Ultrathin PTFE Coating for Hypodermic Needles Enabled by Mussel-Inspired PDA Adhesive Layer

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by

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Abstract

Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer of tetrafluoroethylene, commonly known by its brand name Teflon®, which has many desirable properties such as a low coefficient of friction, high temperature resistance, anti-microbial properties, hydrophobicity, biocompatibility, and chemical resistance. One of the major challenges caused by the non-stick property of PTFE is its poor adhesion to substrates: PTFE coatings can be easily detached from surfaces under frictional forces and shear. The molecule polydopamine (PDA) was discovered as the key protein for adhesion between polytetrafluoroethylene and substrates of many materials, including steel, and thus has been used as a unique approach for coatings. In this undergraduate thesis research, PDA will be examined as an adhesive layer to coat ultrathin PTFE coatings onto stainless-steel hypodermic needles that are subjected to friction during penetration tests to determine effectiveness of reducing forces experienced during needle insertion. The friction and adhesion properties of the coated surface was studied by creating a fixture to hold a thin polyethylene terephthalate (PET) film, and using a Bruker UMT Microtribometer (Bruker UMT) to force needle penetration while measuring the corresponding forces felt by the needle. It was found that the tip of the needle penetrated the PET film at a force on average 44.4% lower than the uncoated needles. During testing, the maximum force felt by coated needles was 125 mN compared to 225 mN for the uncoated needles.
Acknowledgements

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1.0 INTRODUCTION

1.1 Background

PTFE’s hydrophobic and biocompatibility properties make it widely used for medical coatings that provide surface function improvements for medical devices [1]. Some enhancements are improved anti-microbial properties and reduced friction force in order to facilitate insertion into blood vessels, urethra or other body conduits during certain procedures [2]. For example, due to its hydrophobic property, a PTFE coated medical device guide wire or hypodermic needle can prevent blood cells from sticking to it as it navigates through the vascular system of a human body, preventing potential clots or obstructions. To reduce the pain felt by patients, medical devices with smooth surfaces and ultrathin PTFE coatings are desirable to minimize the friction and intrusion caused by the invasive devices. To do this, it is necessary to find a way to improve the adhesion of PTFE to substrates without roughening the substrate surfaces. This is difficult to achieve because PTFE is chemically inert and there are few materials to which it will adhere. Until recently, various surface preparations needed to be performed on the substrates to ensure adhesion of PTFE coatings, which include sanding or grit blasting to roughen substrate surfaces significantly [3]. Roughened surfaces require thicker PTFE coatings to cover the valleys and peaks leading to increased friction, which is especially undesirable on smaller skin penetration devices such as the hypodermic needle [4].

This is where mussels and PDA come into play. Mussels maintain excellent adhesive performance in marine environments involving turbulent and aqueous surroundings due to unique proteins, mimicked by PDA, which allow them to attach to both organic and inorganic surfaces [4]. PDA is biocompatible and can attenuate the adverse biological responses caused by
the intrinsic properties of the coated material, while also increasing material adhesion without roughening the surface [5].

1.2 Scope of the Research

This thesis research focused on using PDA as an adhesive layer to coat ultrathin PTFE coatings onto stainless-steel hypodermic needles that are subjected to friction through the penetration of a PET film of 0.005 inch thickness. It was hypothesized that the adhesion of the PTFE coatings to the hypodermic needles would be improved because of the strong adhesion between the PTFE coating and the PDA layer, and also between the PDA layer and the hypodermic needles. The hypothesis was investigated using a previously verified surface engineering process to fabricate PDA/PTFE coatings and was applied to hypodermic needles. The PDA/PTFE coatings was then be tested against standard hypodermic needles of the same diameter to determine the frictional and penetrative performance of the coatings. The goals of the research are (1) design appropriate fixtures for each portion of the fabrication and testing process.
processes, (2) develop an appropriate process to fabricate ultrathin PTFE coatings with excellent adhesion to the surface of stainless steel hypodermic needles through the use of a PDA adhesion layer, (3) establish methodologies and examine the frictional and penetrative performances of the PDA/PTFE coated hypodermic needles.

1.4 Motivation for the Research

By discerning the tribological behavior of ultrathin PTFE films and their application to nano-engineering, more robust products and systems can be created to benefit the world. In biomedical applications, being able to control surface behavior can increase patient’s health by alleviating pain or reducing bacteria accumulation. For example, PTFE coating on orthodontic braces, archwires and related clamps, clips and springs can prevent food from sticking to these and resist biofilm buildup. Other biomedical applications could include coating medical implants to reduce friction felt by the patient and to reduce material deterioration. PTFE has one of the lowest known coefficients of friction, and thus the technology has unlimited potential, if techniques for strong adhesion in aqueous environments can be found.

1.5 Organization of the Thesis

This thesis is organized into five chapters. The current chapter has presented a background on PTFE applications as well as goals of the research. Chapter two is a review of existing and relevant literature dealing with PDA/PTFE. Chapter three describes the experimental setup and procedures used to conduct the research. Chapter four offers a discussion of the research and the results. Chapter five is comprised of the conclusions and
recommendations for continued research in PDA/PTFE hypodermic needle coatings. Lastly, Appendix A is located on the last page of this thesis and contains data for each of the needle puncture tests.
2.0 LITERATURE REVIEW

2.1 Polydopamine (PDA)

Much of the recent research on PDA was conducted by Lee et al. inspired by the adhesive proteins that are secreted by mussels in their native aqueous environment for attachment to wet and turbulent surfaces [6]. Lee et al. was able to show that PDA adheres to both organic and inorganic surfaces, meaning that there are many potential applications for PDA to serve as a mechanism of adhesion between substrates and materials that are typically resistant to adhesion [7]. PTFE is generally resistant to adhesion, but PDA has been shown to still be able to attach to the material, as can be seen in Figure 1B. While the mechanism of PDA adhesion still is not entirely understood, it is theorized that catechol functional groups found in DOPA and amine in lysine within PDA are a critical factor [7]. Due to the recent discovery of the unique properties of PDA [7], there are few tribological studies of PDA’s adhesive properties between organic and inorganic materials, especially on non-typical substrate geometries.

2.2 Polytetrafluoroethylene (PTFE) Coating

PTFE has drawn much attention due to the many unique properties of the material, especially as a self-lubricating solid lubricant with a low coefficient of friction [8]. As a coating, PTFE offers many potential opportunities to enhance the surface of materials. Researchers usually use surface roughening techniques and/or primer coats to achieve PTFE adhesion to a surface. For primers, polyamide acid [9] and fluorinated ethylene propylene/PTFE blends [6] have been investigated and used. This process typically produces films above 20 µm [6,9] eliminating applications where a thin film is required.
Beckford et al. studied the influence of PDA as a method of adhesion between square stainless steel substrates and a PTFE nanoparticle aqueous solution. Compared to substrates that were just coated with the PTFE nanoparticle aqueous solution, Beckford found that due to the strong adhesion between PDA and PTFE, the PDA/PTFE film was able to withstand approximately 500 times as many rubbing cycles than the PTFE only coat [10]. Furthermore, the study showed that the PDA/PTFE coating was approximately 160 nm in thickness and maintained a coefficient of friction of 0.06 similar to substrates with only a PTFE coating [10].

2.3 Hypodermic Needles

Research has been done by Towler et al. on the influence of the cutting edge configuration of needles and the penetration forces, as well as on the variations of beveled hypodermic needles by Wang et al [11,12]. This thesis research focuses on analyzing the force profile generated from a standard bevel hypodermic needle compared to a PDA/PTFE coated standard bevel hypodermic needle.

A lancet point, also known as a regular medical point, is the typical cutting design for the standard bevel hypodermic needle, and is shown in Figure 1. It is formed from three bevels: a bevel that grinds the end of the tube at a specific angle, and two secondary side bevels that grind the sides of the first bevel to generate a sharp point as the cutting edge [13]. The four different sections of interest for needle penetration are shown in Figure 1C. Section 1 is the needle point; Section 2 is the grinded edges of the bevel; Section 3 is the initial bevel surface cut; and Section 4 is the needle shaft. These sections will be referenced for the remainder of the thesis.
Figure 1. (A) Hypodermic needle with standard three sided bevel. (B) Mussel adhering to PTFE. (C) Section 1 is the needle point, Section 2 is the two grinded edges of the bevel, Section 3 is the initial bevel surface cut, and Section 4 is the needle shaft.
3.0 EXPERIMENTAL TECHNIQUES

3.1 Overview

Dip coating is an extensively used method for thin film deposition due to its low cost and simplicity as well as its independence from substrate shape. Beckford has studied the friction and wear properties of PTFE and PDA/PTFE composite coatings on flat substrates deposited by dip coating [14]. The PDA/PTFE coating procedure developed by Beckford et al. was further developed for this research to fabricate PDA/PTFE coatings on hypodermic needles (Bound Tree Medical, 30-26417BX, 22ga. x 1in.). The stainless steel needles were dipped into a solution mixed according to Lee et al. to introduce the polymerization process of PDA onto the stainless steel needles [14]. When a needle is immersed in an aqueous dopamine solution at pH 8.5 (approximate marine pH), autopolymerization occurs and the needle is coated with an ultrathin adherent PDA layer (< 50 nm). After depositing the PDA, the needles were dipped in an aqueous dispersion of PTFE nanoparticle (TE3859, DuPont) similar to the previously published method by Beckford et al [14]. The samples were then heated to remove water and surfactant.

The frictional and adhesive performance of the PDA/PTFE coatings were next studied using the Bruker UMT. The microtribometer applies a linear load over a specified time period and measures the friction forces as the sample interacts with a test surface. A thin polymer will be used for this research as the object of penetration. Necessary fixtures to hold the PET film (0.005 in) were fabricated. The microtribometer will hold the hypodermic needle with one of the fabricated fixtures and be programmed to repeatedly insert the needle into the polymer sheet in different locations while measuring the resistance/friction forces.
3.2 Hypodermic Needle Fixture Designs

Several fixtures had to be designed before the experiment could be conducted. The Dip Coater (KSV Dip Coater) had a clip designed for typical square substrates, so the attachment shown in Figure 2B was designed and 3D-printed to hold the hypodermic needles during the PDA and PTFE adhesion stages. The design allows for needles of various diameters to be fitted into the holes around the circumference of the fixture. Double-sided permanent adhesive tape was used to hold the needles in place during the dip coating process, with the tape being placed on the top-side of the fixture and the needles being inserted from the bottom with the tip of the needle facing the downwards.

Figure 2. (A) Bruker UMT Fixture. (B) Dip Coating Fixture. (C) Puncture Fixture.
The fixture shown in Figure 2A also had to be fabricated as an attachment for the Bruker UMT so that it could hold the 22 gauge (Outer Diameter 0.028 in, Inner Diameter 0.016 in) hypodermic needles. The design was fabricated by the University of Arkansas machinist and is essentially a scaled down version of the existing Bruker attachment, both shown in Figure 2A.

The Bruker UMT is generally configured for substrates to be mounted onto the main stage where tests are then conducted on a material’s surface. This general configuration would not allow for a film to be penetrated as was the purpose of this thesis research, which led to the fabrication of another fixture shown in Figure 2C. This last fixture allows for an embroidery ring (Joann Fabric and Craft Stores, 3 in. Diameter Wood Embroidery Hoop with Round Edges, 12212429) holding the PET film (0.005 in. thickness) to be placed on a flat surface, while providing ample area for film penetration. In reference to Figure 2, the fixtures are called the Bruker UMT Fixture, Dip Coating Fixture, and Puncture Fixture and will be referenced as such for the remainder of the thesis.

### 3.3 Hypodermic Needle Cleaning Method

The hypodermic needles came from the manufacturer with an attached plastic cap for easy attachment to a syringe, which was removed due to the necessary heating procedure. Once the cap was removed, the needles were separated and subjected to cleaning. The cleaning procedure is the same for coated and uncoated hypodermic needles. The samples were handled using lab gloves and while wearing protective eyewear.

The samples were first placed into a container filled with RO water and 1% by volume of detergent (Liquinox). The solution was allowed to mix at a speed of 700 rpm while being heated
at 40°C for approximately 10 minutes before the needles were placed into the solution. The solution and samples were placed in a sonicator to Degas for 5 minutes, and then sonicated for an additional 5 minutes. The samples were then rinsed with DI water for approximately 1 minute.

The next step was to place the samples into an Acetone solution to be sonicated for 20 minutes. After being sonicated in Acetone, the samples were placed directly into isopropyl alcohol and sonicated for 5 minutes. The final step in the cleaning process is to rinse the samples three times in DI water to remove additional chemicals or surfactants, and then to dry the samples using nitrogen. Samples were held using tweezers when necessary throughout the cleaning process.

3.4 Hypodermic Needle Coating Method

The sample coating method was adapted from the method established by Beckford et al., and is described in detail due to variations due to sample dimensions and required modifications. There are two separate coating procedures for the PDA coating and the PTFE coating, followed by a heat treatment procedure, all described in this section. The area of the sample to be coated shouldn’t be touched in anyway following the Hypodermic Needle Cleaning Method outlined in Section 3.3.

3.4.1 PDA Hypodermic Needle Coating Method

The first step in producing the PDA is mixing DI water and 0.01 molar concentration of Trizma T1503 at a speed of 600 rpm with no heat. After allowing a few minutes for the Trizma to mix,
Dopamine can be added at a concentration of 2 mg/ml of DI water and allowed to mix for an additional 10 minutes.

After the solution appears thoroughly mixed it can be moved to the dip coater and the cleaned samples can be loaded into the fixture and attached to the dip coater, similar to the setup shown in Figure 3A. The solution should be placed onto a magnetic stirrer and set to spin at the slowest possible speed. Using the SG Server program, the dip coater is programmed to insert and remove the hypodermic needles as follows:

**Insertion:** Hypodermic needle is lowered 12mm into the PDA solution at a speed of 40mm/min for 86400 seconds (24 hours).

**Extraction:** Hypodermic needle is removed 5mm above the surface of the PDA solution at a speed of 40mm/min and allowed to sit for 120 seconds (2 minutes) before the fixture is extracted further.

After the PDA extraction is finished the PTFE coating procedure immediately follows.

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**Figure 3.** (A) PDA Hypodermic Needle Coating Setup. (B) Hypodermic Needles after PDA Coat.
3.4.2 PTFE Hypodermic Needle Coating Method

PTFE and DI water is mixed at a ratio of 2:1 at 400 rpm, or lower if foaming occurs. Once the solution has been given time to become homogenous (approximately 5 minutes) it can be placed on the dip coater and the SG Server program can be run. The dip coater was programmed to insert and remove the needles as follows:

**Insertion:** Hypodermic needle is lowered 12mm into the PTFE solution at a speed of 40mm/min for 20 seconds.

**Extraction:** Hypodermic needle is removed 5mm above the surface of the PDA solution at a speed of 40mm/min and allowed to sit for 120 seconds (2 minutes) before the fixture is extracted further.

After the PTFE extraction is finished the heat treatment procedure immediately follows.

![Process Flowchart](image)

*Figure 4. Hypodermic Needle Coating Process Flowchart.*
3.4.3 PTFE Hypodermic Needle Heat Treatment Method

The heat treatment of the PTFE nanoparticle solution should begin within an hour of hypodermic needle extraction. The coated portion of the needle that is critical for testing shouldn’t be touched in any way during the following steps. During this process, the hypodermic needle was secured in the Bruker UMT Fixture since it could withstand the temperatures and keep the coated portion of the needle elevated above the base of the oven. The procedure is as follows:

**Step 1**: Samples are heated in lab oven at 120°C for 2 minutes to remove any excess liquid and surfactant. After samples are removed, proceed directly to Step 2.

**Step 2**: Samples are then placed in an oven at 300°C for 3 minutes. After samples are removed, proceed directly to Step 3.

**Step 3**: Samples are then placed in an oven at 372°C for 3 minutes. After samples are removed, they are allowed to air cool for approximately 5 minutes before being stored until testing.

3.5 Friction/ Penetration/ Adhesion Testing

3.5.1 Bruker UMT Testing Setup

Testing was conducted using a Bruker UMT with a sensor (Bruker, FL-1325) and the initial setup shown in Figure 5. Preliminary testing and analysis was performed to obtain a better understanding of the hypodermic needle insertion forces, with the initial findings described in the Preliminary Testing and Analysis section of this thesis. After studying the initial findings, an
The experimental procedure was formed. This section outlines the experimental procedure that was followed.

The hypodermic needle being tested must first be inserted into the Bruker UMT Fixture. The direction of the needle was such that the bevel cut faced the set screw in the fixture before tightening. The needle was adjusted accordingly so that it was as vertical as manageable while also being secure. The fixture and needle were then placed into the Bruker sensor with the set screw facing to the right, as shown in Figure 5. Once appropriately secured, the sensor is placed onto the Bruker and sensor cables are attached.

*Figure 5. (A) Bruker UMT Fixture and Sensor Placement and Setup. (B) Bruker UMT Testing Configuration.*
A PET film 0.005in thick was used as the object of penetration for the hypodermic needle. A square sheet was cut approximately 6” X 6” with care not to damage or touch the surface and secured by the embroidery ring. The film was then tightened as much as possible before being placed onto the Puncture Fixture and fastened with large binder clips to hold the embroidery ring in position.

3.5.2 Bruker UMT Testing Configuration

Using the UMT software, the Bruker UMT is programmed to measure the lateral force ($F_x$), vertical force ($F_z$), and carriage position ($Z_1$, needle displacement). The testing sequence was programmed to execute a two-step puncture process for each needle before moving two millimeters to the right and executing another puncture until each needle had gone through the sequence three times. Once the needle had gone through three punctures, a new needle was placed into the sensor and new tests were run on the same film. After six punctures had been produced in a straight line, a second row of punctures was started approximately three millimeters perpendicular to the first puncture on the film. The punctures then proceeded to the right until six were made. The needles were alternated on each film from uncoated to coated for consistency, with a typical puncture pattern shown in Figure 6.

The sequence was programmed to lower the needle at a pretouch speed of 0.1mm/sec until a force of 5 mN was registered for Step 1. The sequence then entered Step 2, and proceeded to start measuring the displacement of the needle and recording time. The program was made to apply a linear load by time over the course of fifteen minutes with a max force of 450mN. The sequence ends with the needle being extracted and proceeding to the next puncture when the max
force is felt, the needle displacement reaches 12 mm, or fifteen minutes have passed since Step 1 and the initial touch.

Figure 6. Typical Puncture Pattern.

3.6 Sample Characterization

An optical microscope was used to examine the surfaces of the hypodermic needles before testing. This provides qualitative images that are supportive of surface analysis of the hypodermic needles, and allows for irregularities in the coatings and needle manufacturing to be observed if present. The optical microscope that produced the images analyzed for this thesis took images at (40x) magnification, and had multiple light sources available for adjustment to produce high-quality images. The optical microscope was linked to a computer for digital image capturing and analysis of the needles and PDA/PTFE coatings.
4.0 RESULTS AND DISCUSSION

4.1 Summary of Preliminary Data Collection

A series of tests were initially run to determine possible unforeseen experimental issues. The initial tests were run with five uncoated and five coated needles on four different puncture films. Each needle performed three punctures, and every film was punctured by at least one coated and one uncoated sample. The samples were loaded the same way into the Bruker UMT fixture, but the direction of the beveled edge of each hypodermic needle and the direction of the fixture as it was placed into the sensor wasn’t monitored. Another inconsistency that was noted during the preliminary data collection phase was the tightness of each film; due to the nature of the embroidery ring, it is difficult to reproduce the exact same surface tension for each film.

Corrections for each of these inconsistencies were made to the experimental technique before the final data collection phase commenced. It was determined that all needles for the final phase would go through the cleaning procedure at the same time before being separated into a group to be coated and a group that would stay uncoated. The samples were loaded into the Bruker UMT Fixture as described in Section 3.5.1, so that inconsistencies in the force vs. time and displacement vs. time graphs could be related to the needles, instead of any possible setup conditions. To determine the best way to account for variations in film surface tension, the force vs. time graphs generated for the preliminary data phase were examined. Extremely consistent force profiles can be seen for each of the three needle punctures on the first four films, with few exceptions. This led to the conclusion that to achieve the closest levels of similarity for comparison between each needle, they should be tested on the same film.
The preliminary data collection phase also allowed for an initial data analysis of the ten needles that were tested and helped to determine a better programming sequence to be used in the final data collection phase. Each needle was found to have a similar puncture profile, which is discussed in more detail in Section 4.2.

4.2 Sample Surface Friction and Penetration Forces

4.2.1 Uncoated Sample Analysis

The uncoated samples were subjected to the same testing sequence and environment as the coated samples. The primary purpose of this experiment was to subject the coated and uncoated needles to the same environment and then to compare the performance of both samples. Figure 7 shows a common force and displacement profile for the uncoated needles, with Figure 8 being an annotated version of the same graph. The uncoated needles have very similar force vs. time profiles to the coated needles, as was expected, but with varying peak and shaft $F_z$ force values. As discussed in Section 2.3, the beveled needle is divided into four sections of interest. Table 1 shows the average values of $F_z$ forces felt for all uncoated needle puncture tests over each of the four sections of the needle. Section 1 is the tip of the needle. Preliminary testing led to the conclusion that the tip penetration force was reliant upon the surface tension of the film being penetrated, which is why all coated and uncoated samples were tested on the same film.

It can be seen in Figure 7 that the tip penetration force for the uncoated needle was approximately 240 mN, which was applied at a constant rate over roughly 500 seconds before Section 1 of the needle punctured the PET film. At the same time as Section 1 of the needle broke through the film, frictional forces ($F_x$) and a steady displacement ensued. The
displacement after puncture continues at a steady rate for the duration of the test, until the test is completed at 12 millimeters displacement. Peak 2 and Peak 3 are both characterized by the maximum force seen during the rise in $F_z$ force in their respective local regions, as noted in Figure 8. The dramatic drop in force after puncture is followed by an increase in $F_z$ force until Section 2 of the needle has completely passed through the film. Peak 2 occurs during the transition from Section 2 of the needle to Section 3. Directly after Section 2 of the needle has completely passed through the film, there is a drop in the $F_z$ force followed by a steady increase until Section 3 of the needle has passed through the film. Peak 3 occurs at the intersection of Sections 3 and 4 of the needle, as a transition to the shaft of the needle occurs. The shaft friction is characterized by the average $F_z$ force seen after Peak 3. The Shaft Friction force for Figure 7 goes from approximately 560 seconds until the end of the test.

<table>
<thead>
<tr>
<th>Hypodermic Uncoated Needles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forces ($F_z$)</td>
</tr>
<tr>
<td>Tip Force (Peak 1)</td>
</tr>
<tr>
<td>Peak 2</td>
</tr>
<tr>
<td>Peak 3</td>
</tr>
<tr>
<td>Shaft Friction #1 ($F_z$ Average)</td>
</tr>
</tbody>
</table>

*Table 1. Hypodermic Uncoated Needle Average $F_z$ Values.*

Other interesting areas of the force profile include the nonlinear sample displacement before the constant displacement occurs, and the $F_x$ profile after puncture. The nonlinear displacement portion of the displacement curve is a result of the film flexing as the load is applied and steadily increased, and this is seen in all sample tests, both coated and uncoated. The $F_x$ profile after
puncture is a result of frictional forces being felt by the needle, as well as changes in the direction of needle displacement. The directional changes occur due to the cut made by the bevel in the film not being in the center of the axis of motion of the needle, and due to limitations in centering the needle in the Bruker UMT Fixture. The needle was manually positioned and placed into the Bruker UMT Fixture, which means the needle’s central axis would never truly be perpendicular to the X and Y planes on the puncture surface.

Figure 7. Hypodermic Uncoated Needle Force/Displacement Profile. (Hypodermic Uncoated Needles, Needle 2, Puncture 1, Appendix A)
4.2.2 Coated Sample Analysis

The coated samples had a similar puncture/displacement profile to the uncoated samples which can be seen in Figure 10, but there is more variation between the samples due to differences in the coat of individual needles, as discussed in Surface Characterization of Untested Samples section of this chapter. Differences in the puncture/displacement profile are due to the coating which resulted in an additional peak (Peak 4) due to the end of the coating on the needle and an additional shaft friction force (Shaft Friction #1 is coating friction, Shaft Friction #2 is purely stainless steel friction) due to a portion of the shaft being coated and a portion not being coated.
Figure 11 shows an annotated graph with the peaks and areas of interest labelled. Table 2 displays the average values of $F_z$ forces for all PDA/PTFE coated needle puncture tests for each of the four sections of the needle.

<table>
<thead>
<tr>
<th>Hypodermic PDA/PTFE Coated Needles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Forces (Fz)</strong></td>
</tr>
<tr>
<td>Peak 1 (Tip Force)</td>
</tr>
<tr>
<td>Peak 2</td>
</tr>
<tr>
<td>Peak 3</td>
</tr>
<tr>
<td>Shaft Friction #1 (Fz Average)</td>
</tr>
<tr>
<td>Peak 4</td>
</tr>
<tr>
<td>Shaft Friction #2 (Fz Average)</td>
</tr>
</tbody>
</table>

*Table 2. Hypodermic PDA/PTFE Coated Needle Average Fz Values.*

A direct comparison between the averages of coated and uncoated samples, shown in Table 3, clearly suggests that the PDA/PTFE coating conducted a lower tip force (44.4% lower) and more consistent averages in shaft $F_z$ friction forces due to a lower standard deviation. However, after the uncoated needles penetrated the film it can be seen that the Peak 2, Peak 3, and Shaft Friction #1 averages are all lower than the coated needle’s force values. These findings suggest that the coating was successful at reducing the initial penetration force at the tip of the needle, but led to an increase in other friction quantities. The bar graph shown in Figure 9 compares the uncoated and coated average $F_z$ peak and shaft force values. It’s interesting to note that while the Peak 2, Peak 3, and Shaft Friction #1 forces are higher on the coated needles, the range of average $F_z$ force values across all four sections of the coated needles is lower than the values for the uncoated needles.
### Uncoated vs. Coated Analysis

<table>
<thead>
<tr>
<th>Forces (Fz)</th>
<th>Uncoated Averages (mN)</th>
<th>Coated Averages (mN)</th>
<th>Percent Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tip Force (Peak 1)</td>
<td>225</td>
<td>125</td>
<td>-44.4%</td>
</tr>
<tr>
<td>Standard Deviation (Peak 1)</td>
<td>12</td>
<td>26</td>
<td>117.2%</td>
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<tr>
<td>Peak 2</td>
<td>92</td>
<td>101</td>
<td>10.1%</td>
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<tr>
<td>Standard Deviation (Peak 2)</td>
<td>15</td>
<td>13</td>
<td>-14.5%</td>
</tr>
<tr>
<td>Peak 3</td>
<td>70</td>
<td>82</td>
<td>17.5%</td>
</tr>
<tr>
<td>Standard Deviation (Peak 3)</td>
<td>15</td>
<td>6</td>
<td>-57.4%</td>
</tr>
<tr>
<td>Shaft Friction #1 (Fz Average)</td>
<td>20</td>
<td>36</td>
<td>83.8%</td>
</tr>
<tr>
<td>Standard Deviation (Shaft #1)</td>
<td>4.3</td>
<td>3.5</td>
<td>-18.6%</td>
</tr>
<tr>
<td>Peak 4</td>
<td>N/A</td>
<td>51</td>
<td>N/A</td>
</tr>
<tr>
<td>Shaft Friction #2 (Fz Average)</td>
<td>N/A</td>
<td>21</td>
<td>N/A</td>
</tr>
<tr>
<td>Standard Deviation (Shaft #2)</td>
<td>N/A</td>
<td>4</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*Table 3. Uncoated vs. Coated Analysis of Average Fz Values.*

![PDA/PTFE Coated vs. Uncoated Fz Forces](image)

*Figure 9. PDA/PTFE Coated vs. Uncoated Fz Forces Bar Graph.*
Further analysis of individual needles shows that for each uncoated needle the larger the average $F_z$ force at Peak 1, the more dramatic the difference between Peak 1 and Peak 2. This same characteristic does not apply to the coated samples. The coated samples produced varying Peak 2 profiles. As can be seen in Figure 12, the Peak 2 force is actually slightly larger than the Peak 1 force, which is never seen in uncoated needle tests, even in the preliminary testing round. Both testing rounds had coated needles that occasionally had higher Peak 2 forces than Peak 1 forces. This is seen because of inconsistencies on the surface of Section 2 of the coated needles. Images were taken to verify this hypothesis, and are discussed in Section 4.3. The smooth grinded bevel of the uncoated needles allowed for more consistent peak profiles across the uncoated samples due to the surface having the same roughness and general dimensions. This wasn’t necessarily the case in the coated needles.

The section where the coating had the worst effect was on the Shaft Friction #1 (83.8%) meaning that the PDA/PTFE coating actually increased the forces that would be felt during this portion of penetration at the surface of the film. The cause of this is most likely a combination of an increased bore diameter, as well as uneven adhesion of the coatings. Typical substrate tests, which were the basis of this thesis hypothesis, are conducted on square substrates where the surface friction is tested, but an increased diameter doesn’t affect functionality as it does with needles and bore diameter.
Figure 10. Hypodermic Coated Needle Force/Displacement Profile. (Hypodermic PDA/PTFE Coated Needles, Needle 1, Puncture 1, Appendix A)

Figure 11. Annotated Hypodermic Coated Needle Force/Displacement Profile (. (Hypodermic PDA/PTFE Coated Needles, Needle 1, Puncture 1, Appendix A)
4.3 Surface Characterization of Untested Samples

The sample images shown in Figure 13 were taken with 40x magnification using a Nikon Eclipse E200, with a Luminera Infinity 1 attachment for digital image capture. In Figure 13, (A1), (B1), and (C1) are images of coated needles while (A2), (B2), and (C2) are images of uncoated needles. It’s immediately obvious that there are inconsistencies in the PDA/PTFE coating on each section of the coated needles. The uncoated needles appear to have a similar surface texture in each image and in images (B2) and (C2) no irregularities in the shaft surface can be seen. However, in images (B1) and (C1) there are clear surface formations produced from the coating that are unevenly distributed. Image (A1) shows similar formations located on the inner surface of the needle, but not on the grinded bevel edges of Section 2 of the needle or the tip. The coated
needle tip is clear of any aggregation, and can explain why the PDA/PTFE thin film was effective on this section of the needle, and led to lower penetration forces. Other sections of the coated needles had such non-uniform coats that friction was increased as the uneven texturing passed through the film. Visible protrusions and uneven outer surface textures can be seen in (B1) and (C1), which are sources of increased $F_z$ forces as penetration occurs. No surface abnormalities are seen in any uncoated needle images. A more uniform coat or a method to remove any surface clumping on the coated needles is needed to fully determine whether the coating procedure is depositing a film enhancing properties in Section 2, Section 3, and Section 4 of the needles.
Figure 13. (A1), (B1), (C1) are Images of PDA/PTFE Hypodermic Coated Needles. (A2), (B2), (C2) are Images of Uncoated Hypodermic Coated Needles. (A1/A2) Bevel. (B1/B2) Side View of Section 2/Section 3. (C1/C2) Shaft View.
5.0 CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The hypothesis of this research was that the PDA/PTFE coated hypodermic needles would result in lower penetration forces during puncture of a PET film. While the $F_Z$ forces weren’t lower for each section of the coated needles, Section 1 of the needle was able to penetrate the film at a force on average 44.4% lower than the uncoated needles. The uncoated needles also had a higher maximum force than the coated needles, with the average highest force value being 225 mN for the uncoated samples, compared to only 125 mN for the coated samples. It is concluded that since the PDA/PTFE coating produced a significantly lower maximum force over the course of film penetration, the coating procedure was successful. However, during sample characterization, non-uniform coating was seen on the coated samples. Peak 2 and Peak 3 average force values for the coated samples were both with 20% of the uncoated sample values. While the Shaft Friction #1 force was 83.8% higher for the coated needle, this large percent change was caused by only 16 mN higher average forces. If a more uniform coat can be achieved, it is expected that the $F_Z$ forces felt by the needles at Peak 2, Peak 3, and Shaft Friction #1 would be dramatically reduced.

The PDA/PTFE coat provides great potential in many biomedical applications if equal and consistent particle dispersion can be achieved. For this to be achieved, further testing and experimentation is required.

5.2 Future Work

Nanoparticle induced coatings have unlocked a wide range of possible applications, with unique properties continuing to be discovered. Research has been done on mixing additional particles
with PTFE to produce unique properties with materials such as copper, graphite, etc. Future work in coating hypodermic needles could also focus on increasing the repeatability of each coating and conducting tests with higher quality fixtures. Outside the scope of this thesis, other potential areas for coating investigation include using various needle gauge sizes, different film thicknesses, and alternating the speed of film puncture to determine more about the effects of a particular coating and enhances in penetration.

Additional things to consider are ways in which the research on PDA/PTFE coatings could further benefit medical devices, or other puncture tools. If enhancements in wear are seen in needle penetration, the same improvements may also be found to be useful in tools such as drills, hole punching devices, etc.
References:

## APPENDIX A

### Hypodermic Uncoated Needles

<table>
<thead>
<tr>
<th>Forces (mN)</th>
<th>Needle #1 Punctures</th>
<th>Needle #2 Punctures</th>
<th>Needle #3 Punctures</th>
<th>Uncoated Averages</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1  #2  #3 Avg.</td>
<td>Std. Dev.</td>
<td>#1  #2  #3 Avg.</td>
<td>Std. Dev.</td>
<td>#1  #2  #3 Avg.</td>
</tr>
<tr>
<td>Tip Force (Peak 1)</td>
<td>222 225 227 224 2</td>
<td>2</td>
<td>236 240 241 239 3</td>
<td>2</td>
<td>213 213 209 212 2</td>
</tr>
<tr>
<td>Peak 2</td>
<td>77    80    78   79 2</td>
<td></td>
<td>84    85    86   85 1</td>
<td></td>
<td>110 112 113 112 2</td>
</tr>
<tr>
<td>Peak 3</td>
<td>51    55    52   53 2</td>
<td></td>
<td>72    67    66   68 3</td>
<td></td>
<td>86    88    89   87 2</td>
</tr>
<tr>
<td>Shaft Friction #1 (Fz Average)</td>
<td>18    15    15   16 2</td>
<td></td>
<td>25    21    21   22 2</td>
<td></td>
<td>22    21    21   21 0</td>
</tr>
<tr>
<td>Standard Deviation (Shaft #1)</td>
<td>2     3     3    3 N/A</td>
<td></td>
<td>5     7     8    7 N/A</td>
<td></td>
<td>3     3     3    3 N/A</td>
</tr>
</tbody>
</table>

Table 4. Hypodermic Uncoated Needle Data.

### Hypodermic PDA/PTFE Coated Needles

<table>
<thead>
<tr>
<th>Forces (mN)</th>
<th>Needle #1 Punctures</th>
<th>Needle #2 Punctures</th>
<th>Needle #3 Punctures</th>
<th>Coated Averages</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1  #2  #3 Avg.</td>
<td>Std. Dev.</td>
<td>#1  #2  #3 Avg.</td>
<td>Std. Dev.</td>
<td>#1  #2  #3 Avg.</td>
</tr>
<tr>
<td>Tip Force (Peak 1)</td>
<td>115   114  114   114 0</td>
<td></td>
<td>100  102  103   102 2</td>
<td></td>
<td>158   159  161   159 1</td>
</tr>
<tr>
<td>Peak 2</td>
<td>101   108  128   112 14</td>
<td></td>
<td>107  100  99   102 5</td>
<td></td>
<td>94    83   88    88 6</td>
</tr>
<tr>
<td>Peak 3</td>
<td>76    79    80   79 2</td>
<td></td>
<td>98    84    80   88 9</td>
<td></td>
<td>80    79    78   79 1</td>
</tr>
<tr>
<td>Shaft Friction #1 (Fz Average)</td>
<td>41    38    33   37 4</td>
<td></td>
<td>45    38    38   40 4</td>
<td></td>
<td>27    46    22   32 13</td>
</tr>
<tr>
<td>Standard Deviation (Shaft #1)</td>
<td>5     3     4    4 N/A</td>
<td></td>
<td>4     4     4    4 N/A</td>
<td></td>
<td>4     2     2    2 N/A</td>
</tr>
<tr>
<td>Peak 4</td>
<td>57    61    47   55 7</td>
<td></td>
<td>41    45    53   46 6</td>
<td></td>
<td>N/A   67    N/A  N/A N/A</td>
</tr>
<tr>
<td>Shaft Friction #2 (Fz Average)</td>
<td>19    17    18   18 1</td>
<td></td>
<td>24    26    24   25 1</td>
<td></td>
<td>N/A   23    N/A  N/A N/A</td>
</tr>
<tr>
<td>Standard Deviation (Shaft #2)</td>
<td>2     1     1    1 N/A</td>
<td></td>
<td>7     8     6    7 N/A</td>
<td></td>
<td>N/A   3     N/A  N/A N/A</td>
</tr>
</tbody>
</table>

Table 5. Hypodermic PDA/PTFE Coated Needle Data.