ABSTRACT

YOON, HYOUNIL. Influence of Surface Modification on the Adhesion between Nitinol Wire and Fluoropolymer Films. (Under the direction of Dr. Martin W. King).

One of the current challenges for the medical device industry is how to manufacture and assemble biomedical implants consisting of a metallic wire component and a fluorocarbon film without the use of an adhesive. There are many devices such as guide wires, stent/grafts and embolic protection devices which rely on these components being bonded together in order to function inside the body. This study has evaluated the effect of modifying the surfaces of metallic wire and fluorocarbon film prior to thermally bonding these two components together.

The surface treatments for Nitinol wire included mechanical roughening with sandpaper, treating with atmospheric helium-plasma, and adding a fluorocarbon coating. The surface treatments for fluorinated ethylene-propylene (FEP) film included helium plasma and helium-oxygen plasma under atmospheric conditions. This produced four types of treated and untreated Nitinol wire and three types of treated and untreated FEP film which were combined together and thermally bonded to prepare 12 different types of pull-out test specimens.

A unique pull-out strength test method was developed to assess the level of adhesion between these various candidates. The pull-out force for untreated Nitinol bonded to untreated FEP film was 30.5±2.4 N. Significant improvements of up to 14% in this level of adhesion were obtained with the mechanically roughened Nitinol wire bonded to the helium-plasma treated films and up to 6% of increase with the mechanically roughened Nitinol wire bonded to the helium-oxygen-plasma treated FEP films. However, coating the wire with liquid fluorocarbon monomer mixture (TG-10) and then passing it through a helium-plasma to cure and polymerize

the fluorocarbon coating was not successful. After thermal bonding to FEP film the level of adhesion fell by over 80%.

Scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and contact angle measurements were also taken to characterize the appearance and chemistry of the surfaces before and after modification.

Influence of Surface Modification on the Adhesion between Nitinol Wire and Fluoropolymer Films

by
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A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Master of Science

Textile Management and Technology

Raleigh, North Carolina

2009

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Dedication

This study is dedicated to my mother and father,

and my loving fiancée, Hyunjee.

They are the best supporters for my life.

Biography

Hyounil Yoon was born on December 2nd of 1980 in Kwang-ju, South Korea. After he was born in Kwang-ju where his maternal grandmother lived, he came back to his home in Seoul and grew up in the city. He received his Bachelor of Science in Polymer and Fiber Science in Spring 2002 from Han-yang University in Seoul, South Korea, and then served his military duty in the army from 2003 to 2005. He came to the United States in pursuit of further studies at the College of Textiles, North Carolina State University (Raleigh, NC). He started his master program in Textile Management and Technology (TMT) in Fall 2006 and expects to graduate in May 2009. Upon achievement of his master degree, he plans to proceed to a Ph. D. program in the same college to specialize his interest in textile technology and engineering.

Acknowledgements

I thank God, who is the Savior and the purpose of my life in sending me to the United States. I am thankful for Him to grow my faith in Him and allow me to meet various people and help them while I am studying here in Raleigh. I appreciated meeting Dr. Hoonjoo Lee, who was my senior graduate of Han-yang University in Korea and who came to study in the College of Textiles several years ahead of me so that she could help me plan my study in America.

I thank God for leading me to my advisor, Dr. Martin W. King, who is among the professors in the College of Textiles at North Carolina State University. He has been the most patient person during my progress in this study and the most supportive person for whatever I wished to do, even though it may not have been directly related to my study. What would be the most valuable thing that one can give to another? If it were me, I think it would be the thing that I feel thankfulness and happiness for my present life because I met 'the' person. Thanks to Dr. King, I had a very happy time of two years in my life while I was studying here and also learned a lot academically and grew a lot mentally because of Dr. King.

Lastly but not the least, I thank God for giving me my family. My mom and dad, Yoon-sook Koh and Sang-woo Yoon, are the greatest teachers, supporters, and prayers in my life. My very brilliant and brave younger sister, Sae A, who came to the U.S. ahead of me, has been my mental supporter and reliever during the hard times that I faced. Because of her, my life here was endurable and relieving. I also thank my younger brother, Hyun-woo who is 3 years younger than

me and who always dreams big and thinks practically. He always gives me insightful advice and timely encouragement when I need it such as "I am proud of you, brother!"

Also, this thesis could not have been completed without the assistance of any one of the people listed below. Every help was critical and priceless for me. So I want to say, "Thank you all from my heart!!" I deeply appreciate the individuals below.

Dr. Stephen Michielsen	**Textiles, NCSU**	He shared with me his knowledge of my subject and helped me to keep going forward when I faced critical points in the experimental procedures.
Dr. Ahmed El-Shafei	**Textiles, NCSU**	He gave me directions to plan experiments using the plasma machine and helped me fix the problems.
Eric Johnson	**Crux Biomedical Inc.**	Crux Biomedical Inc. and Mr. Eric Johnson provided me with financial support which essentially allowed me to start my studies in the U.S., be exposed to the biomedical industry, and acquire hands-on experience in R&D of a medical device. It was a countless blessing for me: Thank you! Personally I appreciate his hospitality when I visited Crux Biomedical Inc. in CA. I am very happy to get to know him. I am thankful for learning his professionalism and optimism, and for that he provided practical ideas or advice for my thesis research.
Michael Morrissey	**Fort Wayne Metals**	Fort Wayne Metals and Mr. Michael Morrissey were generous to supply me with a large amount of

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1   Introduction

1.1 Background

It was 26 years ago that the Food and Drug Administration (FDA) set up a new department called Center for Devices and Radiological Health (CDRH). This Center has become responsible for regulating the manufacture, distribution, and clinical use of all medical devices used in the United States. Since 1982 it has set up a detailed list of criteria needed to be considered and evaluated when introducing a new material for use in any medical device. The effect has been to limit the selection of materials that is metals, ceramics, polymers, and adhesives primarily to those that existed either prior to 1982 or that have been approved since that time. This approval process takes considerable time and resources including several millions of dollars to justify and qualify the novel material by the manufacturer.

Within the medical device industry there are currently two types of materials that have most attractive properties and therefore tend to be used in the manufacture and assembly of the same devices. These two materials are:

1) Nitinol, the name derived from its place of discovery (**Ni**ckel **Ti**tanium **N**aval

Ordinance **L**aboratory), shape memory alloy which is biocompatible, superelastic and displays a shape memory effect (1).

2) Various types of fluorocarbon films which are stable and chemically inert in the body and provide non-stick and friction reducing properties (2). These include polytetrafluoroethylene (PTFE), perfluoroalkoxy polymer (PFA), fluorinated ethylene-propylene polymer (FEP), ethylene-tetrafluoroethylene copolymer (ETFE), and polyvinylidene fluoride (PVDF).

Examples of the types of medical devices where these two materials are used include both short-term acute applications, such as guidewires, percutaneous valves, delivery catheters, as well as in long-term chronic or permanent implants, such as endovascular stent-grafts; pacemaker leads; coronary, peripheral, and venous stents; and embolic protection devices. In short term applications the main requirement is to ensure low bending forces and shear forces to permit easy access, for example, of guidewires to tortuous anatomies. For permanent implants the major requirement also relates to fatigue behavior and in vivo degradation. With the US market for stent grafts is currently about $1 billion, and that for coronary stents is about $5 billion, this collection of devices represents a current market of over $6 billion (3).

1.2 Problem Statement

One of the current major challenges for medical device manufacturers is how to assemble or join these two dissimilar materials with a simple, easily engineered, and reliable technique. In particular we are aware that there is a need for a new generation of embolic protection devices. Currently commercial models are manufactured entirely from metal wire which, as discussed in Chapter 2, has certain limitations. We are therefore proposing a new and novel design made from both Nitinol wire and a fluoropolymer film such as fluorinated ethylene-propylene (FEP) (4).

The use of an additional adhesive is not preferred, because the biocompatibility and long term degradation issues related to an additional component take much time and resources to analyze and justify in front of the FDA. Therefore the preferred method of assembly involves thermal bonding. (i.e. the use of heat without any adhesive). Fluoropolymer films, however, are renowned for their non-stick and friction reducing properties. One approach to overcome this situation may be to apply surface modification treatments to either the Nitinol metal wire, or the fluoropolymer film so as to enhance the adhesion between these two dissimilar materials.

1.3 Objectives of the Study

1. The first objective of this study was to develop a reliable and reproducible pull-out strength test method that will measure the level of adhesion or bonding force between wire and film. While the metal wire and polymeric film could be composed of any material, for the purposes of this thesis with the focus on a specific medical product, the materials that were used to develop this test method were Nitinol wire and FEP fluorocarbon film.

2. The second objective was to determine the general level of adhesion between an untreated film and an untreated wire that were thermally bonded together by means of the test method mentioned above using the optimum bonding conditions. Again, because the focus of this thesis has a specific medical product in mind, the untreated materials that were thermally bonded together and tested were Nitinol wire and FEP fluorocarbon film.

3. The third objective was to find which surface treatments to the wire and/or to the film would improve the level of adhesion. A number of different adhesion theories have been listed in Chapter 2 and evaluated. And those surface treatment methods that might have led to improved bond strength either through a mechanical interlocking mechanism or by a chemical bonding mechanism were attempted and tested. Specifically there were 3 treatments that were considered potentially advantageous for the Nitinol wire. They were:

      a) roughening of the smooth metal surface with an abrasive sandpaper;

      b) roughening of the smooth metal surface by the etching action of a helium

plasma; and

c) chemically bonding long fluorocarbon chains to the surface of the wire so that

they could diffuse into the fluorocarbon film during thermal bonding.

In addition, there were 2 treatments that were independently considered potentially advantageous for the FEP fluorocarbon film. They were:

d) roughening of the FEP fluorocarbon surface by the etching action of a helium

plasma; and

e) chemically bonding oxygen-rich polar groups to the surface of the FEP film by a

helium-and-oxygen plasma treatment so they would bond with other polar

groups on the surface of the Nitinol wire during thermal bonding.

4. The fourth objective was to measure the physical and chemical surface properties before and after the various surface modification treatments. These measurements relied on: Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), and a goniometer to measure the static contact angle with distilled water.

1.4 Outline of Thesis

Chapter one provides a general background to the medical device industries and issues that current medical device manufacturers are facing. Chapter one also lists the 4 major goals or objectives in the study. It explains the importance of this thesis topic and the reason why Nitinol wire and FEP film were chosen as the test materials. Chapter two reviews the literature and explains about the background of a specific medical device, a vena cava filter. It also describes current theories of adhesion between dissimilar materials, and discusses about surface treatment methods and characterization techniques. Chapter three describes the materials used in this study, the surface treatment procedures followed, and techniques used to characterize the properties of surfaces before and after modification. Chapter four presents the results and discussion of this experimental work and attempts to explain the findings. Chapter five reviews the initial 4 objectives and draws conclusions about the successfulness of the study and makes practical recommendations. Opportunities for further work are also discussed.

2   Review of Literature

2.1 Designing Vena Cava Filters with Textile Structures

2.1.1 Introduction

The vena cava is the largest vein carrying blood back on the heart. Specifically the inferior vena cava (IVC) is the vein below the heart returning blood from the abdomen and lower limbs, and the superior vena cava (SVC) is the path for blood returning from the brain, upper limbs, and heart (Figure 2.1).

An embolism occurs when a blood clot or thrombus is formed and released in an inflamed vein, associated with pain and swelling. The released clot, called an embolus, is carried by the bloodstream and causes an obstruction in a downstream blood vessel or capillary which is called deep vein thrombosis (DVT). An embolus can be either part of a thrombus, or an air bubble, piece of fat, bone marrow, or tumor tissue (5).

Patients suffering from arteriosclerosis, heart attacks, strokes, certain blood disorders, and congestive cardiac disease, as well as those experiencing surgery or injury with bleeding are predisposed to embolus formation. In fact, when combined with other factors, such as obesity, sitting during long air flights, pregnancy, smoking, birth control

medication, immobility and prolonged bed rest during a serious illness, the incidences of deep vein thrombosis (DVT) and embolism increase significantly (5).

In the event that a circulating clot enters the heart, it will circulate through the pulmonary artery to the lungs, where it will likely cause an obstruction in a capillary. Overtime this may lead to pulmonary insufficiency, difficulty in breathing and chest pain, which are symptoms of pulmonary embolism (PE) (Figure 2.2).

The role of such filters is to trap large flocculent clots measuring greater than 5 mm in size before they arrive in the heart. The filter should hold such thrombi safely in the bloodstream to allow the natural process of clot lysis to be initiated by the plasma protein plasminogen and to permit slow dissolution of the clot over time.

There are currently five alternative approaches for preventing and/or treating pulmonary embolism. They are:

1) post-operative mobilization of the patient with active and passive exercises,

2) thrombolytic therapy, in which, following blood studies, the patient is prescribed

   medication, such as warfarin or heparin,

3) anticoagulation therapy, in which the patient takes medication prophylactically,

   such as low dosage aspirin in order to prevent clot formation,

4) embolectomy, which involves a surgical intervention in order to remove a clot,

and

5) implantation of a permanent or retrievable filter in the inferior vena cava. This

fifth prophylactic approach is becoming increasingly popular for the 23-62% of

patients at risk of DVT and for whom drug therapy is contraindicated (6).
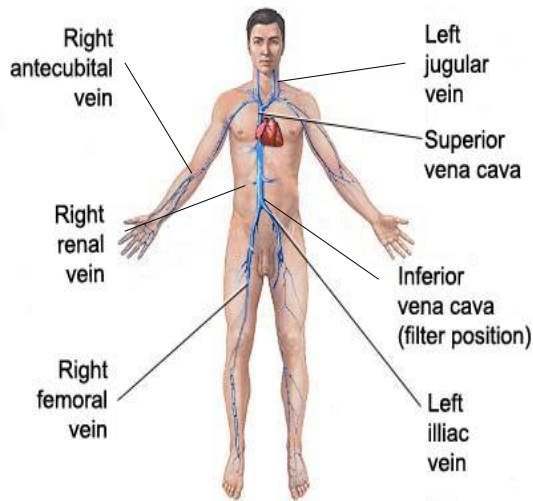
Figure 2.1 Venous System   Figure 2.2 Etiology of Pulmonary Embolism
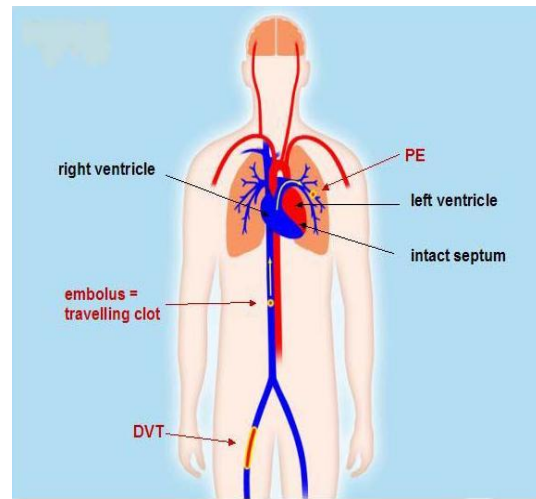
2.1.2 Current Filters for Embolic Protection

2.1.2.1 Filter Insertion and Deployment

The standard site for the placement of vena cava filters is below the renal veins in

the inferior vena cava. However, due to sizing limitations or when there is a high risk of

releasing emboli from the kidneys, vena cava filters can also be placed in the suprarenal position (4.7%) (Figure 2.1) (6). There are three approaches for the percutaneous insertion and delivery, and the specific recommended protocol depends on the specific device and entry site. Generally, non-invasive access through a femoral vein is most frequently used (82%), but alternatively, jugular, subclavian and antecubital approaches have also been found to be clinically successful (Figure 2.1) (6).

Delivery of an inferior vena cava filter requires the filter structure to be collapsed and loaded into a sheath that fits inside a 6-9 French (2-3 mm diameter) size catheter. A guide wire is first inserted into the vein and its position tracked by radiological imaging. Then the guide wire is used to insert the loaded catheter and position the sheath appropriately prior to deployment of the filter by releasing it from the sheath. One of the design requirements for the filter is that, once released, it should expand and push against the internal vessel wall. This ensures that it fits the vessel and generates sufficient radial force so as to prevent migration once implanted. Some degree of over-sizing is obviously a key factor in ensuring stable deployment and good fixation within the vessel, particularly as the vena cava is the most elastic and compliant vein in the body.

2.1.2.2 Materials Selection

At this time all commercial vena cava filters are fabricated from either Nitinol (nickel and titanium alloy), phynox (nickel, cobalt, chromium, iron, and molybdenum alloy), or stainless steel wire in various catheter sheath sizes ranging from 7-14 French (2.3 - 4.7mm diameter). These metals were chosen because they are biostable and have low thrombogenicity. This means that blood is less likely to form clots on the surface, and cells are not encouraged to grow around the device. Moreover, Nitinol is a thermal shape memory alloy that is self-expanding after deployment and exposure to body temperature (7).

2.1.2.3 Types of Embolic Protection Filters

There are three main types of filters used for embolic protection. They are the permanent, retrievable and temporary filters. In the past, the use of permanent filters was considered the best therapy for patients with DVT. However, with increasing experience of late complications, surgeons are seeing merit in moving towards retrievable devices that can be withdrawn when the risk of PE has been lowered by drug or other treatments after a period of 2-8 weeks. Temporary filters are designed for deployment and use during certain surgeries and interventions, such as angioplasty and thrombectomy that last for only a few hours. For this reason they remain tethered to their guide wires throughout deployment.

Because of the need for large multi-centered randomized clinical trials to determine their safety, efficacy and optimal usage, only seven permanent commercial filters and four retrievable filters have received approval from the Food and Drug Administration for clinical use in the USA (5), (8), (9). A number of temporary filters are still under development (10).

Permanent Filters

All commercial IVC filters have evolved with a similar overall conical shaped design. Of the seven different permanent filters currently available in the United States, their styles have evolved into three types: conical, basket and multilayered (Figure 2.3) (11). With respect to their filtering ability against emboli, the basket and multilayered designs are considered more efficient than the conical design (12). Even though permanent filters function relatively well, they have long-term complications.

(a)   (b)   (c)   (d)
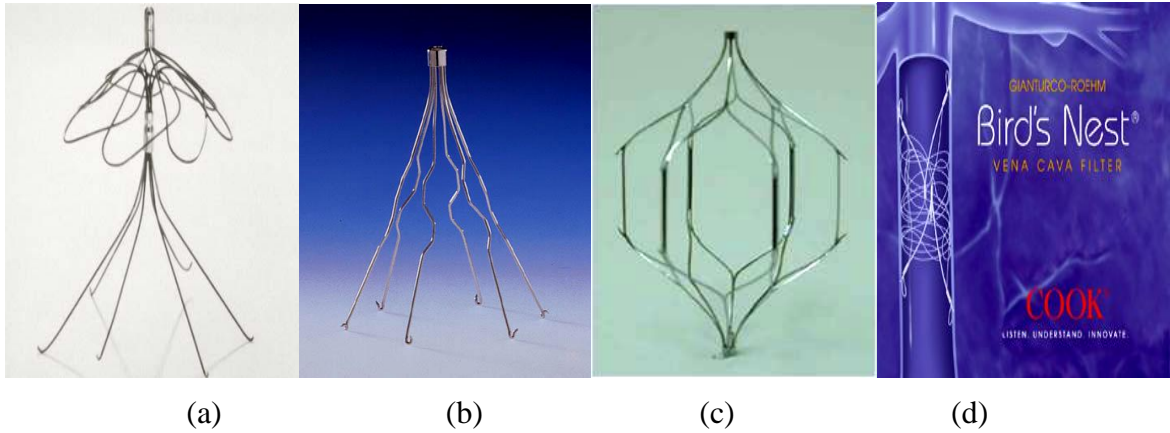
Figure 2.3 Permanent Vena Cava Filters

(a) Simon Nitinol filter (Bard), (b) Over-the-wire stainless steel Greenfield filter
(Boston Scientific), (c) TrapEase filter (Cordis Endovascular), and (d) Bird's nest filter (Cook)

Retrievable Filters

Retrievable filters can avoid some long-term complications because they can be retrieved from the body when they are no longer needed. However, they are usually retrieved within a relatively short term of 4-6 weeks. So sometimes the implantation time is too short to solve the clinical problem such as DVT. The design of retrievable filters is similar to that of permanent filters (Figure 2.4). One significant difference is that retrievable filters have hooks at either one or both ends so that the filter can be retrieved by a wire when the filter is no longer needed.

| (a) | (b) | (c) | (d) |
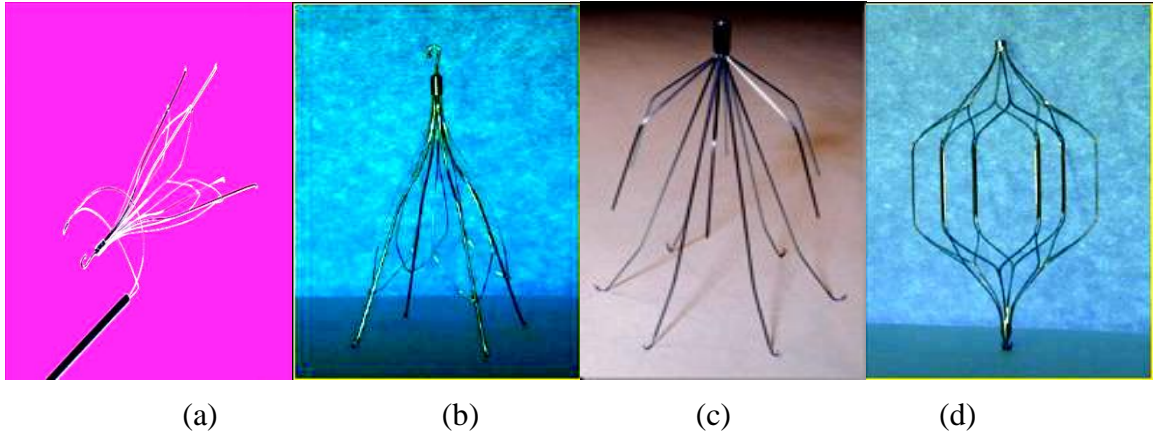
Figure 2.4 Retrievable Vena Cava Filters

(a, b) Gunther tulip filter (Cook), (c) Recovery filter (Bard), (d) OptEase filter (Cordis Endovascular)

Temporary Filters

The role of a temporary filter is different from that of a permanent or retrievable device. Its purpose is to collect thrombi and debris that might be released into the blood stream during angioplasty and thrombectomy interventions. It is therefore attached to the tethering catheter while inside the body. Temporary filters are generally inserted into the jugular or femoral veins. Because of their short term use, temporary filters do not have barbs that might penetrate the wall of the vena cava (Figure 2.5). However, for this very reason, temporary filters have a greater chance to migrate, and, under certain circumstances adverse incident reports of filter migration into the heart have been reported (13). Up to now no temporary filters have received FDA approval.
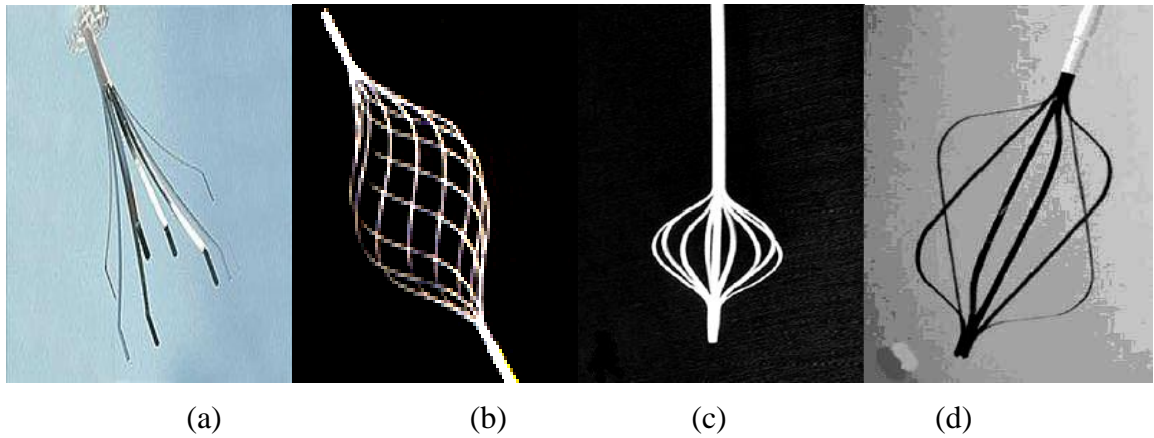
Figure 2.5 Temporary Vena Cava Filters

(a) Tempofilter II (B. Braun), (b) Gunther filter (Cook), (c) Neuhaus protect filter (Toray), (d) Antheor filter (Boston Scientific)

2.1.3 Complications with Current Vena Cava Filters

Although vena cava filters have been in clinical use since the 1960's, they have not always been safe and effective due to late complications. A number of complications have been reported in the literature, including: recurrent pulmonary embolism (2-5%), inferior vena cava thrombosis (6-30%), access site thrombosis (2-28%), filter migration (3-69%), tilting (15-20%) (Figure 2.6), penetration of the vena cava wall (9-24%), structural fracture of the filter (1%), and guidewire entrapment (<1%) (Figure 2.7) (14).

The high percentage of complications and adverse incidents demonstrates a range of limitations for IVC filters. The frequencies are influenced by many factors, such as style of filter, design, material, site of deployment, access approach, patient anatomy,

pathology, and disease state.   Clearly with such a high and unsatisfactory level of complications, there is a need for a more versatile, functional and durable device.

Figure 2.6 Radiographic Image of IVC Filter Deployed with Tilted Orientation

Figure 2.7 Radiographic Image Showing IVC Filter Released from Sheath, but Entangled

2.1.4 "Ideal" Inferior Vena Cava Filter Design

As can be seen in Figures 2.3, 2.4, and 2.5 and from the reports of clinical complications, the use of wire structures as IVC filters has a wide variability and lack of consistency in their clot trapping efficiency, their ability to be self-centering, and their tendency to experience migration and thrombosis.   It would therefore be useful as part of

the process of new product design and development to identify, prioritize and attempt to quantify the desirable features and characteristics of the "ideal" IVC filter design. To this end, we offer the following list of ten requirements. They are in no particular order.

- Non-thrombogenic

- High filtration efficiency for emboli measuring at least 5 mm

- No impedance of flow and minimal turbulence

- Low thrombosis at access site

- Ease of insertion and retrieval

- Secure fixation within the vena cava

- Minimal damage to luminal wall of vena cava

- No perforation of vena cava wall

- Magnetic resonance imaging compatibility (15)

- Low cost

What the specific design inputs are for the various requirements, and how you measure them quantitatively to ensure validation of prototype candidates, is still under development. However, we offer the following prototype design with its unique textile structure as a potential idea for the next generation of IVC filters (Figure 2.8).

The proposed filter consists of a Nitinol wire, which is formed into a figure of eight. One of the lobes of the figure of eight contains an open mesh of PTFE yarns with known pore size openings, which provide a consistent clot trapping performance. The wire and mesh are fine and flexible enough to allow the device to be easily loaded, deployed and retrieved into and from a 6 French (2mm diameter) sheath. This gives the device a low profile, and, given that it is available in two sizes (S = 17-21mm ID, L = 22-28mm ID), this permits its use with a wide range of patient anatomies, including the jugular and femoral positions.
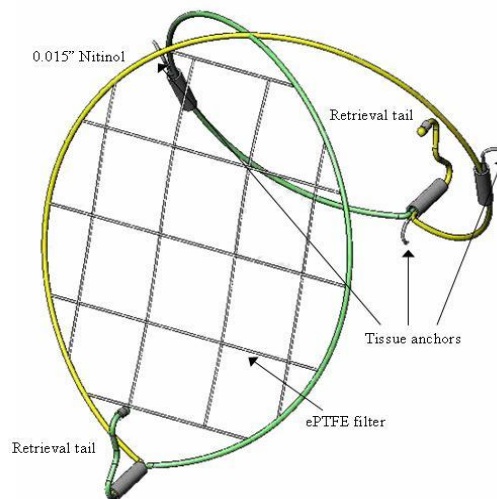
Figure 2.8 Proposed New Prototype IVC Filter Based on a Textile Construction

The simplicity of the design ensures that once deployed, it is self-centering. And, as long as the selection of the size deployed is greater than the diameter of the vena cava, then the likelihood of migration is minimized by the incorporation of small tissue anchors. In addition to having radio-opaque features that ensure it can be readily visualized by radiography, the device contains retrieval hooks on both sides to facilitate the ease of retrieval when used as a retrievable filter. Animal trials are continuing to assess the ease of deployment and retrieval after $1 - 10$ weeks *in vivo.*

2.2 Adhesion between Dissimilar Materials

The major challenge in designing this new generation of flexible textile filters concerns the method of assembly of the metallic and polymeric components, particularly in assuring good adhesion between the proposed Nitinol wire surface and the FEP polymeric film or fiber. It is important that bonding between the wire surface and the polymeric film or fiber be achieved without the use of an additional adhesive. This is because there would be considerable time, energy and money required to demonstrate acceptable initial and long term biocompatibility of an additional adhesive in front of the FDA. For this reason a simpler approach is always preferred, namely, to use direct thermal bonding between the metallic wire and the polymeric film without the addition of an intervening adhesive layer.

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The remainder of this chapter deals with the science and technology of adhesion between metal and thermoplastic polymeric surfaces and the use of surface modification techniques that could be employed to improve the level of adhesion between these components when assembled by thermal bonding. It reviews the current state-of-the-art regarding adhesion phenomena between metals and polymeric films in general, and between Nitinol wire and FEP film in particular.

2.3 Principles of Adhesion

Here is a list of the main theories that describe the principles of adhesion (16). The four traditional theories have recently been expanded to seven theories as the concept of "adsorption/surface reaction" has been broken down into four separate mechanisms (Table 2.1).

Table 2.1 Theories of Adhesion

Traditional	Recent	Scale of Action
Mechanical Theory	Mechanical Interlocking	Microscope
Electrostatic	Electrostatic	Microscope
Diffusion	Diffusion	Molecular

Table 2.1 (continued)

	Wetting	Molecular
Adsorption/ Surface Reaction	Chemical Bonding	Atomic
	Weak Boundary Layer	Molecular
	Acid-Base	Molecular

2.3.1 Mechanical Interlocking Theory

According to the mechanical interlocking theory, adhesion occurs by the penetration of adhesives into pores, cavities, and other irregularities on the surface of the substrate or adherend. The trapped air at the interface of the adhesive leads it to be concluded that an adhesive penetrating into the surface roughness of two adherends can bond the two. In the case such as this study, where there is no adhesive, the polymeric film layer must be soft enough to penetrate into the surface roughness of the wire. This requires one to use the optimal applied pressure and surface temperature during thermal bonding. Note that there is supportive data in the literature that relates bond strength and durability to increased surface roughness (17). It may therefore be possible to increase the bond strength between Nitinol wire and a fluorocarbon polymeric film by simply roughening the surface of the wire and take advantage of this mechanical interlocking theory.

2.3.2 Electrostatic Theory

This theory explains that adhesion takes place because of electrostatic effects between adhesive and adherend. Theoretically, an electron transfer takes place between the adhesive and the adherend as a result of the electronic imbalance of the two. Thus the electrostatic forces in the form of an electrical double layer are formed at the adhesive-adherend interface. This theory gains support from the fact that electrical discharges have been detected when an adhesive is peeled from a substrate. So when explaining adhesion between a polymeric film and a metallic wire, the electrostatic mechanism does provide a plausible explanation (18). However, the contribution to the adhesion strength may be only minor when compared to that of chemical bonding.

2.3.3 Diffusion Theory

This theory suggests that adhesion is developed through the inter-diffusion of molecules in and between the adhesive and adherend. The diffusion theory is primarily applicable when both the adhesive and adherend are polymers with relatively long-chain molecules capable of movement. The diffuse interfacial (interphase) layer typically has a thickness in the range of 10Å -1,000 Å, which is in the measurable range for XPS analysis when samples are probed to a depth of up to 100 Å. Clearly in this study, the untreated metallic wire does not experience a diffusion mechanism when bonding. But after

fluorocarbon coating the wires may present long-chain fluorocarbon molecules on their surfaces which may be capable of taking part in a diffusion mechanism with the adjacent FEP film. The assumption here is that the elevated temperature used during thermal bonding would be sufficiently high to ensure inter-diffusion of long-chain molecules from both surfaces, thus leading to higher bond strength.

2.3.4 Wetting Theory

In this theory, adhesion results from molecular contact between the two materials and the surface forces that develop between them. The process of establishing continuous contact between the adhesive and the adherend is called *wetting*. For an adhesive to wet a solid surface, the adhesive should have a lower surface tension than the critical surface tension of the solid.

Figure 2.9 illustrates how complete and incomplete wetting of an adhesive can spread over a surface (19). Good wetting means that the adhesive flows into the valleys, cracks, and crevices. Poor wetting means that the adhesive forms bridges over the valleys, cracks, and crevices; and this results in a reduction of the actual contact area. This lower overall contact area causes lower bond strength. In the bonding procedures followed during wire/film assembly it is assumed that high enough applied pressures and elevated

temperatures will be used to cause FEP polymer softening and flow, and so ensure complete and continuous surface wetting.
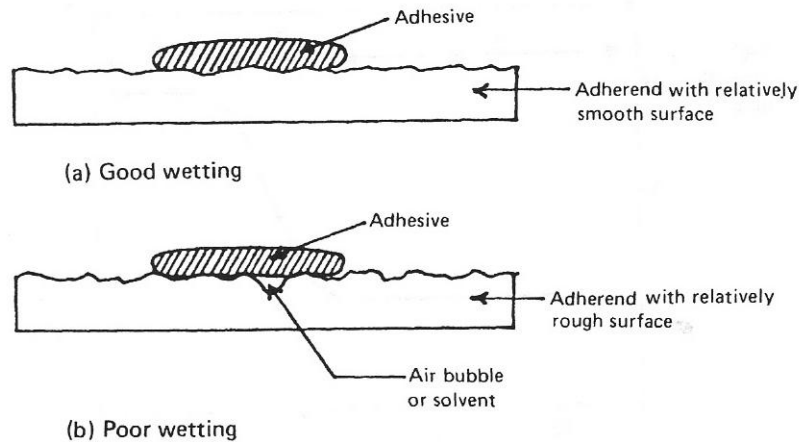
Figure 2.9 Examples of Good and Poor Wetting by an Adhesive Spreading across a Surface (19)

2.3.5 Chemical Bonding

Various types of interactions can occur between surfaces. They include covalent bonds, hydrogen bonds, van der Waals forces, and ion-dipole interactions (Table 2.2). Clearly covalent bonds and ion-ion polar interactions generate the highest energy levels and result in the strongest chemical bonds and highest adhesion values between two independent surfaces at an interface. In this study, attempts to increase the surface oxygen content of fluorocarbon films with the use of helium-oxygen plasma treatments may allow

us to increase the level of hydrogen bonding and the hydrophilicity of the film, and hence achieve a stronger adhesive bond with the metallic wire.

On the other hand, by applying a fluorocarbon coating to the Nitinol wire, we could induce weaker dipole-dipole interactions between the wire and the fluorocarbon film which may lead to reduced adhesion strength.

Table 2.2 Examples of Energies of Atomic Interactions and Chemical Bonds

Type	Example	E (kJ/mol)
Covalent	$C-C$	350
Ion-Ion	$Na^+\cdots Cl^-$	450
Ion-Dipole	$Na^+\cdots CF_3H$	33
Dipole-Dipole	$CF_3H\cdots CF_3H$	2
London Dispersion	$CF_4\cdots CF_4$	2
Hydrogen Bonding	$H_2O\cdots H_2O$	24

2.3.6 Weak Boundary Layer Theory

This theory was first explained by Bikerman, who claimed that bond failure inevitably occurred at a weak boundary layer and not necessarily at the bonded interface between the two adhering components (20). In this study of Nitinol wire, given that the

titanium oxide boundary layer on the outer surface of the Nitinol is well integrated into the alloy through well controlled exacting chemical etching and annealing processes, the possibility of failure through a weak boundary layer mechanism is not at all likely to occur.

2.3.7 Acid-Base Theory of Adhesion

This specific example of chemical bonding involves the formation of a Lewis acid and a Lewis base, when compounds are able to accept and donate respectively an electron pair (21). In this study, this may happen when fluorocarbon gas is exposed to helium plasma, thus creating a negative fluorine Lewis acid which will react chemically with a Lewis base at the surface of the Nitinol wire.

2.3.8 Summary of Adhesion

Therefore in conclusion, in order to increase the level of adhesion between Nitinol wire and FEP film we need to consider strategies that will ether

1) increase mechanical interlocking, or

2) increase the energy level associated with chemical bonding, or

3) increase the opportunity for inter-diffusion of long-chain molecules into the

other substrate.

To achieve this, we plan to

a) increase the surface contact area of Nitinol by roughening the wire,

b) increase the surface contact area of Nitinol wire and the FEP film by

etching with helium-plasma treatment,

c) change the surface chemistry of FEP film and increase the chemical

bonding by treating with helium-oxygen-plasma treatment, and

d) add long-chain fluorocarbon molecules to the Nitinol surface by

fluorocarbon coating treatment of the wire.

2.4 Surface Modification Techniques

Surface treatments take an important role in bonding materials that have different surface energies such as metals and polymers. Polymers especially have an inherently lower surface energy than metals, so polymers tend to form intrinsically poor adhesive bonds without some types of surface treatment. The important feature of surface treatments is that they only affect the properties of the region near the surface, and do not alter the

bulk properties of the substrate. Table 2.3 shows a simple classification of surface treatment techniques (22). In this study mechanical roughening and plasma treatments including surface coating were chosen to be the simplest and most likely approaches to increase the bonding strength between Nitinol wire and FEP film.

Table 2.3 Classifications of Surface Treatment Techniques

Treatment Methods					
Mechanical	Flame	Plasma	Laser	Chemical	Cleaning

Figure 2.10 provides an illustration of how the functionality of interfaces, particularly between polymers and Nitinol, can be modified so as to improve the adhesion between polymer and metal surfaces. In the upper figure the Nitinol wire has already acquired an oxide layer. So to improve adhesion, the FEP polymer surface needs exposure to oxygen plasma in order to acquire functional groups with high polarities. In the lower Figure 2.10 the alternative approach of treating the Nitinol wire is illustrated. By coating the surface of the Nitinol with long-chain fluorocarbon species by treating with a fluorocarbon monomer mixture and subsequent helium-plasma, the metal's interfacial properties will be improved. If the long-chain fluorocarbon species can diffuse during

thermal bonding into the FEP polymer surface, then the bonding strength would be increased and the level of adhesion improved.
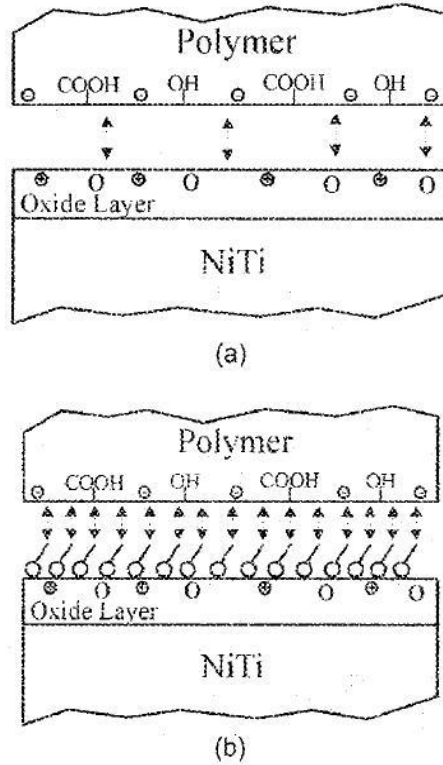
Figure 2.10 Schematic Illustration of Functional Interfaces at Polymer and Nitinol Surfaces

2.4.1 Mechanical Treatment

Surface roughening of plastics and/or metals accomplishes the same purposes. By roughening the surface of substrates, the contacting surface area increases. Usually hand-

sanded or sand-blasted methods are used to improve surface roughness. In the thermal bonding procedures during wire/film assembly it is assumed that increasing the surface area of the Nitinol wire will increase the bonding strength of the wire to FEP film. In addition, bonding strength may also be enhanced due to the mechanical interlocking or interdigitation between the roughened wire and polymer surfaces. This approach has been reported by Caroll et. al. who have shown that the level of adhesion of Nitinol wire to polymer coatings is best when the state of the wire's surface is roughest (23).

2.4.2 Plasma Treatment

Plasma is a collection of charged particles containing positive and negative ions. Plasma is electrically conductive and influenced by a magnetic field. According to Liston, four major effects of plasma on surfaces are normally observed. The effects are:

1) cleaning of organic contamination from the surfaces;

2) material removal by ablation (micro-etching) to increase surface area or to

   remove a weak boundary layer;

3) crosslinking or branching to strengthen surface cohesion;

4) and surface chemistry modification to improve chemical and physical

   interactions at the bonding interface. Surface modification alone, or in

combination with any or all of the competing reactions, provides a means to

dramatically improve the strength of adhesive bonds (24-27).

2.4.2.1 Atmospheric Plasma

Atmospheric plasma systems have been developed and have many advantages

compared to previous types of surface treatment systems, such as 3D corona. The superior

points of atmospheric plasma treatment are:

1) extremely low currents in the plasma cloud (100µA);

2) noiseless;

3) very little ozone generation;

4) low plasma flow temperature (ambient); and

5) relative ease to introduce special additives for surface modification (28).

 With regards to plasma treatment of plastic films, the literature indicates that a

helium-plasma treated FEP polymer showed significant increases in film/film bond or peel

strength compared to that of untreated FEP film (29). Also another type of fluoropolymer

film, ETFE, treated with oxygen-plasma showed a 20 times increase in bond strength in an

adhesive bonded double-lap shear test (30).   Another example of improved adhesion

between metal and polymer surfaces is reported by Grundmeies et. al., who used an oxygen atmospheric plasma to introduce polar groups to the surface of polyethylene polymer. Subsequent processing of the metal/polymer composite led to improved interfacial bonding (31). In a study to improve the adhesion of FEP film to copper metal, Inagaki et. al. showed that hydrogen atmospheric plasma treatments increased the hydrophillicity of the FEP film, which resulted in an improvement in the peel strength to copper metal. These references support the assumption that helium and/or helium-oxygen plasma treatments of FEP film may increase the bonding strength between the film and Nitinol wire.

2.4.3 Fluorocarbon Coating

Fluorochemical finishes are the most widely used repellant finish in the textile industry. Fluorocarbon finishes are currently the best repellent finishes and, also they are known for their durability under physical, chemical, and thermal stresses (32).

In an example from the literature, Yahia et. al., has demonstrated that superior bonding strength can be achieved between Nitinol treated with plasma polymerized tetrafluoroethylene (TFE) fluoropolymer and a fluorocarbon coating (33). This supports the idea that adding a hydrophobic surface treatment to metal wire may improve its bonding strength when thermally bonded to other hydrophobic fluorocarbon surfaces.

3 Materials and Methods

3.1 Materials

The sample of fluorinated ethylene-propylene (FEP) film was supplied by CS Hyde Company (Lake Villa, IL). The film was 2 inch wide and had a thickness of 0.005 inch. The film was transparent. It was shipped and stored wound on a roll in an unsealed plastic bag. FEP film was selected because it is a biocompatible polymer recognized and accepted by the FDA for use in biomedical devices. It is thermoplastic as well as having similar mechanical properties and chemical inertness to those of PTFE. In a study reported by Chang et. al., FEP film from among a number of fluorocarbon candidates, was found to give the highest peel strength to metals (34).
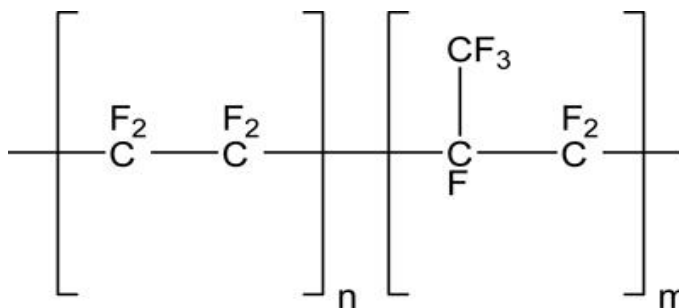
Figure 3.1 Chemical Structure of Fluorinated ethylene-propylene (FEP)

The sample of 0.015" diameter Nitinol wire was shipped by Fort Wayne Metals (Fort Wayne, IN). It was silver colored, chemically etched and annealed. Because of the annealing process, the as-received wire was very elastic (Table 3.1). The continuous wire sample was delivered and stored on a roll in a blue unsealed plastic bag. According to Fort Wayne Metals, the chemical composition of the material shall be equal to or better than those defined by ASTM F20063 (35).

Table 3.1 Chemical Composition of Nitinol Wire Supplied by Fort Wayne Metals

Element	Weight (%)
Nickel	54.5 to 57.0
Titanium	Balance
Carbon	< 0.05 (500 PPM maximum)
Cobalt	< 0.05 (500 PPM maximum)
Copper	< 0.01 (100 PPM maximum)
Chromium	< 0.01 (100 PPM maximum)
Hydrogen	< 0.005 (50 PPM maximum)
Iron	< 0.03 (300 PPM maximum)

Table 3.1 (continued)

Niobium	< 0.025 (250 PPM maximum)
Oxygen	< 0.05 (500 PPM maximum)
Any Single Trace Element	< 0.1
Total Trace Elements	< 0.25

3.1.1 Cleaning Methods

3.1.1.1 Initial Cleaning Method

Prior to any characterization, analysis or surface treatment both the FEP film and the Nitinol wire were exposed to the following 5 step initial cleaning process.

1. The materials were cut into small pieces: the wire into 2 inch long specimens and

   the film into 2inch long and 1 inch wide rectangles.

2. The specimens of cut films and wires were put into an ultrasonic bath and

   immersed in a 2% Triton X100 aqueous monomer mixture. The ultrasonic bath

   was run for 5 minutes to remove most aqueous soluble contaminants.

3. The film and wire materials were then rinsed in running distilled water.

4. The film and wire materials were then returned to the ultrasonic bath, and this

time immersed in distilled water. The ultrasonic bath was then run for 5 minutes.

5. In next step, the film and wire specimens were cleaned in the ultrasonic bath for 5 minutes with hexane in order to remove most of the remaining oily contaminants. The hexane was ACS Grade, at least 98.5% pure (60-65% n-hexane) as supplied by VWR International (36). The specimens were then dried for one hour in a hot air oven at 110ºC.

3.1.1.2 Second Cleaning Method

When it was found that the initial cleaning method led to the appearance of beads or blisters on the surface of the untreated and helium-plasma treated FEP film (See Results Section 4.1), it was decided to delay the drying step and to add an additional sixth step so as to remove any residual hexane with an aqueous wash. The sixth step in the Second Cleaning Method is described below.

6. In a sixth step, the film and wire materials were rinsed again in running distilled water and then dried for one hour in a hot air oven at 110°C.

3.1.2 Storage

The cleaned wires and film specimens were stored in fluoropolymer containers (Fluoroware® Inc., Chaska, MN) which had previously been cleaned with hexane and blown dry with nitrogen gas before storing the materials.

3.2 Preliminary Testing

3.2.1 Tensile Test for Verifying the Isotropic Nature of the FEP Film

To verify whether or not the FEP film had an isotropic structure, a set of tensile breaking force measurements was performed using strip shaped specimens cut in the machine direction and in the cross direction. The equipment and conditions for performing the mechanical testing were as follow:

- MTS Model# 1122 (Eden Prairie, MN)

- Capacity of load cell: 250N

- Crosshead speed: 0.1mm/sec

- Initial gauge length: 0.6"

- Type of clamps: pneumatic (100psi pressure)

- Jaw faces: flat metal with 120 grit sandpaper surface covering

The film specimens are described below:

- FEP film 0.005 inch thick (see Section 3.1)

- Specimen size: 2" x 1/8"

- Number of repeat tests: 6

And the Table 3.2 shows the results of tensile testing.

Table 3.2 The Results of Tensile Breaking Force and the Student T-test

Breaking Force	Spcm #	Machine Direction (N)	Cross Direction (N)
	1	7.1	5.2
	2	6.2	7.3
	3	6.5	6.0
	4	6.4	4.9
	5	N/A	7.0
	6	N/A	6.2
	Mean	6.6	6.1
	SD	0.3	0.9

*T-test result: p= 0.33 (NOT significantly different)

From these results, I concluded that the FEP film received from CS Hyde was isotropic in structure.

3.2.2 Validation of Thermal Bonding Conditions

- Given that 0.005 inch thickness of FEP film was considered to be the most suitable in terms of handling, processablility and flexibility for the next generation of vena cava filter, 0.002 inch and 0.010 inch thicknesses were not selected.

- Given that the glass transition temperature of FEP is known to be 260°C; FEP film bonding strength was measured after thermally bonding at 270°C, and 280°C. These temperatures were measured on the top metal plate with a thermometer probe, RPK-PYRMTR (Geo Knight & CO. INC, Brockton, MA), that had been previously calibrated.

- The duration of thermal bonding was selected at 30 seconds and 60 seconds.

- The heat press used was a DC5 supplied by Geo Knight & CO. INC (Brockton, MA). The base was made from 0.3 inch thick compressible foam rubber so that the applied pressure was minimal once the top plate was in touch with specimen.

As a result of these preliminary trials, there was insufficient bonding between two layers of FEP film at 270°C. By using 280°C for 30 seconds, a strong bond between 2 layers of FEP film was achieved, and it took considerable manual strength to remove the Nitinol wire from between the FEP films to which it had been thermally bonded.

3.3 Material Treatments

3.3.1 Plasma Treatments

General factors of the Atmospheric Plasma Machine are as follow.

- Power: 675 W;

- Timing: 2 minutes;

- Volume use of helium gas: 40 SLPM (Standard Liters Per Minute);

- Volume use of oxygen gas: 0.4 SLPM;

- Volume use of argon gas: 0.95 SLPM;

- Gap distance between electrode and metal conveyor plate: 0.09";

- Samples to be treated by the plasma were placed on a rectangular 27 inch x 14.5 inch

    metal plate which was moved by an electric motor and drive chain under the plasma-

    emitting electrode.
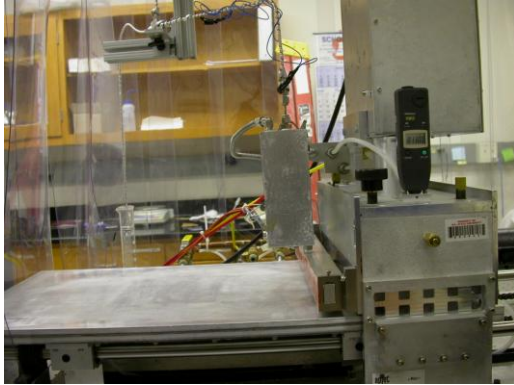
(a)   (b)

(c)   (d)

Figure 3.2 Components of the Atmospheric Plasma Machine Used in the Plasma Treatments

(a) Atmospheric Plasma Machine, (b) Power Generator (right bottom), Temperature Controller (right top), and Gas Flow-meters (left), (c) Helium, Oxygen, and Argon Gas Tanks, (d) TG-10 Monomer Mixture and Supply Pump

3.3.1.1 Helium-plasma Treatment

- Either 7 or 14 of cleaned 2 inch-long wire specimens were aligned longitudinally on the metal plate. When treating for FEP films, 7 pairs of specimen-shape-cut films were

aligned in two rows on the metal plate.

- 40 standard liter per minute (SLPM) of helium gas was supplied to the electrode as recommended by previous study with the machine.

- 675watts of electric power was applied to the electrode to generate the helium plasma.

- The conveyor plate was moved into position under the helium-plasma-emitting electrode and held there for 2 minutes.

- After 2 minutes the electric power was switched off and the helium valve was closed.

- The conveyor plate was moved away from the electrode.

- The helium treated FEP films were stored in a Fluoroware® container for a period of time ranging from several hours up to a maximum of one day in a vacuum desiccator at room temperature prior to the characterizations using XPS, SEM, and a goniometer and prior to a thermal bonding with Nitinol wire.

- Pieces of tape were attached at each end of the parallel wires aligned in a row, which were then flipped over so as to treat the other side of the wires with helium-plasma only.

- The other side of the 7 (or 14) wires was then exposed to the same helium plasma conditions for another 2 minutes.

- The helium treated wires were stored in a Fluoroware® container for a period of time ranging from several hours up to a maximum of one day in a vacuum desiccator at room temperature prior to the characterizations using XPS and SEM and prior to a thermal bonding with FEP film.

3.3.1.2 Helium-oxygen Plasma Treatment

The procedure was the same to that of helium-plasma treatment except for opening and closing the oxygen (0.4 SLPM) valve in addition to the helium valve at the same time.

3.3.1.3 Fluorocarbon Coating Treatment

A fluorocarbon monomer mixture (known as TG-10) having the following constituents was supplied by DAIKIN AMERICA (Orangeburg, NY). The chemical composition of this fluorocarbon cocktail is shown in the Figure 3.3.
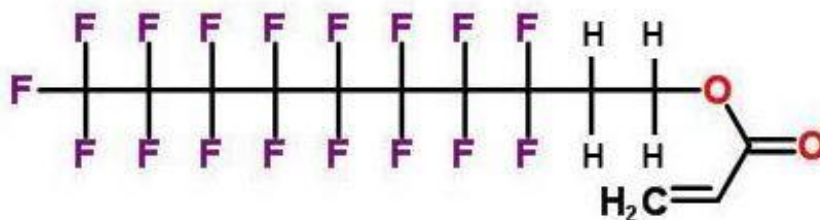
(a)
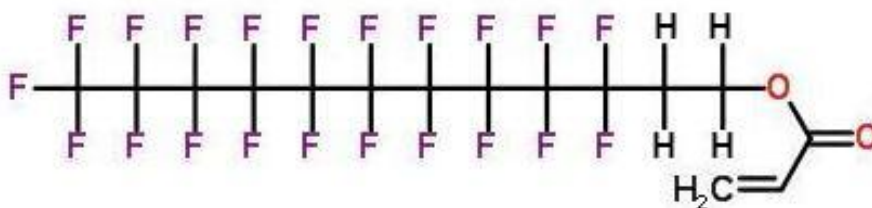
(b)

Figure 3.3 Chemical Composition of TG-10 Fluorocarbon Monomer Mixture

(a) 70-90% of 1,1,2,2-Tetrahydroperfluorodecyl acrylate: $C_{13}H_7F_{17}O_2$

(b) 10-30% of 1,1,2,2-Tetrahydroperfluorododecyl acrylate: $C_{15}H_7F_{21}O_2$

In order to coat fluorocarbon on the Nitinol wires, three steps were needed.

(1) Surface activation: It was first necessity to activate the wire with a

helium-plasma treatment for 1 minute.

(2) Fluorocarbon (FC) coating: The fluorocarbon monomer mixture (TG-

10) was delivered at a speed of 0.45 ml/min from the pump through a

nozzle connected to the metal sprayer, a part of the machine in front of

44

the electrode. The sprayer part was heated up to 170°F, so the TG-10

monomer mixture was vaporized. While the activated Nitinol wires were

exposed to the vaporized TG-10 for 1 minute, argon gas (0.95 SLPM)

was sprayed at the same time to make the surrounding atmosphere inert.

(3) Curing or polymerizing: For the last step, the Nitinol wires which were

wet by the TG-10 vapor were exposed under helium-plasma for 3

minutes to get the TG-10 cured or polymerized. Once this process was

complete, the wires were flipped over and the helium plasma turned on

again to permit the polymerization reaction to occur on the other side.

After all the fluorocarbon coating process was done, specimens were stored in the

Fluoroware® containers for a period ranging from several hours up to one day in a vacuum

desiccator prior to characterization of the surface and thermally bonding them with FEP

film.

3.3.2 Mechanical Roughening of the Wire

In order to roughen the wire mechanically in a reproducible and consistent fashion

a 2 inch long Nitinol wire specimen was mounted in the bit of a drill and operated at a

speed of 700 rpm prior to being cleaned (Figure 3.4). The drill was mounted vertically downwards in an MTS mechanical tester (Model# 1122, Eden Prairies, MN) with the Nitinol wire held firmly between 2 pieces of unused 120 grit sandpaper at a lower jaw pressure of 100 psi. The drill was operated at a speed of 700 rpm for a period of 2 minutes. This caused the wire to acquire a roughened appearance.
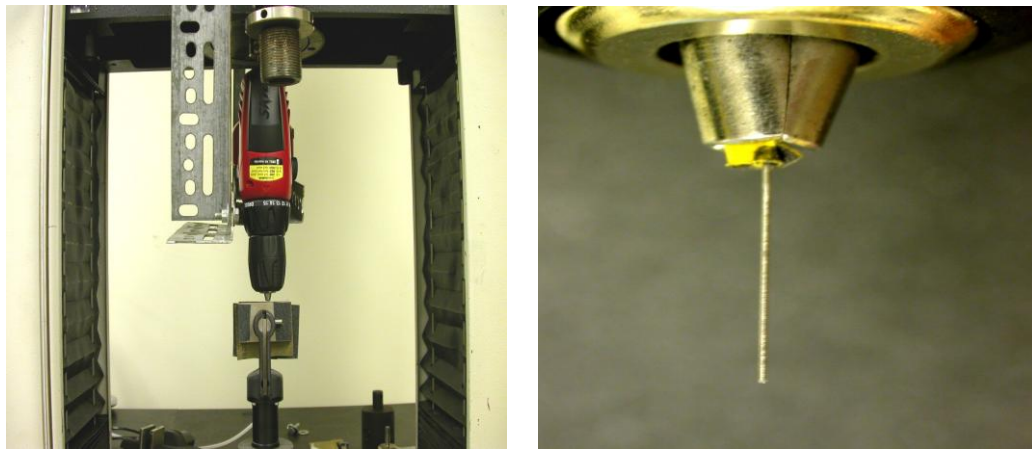
Figure 3.4 Images of the Drill Mounted in the MTS Mechanical Tester

3.4 Material Characterization Methods

3.4.1 Scanning Electron Microscopy (SEM)

Photographic images were taken at a series of magnifications by a Hitachi S-3200N SEM (Schaumburg, IL) machine in the Analytical Instrumentation Facility at North Carolina State University. An accelerating voltage of 20 kV was used to view the images of untreated and treated wires, whereas an accelerating voltage of 5 kV was used to view the FEP film samples. These FEP film specimens were prepared for SEM viewing by mounting each specimen on a piece of carbon tape to an aluminum stub and then sputter coated the stub with gold/palladium in a DESK II sputter coater (Moorestown, NJ).

3.4.2 X-ray Photoelectron Spectroscopy (XPS)

XPS data were acquired using survey scans on a Riber LAS-3000 XPS machine (Paris, France) in the Analytical Instrumentation Facility at North Carolina State University. The FEP film samples were cut to about 0.5 inch square size, and mounted on a specimen stub with conductive tape.

The Nitinol wire samples were cut to about 0.6 inch in length, and about 16 of them were aligned on the stub with a minimum of distance between them. The Riber LAS-3000 XPS machine has a Mg Kα (1253.6 eV) x-ray source, has approximately 10^{-10} Torr of base

pressure, and the take-off angle was 75º. Three repetitive survey scans were done for each sample.

3.4.3 Contact Angle Measuring Equipment

A Model 200-F1 Standard Goniometer made by Ramé-hart Instrument Company (Netcong, NJ) was used to measure the contact angle measurements. ASTM Method D5946-04 was followed in order to generate the contact angle data. This means that a 0.05 ml droplet of double distilled water was placed on the surface of the untreated and treated films, and the contact angle was measured within the next 60 seconds. More than twelve repeat measurements were recorded for each sample of FEP film.

Figure 3.5 Model 200-F1 Standard Goniometer

3.5 Mechanical Testing of Composite Specimen

3.5.1 Specimen Preparation
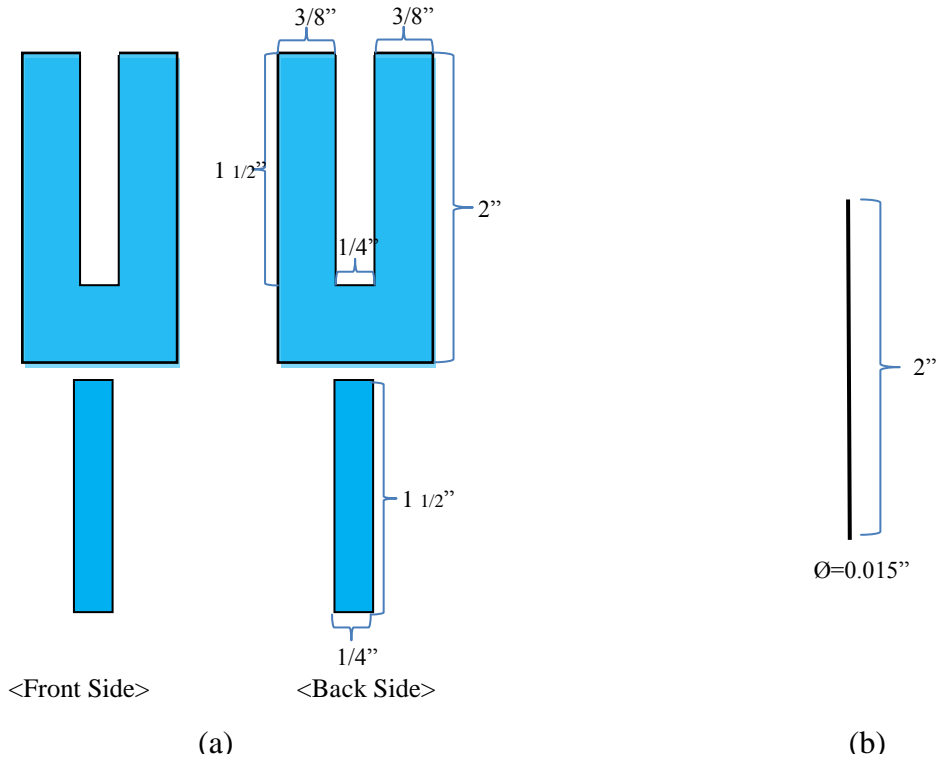
Figure 3.6 FEP Film and Nitinol Wire Specimens for Pull-out Strength Test

(a) Dimensions of the FEP Film Specimen, (b) Dimensions of the Nitinol Wire Specimen

In order to be able to measure the level of adhesion between the Nitinol wire and the FEP film it was necessary to find a pull-out strength test method that gives consistent and reproducible results. In the past most adhesion strength tests have relied on measuring

the peel strength between two adhering film components (37), (38), (39). This type of test would not apply here where we were attempting to measure the level of adhesion between a polymeric film and a straight wire. So after many unsuccessful attempts using test procedures from elsewhere, a new specimen size and shape was designed that appeared to be easy to prepare and gave consistent results.

3.5.2 Specimen Assembly

The shape and dimensions of the 4 film components and the one wire component are shown in Figure 3.6. DC5 heat press was used to assemble the 5 components by thermal bonding. The single composite specimen ready for testing is shown in Figure 3.7. The wire component was sandwiched in between by a front and back layer of FEP film.
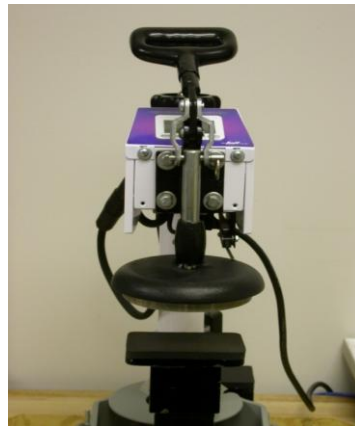
Figure 3.7 DC5 Heat Press Machine

3.5.3 Pull-out Test Method

The wire and two layers of film are clamped firmly in the bottom jaw. (This prevents wire slippage). While the top jaw clamps only two layers of FEP film. The distance of bonding between the wire and the FEP film is strictly controlled at 0.5 inch due to the shape and size of the film components. Also the wire sticks out beyond the double film sandwich to prevent any sealed end effects (Figure 3.8).
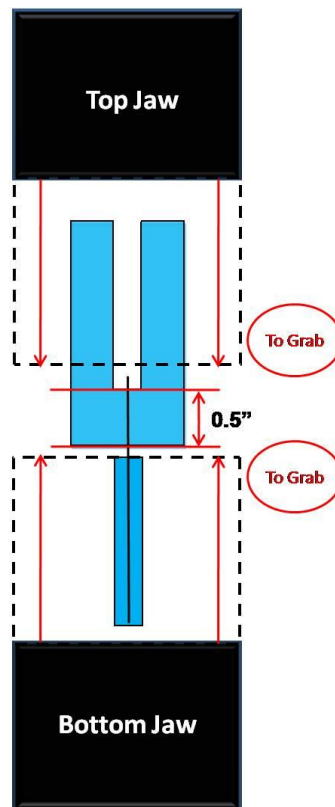
Figure 3.8 Single Composite Pull-out Strength Specimen Ready to Test

Table 3.3 Preparation of Composite Specimens

Group	Nitinol Wire	FEP Film	Number of Nitinol Composite Specimens
1	Untreated Wire	He-treated Film[1]	6
2	Untreated Wire	HeO$_2$-treated Film[2]	6
3	Untreated Wire	Untreated Film	6
4	He-treated Wire[3]	He-treated Film	6
5	He-treated Wire	HeO$_2$-treated Film	6
6	He-treated Wire	Untreated Film	6
7	FC Coated Wire[4]	He-treated Film	6
8	FC Coated Wire	HeO$_2$-treated Film	6
9	FC Coated Wire	Untreated Film	6
10	Mech-roughened Wire[5]	He-treated Film	6
11	Mech-roughened Wire	HeO$_2$-treated Film	6
12	Mech-roughened Wire	Untreated Film	6

* [1] He-treated Film: Helium-plasma-treated Film; [2] HeO$_2$-treated Film: Helium-oxygen-plasma-treated Film;

[3] He-treated Wire: Helium-plasma-treated Wire; [4] FC Coated Wire: Fluorocarbon Coated Wire; and

[5] Mech-roughened Wire: Mechanically Roughened Wire

4   Results and Discussion

4.1 Results of Material Characterization

4.1.1 Scanning Electron Microscopy (SEM)

The surface appearances of the FEP film samples after the initial cleaning method as viewed under scanning electron microscopy at different magnifications are seen in Figures 4.1, 4.2, and 4.3. The photomicrographs in Figure 4.1 of the cleaned untreated FEP film show a smooth surface interrupted with small circular beads or blisters measuring 1-3µm in diameter. Following helium-plasma treatment, the FEP film has a similar appearance (Figure 4.2). However the 1-3µm diameter circular beads or blisters appear to have been flattened and roughened.

As a result of the helium-oxygen plasma treatment, the surface of the FEP film appeared to be much smoother, being free of any beads or blisters (Figure 4.3). This confirms that the use of a helium-oxygen plasma provides a surface "cleaning" effect to FEP film. A similar, but less evident surface "cleaning" effect is observed after a plasma treatment with only helium. These SEM observations support the view that the primary effect of helium based plasma is an ablative one, with a tendency to remove material from the outer surface.
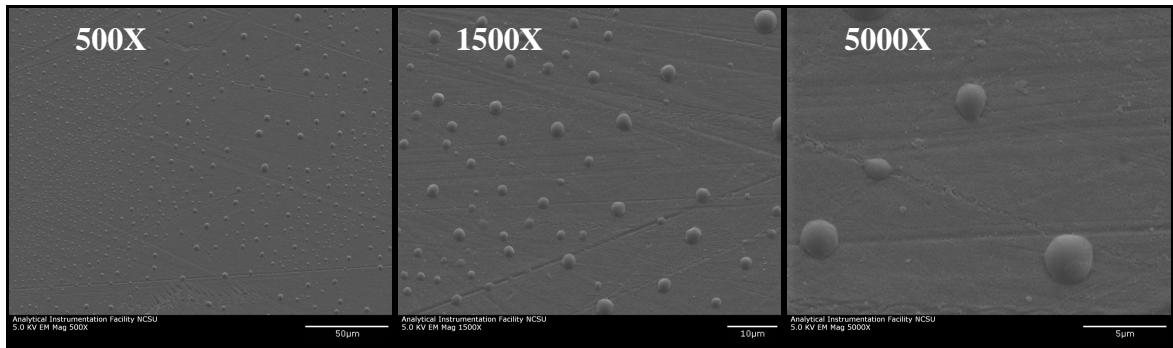
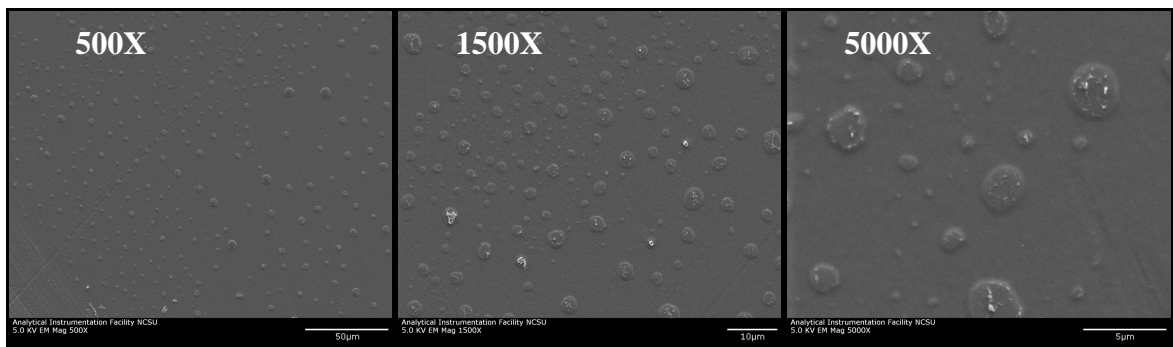Figure 4.1 Untreated FEP Film Cleaned by Initial Cleaning Method

Figure 4.2 Helium-plasma Treated FEP Film Cleaned by Initial Cleaning Method

Figure 4.3 Helium-oxygen-plasma Treated FEP Film Cleaned by Initial Cleaning Method

Figures 4.1, 4.2, and 4.3 are good examples for showing the "cleaning" effect of the plasma and how strong the effect is depending on the kind of gases that are used in the plasma treatment. However, strictly speaking the images indicate that a reliable cleaning method was not established yet. We were able to get Energy-dispersive X-ray Spectroscopy (EDS) analysis on both a blistered spot and on a smooth surface of the FEP film. According to the result of EDS, the composition of the blister was 54% of carbon and 46% of fluorine (Appendix B). There was a fair amount of increase in carbon percentage and decrease in fluorine percentage by comparing an EDS result from the smooth surface of the same FEP film: carbon=28% and fluorine=72% (Appendix B). We assumed that this happened because there were some residues of hexane solution on the FEP film surface after cleaning the film with the hexane in an ultrasonic bath for 5 minutes and immediately drying in a hot air oven.

The following SEM images in Figures 4.4 - 4.6 which were taken after we completed the second cleaning procedures of the FEP film proved that we acquired a reliable way of cleaning the FEP film surfaces uniformly. Note there are no apparent beads or blisters in these photomicrographs.

Figure 4.4 Untreated FEP Film Cleaned by Second Cleaning Method

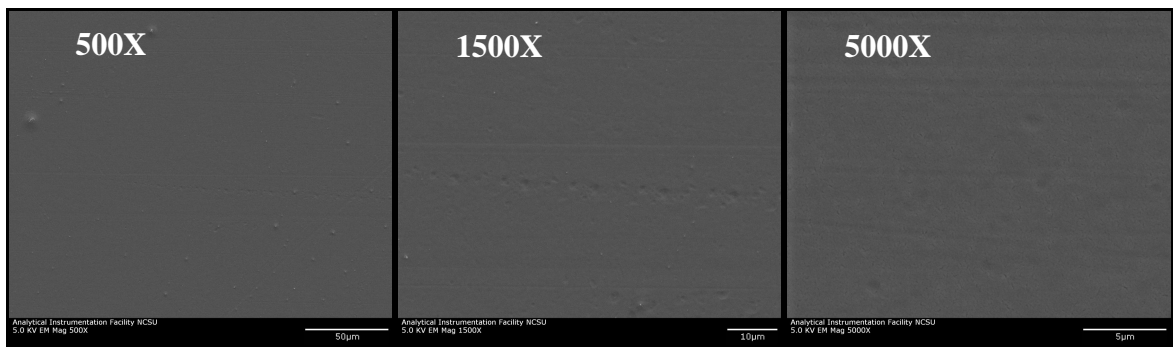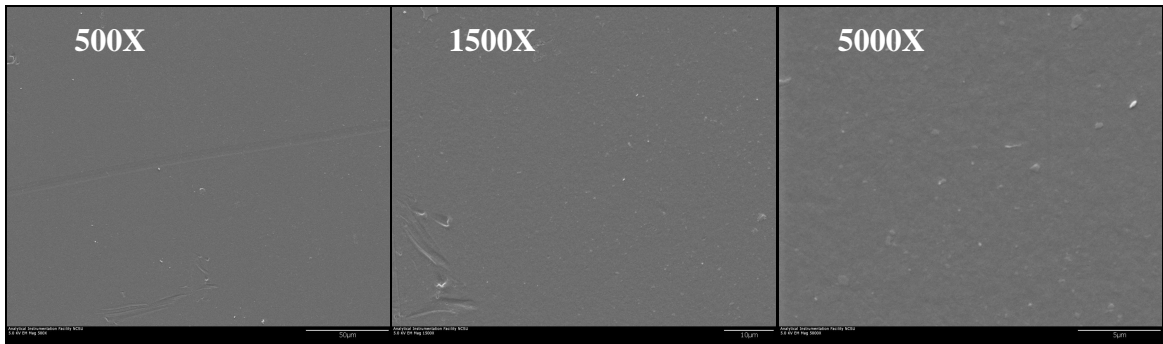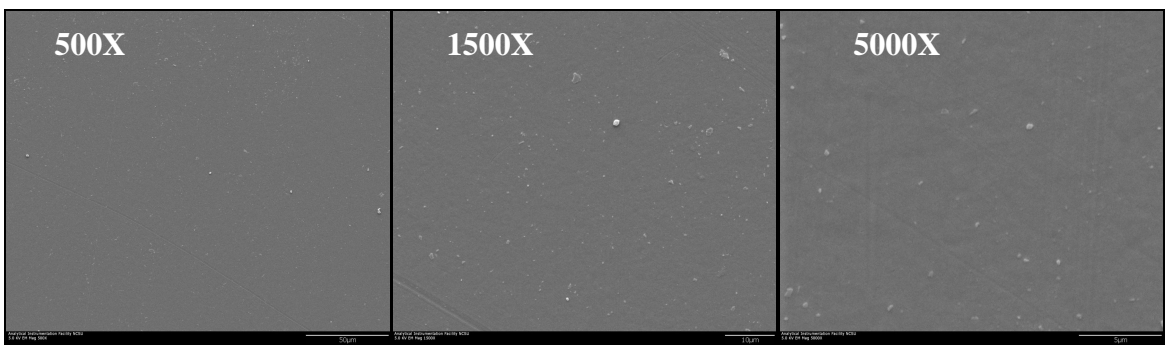Figure 4.5 Helium-plasma Treated FEP Film Cleaned by Second Cleaning Method
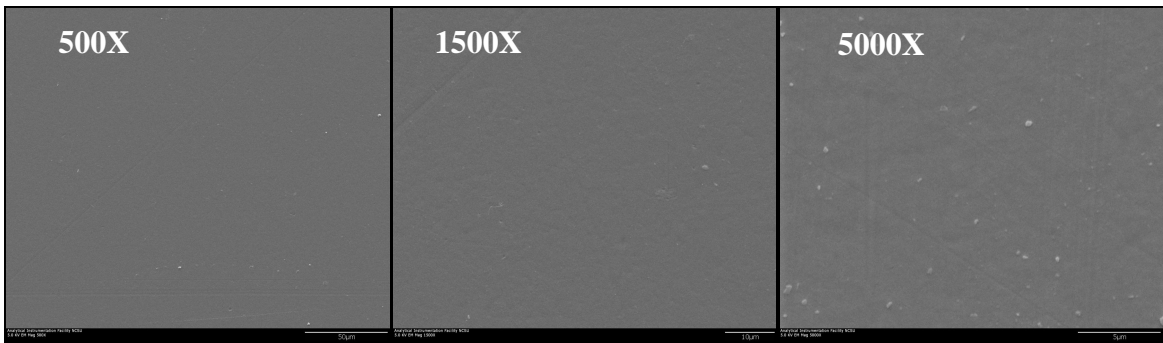
Figure 4.6 Helium-oxygen-plasma Treated FEP Film Cleaned by Second Cleaning Method

The SEM photomicrographs of the Nitinol wire samples as viewed at different magnifications before and after the different treatments are shown in Figures 4.7 - 4.10. The cleaned untreated wire has a smooth appearance containing longitudinal cracks or striations (Figure 4.7). In comparison, the helium-plasma treated Nitinol has a similar smooth appearance except that in addition to longitudinal cracks, less well oriented white bands of material were also visible on the surface (Figure 4.8). The composition of these white bands is not fully known. Evidence from EDS spectra taken during SEM viewing suggests that they contain aluminum (Appendix B). Such aluminum could have originated from small excited particles released from the aluminum conveyor plate on the plasma machine. Alternatively, other elements such as zinc, fluorine, and calcium were observed by XPS on the helium plasma treated Nitinol wire surface (Table 4.2).

The appearance of the fluorocarbon-coated Nitinol wire in Figure 4.9 has several unique features. The photomicrographs show clear evidence of polymerized or cured fluorocarbon deposits on the surface of the wire. These deposits vary from small globular regions measuring about 10 μm across, through intermediate sized craters measuring about 100 μm in diameter, to large continuous deposits standing over 20 μm thick on top of the wire.

The mechanically roughened Nitinol wire is easy to recognize under SEM (Figure 4.10). The photomicrographs show clear evidence of material having been removed non-

uniformly by the circumferential motion of the 120 grit sandpaper that has left a roughened surface topography with an uneven thickness along its length and circumferential striations.
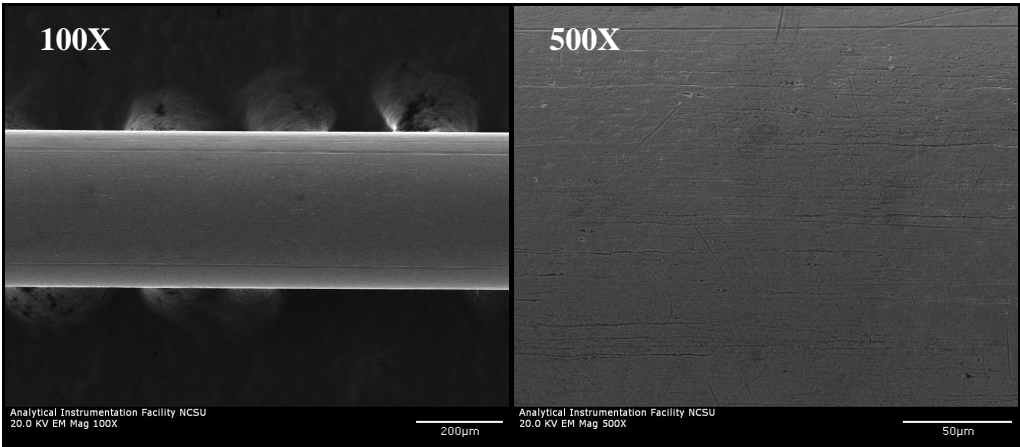
Figure 4.7 Untreated Nitinol Wire
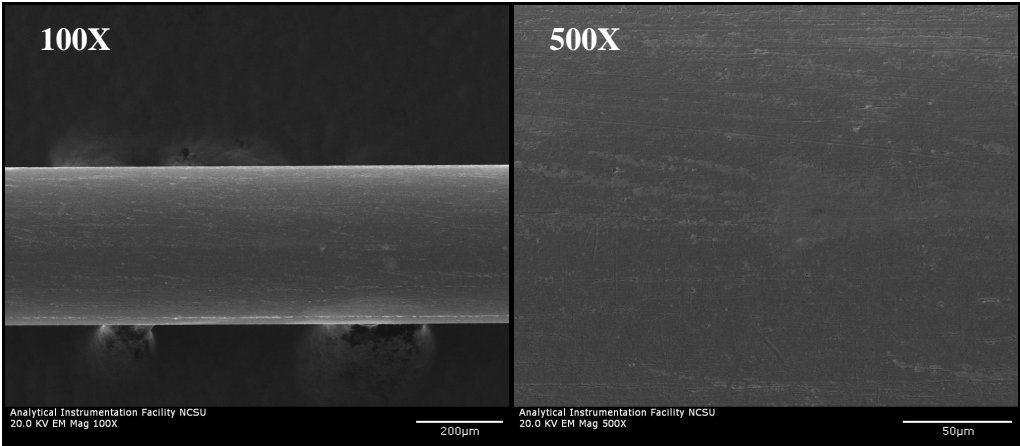
Figure 4.8 Helium-plasma Treated Nitinol Wire
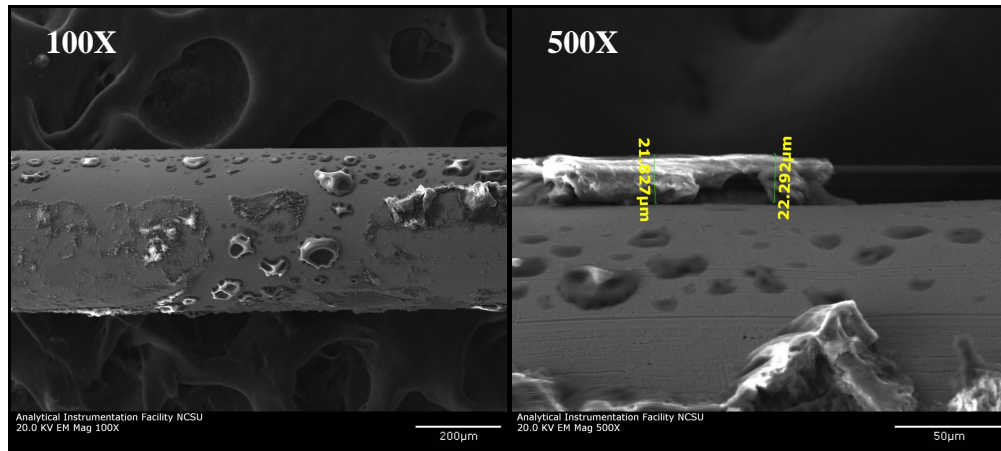
Figure 4.9 Fluorocarbon (FC)-coated Nitinol Wire
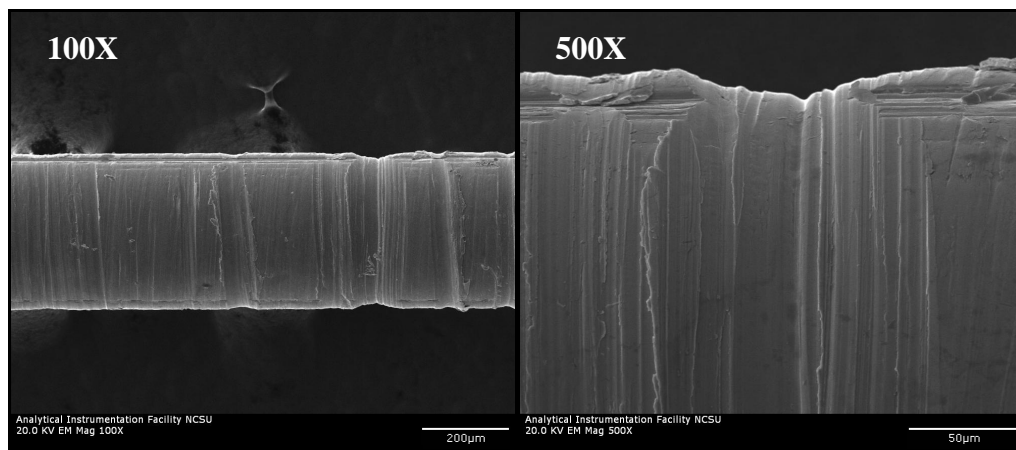
Figure 4.10 Mechanically Roughened Nitinol Wire

4.1.2 X-ray Photoelectron Spectroscopy (XPS)

4.1.2.1 XPS Results of the FEP Film

The surface elemental analyses of the FEP films before and after plasma treatments as measured by XPS are shown in Table 4.1. The individual spectra of XPS scans for the untreated and treated surfaces are presented in Appendix C. Given that FEP film is a copolymer of tetrafluoroethylene (C_2F_4) and hexafluoropropylene (C_3F_6) both these monomers have twice as many fluorine atoms as carbon atoms. The theoretical elemental composition of a totally pure and homogeneous FEP copolymer film would therefore be C=33% and F=67%. The experimental XPS values for the cleaned and untreated FEP film surface are close to these theoretical values, which is reassuring as to the purity and homogeneity of the cleaned, as received FEP film.

The cleaned untreated fluorocarbon film surface contains only a trace of oxygen (0.80%). This oxygen level is increased significantly by 160% and 290% by applying helium plasma and helium-oxygen plasma treatments to the FEP film respectively. This suggests that there remains a residual level of oxygen (or air from the atmosphere) close to the film as it passes through a helium-only plasma. While the surface oxygen level increases, so the percentages of carbon and fluorine in Table 4.1 fall with increasingly active plasma treatments.

Table 4.1 Composition of Elements of FEP Films Detected by XPS

	Untreated	Helium-plasma Treated	Helium-oxygen-plasma Treated
Oxygen (%)	0.80	2.1	3.1
Carbon (%)	31.	30.	31.
Fluorine (%)	68.	68.	66.

4.1.2.2 XPS Results of the Nitinol Wire

Table 4.2 lists the surface elemental analyses of the Nitinol wire before and after plasma treatments and mechanical roughening as measured by XPS.

The first unexpected value is the approximately 60% carbon on the surface of the cleaned wire. For a pure chemically-etched and annealed Nitinol round wire it is evident that it contains an organic surface finish, not previously declared by the suppliers. Then with helium-plasma treatment and fluorocarbon coating, the level of this surface finish was reduced. Concurrently either the level of oxygen and titanium increased or the fluorine content increased with these two treatments respectively. With the helium-plasma treatment, the level of surface titanium increased to nearly 9%, while the surface oxygen increased to nearly 43%. These data suggest that the helium plasma had an ablative, etching or surface cleaning effect revealing elements previously below the surface of the as

received Nitinol wire. This suggestion is supported by the increases in titanium and oxygen on the surface of the wire. At the same time fluorine and traces of zinc have appeared. Such elements may have been exposed by plasma etching, or alternatively may have arisen because of surface contamination.

Table 4.2 Composition of Elements of Nitinol Wires Detected by XPS

	Untreated	Helium-plasma	Fluorocarbon Coated	Mechanically Roughened
Carbon (%)	59.3	32.4	23.8	62.6
Oxygen (%)	35.7	42.9	13.3	33.2
Titanium (%)	2.96	8.86	1.92	2.95
Calcium (%)	2.03	2.35	None	1.17
Fluorine (%)	None	12.8	57.7	None
Zinc (%)	None	0.75	None	None
Silicon (%)	None	None	3.23	None

The increase in surface fluorine content as a result of fluorocarbon coating and helium-plasma treatment was most successful. If the Nitinol wire was totally covered by a thin layer of TG-10 fluoropolymer (assuming a 80:20 mixture of the two components) then

the theoretical elemental analysis would be carbon: 25.4 %, fluorine: 57.6 %. The XPS fluorine content, which increased from around 13% to nearly 58% (Table 4.2), is close to the ideal percentage value of the fluorine in the TG-10. This suggests that the wire is almost entirely covered by a thin layer of fluorocarbon polymer. However other contaminants, such as silicon, were also identified at the surface of the treated Nitinol wire.

The elemental analysis of the mechanically roughened Nitinol wire surface is very similar to that of the original cleaned Nitinol wire. The surface roughening procedure therefore did not change the chemistry of the wire's surface. It only changed the surface topography (Table 4.2).

4.1.3 Contact Angle of FEP Film Samples

The averages and standard deviations for the contact angle measurements of the untreated and treated FEP films are shown in Table 4.3. The raw data for each set of measurements are listed in Appendix C.

As can be seen in Table 4.3, the average value for the cleaned untreated FEP film is 104 degrees. This compares well with other contact angle measurements of 110 degrees found in the literature and confirms that this untreated fluoropolymer film is inherently hydrophobic in character. After treatment with only helium or helium-oxygen plasma, however, the average contact angle changed significantly to a lower value (Table 4.3).

Contact angles of 85 and 82 degrees are now less than 90 degrees, which means that both plasma treatments altered the surface of the FEP film from being inherently hydrophobic to being inherently hydrophilic. This confirms the previous observations of Tanaka et. al. who showed that the contact angle of helium-plasma treated FEP and helium-oxygen-plasma treated FEP fell to 76 degrees and 74 degrees respectively (40).

Table 4.3 Contact Angle Measurements of Differently Treated FEP Films

	Untreated	**Helium-plasma Treated**	**Helium-oxygen-plasma Treated**
Average (°)	104	85	82
Standard Deviation (°)	7	10	5
Total Number of Observations	21	12	18

When the results for helium-plasma treated film were compared to those for helium-oxygen plasma treated film, the statistical analysis using a student t-test was unable to confirm any significant difference (Table 4.4). This may have been due to the inferior control over the helium-plasma process, which led to a high value of 10 degrees for the standard deviation. Alternatively, residual oxygen or the presence of air may have served

as a trace contaminant in the atmospheric helium-plasma process which led to the formation of polar groups and increased hydrophilicity at the FEP film surface.

Table 4.4 Student t-test Results of Contact Angle Measurements

	Untreated vs. Helium-plasma Treated	Untreated vs. Helium-oxygen-plasma Treated	Helium-plasma Treated vs. Helium-oxygen-plasma Treated
P-value	5.6e-05	3.7e-13	0.43

* Significant difference were assumed to exist if $p \leq 0.05$

4.2 Result of the Polymer/Wire Pull-out Test

The pull-out force results for the 12 combinations of wire and film have been averaged and the means and standard deviations listed in Table 4.5. The original data are to be found in Appendix D.

Statistical analysis in the form of a student t-test has been performed on the various pairs of pull-out force data. Their respective p values are presented in Appendix F. In this table it is assumed that significance occurs at the 95% confidence interval and that when $p \leq 0.05$ that the two sets of data have significantly different means.

Table 4.5 Pull-out Force Order According to Student T-test Results

		Mean (N)	Standard Deviation (N)
1st	Mech-wire/ He-film	34.9	1.2
2nd, 3rd	Mech-wire/ HeO2-film	32.2	1.2
	Un-wire/ He-film	32.1	2.0
4th	Un-wire/ Un-film	30.5	2.4
5th, 6th	Mech-wire/ Un-film	30.1	1.7
	He-wire/ Un-film	29.9	2.1
7th	Un-wire/ HeO2-film	28.4	1.6
8th, 9th	He-wire/ He-film	24.1	4.3
	He-wire/ HeO2-film	23.3	5.4
10th, 11th, 12th	FC-wire/ He-film	5.13	0.63
	FC-wire/ Un-film	4.88	1.5
	FC-wire/ HeO2-film	4.77	0.46

On inspecting the values in Appendix F it is evident that some of the p values are below 0.05 while others are above 0.05. This means that some of the mean pull-out force results are too close to one another to confirm that they are significantly different. In fact, when viewing Table 4.5 it is clear that there are only seven significantly different groups of mean pull-out force into which the 12 combinations of wire and film fall. In any one group it is not possible to claim that one combination of wire and film has a significantly stronger pull-out force then any of the other combinations in the same group!

Firstly it is worth noting that the untreated wire/untreated FEP film combination generated a mean pull-out force of 30.5N. And there are those combinations that are significantly stronger than this value and there are those combinations that are significantly weaker than this.

This value of 30.5N for pull-out force is of interest since it measures the maximum load supported by about 0.5 inch of wire sandwiched between FEP films (See Chapter 3). While this has no direct bearing on the clinical use of this assembly, it is worth noting that researchers have recorded a maximum migration force of a stent-graft within an artery to be about 20N force (41). Therefore the design of any new embolic protection device has to not only meet, but exceed this requirement.

The strongest combination was achieved by the mechanically roughened wire being thermally bonded to the helium-plasma treated FEP film. With a mean pull-out force of

34.9N, this represented a 14% increase in bonding strength over the untreated wire and film. Likewise the mechanically roughened wire when thermally bonded to the helium-oxygen plasma treated film also showed some improvement in adhesion. However this represented only 5-6%. Clearly the effect on mechanical roughening is more significant than the chemical or plasma treatments that were undertaken. We assume this was due to the increase in contact area as well as some improvements in interdigitation or mechanical keying after thermal bonding.

The effect of applying a helium-plasma treatment to Nitinol wire did not result in any improvement in adhesion with fluorocarbon films. All 3 helium-plasma treated wire samples showed some fall in mean pull-out force compared to the untreated control combination. This suggests that even if helium-plasma initiates more polar groups on the Nitinol surface, (Table 4.2), either the smoother surface caused by the etching away of material or the presence of fluorine contamination has had a greater effect on the level of adhesion to FEP film.

Fluorocarbon coating of Nitinol wire had a disastrous effect on the adhesion properties after thermal bonding of the coated wire to FEP film. All 3 combinations with different types of FEP film resulted in the same significantly inferior performance. In fact they all showed a loss in pull-out force in excess of at least 80% compared to the untreated combination. This suggests that the diffusion mechanism involving long-chain

fluorocarbon molecules diffusing into the other component after thermal bonding simply did not occur. There was clear XPS and SEM evidence that fluorocarbon species were attached to the surface of the coated Nitinol wire. But such species were not flexible long chains that were able to diffuse into the FEP polymer. This experiment confirms that fluorocarbon compounds possess a very low dipole-dipole adhesive energy that "lubricates" rather than contributing to high bonding strengths (42).

When evaluating the effect of helium-plasma treatment on the FEP film we see in some cases a positive effect over the untreated film. For example, when thermally bonded to untreated Nitinol wire or mechanically roughened wire the level of adhesion to the helium-plasma film is significantly superior to untreated FEP film. This means that the chemical modification of adding oxygen and polar groups to the fluoropolymer surface does enhance its ability to bond to Nitinol wire. However this chemical effect is of secondary importance when compared to the mechanical roughening effect.

In comparison, when evaluating the effect of helium-oxygen plasma treatment on FEP film, we see in almost all cases that there is a negative effect over the untreated film. Why should this be when the helium-plasma treatments referred to above show a positive effect, and chemically the helium-oxygen plasma is continuing to modify the surface chemistry. The answer may be found in Figures 4.1, 4.2, and 4.3 which show that after helium-oxygen plasma treatment on the surface of the FEP film is much smoother than

either the untreated or the helium-plasma treated FEP films. This result reinforces our finding that the mechanical interlocking theory of adhesion appears to play a more important role than the chemical bonding theory (17).

5   Conclusions and Future Work

In Chapter 1, Introduction, there are listed four specific objectives or goals for this study. They have driven the direction and experimental strategies for undertaking the study and have produced a series of results which have been discussed in Chapter 4. This chapter, Chapter 5, reviews those four objectives one at a time, and determines whether or not they have been achieved.

The first objective was to develop a pull-out force test method that would be suitable to measure reliably and reproducibly the level of adhesion between metallic wire and polymeric film. This objective has been achieved! One of the outcomes of the study is the design and development of a reliable and precise test method for measuring the wire/film pull-out force. In this test method the wire was thermally bonded in a sandwich between two pieces of FEP film. The design of specimen shape and the testing approach are novel and they do not duplicate a previous standard test method. By taking only 6 repeat measurements for pull-out force for each of the 12 combinations of wire and film the average coefficient of variation was 11.0%. This is considered an acceptable level of variability for this type of *in vitro* laboratory test method.

The second objective was to determine the level of adhesion or pull-out force after thermally bonding an untreated Nitinol wire specimen to an untreated FEP fluorocarbon film using the test method described above. This was also accomplished. The mean and standard deviation for the pull-out force between cleaned and untreated Nitinol wire and cleaned and untreated FEP fluorocarbon film was 30.5N and 2.4N respectively. It must be realized that this particular force is highly dependent on the geometric shape and size of the 3 layer thermally bonded pull-out test specimen and the extent of wire/film overlap and bonding. As such this absolute value has little direct importance in comparison with the bonding strength reported by others in the literature. Nevertheless, it serves as a base line for comparison of all the other 11 thermally bonded combinations of treated and untreated wire with treated and untreated FEP film. Let's see how it compares!

In the third objective five different surface treatment methods were investigated, three for the Nitinol wire, and two for the FEP film. And before each of these surface modification treatments were included in this study, they were optimized and evaluated so as to confirm that the surface had indeed been modified, either physically, or chemically, or both. Let us review the outcome of each surface treatment method in turn.

(1) Roughening of the smooth metal wire surface with abrasive sandpaper had a significant and positive effect on the level of metal/wire adhesion. Increases of up to 14% were achieved in the wire/film pull-out force when mechanically

roughened Nitinol was used for thermal bonding. This supports the adhesion
theory of mechanical interlocking.

(2) Treating the wire with helium-plasma did NOT improve the level of adhesion
between the wire and the FEP film. In fact the use of helium-plasma treatment
on the wire decreased the wire/film pull-out force by between 2-24%. Clearly
the helium-plasma neither contributed to roughening the wire's surface, nor
added any desirable chemical species that could have reacted with the FEP film
to improve the chemical bonding. In fact, there is evidence to suggest that the
helium-plasma most likely etched the surface of the wire and made it smoother,
or exposed chemical elements in the wire that had no chemical affinity for the
FEP film.

(3) The third treatment to the Nitinol wire involved adding a coating of
fluorocarbon polymer. While the fluorine content on the wire's surface
definitely increased significantly, the modification to the Nitinol's surface had a
disastrous effect on the level of adhesion between the wire and the FEP film.
The significant fall in wire/film pull-out force due to this fluorocarbon coating

was between 83-84%! Clearly the concept of diffusion of long-chain

fluorocarbon molecules from the surface of the Nitinol into the FEP film did not

work at thermal bonding temperatures. This may have been due to the fact that

the fluorocarbon coating was intermittent and not a continuous layer or that the

fluorocarbon species were only short chains and so served to lubricate the two

components, rather than add to their adhesion.

(4) One of the surface treatments applied to the FEP film was that of a helium-

plasma. Its primary role would have been to clean the FEP film of surface

contaminants by its ablative or etching action. This could lead either to a

rougher or a smoother film surface. There is evidence to suggest that this

helium-plasma was also responsible for adding oxygen containing polar groups

to the film's surface and making it significantly more hydrophilic (Table 4.3).

Consequently it is not surprising that, as a result of helium-plasma treatment to

the FEP film, the mean wire/film pull-out force increased marginally, yet

significantly by 5-14%. This small improvement in adhesion is interpreted to be

due primarily to increased chemical bonding. However the impact of this

chemical bonding effect is much less than the mechanical interlocking discussed earlier.

(5) The second surface treatment applied to the FEP film was that of helium-oxygen plasma. This surface modification has been well established as a means of attaching oxygen rich, polar species to the film's surface. While evidence from XPS clearly supports this effect, and significant chemical changes and increased hydrophilicity were observed after this treatment, nevertheless the effect on adhesion was generally negative. In most cases after helium-oxygen plasma treatment to the FEP film the mean wire/film pull-out force decreased significantly by 7-28%. What might have contributed to this fall in adhesion level? One possible explanation is the really effective cleaning action that a helium-oxygen plasma can have on a polymeric film surface. If such a treatment results in a much smoother surface, as seen in Figure 4.3, this may explain our findings in terms of the mechanical theory of adhesion.

In the fourth objective a number of surface characterization techniques were used to investigate the appearance, and physical and chemical changes at the surfaces of the Nitinol wire and FEP film as a result of the different surface treatment methods. All three

techniques, scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and a goniometer to make contact angle measurements, were successfully employed and were able to provide supportive data about the changes experienced by the treated Nitinol wire and the treated FEP fluorocarbon film.

One disappointment that was not achieved during this study was the measurement of advancing and receding contact angles for the untreated and treated Nitinol wire. It was hoped that this would assist in explaining the level of hydrophilicity/hydrophobicity of the wire before and after its series of surface treatments.

Recommendations

From the results of this study the following recommendations are made about how to improve the level of adhesion between Nitinol wire and FEP film.

(1) Improve the level of adhesion by mechanically roughening the surface of the Nitinol wire, and treating the FEP fluorocarbon film with a helium-plasma as described in this thesis prior to thermally bonding these two components together.

(2) The following treatments to the Nitinol wire are NOT recommended, as they will result in an inferior level of adhesion between the Nitinol wire and the FEP film.

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Treating the wire with a helium-plasma and giving the wire a fluorocarbon coating as described in this thesis.

(3) The following treatment to the FEP fluorocarbon film is NOT recommended as it will result in an inferior level of adhesion between the Nitinol wire and the FEP film: treating the FEP film with a helium-oxygen plasma as described in this thesis.

Future Work

In this study the level of adhesion has been measured catastrophically and once on the day following thermal bonding. This evaluated the immediate level of adhesion, but does not assess this property during use and over time. It will be necessary to perform fatigue testing under various conditions of accelerated frequency, temperature, and in liquids at different pH values, for example at the pH of human blood. Such accelerated mechanical fatigue testing will give better prediction of how the bonded components will behave in the body under real life conditions.

The materials used in this study are not the only ones being used or considered by manufacturers of medical devices. Other types of metallic wire, such as stainless steel and elgiloy, could also be included in this type of bonding experiment. Other types of fluorocarbon films could equally be included in future bonding studies. They could involve polytetrafluoroethylene (PTFE), perfluoroalkoxy polymer (PFA), ethylene-

tetrafluoroethylene copolymer (ETFE), and polyvinylidene fluoride (PVDF) in place of the FEP film used in this work.

Alternative high vacuum plasma treatments could be tried. Adding 100% reactive gases, such as oxygen, is known to increase the number of polar groups and increase the material's hydrophilicity.

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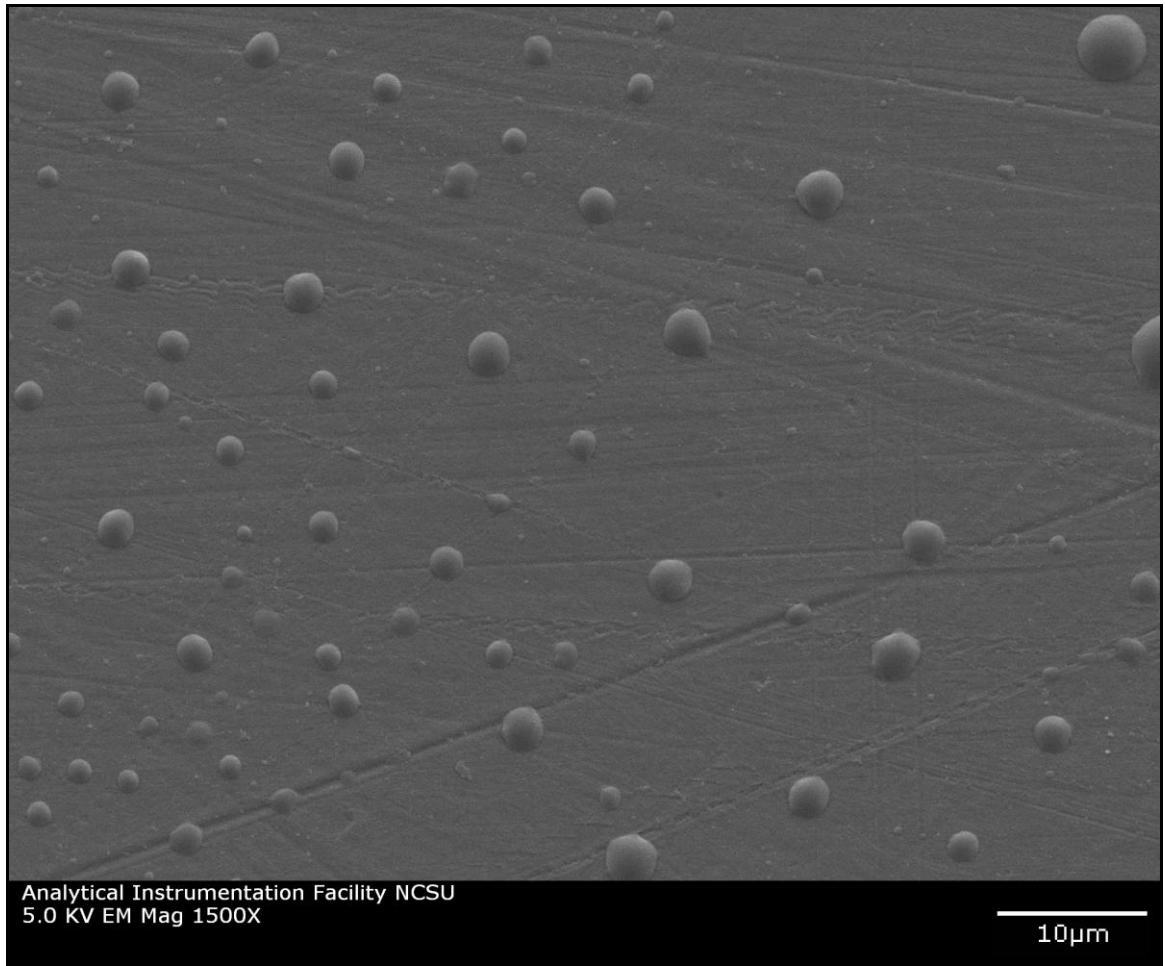
APPENDICES
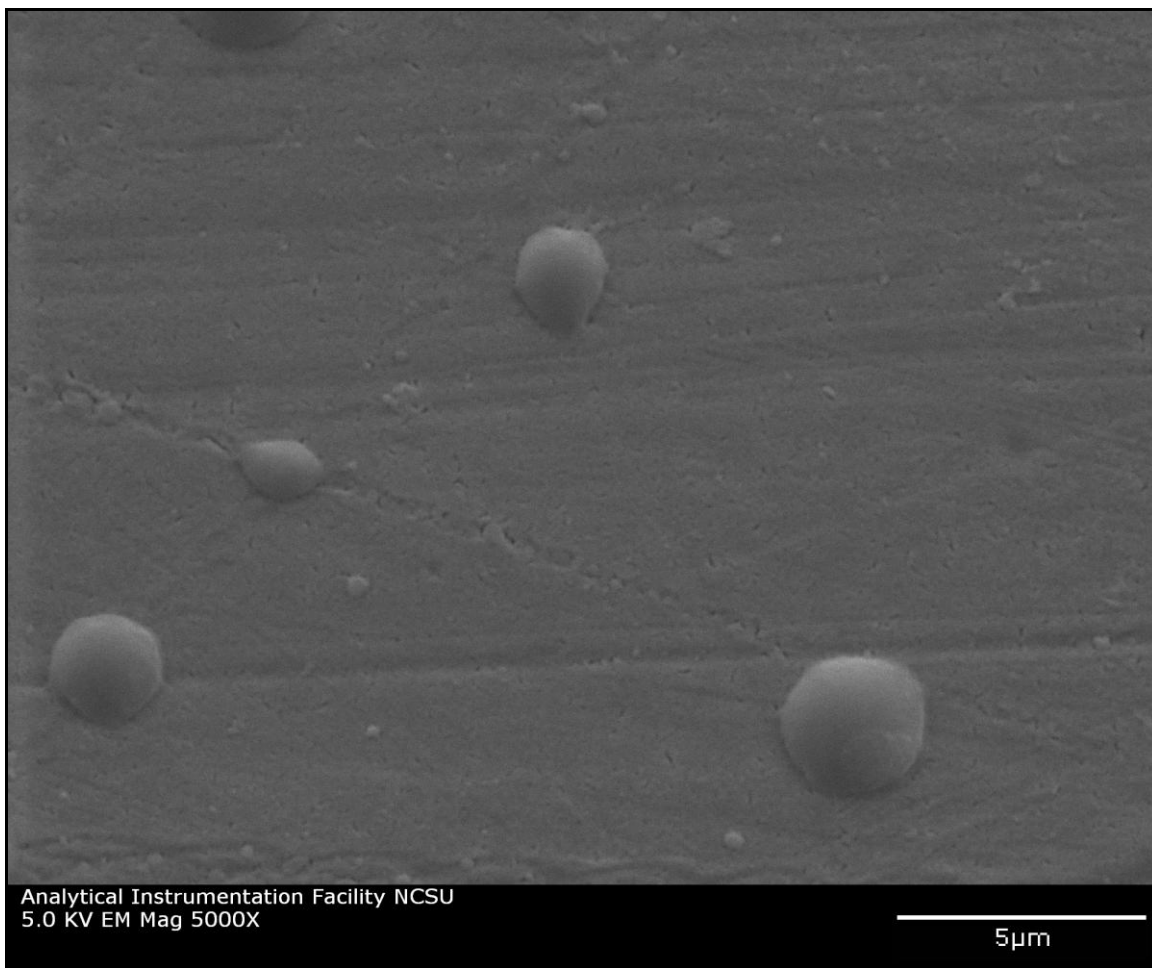
Appendix A: Images of Scanning Electron Microscopy (SEM)

A.1 Fluorinated ethylene propylene (FEP) Films (Initial Cleaning Method)

Analytical Instrumentation Facility NCSU
5.0 KV EM Mag 500X
50µm
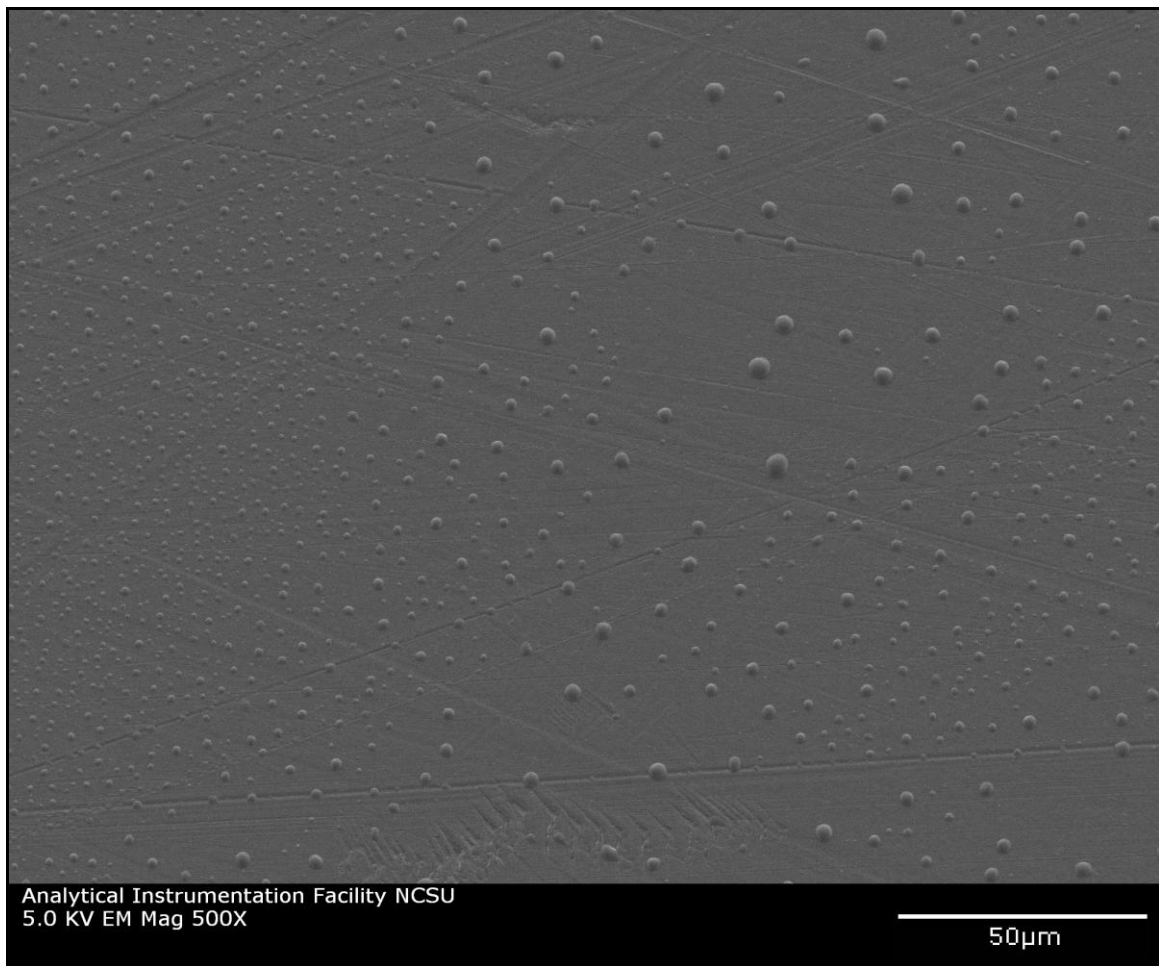
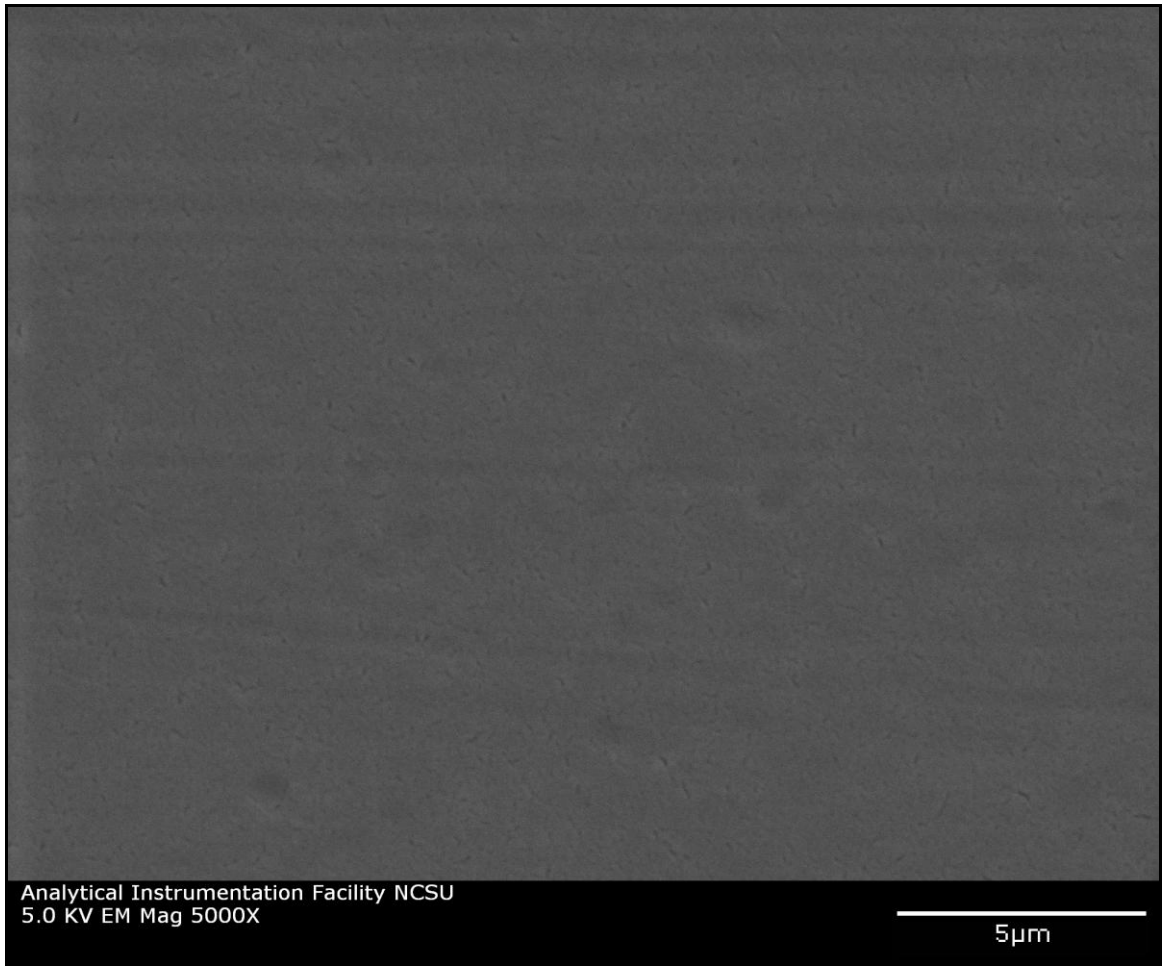**A.1.a-1 Untreated FEP Film; Mag. 500X**

A.1.a-2 Untreated FEP Film; Mag. 1500X

A.1.a-3 Untreated FEP Film; Mag. 5000X
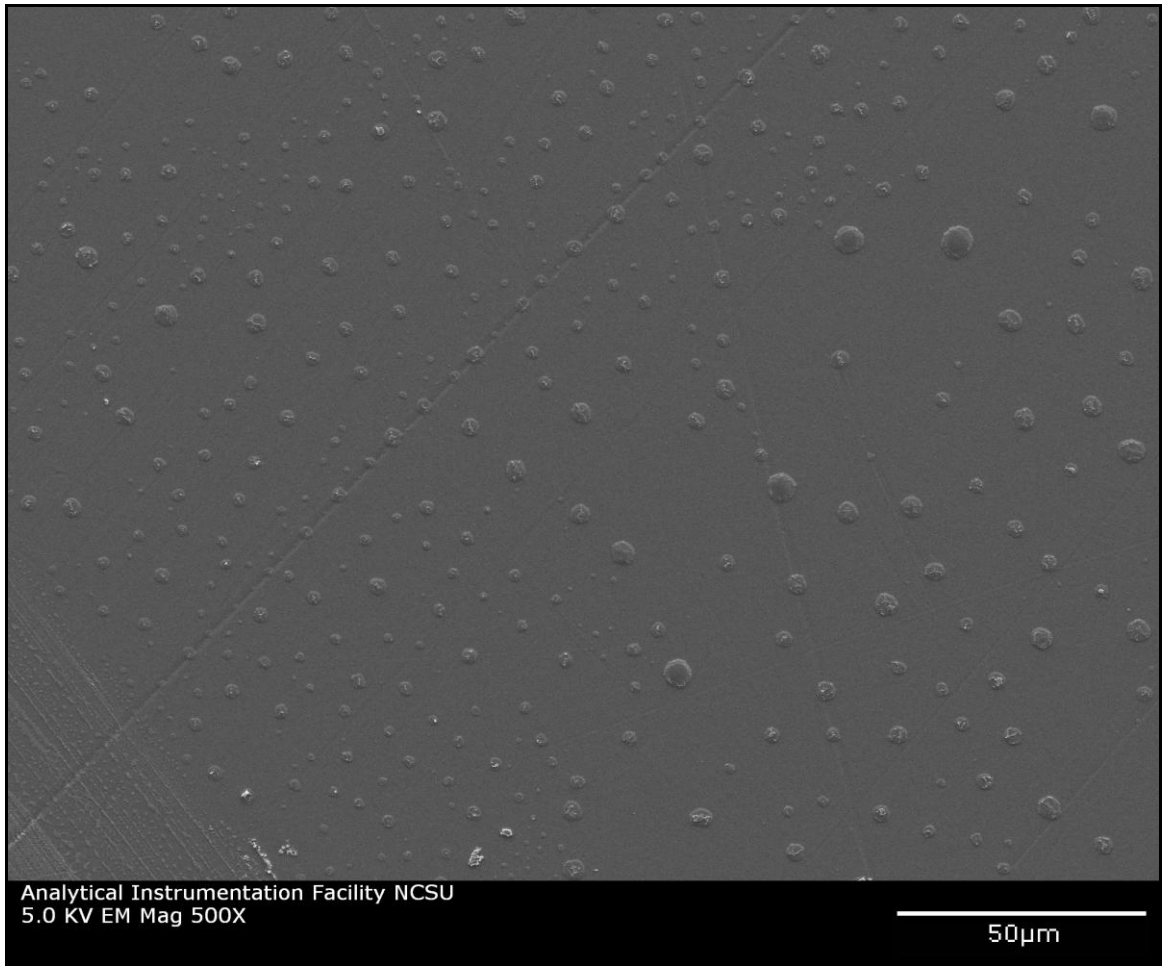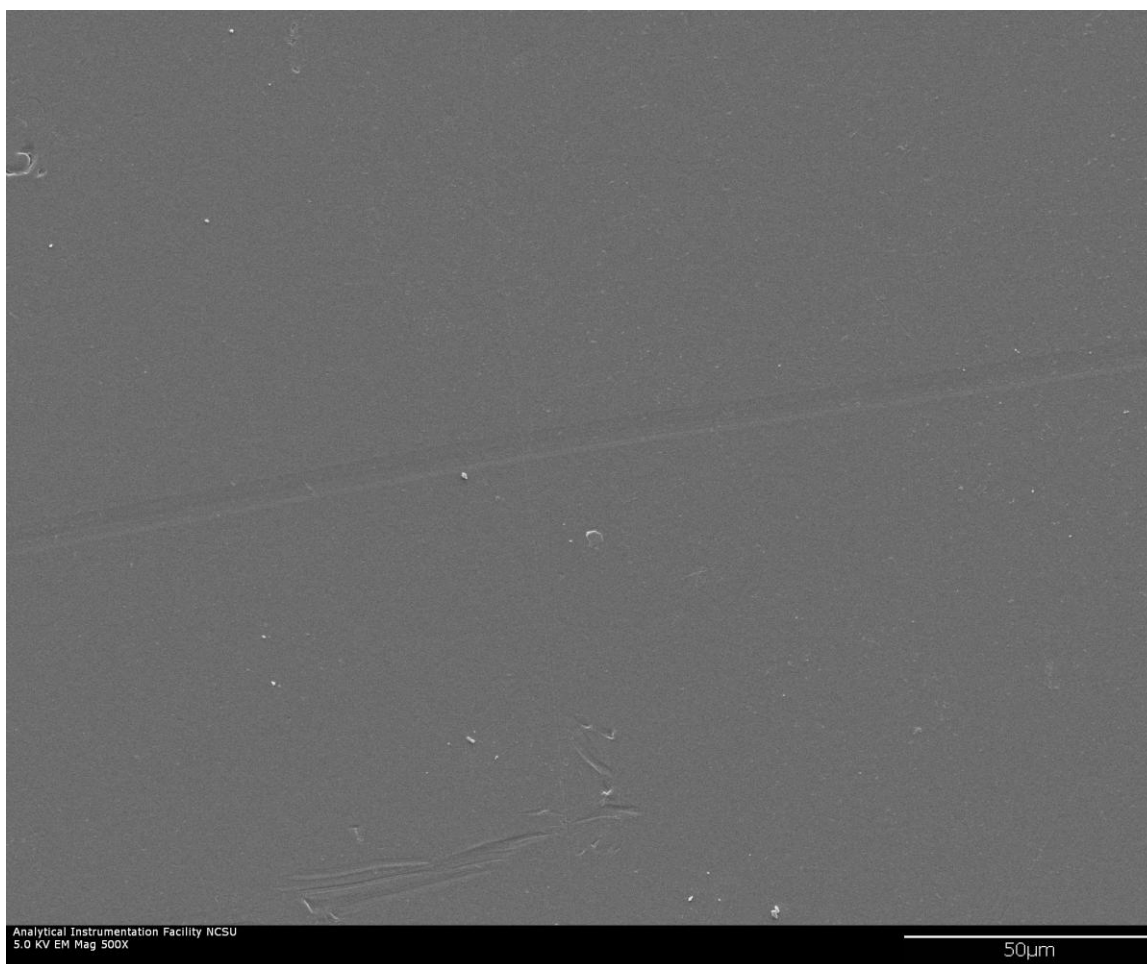
A.1.b-1 Helium-plasma treated FEP Film; Mag. 500X
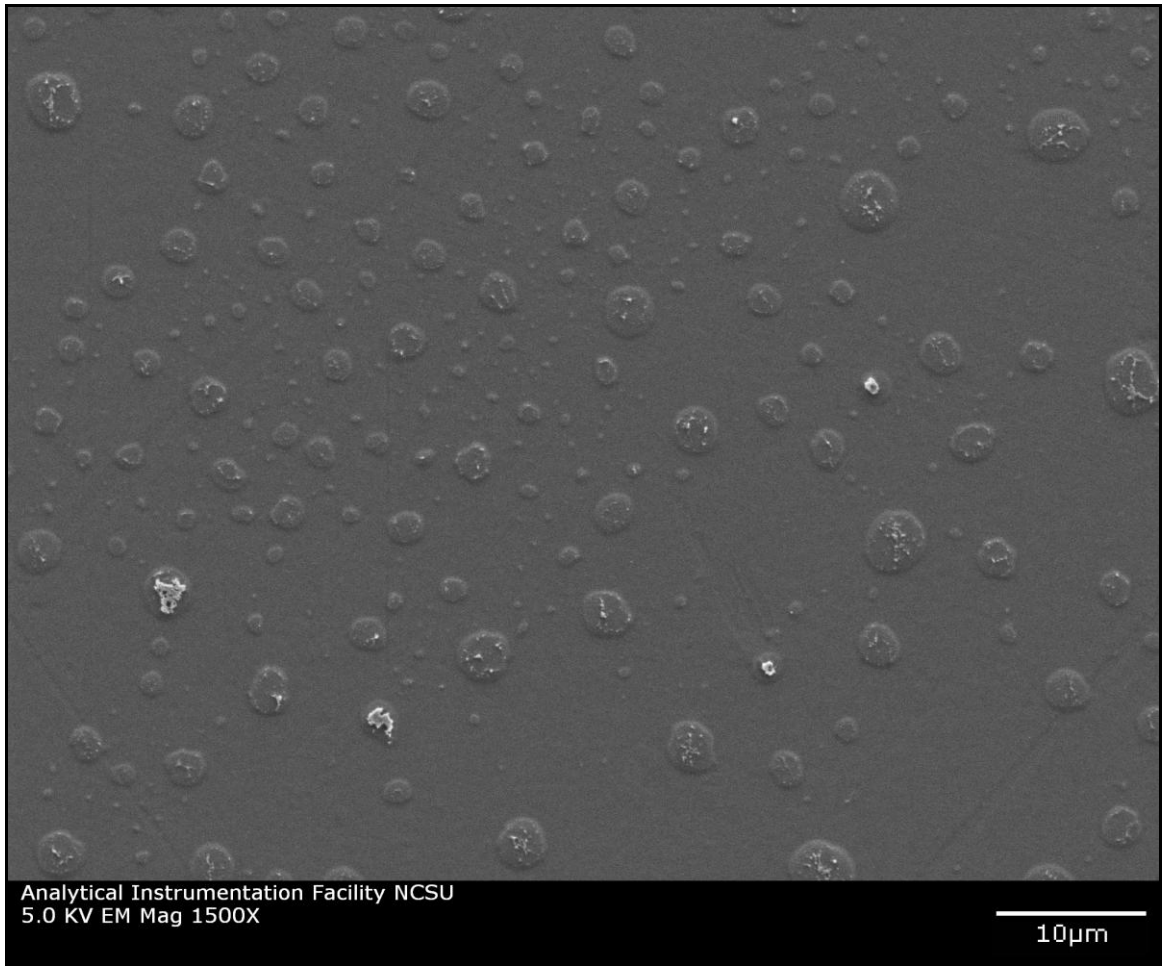
A.1.b-2 Helium-plasma treated FEP Film; Mag. 1500X
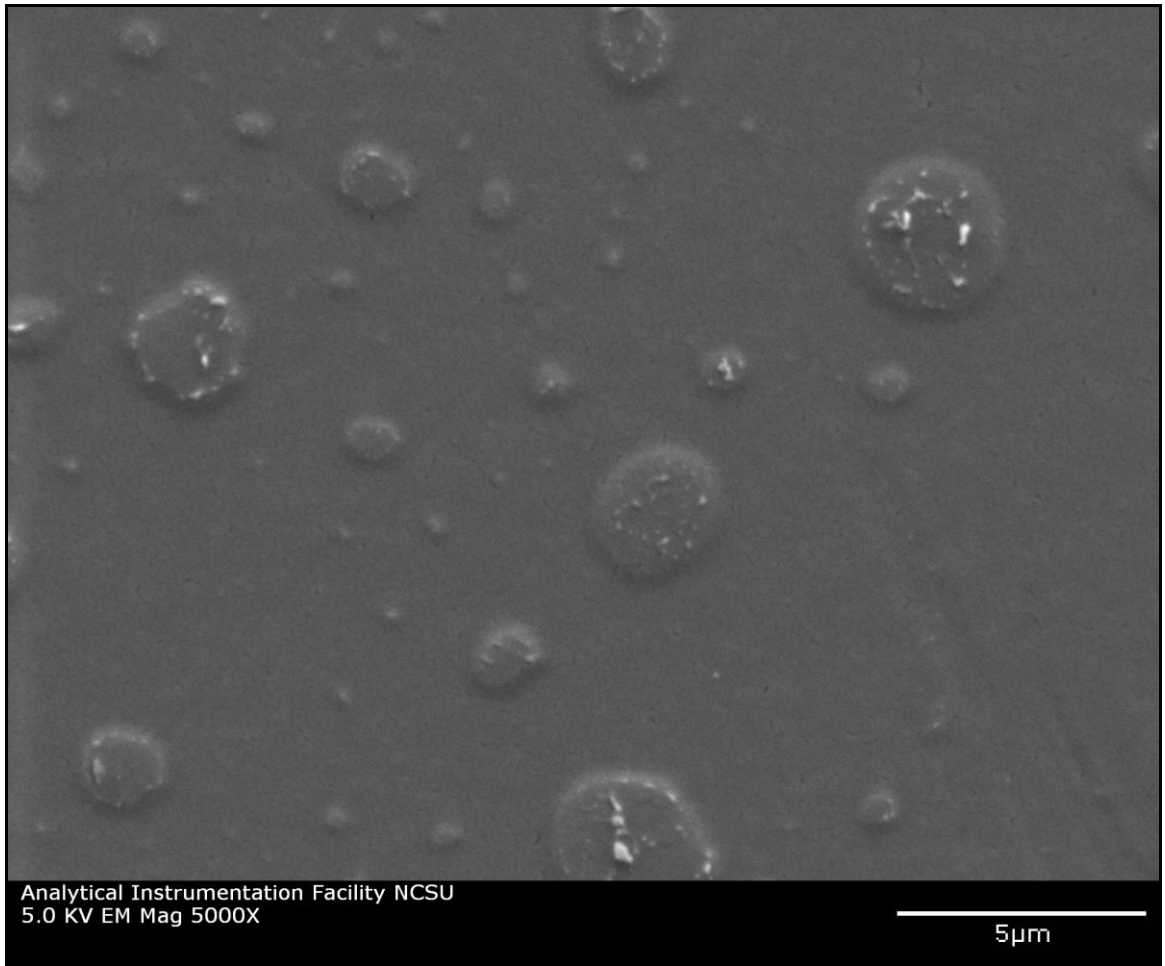
A.1.b-3 Helium-plasma treated FEP Film; Mag. 5000X
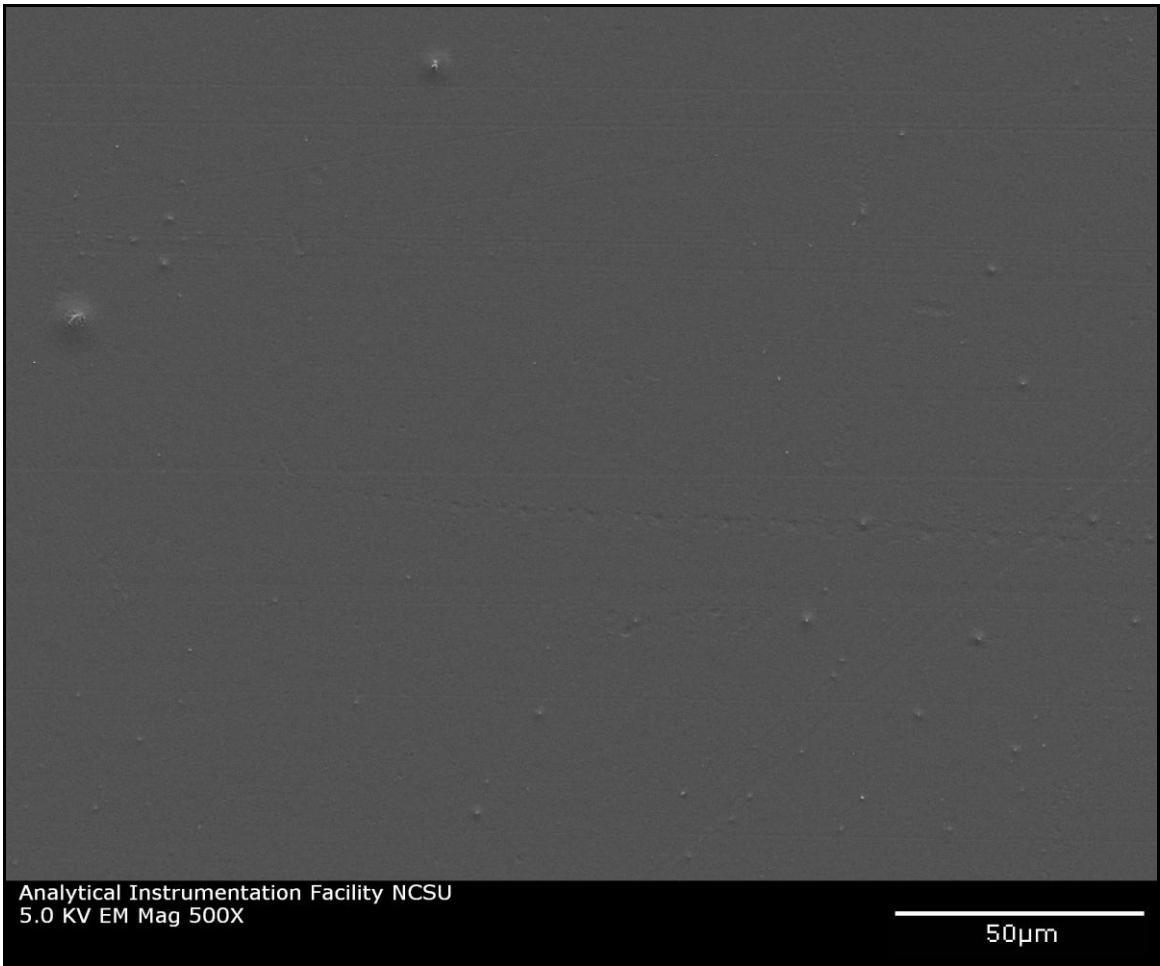
A.1.c-1 Helium-oxygen-plasma treated FEP Film; Mag. 500X
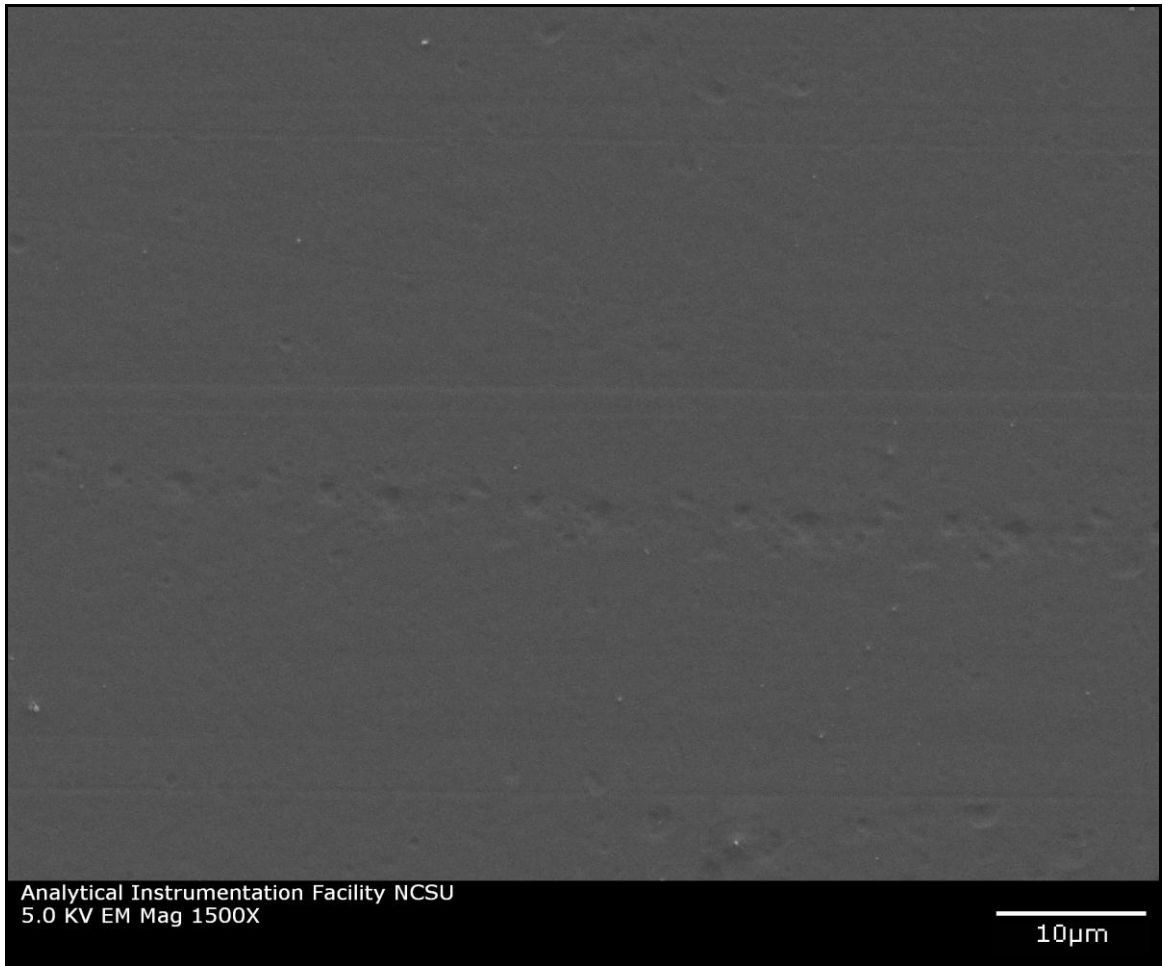
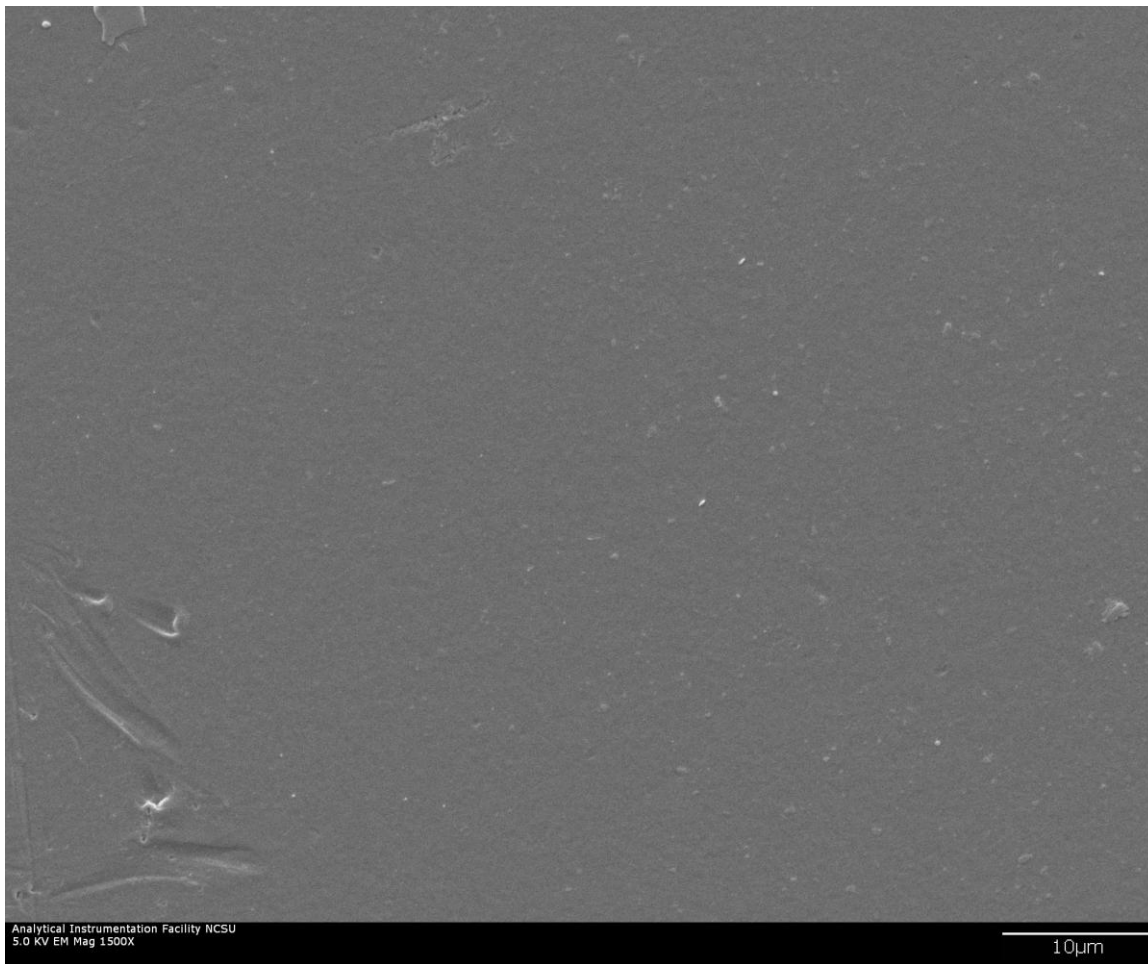**A.1.c-2 Helium-oxygen-plasma treated FEP Film; Mag. 1500X**

A.1.c-3 Helium-oxygen-plasma treated FEP Film; Mag. 5000X

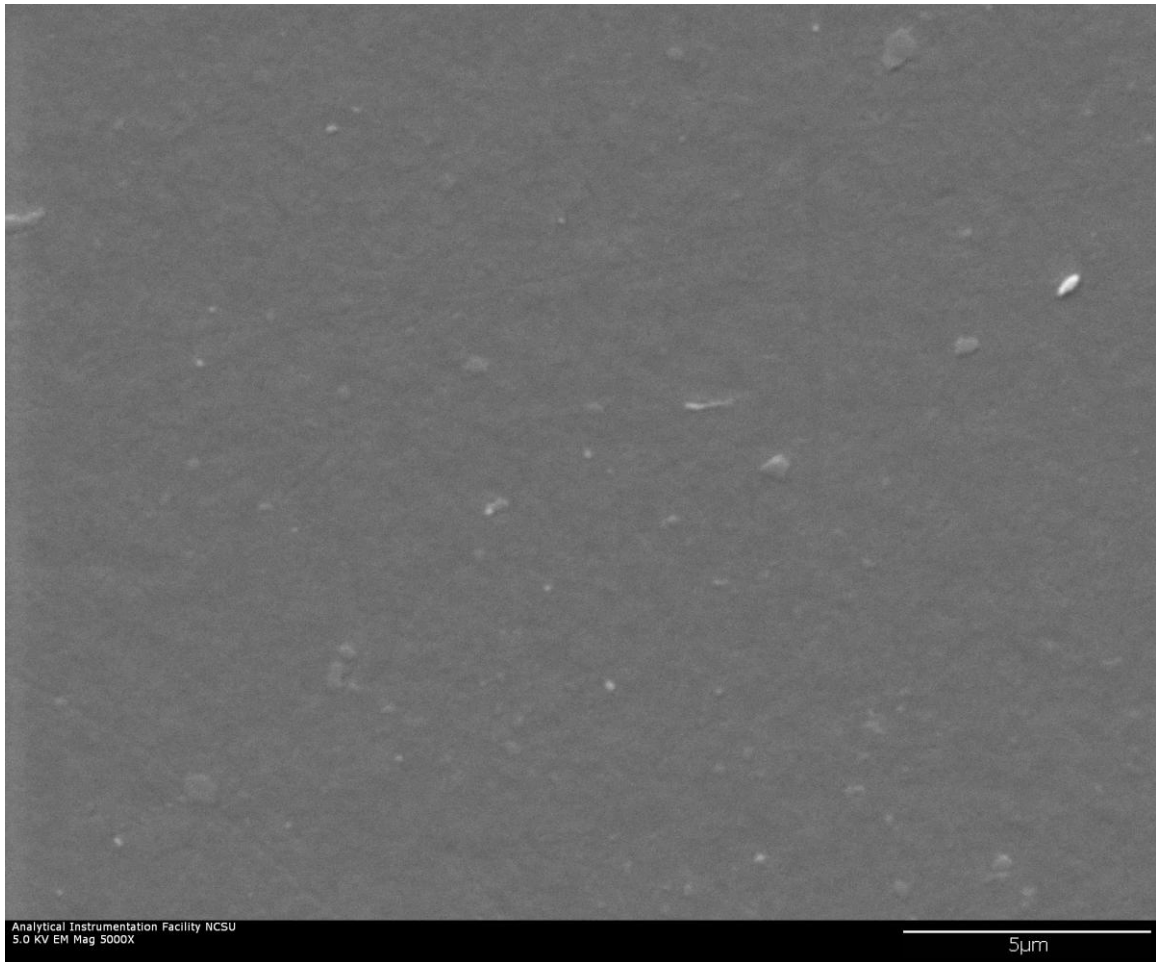**A.2 Fluorinated ethylene-propylene (FEP) Films (Second Cleaning Method)**
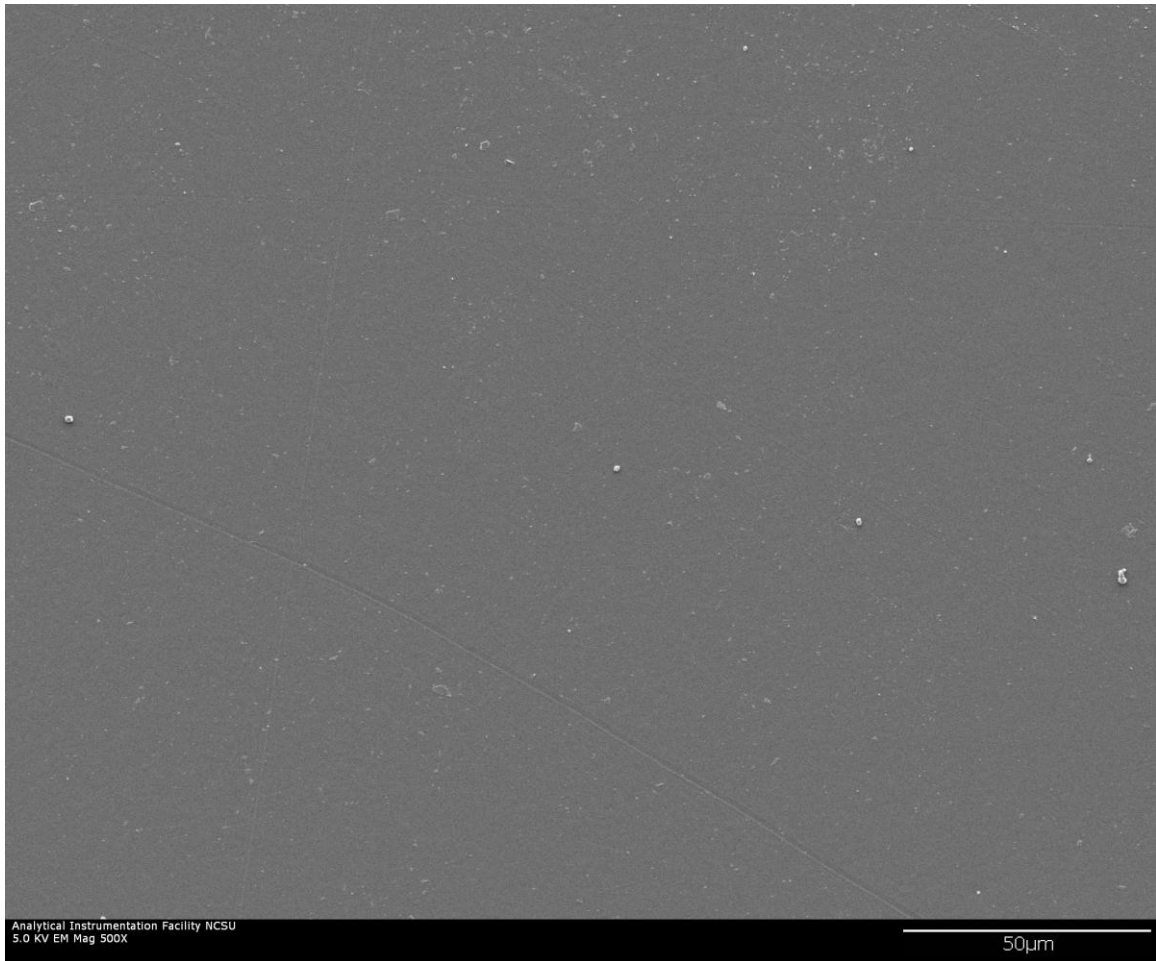

A.2.a-1 Untreated FEP Film; Mag. 500X
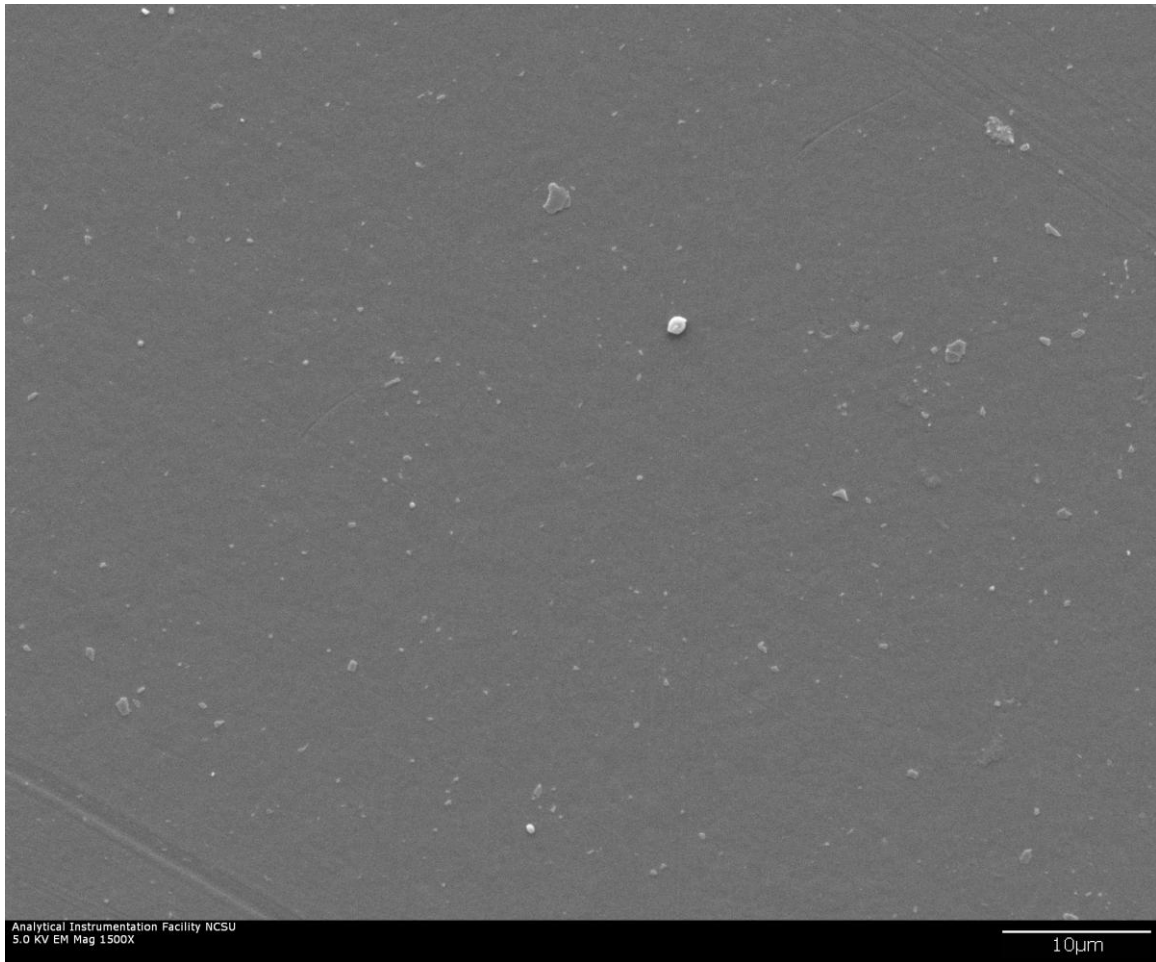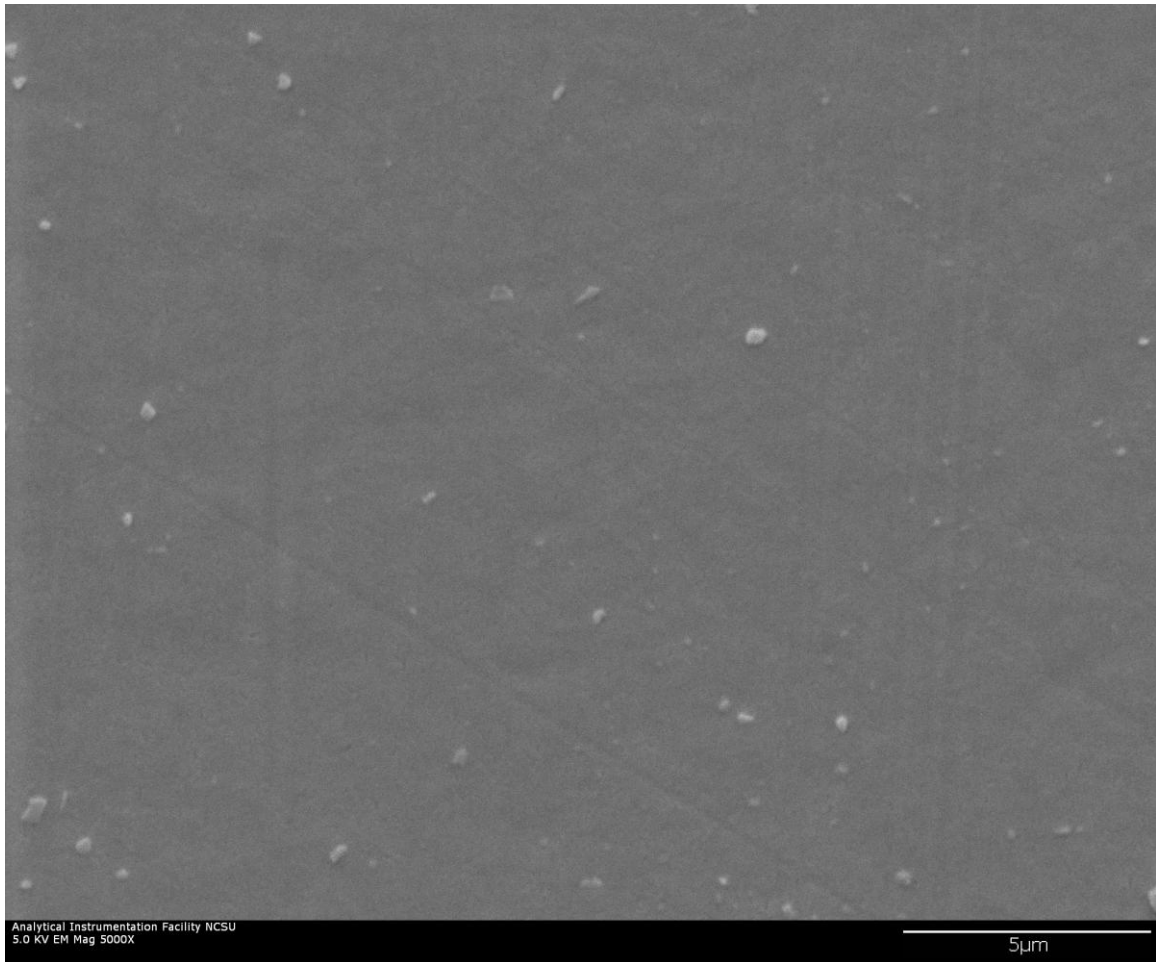
A.2.a-2 Untreated FEP Film; Mag. 1500X
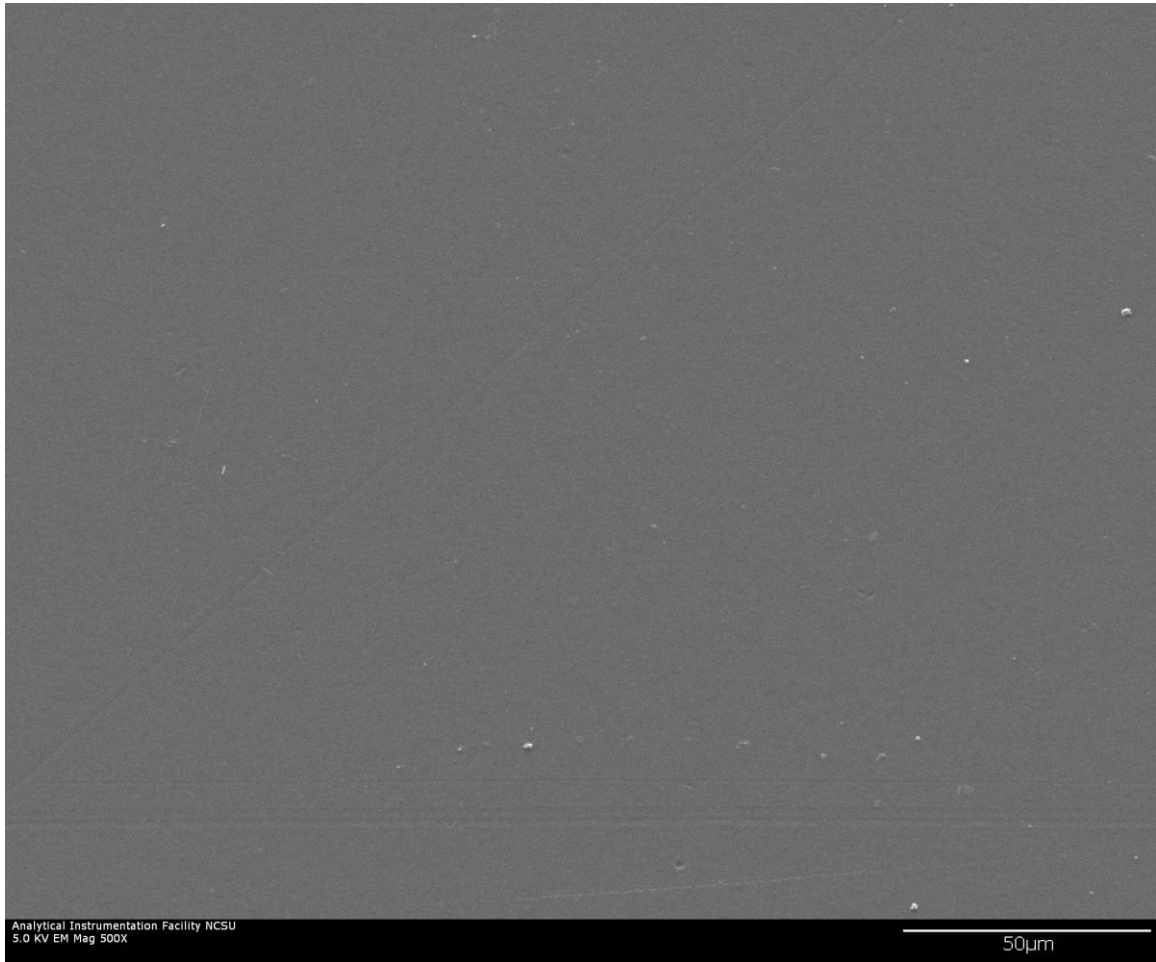
A.2.a-3 Untreated FEP Film; Mag. 5000X

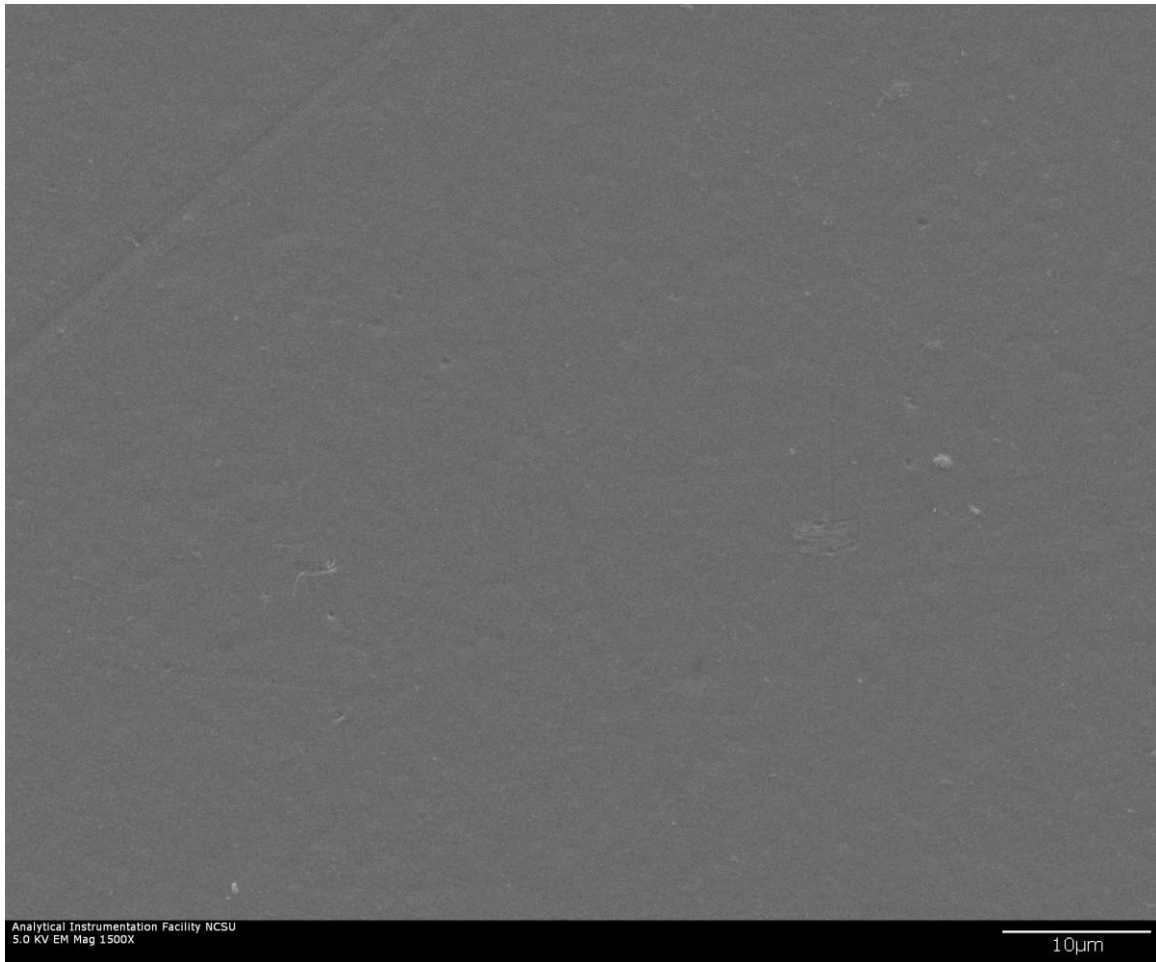**A.2.b-1 Helium-plasma treated FEP Film; Mag. 500X**

A.2.b-2 Helium-plasma treated FEP Film; Mag. 1500X

A.2.b-3 Helium-plasma treated FEP Film; Mag. 5000X

A.2.c-1 Helium-oxygen-plasma treated FEP Film; Mag. 500X

Analytical Instrumentation Facility NCSU
5.0 KV EM Mag 1500X
10µm

A.2.c-2 Helium-oxygen-plasma treated FEP Film; Mag. 1500X
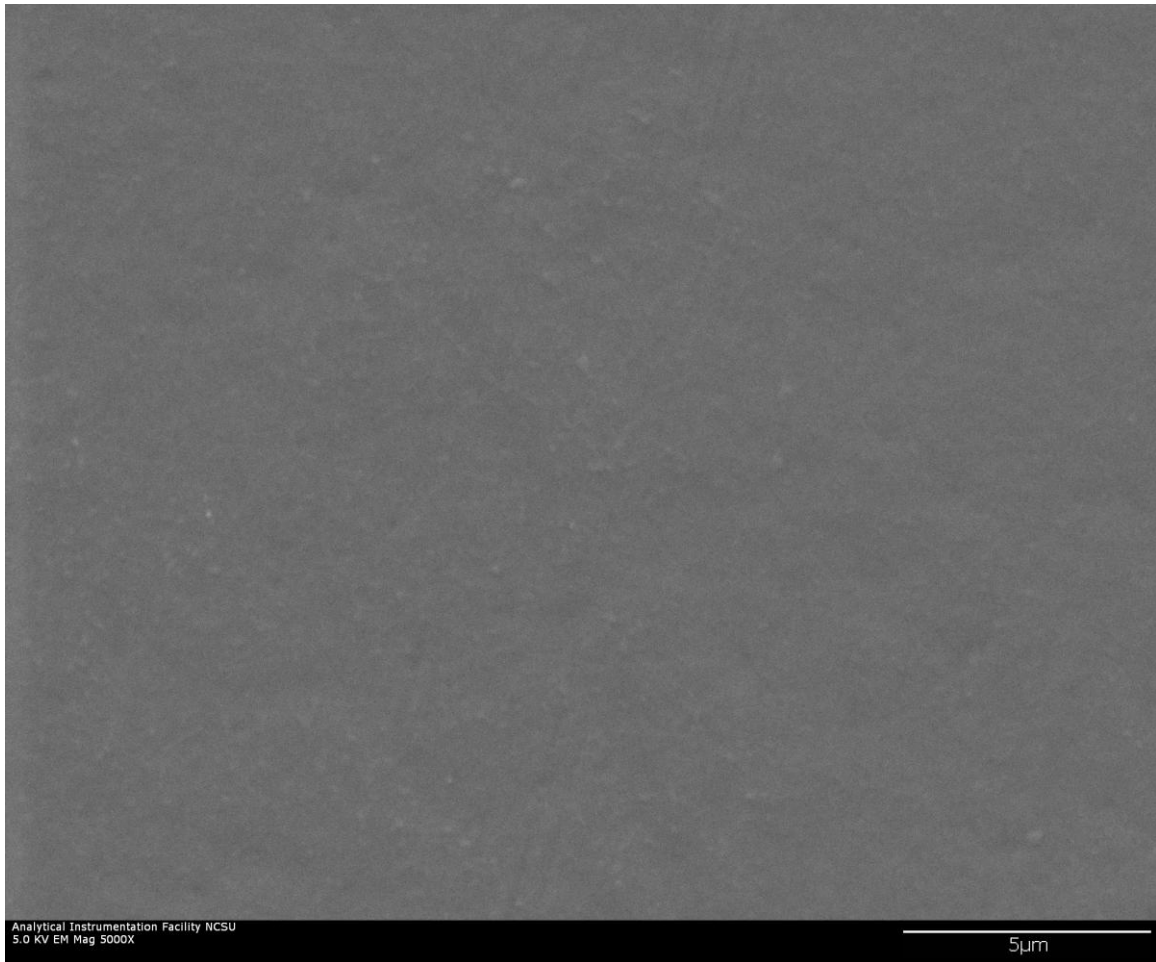
A.2.c-3 Helium-oxygen-plasma treated FEP Film; Mag. 5000X

A.3 Nitinol Wires

Analytical Instrumentation Facility NCSU
20.0 KV EM Mag 100X
200μm

A.3.a-1 Untreated Nitinol Wire; Mag. 100X

Analytical Instrumentation Facility NCSU
20.0 KV EM Mag 500X

50μm
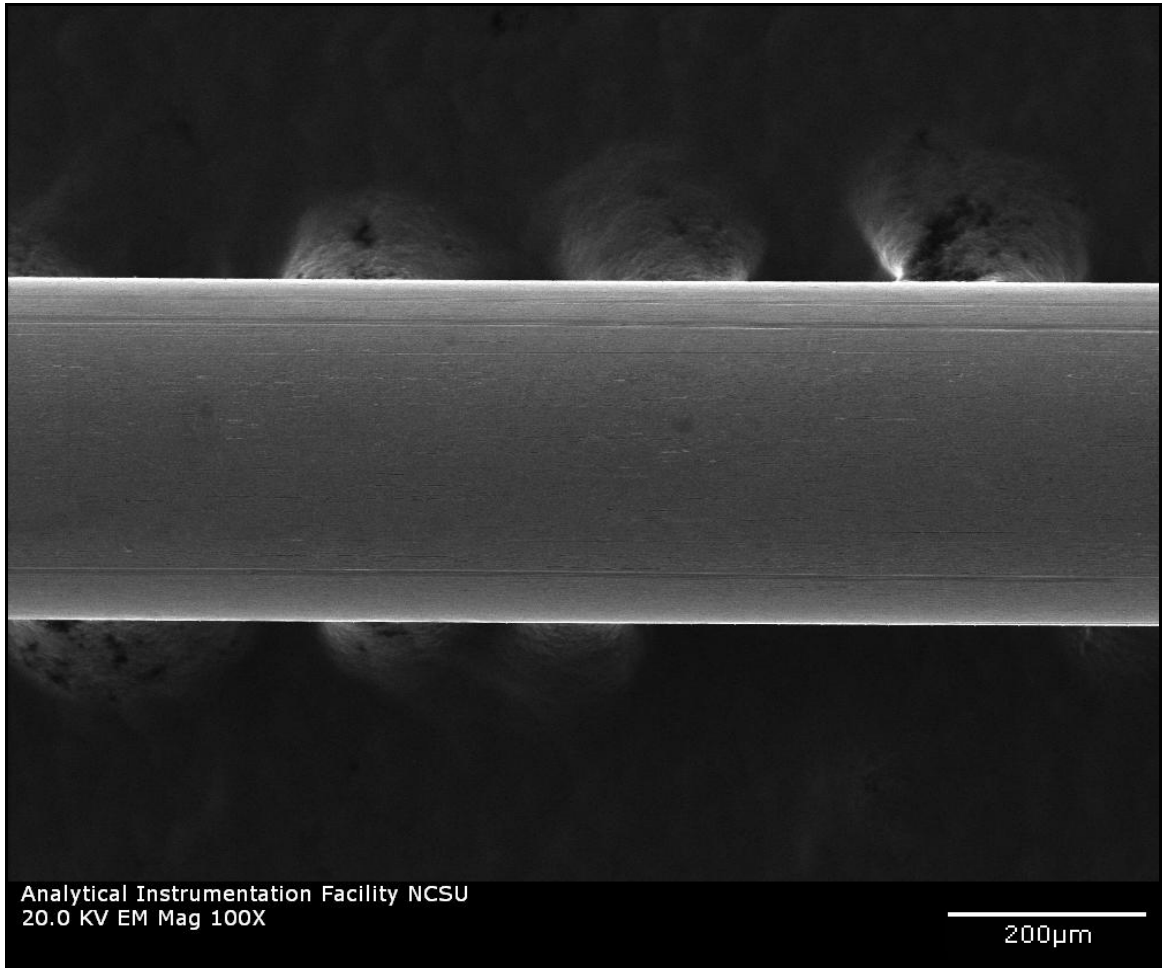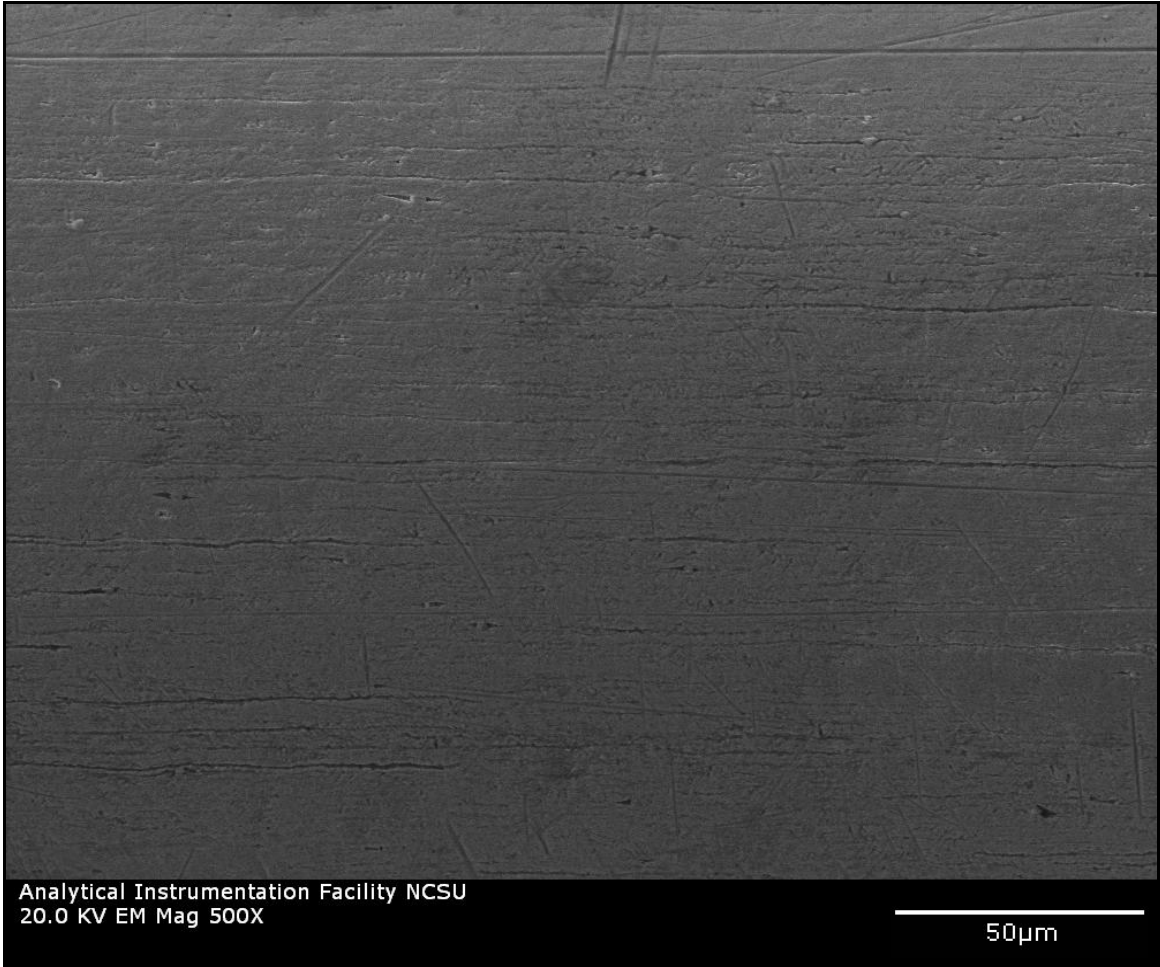
A.3.a-2 Untreated Nitinol Wire; Mag. 500X

A.3.b-1 Helium-plasma treated Nitinol Wire; Mag. 100X

Analytical Instrumentation Facility NCSU
20.0 KV EM Mag 500X

50μm

A.3.b-2 Helium-plasma treated Nitinol Wire; Mag. 500X

Analytical Instrumentation Facility NCSU
20.0 KV EM Mag 100X

200μm
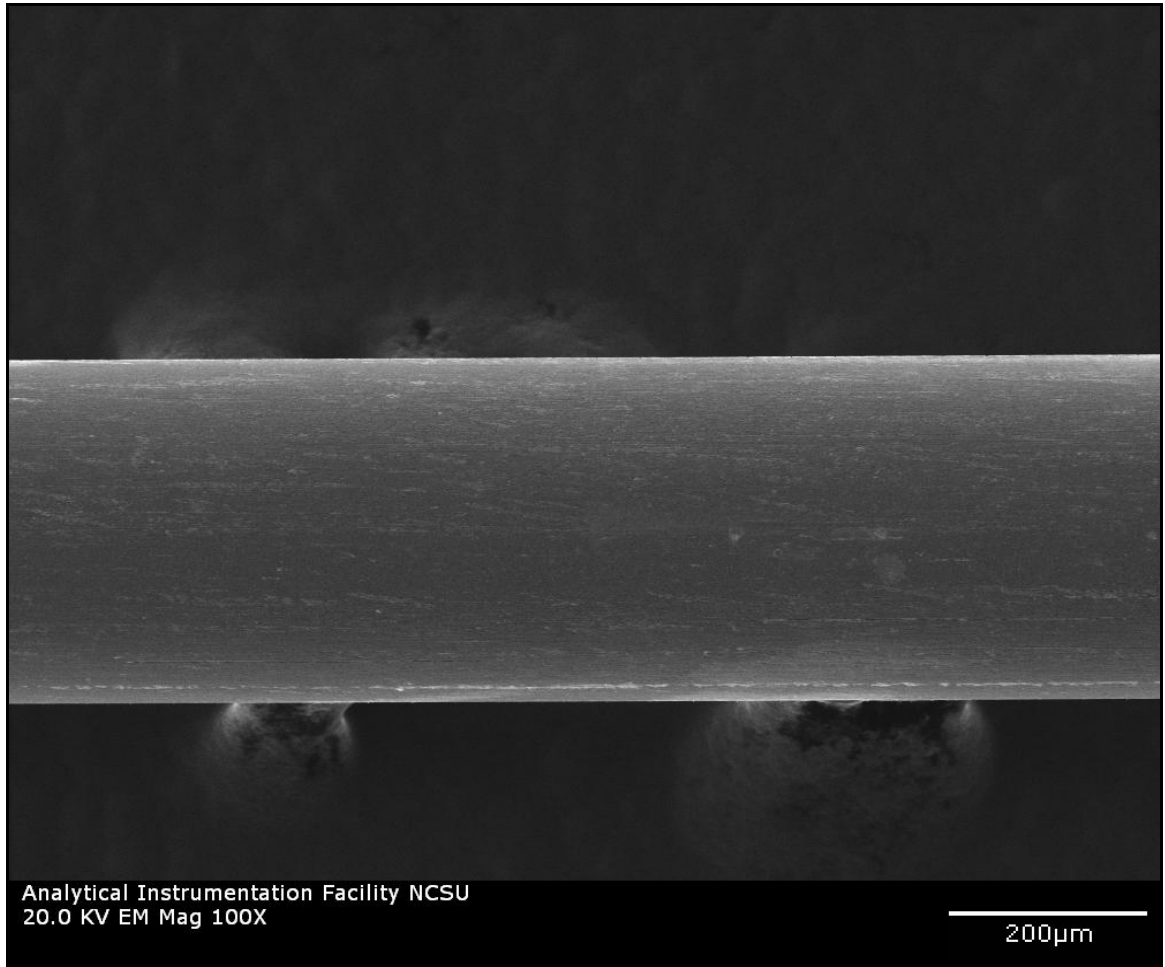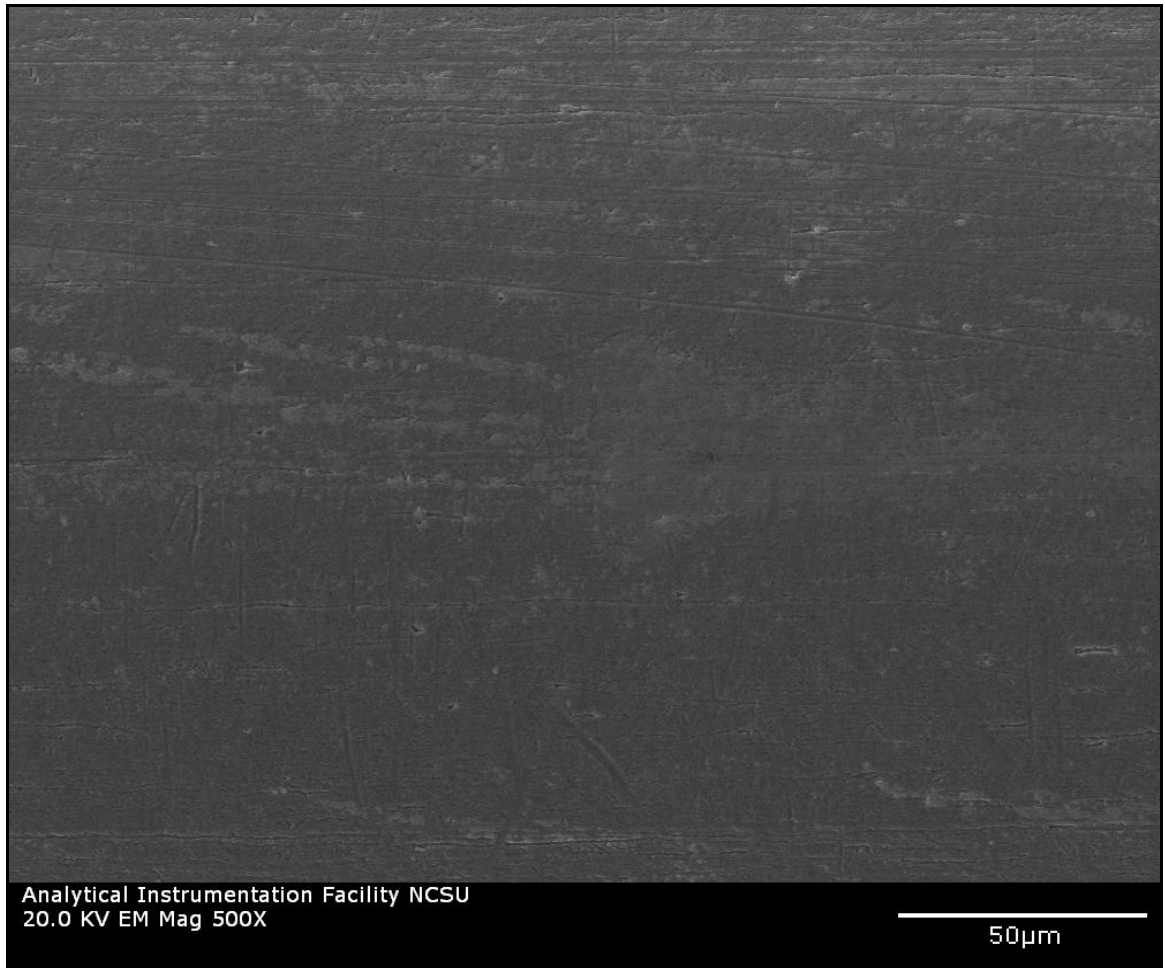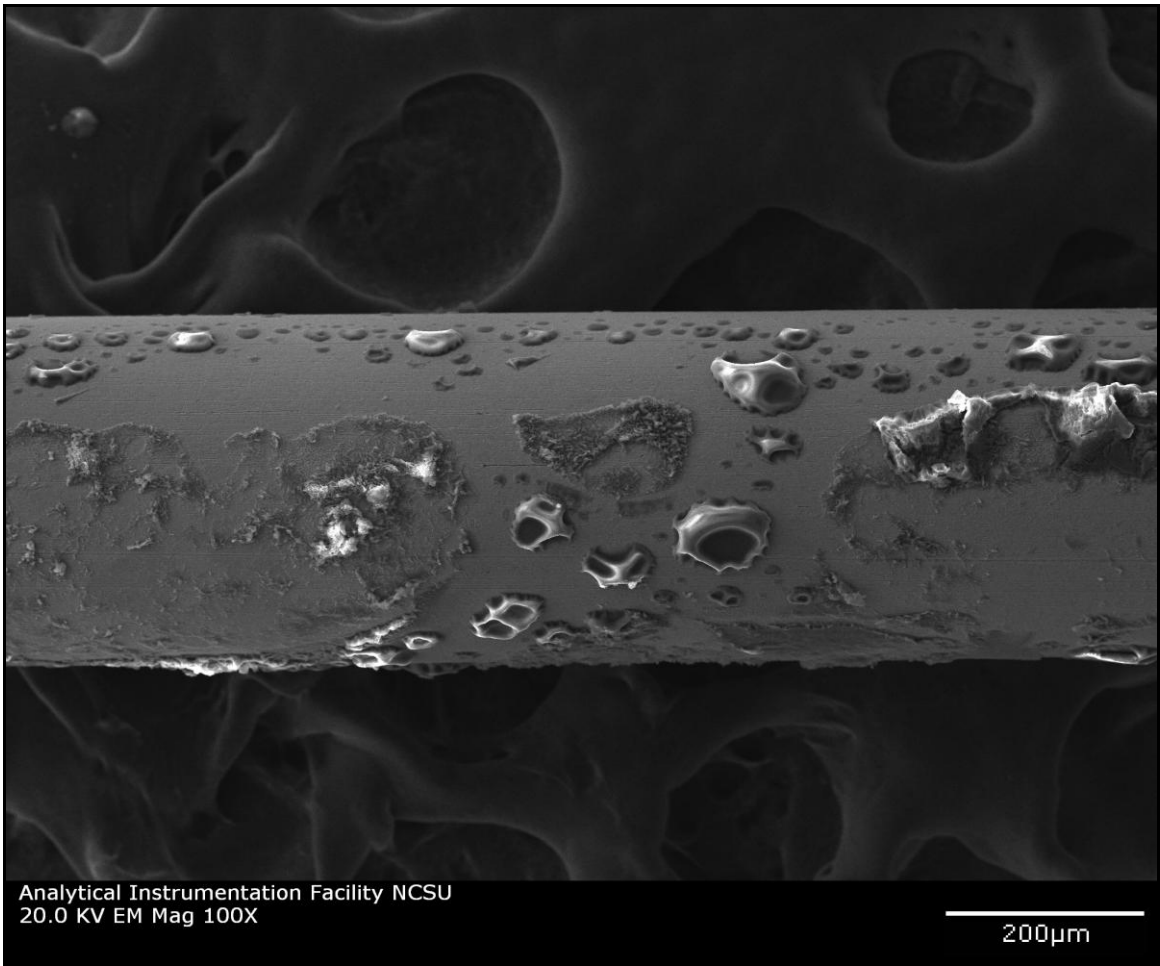
A.3.c-1 Fluorocarbon(FC)-coated Nitinol Wire; Mag. 100X
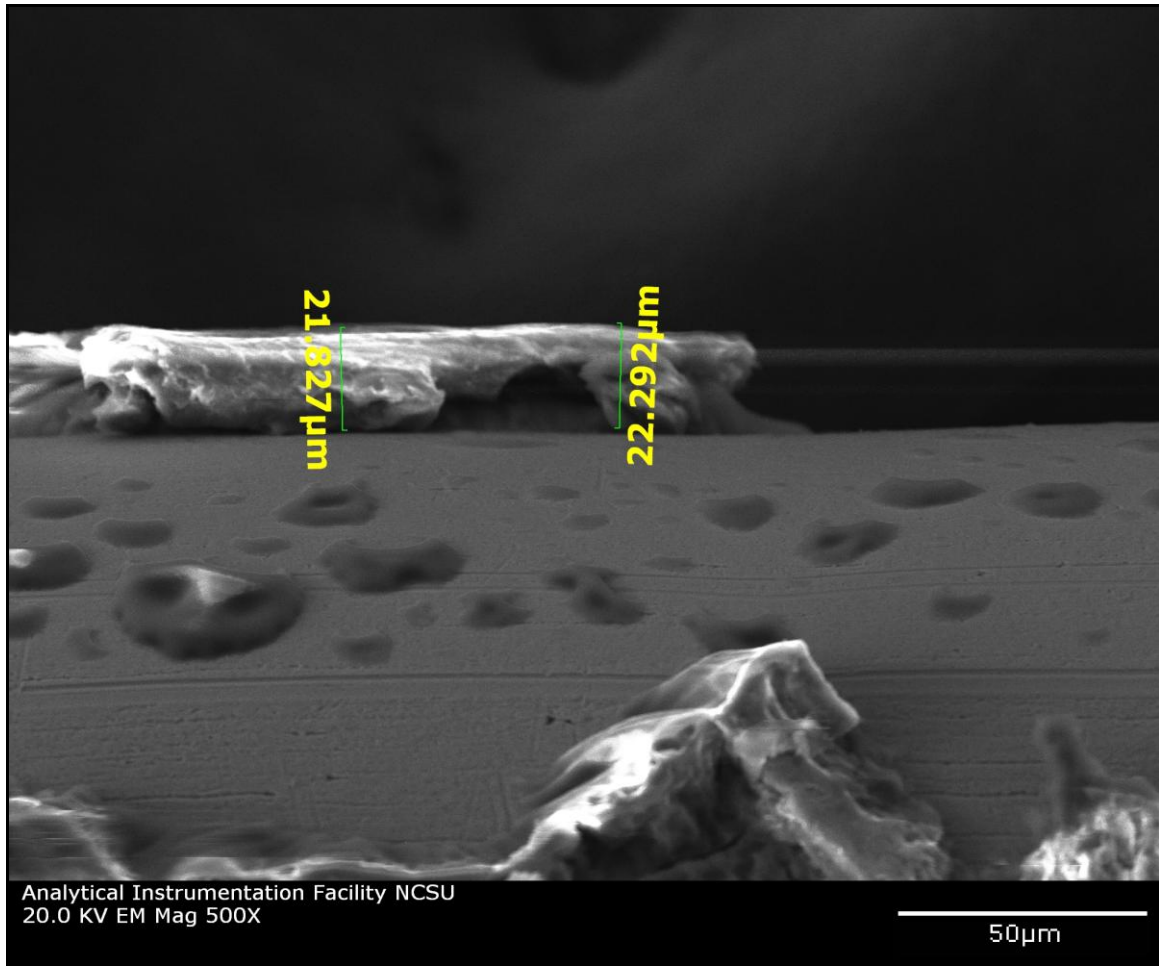
A.3.c-2 Fluorocarbon(FC)-coated Nitinol Wire; Mag. 500X
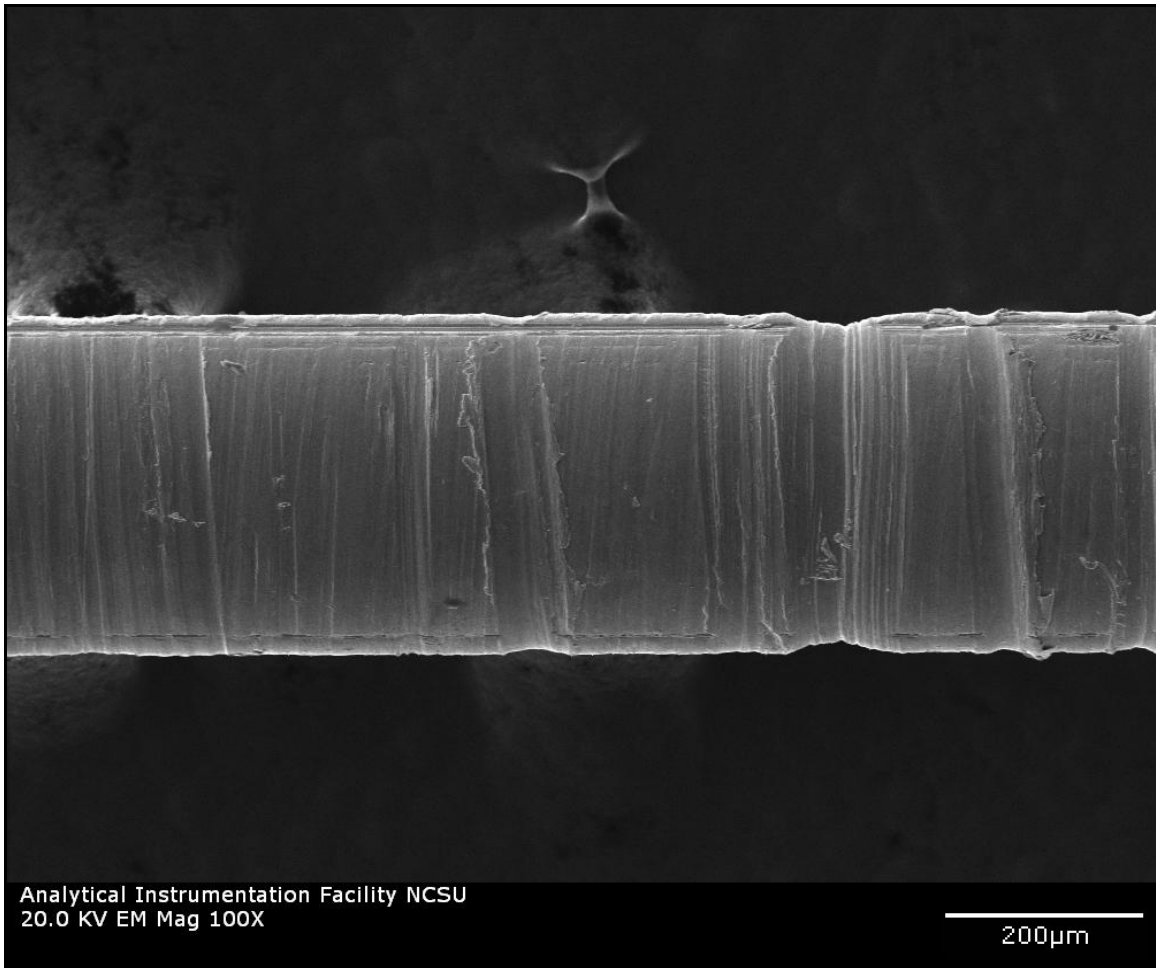
A.3.d-1 Mechanically-roughened Nitinol Wire; Mag. 100X
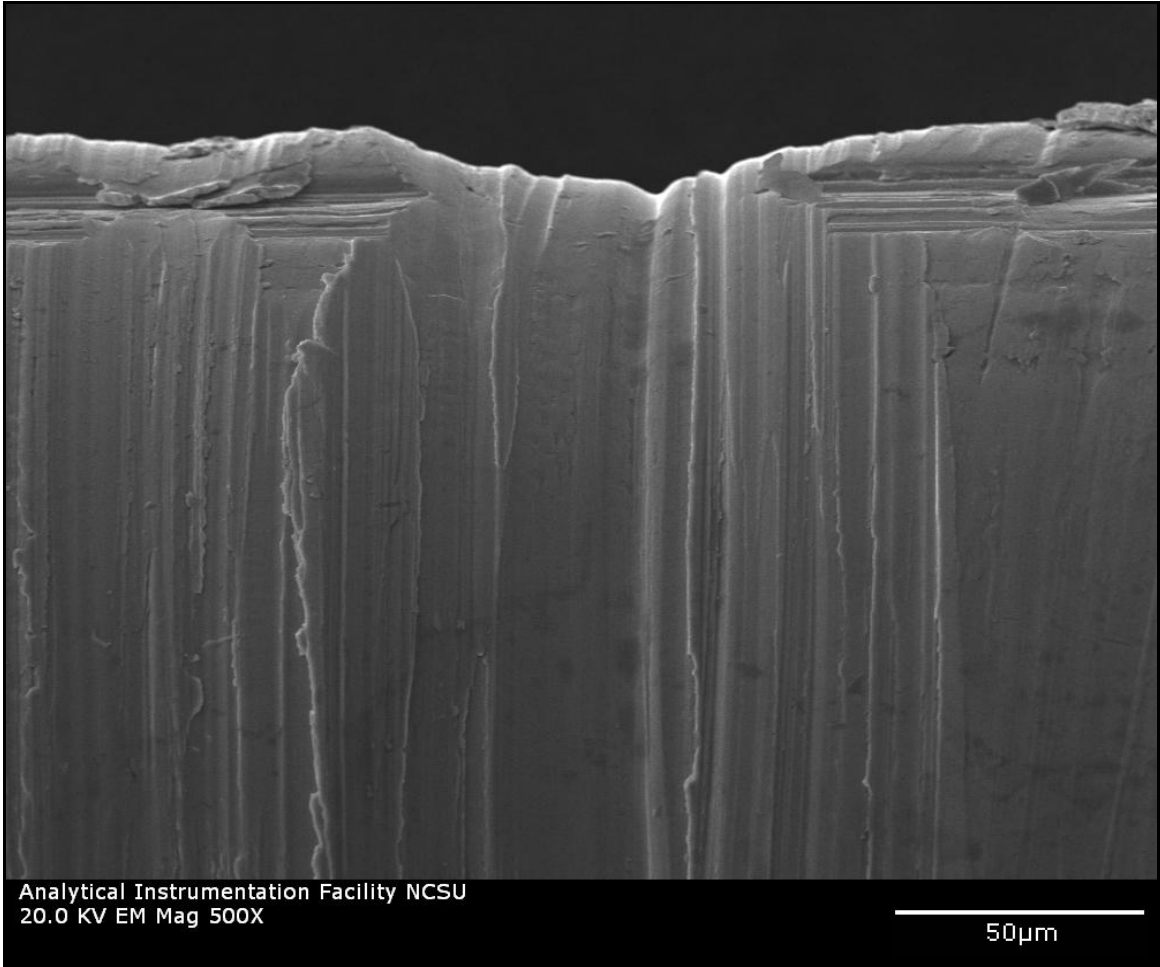
A.3.d-2 Mechanically-roughened Nitinol Wire; Mag. 500X

Appendix B: Energy-dispersive X-ray Spectroscopy (EDS)

B.1 Fluorinated ethylene-propylene (FEP) Film
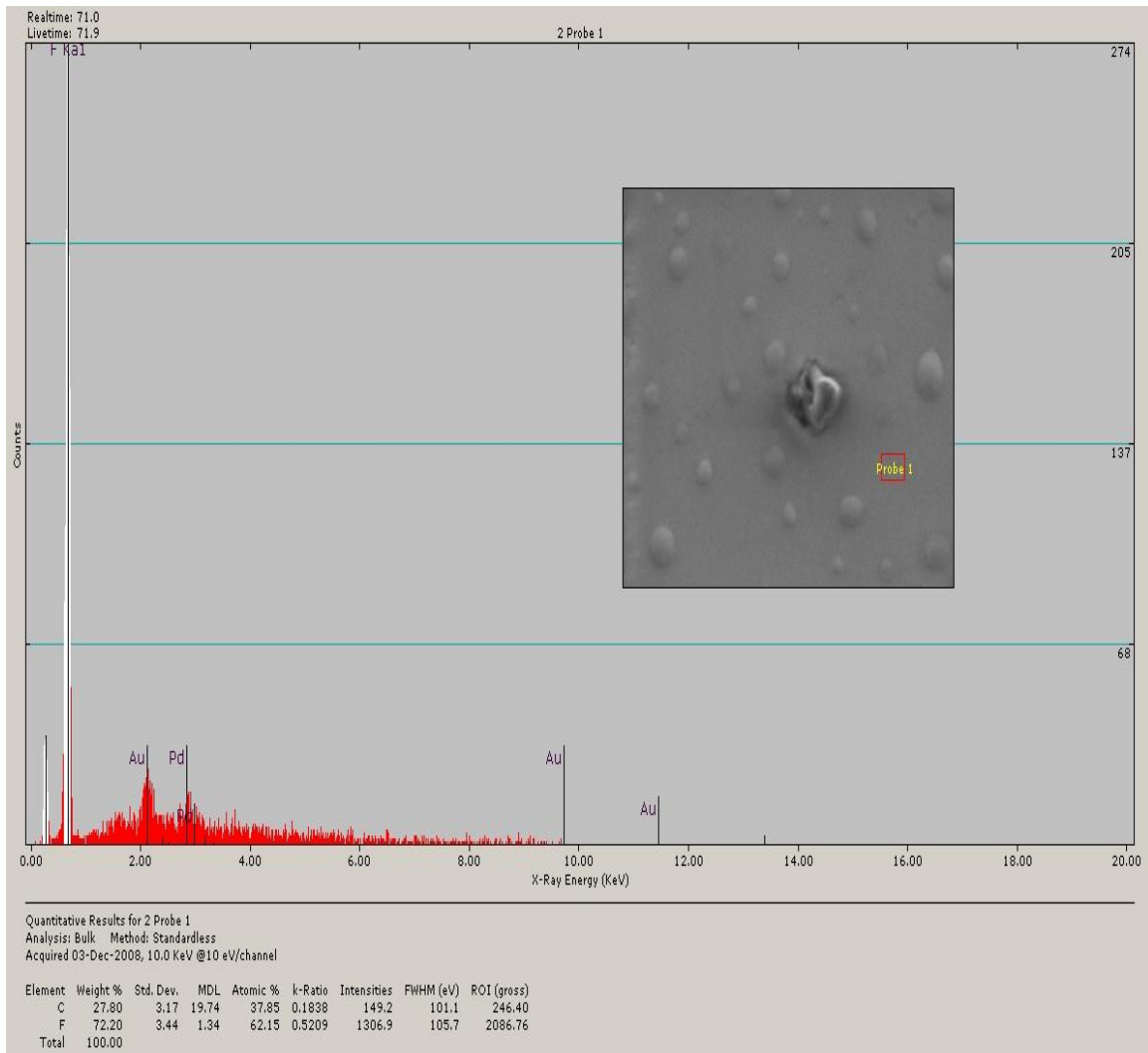
B.1.a A Smooth Spot of Untreated FEP Film
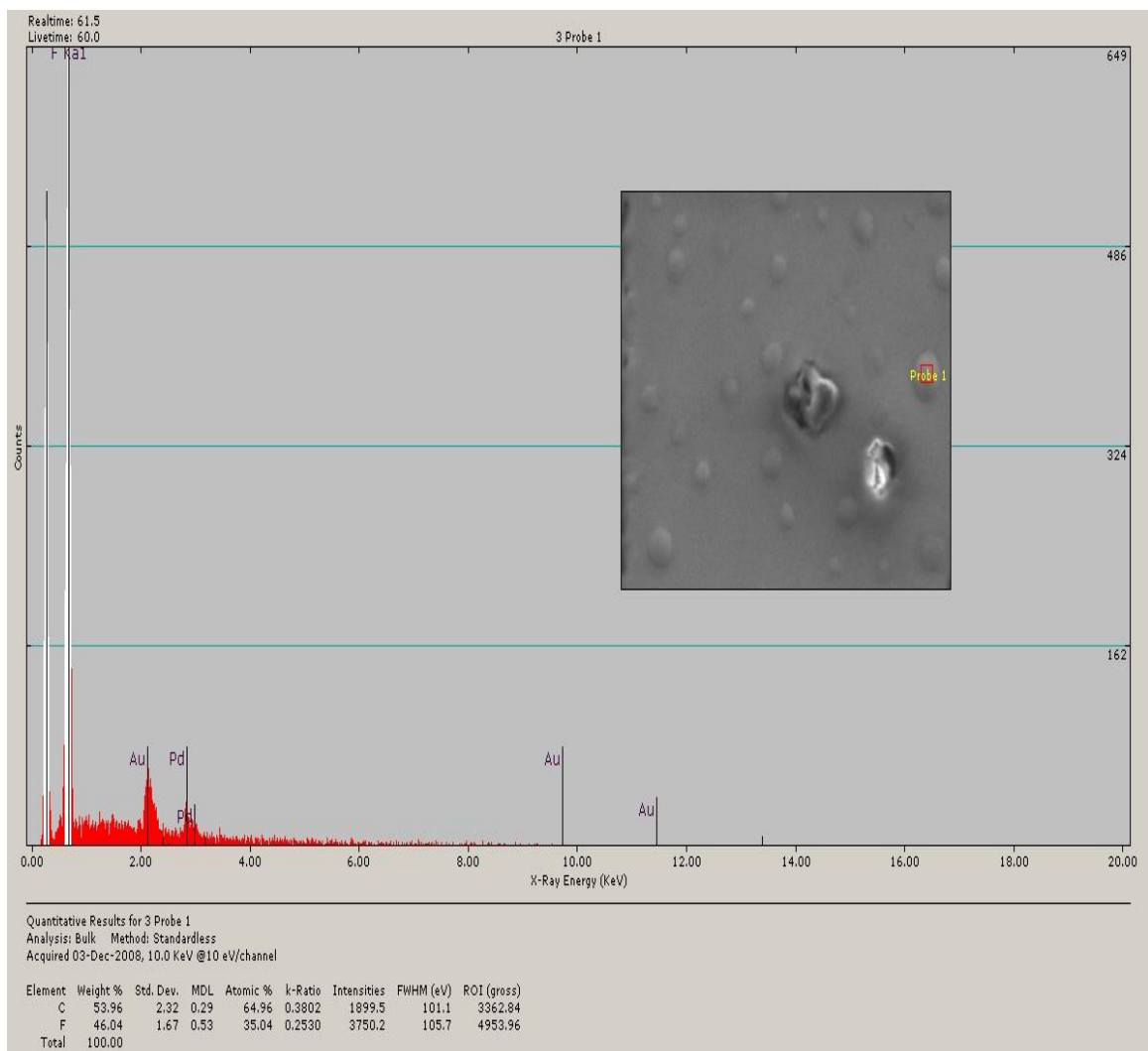
B.1.b A Bumped Spot on the Untreated FEP Film

B.2 Nitinol Wire
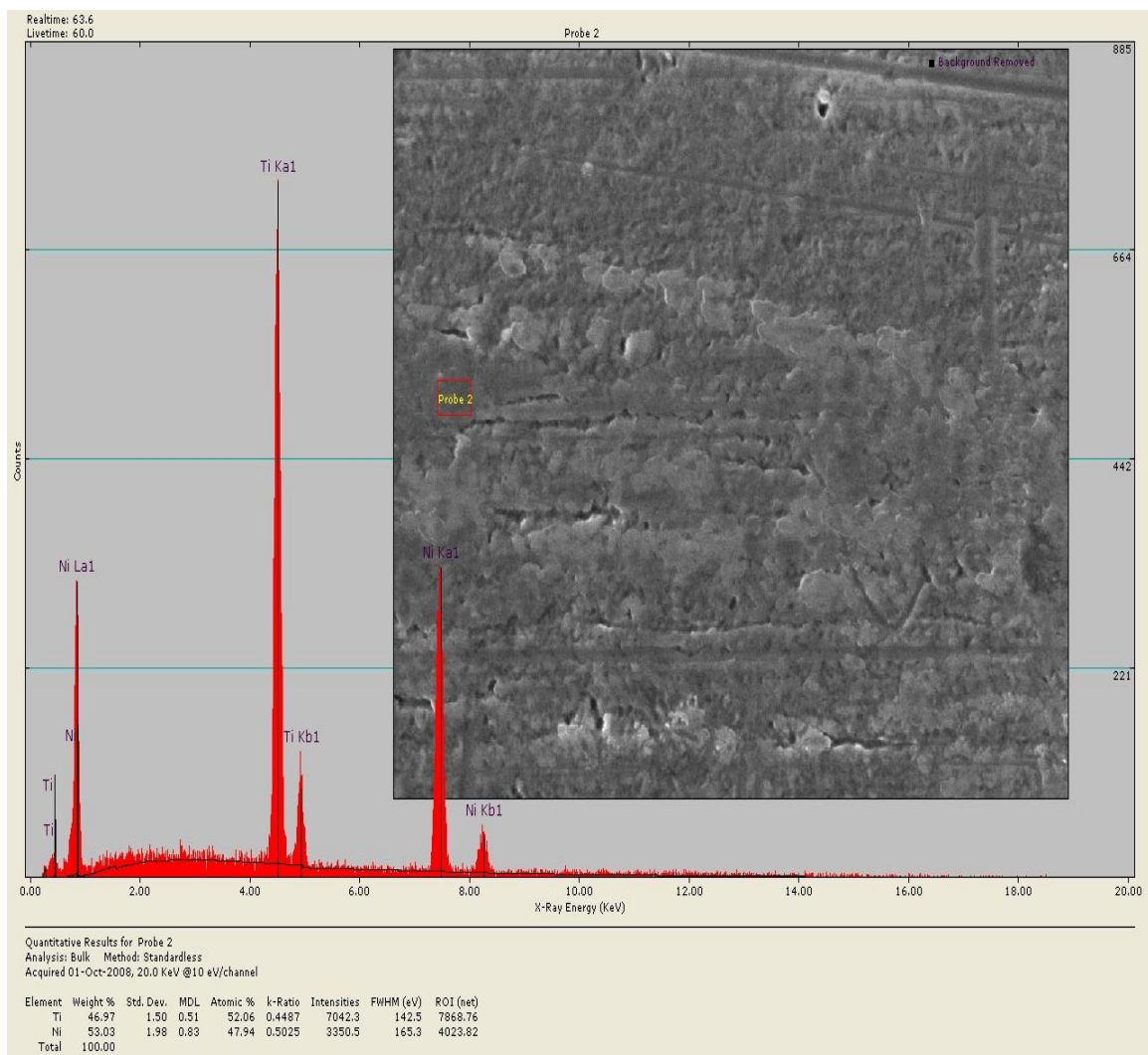
B.2.a A Clean Spot on the Helium-plasma Treated Nitinol Wire Surface
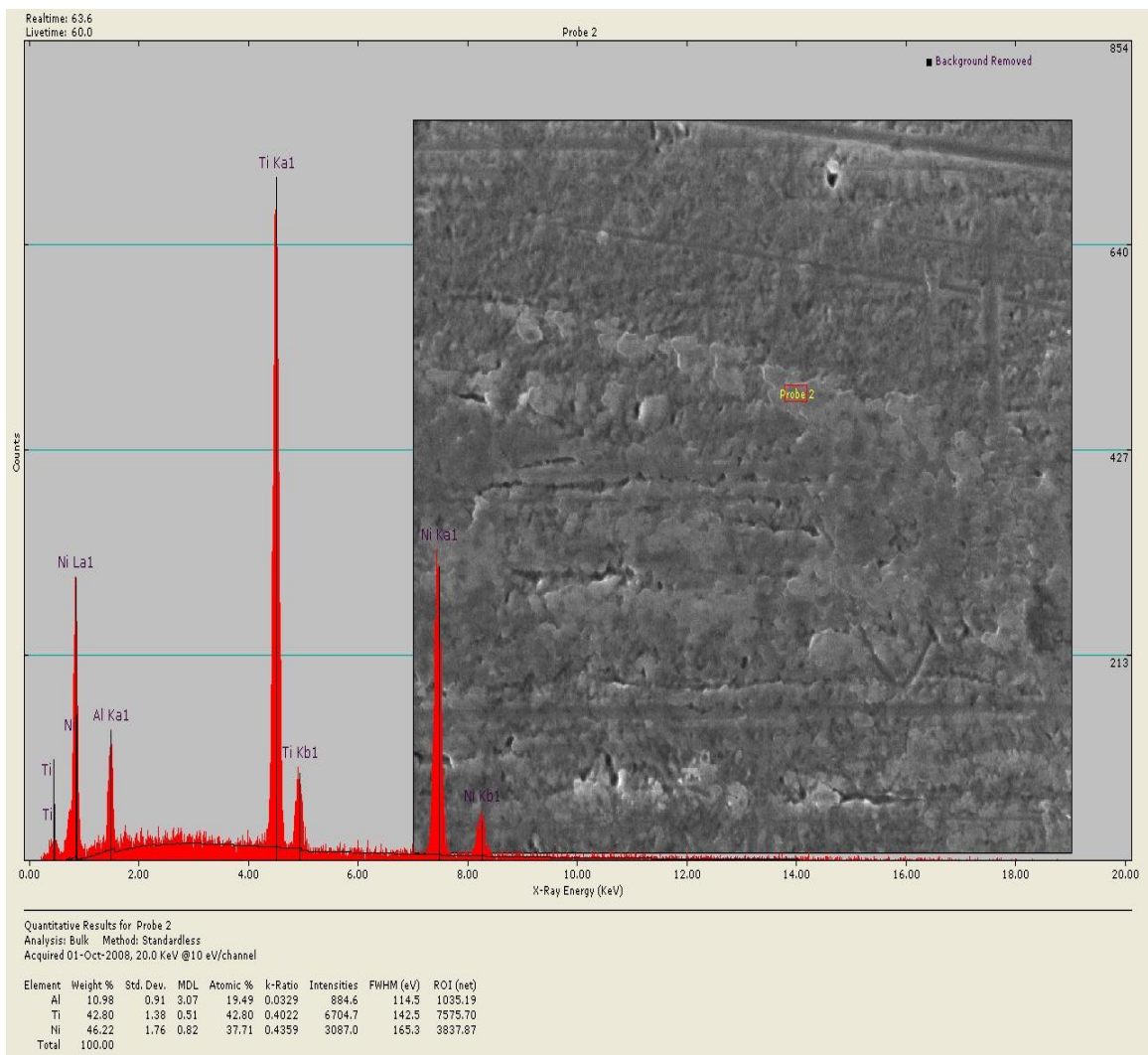
B.2.b A Contaminated Spot on the Helium-plasma Treated Nitinol Wire Surface

Appendix C: Spectra of X-ray Photoelectron Spectroscopy (XPS)

C.1 Fluorinated Ethylene-propylene (FEP) Films

x 10⁴

Name	Pos.	FWHM	Area	At%
O 1s	526	6.08962	4763.3	0.80
C 1s	285	3.22869	65195.0	31.19
F 1s	682	3.49165	605738.0	68.02
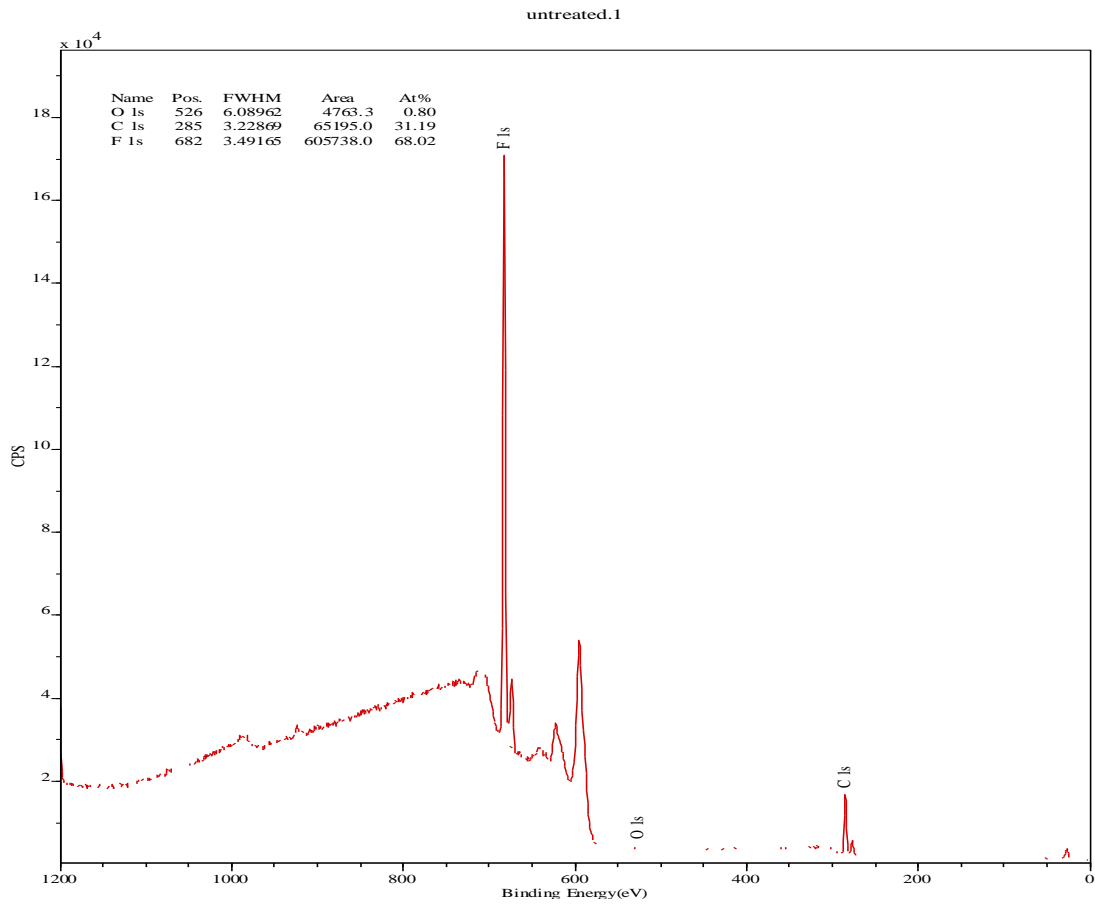
CasaXPS (This string can be edited in CasaXPS.DEF/PrintFootNote.txt)

C.1.a XPS Spectrum of Untreated FEP Film

Name	Pos.	FWHM	Area	At%
O 1s	528	4.32722	12566.7	2.08
C 1s	284	3.77823	63231.4	29.82
F 1s	682	3.71747	615098.1	68.10
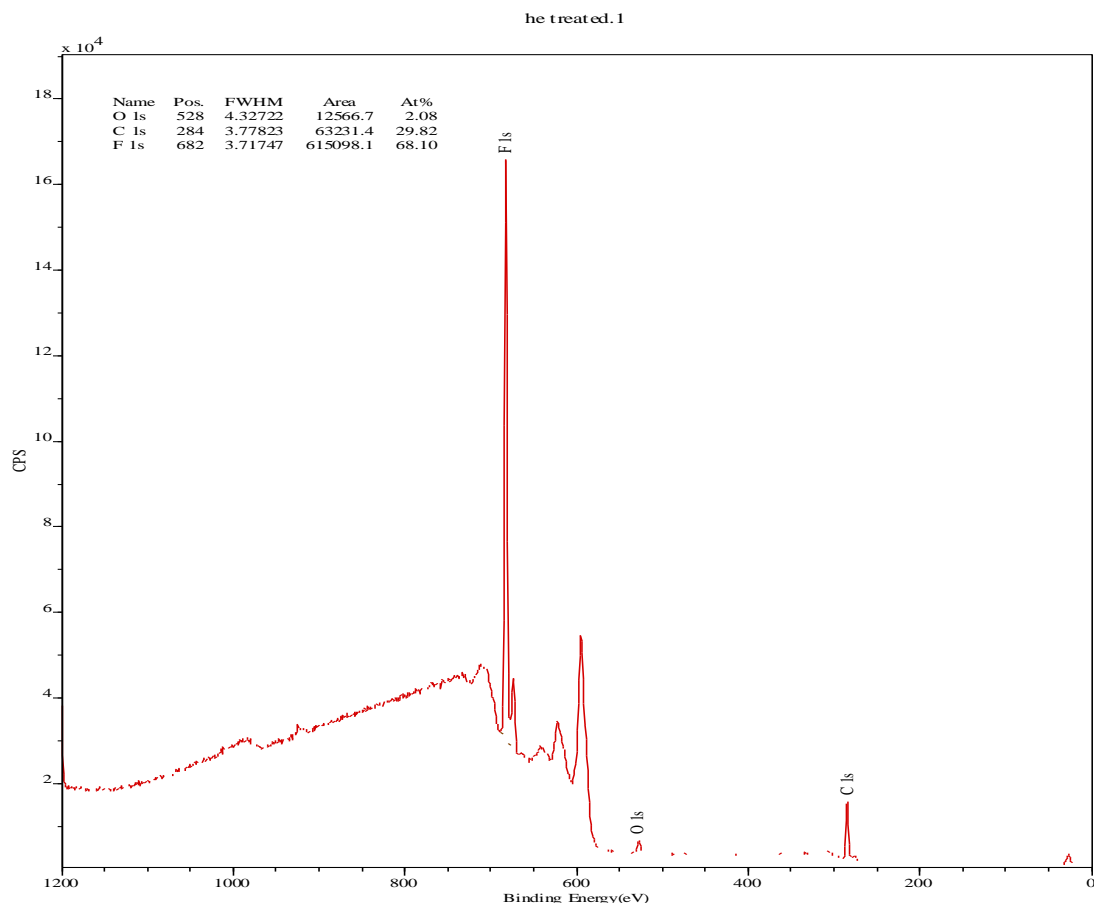
C.1.b XPS Spectrum of Helium-plasma Treated FEP Film
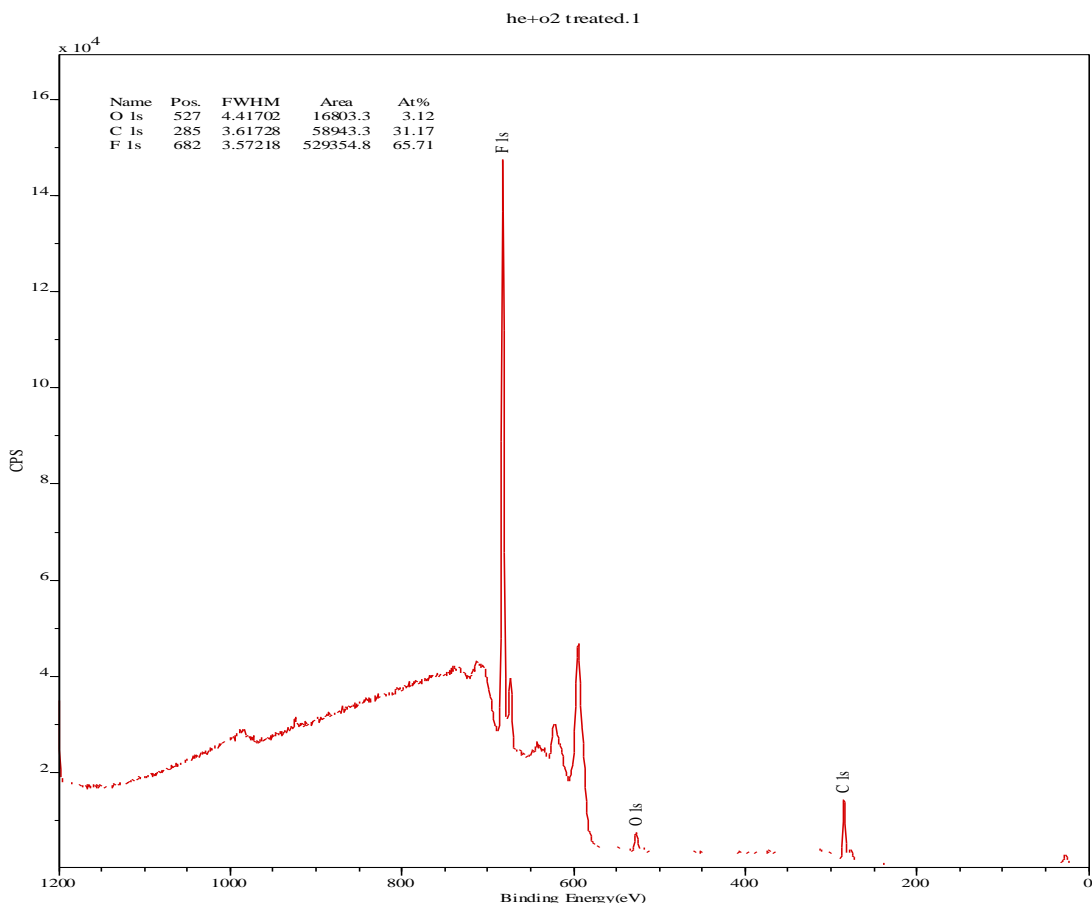
C.1.c XPS Spectrum of Helium-oxygen Plasma Treated FEP Film

C.2 Nitinol Wires

Name	Pos.	FWHM	Area	At%
O 1s	532	4.44853	26348.6	35.69
Ti 2p	458	2.1638	6060.5	2.96
C 1s	285	2.53019	15362.1	59.31
Ca 2p	347	2.52025	2703.0	2.03

CasaXPS (This string can be edited in CasaXPS.DEF/PrintFootNote.txt)
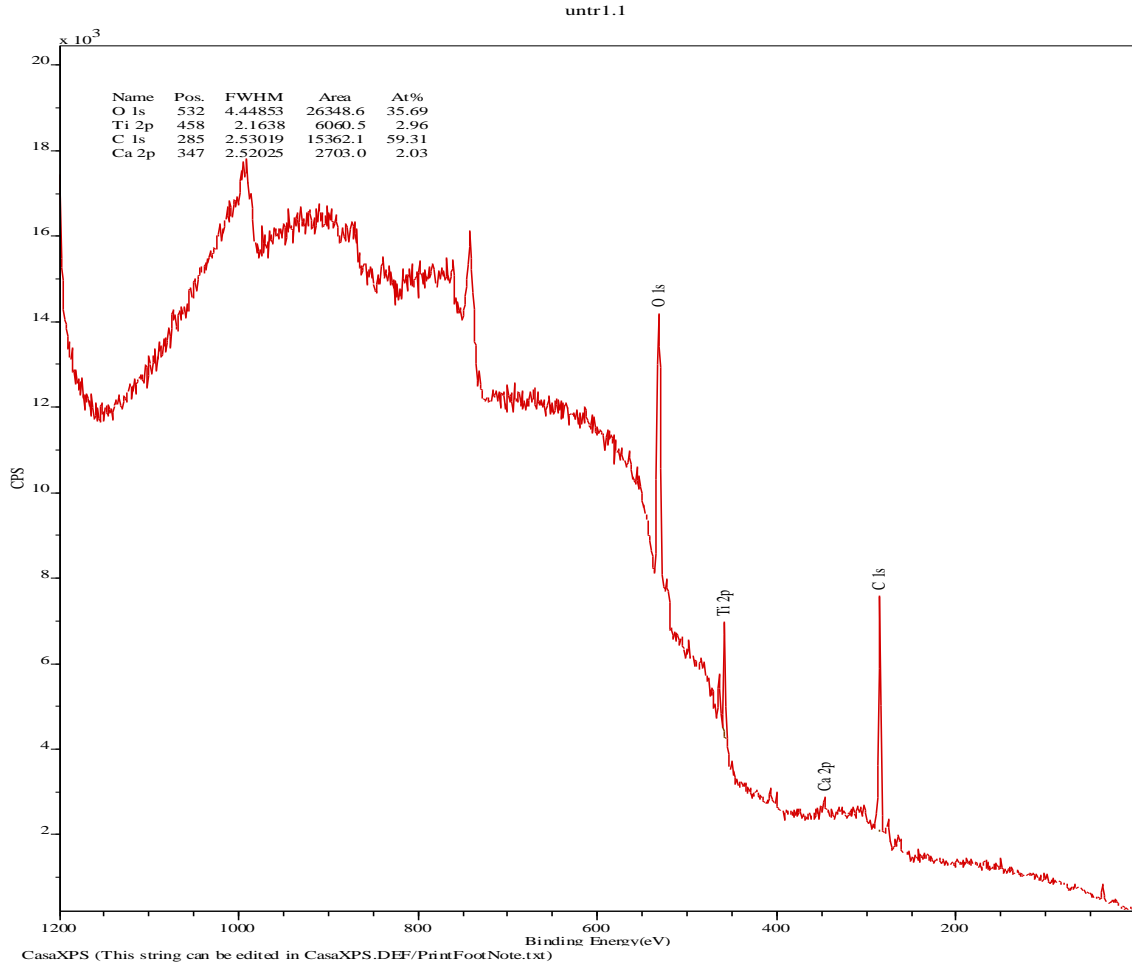
C.2.a XPS Spectrum of Untreated Nitinil Wire

Name	Pos.	FWHM	Area	At%
C 1s	285	2.08879	9643.8	32.40
O 1s	531	3.62634	36370.0	42.88
F 1s	685	2.57546	16168.4	12.75
Ti 2p	459	2.0074	20836.4	8.86
Zn 2p	1023	2.80986	6123.1	0.75
Ca 2p	348	2.65366	3590.6	2.35
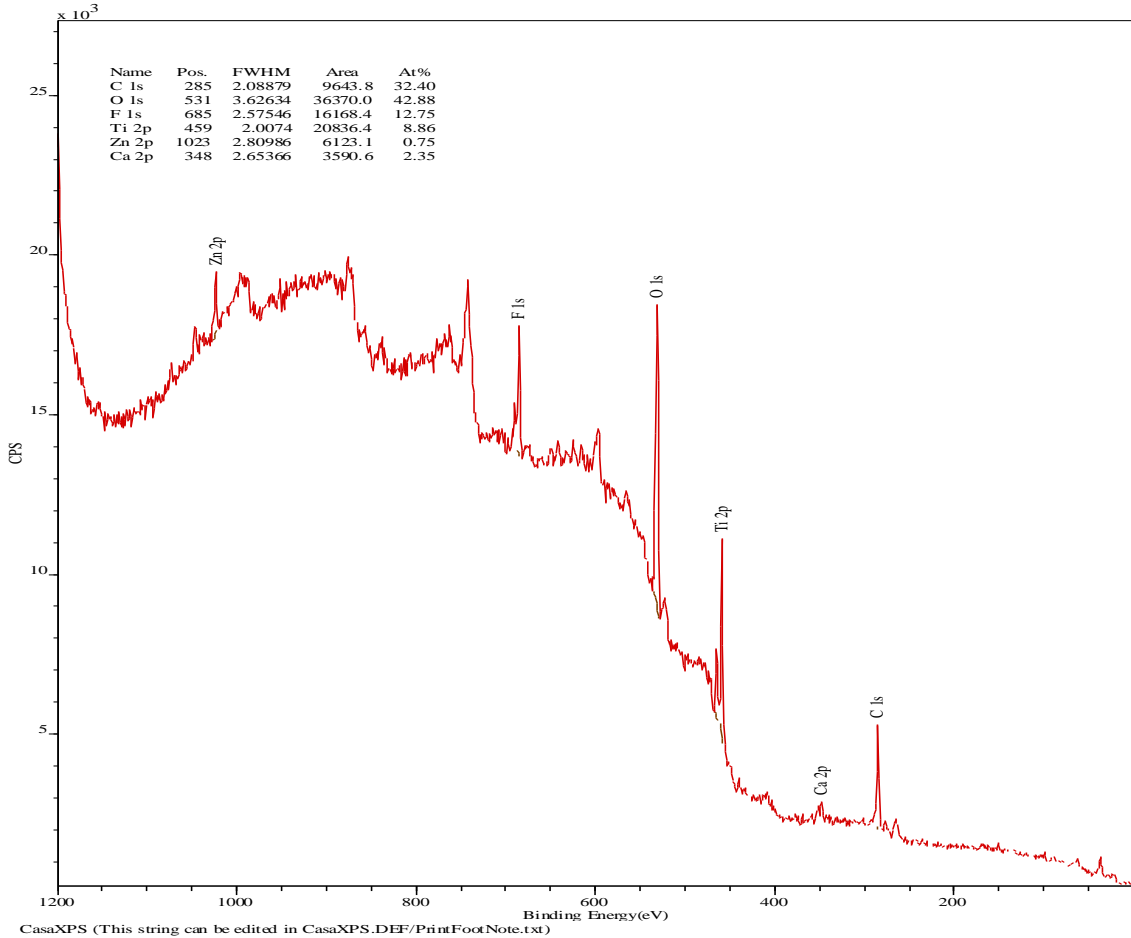
CasaXPS (This string can be edited in CasaXPS.DEF/PrintFootNote.txt)

C.2.b XPS Spectrum of Helium-plama Treated Nitinil Wire

Name	Pos.	FWHM	Area	At%
F 1s	690	4.2328	95159.2	57.71
O 1s	533	4.01774	14702.5	13.33
C 1s	292	5.27697	9217.7	23.82
Ti 2p	459	2.42213	5862.8	1.92
Si 2p	99	2.16086	1079.8	3.23

CasaXPS (This string can be edited in CasaXPS.DEF/PrintFootNote.txt)
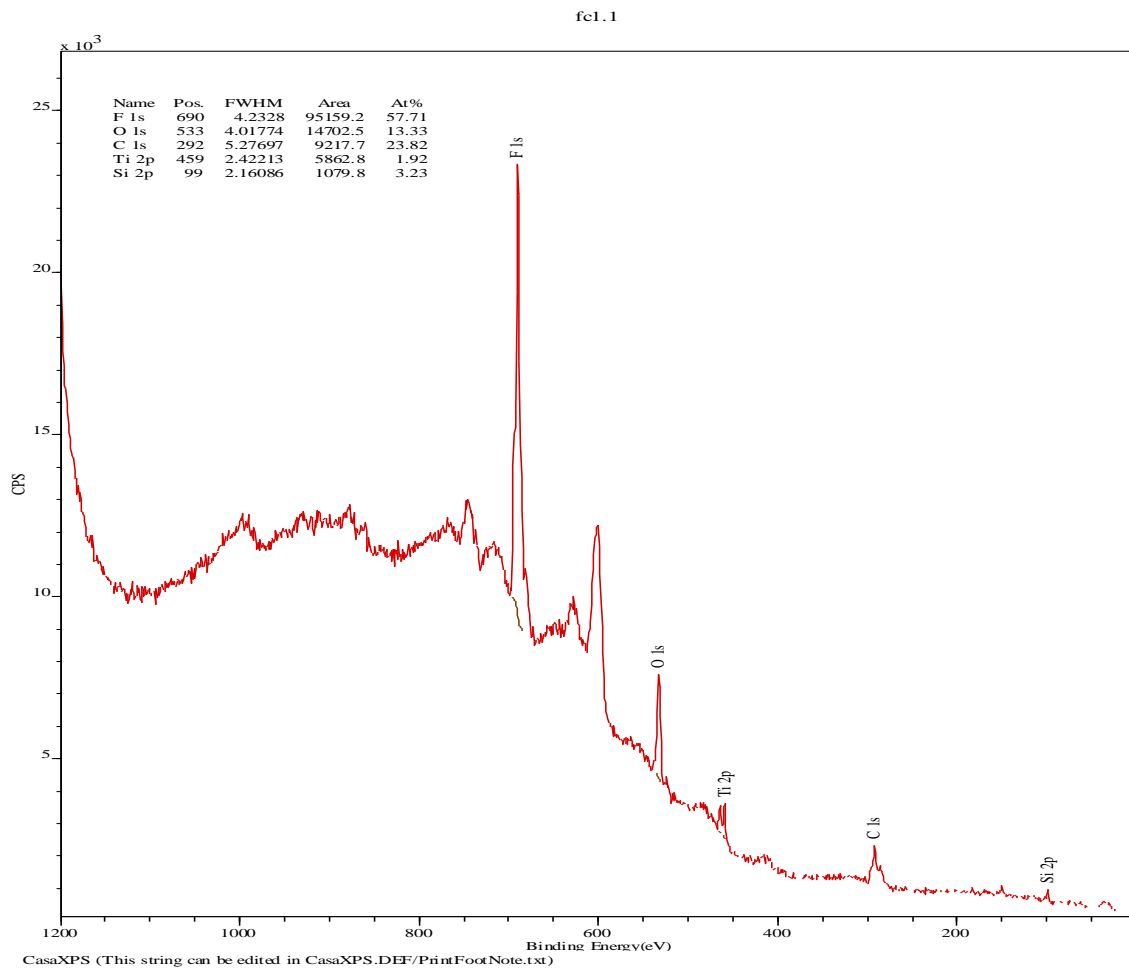
C.2.c XPS Spectrum of Fluorocarbon(FC)-coated Nitinil Wire

mech1.1

Name	Pos.	FWHM	Area	At%
C 1s	285	2.47979	18303.7	62.63
O 1s	532	4.39775	27684.3	33.24
Ti 2p	458	2.22334	6821.5	2.95
Ca 2p	347	2.80611	1754.7	1.17
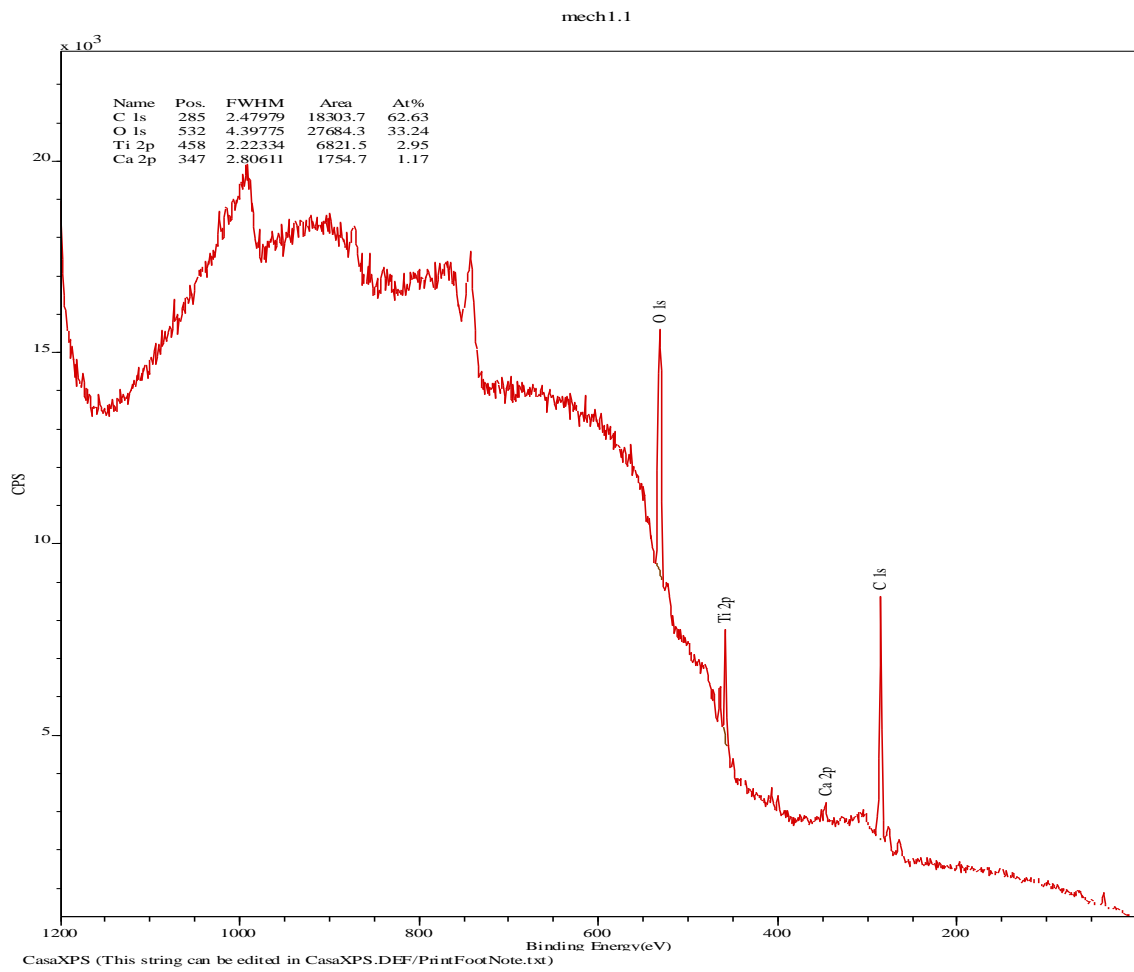
C.2.d XPS Spectrum of Mechanically-roughened Nitinil Wire

Appendix D: Contact Angle Measurement

D.1 Contact Angle Measurements of FEP Films

Untreated		Helium-plasma Treated		Helium-oxygen-plasma	
Angles (°)		Angles (°)		Angles (°)	
UN-1a.txt	98	He-1a.txt	68	O2-1a.txt	80
UN-1b.txt	94	He-1b.txt	85	O2-1b.txt	89
UN-2a.txt	92	He-1c.txt	66	O2-2a.txt	86
UN-2b.txt	93	He-2a.txt	74	O2-2b.txt	86
UN-2c.txt	92	He-2b.txt	89	O2-2c.txt	96
UN-3a.txt	93	He-2c.txt	92	O2-2d.txt	83
UN-3b.txt	108	He-2d.txt	98	O2-2e.txt	84
UN-4a.txt	107	He-2e.txt	80	O2-2f.txt	82
UN-4b.txt	107	He-3a.txt	96	O2-3a.txt	84
UN-5a.txt	108	He-3b.txt	94	O2-3b.txt	81
UN-5b.txt	109	He-3c.txt	93	O2-3c.txt	86
UN-6a.txt	111	He-3d.txt	85	O2-3d.txt	79
UN-6b.txt	114			O2-4a.txt	79
UN-7a.txt	106			O2-4b.txt	77
UN-7b.txt	105			O2-4c.txt	78

D.1 (continued)

UN-7c.txt	106			O2-4d.txt	76
UN-7d.txt	105			O2-4e.txt	79
UN-8a.txt	108			O2-4f.txt	76
UN-8b.txt	110				
UN-8c.txt	106				
UN-8d.txt	108				
Average	**104**	**Average**	**85**	**Average**	**82**
SD	**7**	**SD**	**10**	**SD**	**5**

Appendix E: Mechanical Pull-out Test

E.1 The Results of Pull-out Test
(Load: N)

	Un-wire/ Un-film	Un-wire/ He-film	Un-wire/ HeO2-film	He-wire/ Un-film	He-wire/ He-film	He-wire/ HeO2-film	FC-wire/ Un-film	FC-wire/ He-film	FC-wire/ HeO2-film	Mech-wire/ Un-film	Mech-wire/ He-film	Mech-wire/ HeO2-film
#1	26.3	32.4	26.6	32.5	22.2	29.3	4.70	4.90	4.80	29.4	35.6	32.8
#2	31.5	28.0	28.7	25.6	17.5	18.3	8.00	4.60	4.10	28.0	36.4	31.7
#3	31.0	32.2	31.5	30.4	21.9	19.3	4.20	5.30	4.60	30.2	32.7	33.9
#4	33.6	34.2	28.4	29.8	31.3	18.1	3.70	5.10	5.30	28.6	34.3	32.2
#5	28.6	33.8	27.9	30.2	24.7	23.1	5.10	4.50	4.40	32.0	35.1	29.9
#6	31.7	31.7	27.3	30.8	27.1	31.6	3.60	6.40	5.40	32.6	35.5	32.6
Mean	30.5	32.05	28.4	29.9	24.1	23.3	4.88	5.13	4.77	30.1	34.9	32.2
Standard Deviation	2.4	2.0	1.6	2.1	4.3	5.4	1.5	0.63	0.46	1.7	1.2	1.2

Appendix F: P-values of the Pull-out Test Results Using a Student T-test

F.1 P-values of the Pull-out Test Results Using a Student T-test

| | : Significantly Different | | : Not Significantly Different |

	Un-wire/ Un-film	Un-wire/ He-film	Un-wire/ HeO2-film	He-wire/ Un-film	He-wire/ He-film	He-wire/ HeO2-film	FC-wire/ Un-film	FC-wire/ He-film	FC-wire/ HeO2-film	Mech-wire/ Un-film	Mech-wire/ He-film	Mech-wire/ HeO2-film
Un-wire/ Un-film												
Un-wire/ He-film	0.28											
Un-wire/ HeO2-film	0.14	0.01										
He-wire/ Un-film	0.70	0.13	0.23									
He-wire/ He-film	0.02	0.02	0.08	0.03								
He-wire/ HeO2-film	0.03	0.01	0.09	0.04	0.79							

F.1 (continued)

	Un-wire/ Un-film	Un-wire/ He-film	Un-wire/ HeO2-film	He-wire/ Un-film	He-wire/ He-film	He-wire/ HeO2-film	FC-wire/ Un-film	FC-wire/ He-film	FC-wire/ HeO2-film	Mech-wire/ Un-film	Mech-wire/ He-film	Mech-wire/ HeO2-film
FC-wire/ Un-film	1.8e-08	1.2e-09	3.0e-10	4.2e-09	7.2e-05	3.8e-5						
FC-wire/ He-film	7.4e-07	1.3e-07	2.1e-08	3.1e-07	1.6e-4	5.9e-4	0.74					
FC-wire/ HeO2-film	1.1e-06	2.7e-07	6.9e-08	5.7e-07	1.6e-4	5.6e-4	0.87	0.32				
Mech-wire/ Un-film	0.81	0.13	0.12	0.84	0.03	0.03	2.9e-10	3.4e-08	9.7e-08			
Mech-wire/ He-film	0.01	0.02	3.0e-05	1.6e-3	2.0e-3	4.1e-3	2.1e-11	7.1e-11	7.6e-10	5.6e-4		
Mech-wire/ HeO2-film	0.19	0.90	1.8e-3	0.07	0.01	0.01	4.6e-11	2.6e-10	2.2e-09	5.5e-2	4.7e-3	