4. Conclusions

Dopamine monomers and trimers were used to study self-assembly of dopamine films using molecular dynamics simulations. The film thickness, water content, and dopamine oligomer ratio were studied to understand the formation of hydrogen bonds in the film. An increase in the number
of hydrogen bonds present in the films was observed when the film thickness increased, the water content increased, and when mixing of the oligomer content occurred. In each scenario a greater separation between molecules was observed where the hydrogen bonding occurred. Dopamine trimers were observed to form layers, all interacting via pi-pi interactions. Dopamine monomers occasionally formed pi-pi stacks, however, because the non-flat surface of the monomers, pinwheel formations were also observed. The simulations presented here, in cooperation with experiments are presented in the paper “Rapid Deposition of Uniform Polydopamine Coatings on Nanoparticle Surfaces with Controllable Thickness”. We have shown that mixing a dopamine solution facilitates the formation of hydrogen bonds, thus increasing dopamine deposition on metal surfaces.8

6.1.5. References


Coauthored paper 2:

6.2. Rapid deposition of uniform polydopamine coatings on nanoparticle surfaces with controllable thickness

The following portion of the supplementary material was part of a collaborative study which was published in the journal Langmuir titled “Rapid deposition of uniform polydopamine coatings on nanoparticle surfaces with controllable thickness”.

Coauthors:

Orishchin, Nazar; Crane, Cameron C; Brownell, Matthew; Wang, Tengjiao; Jenkins, Samuel; Zou, Min; Nair, Arun; Chen, Jingyi

6.2.1. Introduction

Experimental investigations of PTFE thin films found that PTFE molecules oriented more normal to the substrate as the annealing duration was lengthened.\textsuperscript{1} Changes in the topography and adhesive properties of PTFE films was also reported after annealing at different temperatures.\textsuperscript{2} In collaboration with experimental research, molecular dynamics simulations of PTFE were performed to investigate the effects of annealing on the shape of PTFE particles. Coarse-grained models were used and steered molecular dynamics (SMD) simulations performed to simulate the tip of an AFM probe as it scratches the surface of a particle.\textsuperscript{3-5} The adhesive capabilities of PTFE particles are also investigated to understand how the shape of a particle affects its adhesive properties.
6.2.2. Methods

Molecular dynamics models of PTFE molecules were used to calculate the effects that temperature has on the geometry of PTFE particles. A 24 Å diameter bundle of PTFE was created and equilibrated at 26.85 °C using an NVT ensemble, the ReaxFF potential and LAMMPS simulating package. The temperature was then raised to 226.85 °C and again to 326.85 °C and the radius of curvature was measured at each temperature.

The coarse-grained potential described in Chapter 2 was also used to model two columnar (or spherical), or spindle (or needle) shaped PTFE particles. The particles were equilibrated and the number of interacting fibers of each particle observed, indicating which particle and orientation had higher adhesion forces. A steered molecular dynamics (SMD) simulation was performed on the columnar particle to mimic an AFM probe. A single section of the PTFE particle is attached to a spring to simulate the effects of an AFM as it scratches the particles. Observations of the deformation and forces on the particle during scratch are reported. All coarse-grained models are performed at 326.85 °C. Results are visualized in VMD.

6.2.3. Results

A bundle of PTFE chains was equilibrated at 26.85, 226.85, and 326.85 °C to investigate the morphology change of the material during annealing. The radius of curvature of the bundle is measured at each temperature by fitting a second-degree polynomial to the average atom positions. The radius of curvature is taken to be the radius of curvature at the apex of the polynomial. As the temperature of the PTFE bundles increased, the radius of curvature decreased (Figure 6.2.1). This result adds to previous literature which states annealing affects PTFE films, by providing the insight to how that change occurs. The reason the topography changes during annealing is because
the individual particles of PTFE are curling, which creates an uneven topography after annealing is complete.\(^9\)

![Figure 6.2.1](image)

**Figure 6.2.1** (A) Plot of the temperature of the PTFE bundle vs the radius of curvature. As the temperature increases, the radius of curvature also decreases, indicating the bundle is curling. (i) PTFE bundle at 26.85 °C, a single chain is highlighted in green to show the change in single chain positioning with the increase in temperature. (ii) The bundle at 223.85 °C. (iii) The bundle at 326.85 °C.

Experiments report an increase in wear resistance of PDA/PTFE composites after annealing. Annealing also causes a change in the shape of PTFE particles. We next investigated how the shape of two particles affected the relative adhesion between said particles. Two particles were selected to compare, the columnar particles and the spindle particles (Figure 6.2.2A&B). The spindle particles are placed perpendicular to each other (Figure 6.2.2C&D) and parallel (Figure 6.2.2E&F). Each model was equilibrated at 26.85 °C and the number of interacting fibers between particles was counted. The columnar particle had 136 interacting fibers, the perpendicular spindle particles had 159 and the parallel spindle particles had 70. The shape of the particle affects the contact area of the particle, which ultimately affects the number of fibers which can adhere to other particles. It was apparent by the simulation results that the PTFE film with the weakest adhesion would have many parallel spindle particles. Experimental results agreed with the conclusion and
showed that an initial increase in wear resistance is seen when PTFE films are annealed, but if annealed too long, the films form a greater number of spindle particles and have a lower wear rate.\(^9\)

**Figure 6.2.2** Two different PTFE particles are shown, one in orange and the other in yellow. The blue colored fibers are the fibers from the orange particle and adhering to the yellow particle. The cyan colored fibers are the fibers from the yellow particle which adhere to the orange. (A) Two columnar particles and (B) the interacting fibers. (C) Two spindle shaped particles placed perpendicular to each other, and (D) the interacting fibers. (E) Two spindle shaped particles placed parallel to each other, and (F) the interacting fibers. (G) A graph of the total number of fibers in the columnar, spindle perpendicular, and spindle parallel models.

Running lines are observed to lie in the wear tracks of PTFE films after scratch tests are completed. To simulate the effects of an AFM tip on PTFE particles, we used SMD to attach a spring to the end of a group of fibers on the PTFE particle (shown in red Figure 6.2.3A–D). A spring applies a force on the fibers and the fibers are pulled out of the particle. As the fibers directly attached to the spring are removed from the particle, the surrounding fibers (shown in blue Figure 6.2.3A–D) are deformed slightly. The force on the fibers plateaus as they shear out of the particle (Figure
Just before the PTFE fibers begin to shear out of the particle, the maximum force of approximately 50 pN is achieved. A colormap showing the force distribution throughout the particle is shown in Figure 6.2.3F. The forces felt throughout the particle are localized to the point where the SMD test was performed. Various experiments of PTFE films have observed strands of PTFE remaining on the surface of the film after scratch has occurred. In our simulations, we showed that strands of PTFE can be separated from particles during scratch with an AFM, confirming experimental observations of the origin of these fibers.

Figure 6.2.3 (A) An equilibrated columnar PTFE particle showing the fibers where a spring is attached to simulate the AFM tip (red), the fibers which are touching the directly affected fibers (blue), and the rest of the particle (yellow). (B) The particle once most of the directly affected fibers are being removed from the particle. (C) An isolated image of only the affected fibers from the equilibrated particle. (D) An isolated image of only the affected fibers as the affected fibers are being removed. (E) Plot of the fiber displacement vs the force felt by the spring. (F) a color plot of the forces felt throughout the particle during the SMD simulation.
6.2.4. Conclusions

Molecular dynamic simulations were performed to investigate the affects annealing has on the particle shape of PTFE. We observed a decrease in the radius of curvature as the annealing temperature increased, indicating that the change in PTFE film topography observed in experiments was due to the curling of PTFE chains during annealing. We also investigated the adhesion between spindle and columnar shaped PTFE particles. We observed that the shape of particles greatly affects the interacting surface area of the particles, and thus the adhesion. Spindle shaped particles oriented parallel to each other resulted in the lowest number of interacting fibers. These results explain why experiments of PTFE films observe parallelly oriented spindle shaped particles after scratch, it allows the indenter to pass through the spindle shaped particles easier than if they were oriented in another direction. SMD simulations were also performed on a single PTFE particle, showing that the lines running through the wear track of AFM images were strands of PTFE removed during scratch.

6.2.5. References


