2007

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HYDROGEN PLASMA SURFACE MODIFICATION
OF POLYTETRAFLUOROETHYLENE

A Thesis

Presented to

The Faculty of the Department of Chemical and Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Brian Keith McCoy

May 2007

UMI Number: 1445249

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ABSTRACT

HYDROGEN PLASMA SURFACE MODIFICATION OF
POLYTETRAFLUOROETHYLENE

by Brian K. McCoy

Polytetrafluoroethylene (PTFE) was treated in a glow discharge hydrogen plasma and the subsequent surface modifications were evaluated by contact angle measurement, atomic force microscopy (AFM), and x-ray photoelectron spectroscopy (XPS). The wetting behavior of several test liquids increased with continued exposure to hydrogen plasma. Hydrogen plasma treating the PTFE surface led to an increase in surface tension, as calculated from contact angle data. Surface roughness decreased with increased exposure to the hydrogen plasma. Surface analysis by XPS detected the loss of fluorine and binding of nitrogen, oxygen, and carbon functional groups. Longer plasma treatment times resulted in a greater loss of fluorine and increased functional group binding. Atmospheric exposure post plasma treatment aided in surface sorption of nitrogen and oxygen groups.

ACKNOWLEDGMENTS

The author wishes to thank Dr. Guna Selvaduray for his guidance and support in seeing this research through to completion and Drs. Steven Shannon and Javad Dorosti for guidance and serving on the thesis committee. The author would also like to thank Dr. Angela Craig of Evans Analytical Group for donating her time and experience with XPS analysis. Finally, the author would like to thank April McCoy for her unwavering support and enthusiasm.

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CHAPTER ONE

INTRODUCTION

The advancement and extended use of medical implants has created dynamic interfacial reactions between synthetic materials and constituents of the human body [1]. A way of mediating these interactions while maintaining the integrity of the implant is to modify the surface of the implant. This method has the potential to allow the tailoring of a surface to obtain specific interactions, whether it is with blood, tissue, bone or biological fluids. A common method for altering the surface properties of polymers is plasma surface modification, which is typically employed to alter adhesion characteristics. This investigation was concerned with altering the interfacial behavior of polytetrafluoroethylene (PTFE) for implantation into a biological environment; however, the results may be of interest to many other industrial applications.

A special area of host/implant compatibility is blood-material interactions (BMI). Extended contact of blood with synthetic materials presents many unique problems, one of which is that the hemostatic* function of blood may be induced by the implanted device's surface. This intrinsic process may respond to the artificial surface as if it were an injured vessel and initiate the blood coagulation cascade, forming blood clots, known as thrombus, which may interfere with the function of the device or biological processes such as circulation [1]. All artificial surfaces in contact with blood induce some level of thrombus, with the degree of blood coagulation induced by the implant determining patient survival rate, implant acceptance/rejection, and the overall bio-functionality [1].

* A biological process that prevents hemorrhaging by coagulating into clots.

The occlusion of an artificial vascular device is generally a problem of adhesion, and therefore surface specific.

While many investigations attempting to correlate specific material properties to thrombogenicity have been completed, there is a lack of definitive clarity on the matter. Materials selection for blood compatibility can be tested, but there are inconsistencies in their behavior. There are many reasons for this, the first being that there are few standardized tests for BMI. Second, similar materials may not exhibit the same level of blood compatibility due to slight variations in surface homogeneity, *e.g.*, charge, topography, and chemistry. Furthermore, variations in blood flow and blood constituents during testing alter the interaction along the implant surface, which challenges the identification of set material characteristics [1-3].

In the case of polymers it has been found that a material's surface tension, charge, chemistry, and roughness are key properties which affect thrombogenicity on implanted surfaces [1, 2]. It has also been suggested that there exists a dedicated range of surface tension that prevents the adhesion of platelets, and is therefore compatible to blood from a thrombogenic perspective [3, 4]. However, there is disagreement as to what that surface tension range is, and if the postulated models follow for homogeneous and heterogeneous surfaces.

This study was undertaken to investigate the chemical and physical effects of hydrogen plasma modification of PTFE, a commonly implanted polymer that exhibits high thermal stability, chemical inertness, low coefficient of friction, and low surface tension [5]. PTFE is currently being researched as a material for small diameter vascular

grafts and coatings on stents. These types of devices require blood to flow through small diameter vessels and stent strut pitches. Even low levels of thrombus on these devices can occlude blood pathways, necessitating a complete evaluation of surface and the corresponding BMI.

The motivation for this work arises from the need to fully characterize the plasma modified PTFE surface before biocompatibility testing in order to gain a fundamental understanding of any relationships that may exist between the two. Understanding how a material interacts within a given biological environment allows for the selection of appropriate materials for implantable devices. Most studies of this kind have attempted to correlate heterogeneous specimens without full evaluation of the surface, which may provide misleading or incomplete results. The intrinsic low surface tension of PTFE enabled the creation of a positive wettability gradient without the need to deposit unique chemistries which may increase the complexity of biocompatibility testing.

This study was accomplished by hydrogen plasma modifying PTFE with varying plasma treatment times to alter the surface roughness, surface tension, and surface chemistry. This research was also aimed at designing a repeatable surface modification protocol, which will be necessary to facilitate future biocompatibility testing. After processing the physical and chemical characteristics of the surface were determined and the results were compared to established theories.

In keeping with the interdisciplinary nature of this study it is appropriate to provide key concepts and related theories. Chapter 2 contains the necessary background information regarding PTFE structure, surface tension, and plasma modification. A review of previous work and theories is contained in Chapter 3. The hypothesis and research objectives are addressed in Chapter 4, and the experimental methodology is presented in Chapter 5. The experimental results can be found in Chapter 6, and a discussion of the values in regard to previous work is in Chapter 7. Conclusions and recommendations for future work are presented in Chapter 8.

CHAPTER TWO

BACKGROUND

What began as a waxy deposit in the cylinder of a refrigerant gas has since become the polymer of choice for many industrial and medical applications. The adventitious discovery of PTFE in 1938 by Dr. Roy Plunkett conferred a unique class of polymers, fluoropolymers, which have since found use in everything from missiles to frying pans [6]. The prolific use of PTFE can be explained by its extraordinary properties of chemical inertness and low coefficient of friction, both of which are a result of chemical structure and processing conditions. In this chapter the background information on the structure and properties of PTFE, as well as surface theory, plasma generation, and polymer surface modification, are presented.

2.1 PTFE Structure and Properties

PTFE is a carbon backbone polymer that is readily synthesized by emulsion polymerization of tetrafluoroethylene, forming repeating linear chains of $(-\text{CF}_2-\text{CF}_2-)_n$ which is illustrated in Figure 1. This atomic arrangement conforms to a helical carbon backbone with a dihedral angle between 160° and 165° , forming a complete sheath of fluorine atoms around the carbon backbone, as depicted in Figure 2 [6]. High fluorination of the carbon backbone decreases the amount of unfulfilled bonds, leading to a polymer with a low intrinsic surface tension of 22.5 mN/m [6]. PTFE covalent bond energies are among the strongest in single bond organic chemistry, with C-F bond energies of 481 kJ/mol (4.99 eV/atom) and C-C bond energies of 348 kJ/mol (3.61

eV/atom), making them harder to dissociate as compared to other single bond polymers [6]. The steric effects of the fluorine atoms perfectly balance the charges across the polymer chain cross section and are therefore non-polar. High bond energies, non-polar structural arrangement, and tight intermolecular packing are responsible for PTFE's chemical inertness.

Figure 1. Illustration of the polymerization of tetrafluoroethylene into PTFE.

Figure 2. Illustration of a PTFE chain, a carbon core surrounded by fluorine atoms.

The tightly packed polymer morphology facilitates chain alignment, allowing high polymer crystallinities of 70-90% [6]. Bond forces between two adjacent polymer chains are significantly lower than the forces within one chain, which are typically 3 kJ/mol [6]. This low molecular cohesion is partially responsible for a coefficient of

friction of 0.1, the lowest of any material; however, it also facilitates mechanical creep due to chain movement [6]. The unbranched morphology and low interpolymer chain attraction requires very long chain lengths, increasing the melting point of PTFE to nearly 300 °C [6].

2.2 Surface Tension

Surfaces are distinctly different from the bulk because there are no neighboring atoms or ions bound on one side. This may leave unfulfilled bonds at the surface, which in turn affect the interactions with the material's surroundings. These unfulfilled bonds are stored energy, which is historically referred to as surface tension (γ), but is technically the excess specific surface free energy [7]. This is because it is the energy associated with a certain area of surface that deviates from the ideal, such as a change in the number of nearest neighbors. Surface tension is an interfacial “tension” because the surface is merely a boundary between two phases, such as a liquid/gas boundary. Systems with lower surface tension are thermodynamically more stable, so high surface tension systems tend to bond in order to decrease their excess free energy.

Thermodynamically, surface tension is the net work required to reversibly transfer matter from the bulk to the surface, and thereby increase the surface area, as defined in Equation 1:

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{T,P,n} \quad \text{Equation 1}$$

where G is the Gibbs free energy of the total system, A the interfacial area, T the temperature, P the pressure, and n the total number of moles [7-10]. Helmholtz free

energy (F) is often substituted for Gibbs free energy (G) in Equation 1 because surface studies are conducted at constant volume. Although it is the excess free energy per unit area at the surface with actual units of J/m^2 , it is generally reported under the mechanical analog of force per unit length with units of mN/m .

There is often confusion regarding the differences between surface tension, surface energy, and surface free energy. Surface tension is an excess energy component, whereas surface energy and surface free energy are not. Surface energy (u^s), also termed specific surface energy, is the internal energy of the surface (U^s) divided by the area:

$$u^s = \frac{U^s}{A} \quad \text{Equation 2}$$

Surface free energy (f^s), also known as the specific surface free energy, is the surface Helmholtz free energy (F^s) divided by the area, as see in Equation 3:

$$f^s = \frac{F^s}{A} \quad \text{Equation 3}$$

For a two component solute/solvent system in equilibrium, f^s is related to γ by

Equation 4:

$$\gamma = f^s - (\Gamma_1 \mu_1 + \Gamma_2 \mu_2) \quad \text{Equation 4}$$

where Γ is the surface concentration^{*} and μ the chemical potential, with subscripts 1 and 2 denoting each component[†]. A complete thermodynamic derivation of Equations 2-4 is given by Ip and Wu [8, 10].

^{*} Number of moles divided by the area

[†] It should be stated that μ_1 and μ_2 are the same value in equilibrium

The confusion between surface free energy and surface tension often occurs when Equation 4 is solved for a single species, rather than a multi component system. Through evaluation of Equation 4, the surface free energy can only be equal to the surface tension if there is no adsorption of component 2 at the surface of component 1. For $\Gamma_1\mu_1 + \Gamma_2\mu_2$ to be zero a pure liquid must be in contact with only its own vapor, where the activity of component 1 becomes unity and the chemical potential of component 1 is zero. This is impossible because of the air associated with the vapor, which cannot be completely evacuated, which creates a multi component system [8, 10]. Since surfaces are defined as phase boundaries, all surfaces reside in multi component systems.

Surface tension is the sum of two distinct forces, dispersive (γ^d) and polar (γ^p), where $\gamma = \gamma^d + \gamma^p$ [7,10]. Dispersive forces, also known as London forces, are the result of transient charges spontaneously generated over the atom and molecular chain. Although PTFE has zero net charge across the chain, this is an average of electron interaction over time. At any given instantaneous time the electrons may be interacting across the interatomic bond, causing dispersive forces. On the other hand, polar forces are due to permanent dipole or induced dipole interactions. Polar surfaces are often hydrophilic, while dispersive forces are often hydrophobic.

In the case of liquids, surface atoms have high mobility and are able to achieve an equilibrium state through the reduction of surface area [7, 10]. However, atoms on the surface of a solid have low mobility and are unable to reduce their surface area, creating a two component surface stress (τ) of surface tension and mechanical surface stress. For an

isotropic solid that is unable to reach an equilibrium shape the surface stress (τ) is given by Equation 5:

$$\tau = \gamma + \frac{A \partial \gamma}{\partial A} \quad \text{Equation 5}$$

where τ is the total surface stress, and A is the area [7]. It is not possible to measure the surface stress of the solid directly and there are no methods for decoupling mechanical surface stresses from the surface tension. For this reason, τ is often referred to as the solid surface tension (γ_s). For liquids, the second term in Equation 5 goes to zero, and therefore the surface tension is equal to the surface stress.

If there is a liquid-solid interface, then adhesion between the two can be partly determined by the corresponding interfacial tension. If the atoms in the liquid have a stronger attraction to the surface atoms of a solid, rather than among themselves, then wetting of the surface occurs. A de-wetting surface is just the opposite, where the atoms in the liquid are more strongly attracted to each other than to the surface of the solid and therefore do not wet the surface.

One approach to measuring the wetting phenomenon, and therefore estimating the interfacial tension, is by placing a drop of liquid on a solid's surface and measuring the contact angle (θ) between the solid and the tangent to the droplet, as illustrated in Figure 3, where γ_{sv} , γ_{lv} , γ_{sl} are the interfacial energies and subscripts S, L, and V denote the solid, liquid and vapor phases, respectively. The droplet's shape in Figure 3 conforms to the solid substrate so that there is a minimum total interfacial energy at the liquid-solid-vapor boundaries. Measurement of contact angles yield data which reflect the thermodynamics of a liquid/solid/vapor interaction. A surface that is completely wet by water would have

a contact angle of 0° , while for hydrophilic surfaces $\theta < 90^\circ$, and for hydrophobic surfaces $\theta > 90^\circ$ [9]. Because the solid/liquid/vapor phases are in equilibrium it is possible to derive a force balance equation, Equation 6, also known as Young's equation, using the contact angle of the liquid:

$$\gamma_v = \gamma_l + \gamma_v \cos \theta \quad \text{Equation 6}$$

Figure 3. Illustration of the equilibrium force balance and contact angle of a liquid on a solid surface.

The morphology of the solid surface and size of the liquid drop also contribute to the contact angle [7]. Surface roughness may alter the contact angle in one of two ways. First, as compared to a smooth surface, the rough morphology may impede the advancing contact angle. This will cause hysteresis between advancing and receding contact angles. Second, the surface area of a rough surface is larger than that of a smooth surface; therefore the liquid drop encounters more surface area for the same drop circumference. The size of the liquid drop has also been observed to alter the contact angle, whether through gravitational force or evaporation. Larger volumes of test liquid experience a greater deformation and have been observed to have a plateau rather than a hemispherical

shape. This hinders direct comparison of contact angle data, as many authors fail to fully describe experimental protocol.

What is of interest to this investigation is the solid surface tension (γ_s), as γ_{lv} is easily measured through one of several ways, *e.g.*, pendant drop or Du Nouy ring. Most solids in contact with vapor have a limited amount of vapor adsorption which lowers the surface tension of the substrate, such that γ_s is not equal to γ_{sv} . As can be seen in Figure 3, there is a tensor force, γ_{sv} , acting in the opposite direction of the drop, along the substrate. In addition to γ_{sv} there is another tensor component, the equilibrium spreading pressure (π_e), which acts in the same direction as γ_{sv} , where π_e is the decrease in solid surface tension due to vapor adsorption, as seen in Equation 7:

$$\gamma_{lv} \cos \theta = \gamma_s - \gamma_{sl} - \pi_e \quad \text{Equation 7}$$

Therefore the solid surface tension (γ_s) is equal to the sum of the solid/vapor interfacial tension and the equilibrium spreading pressure, as seen in Equation 8:

$$\gamma_s = \gamma_{sv} + \pi_e \quad \text{Equation 8}$$

Most methods of estimating γ_s are based on calculation of the surface tension for a liquid that completely wets the surface. Many empirical methods have been used to estimate γ_s , such as Owens-Wendt, Zisman, Acid-Base theory, etc. These have been thoroughly examined in textbooks [7, 10]. However, the method used in this investigation, the Harmonic Mean Theory, will be described. The harmonic mean, Equation 5, is one of three Pythagorean means which is always smaller than the arithmetic mean and larger than the geometric mean:

$$H(X_1, \dots, X_n) = \frac{n}{\frac{1}{X_1} + \dots + \frac{1}{X_n}} \quad \text{Equation 9}$$

where H is the harmonic mean, X represents the term to be averaged, and n is the number of terms to be averaged.

The Harmonic Mean Theory divides the surface tension into two components, dispersive (γ^d) and polar (γ^p), and mathematically sums their contributions. Combining Equations 6, 8, and 9 for two liquids yields Equations 10 and 11:

$$(1 + \cos \theta_1) \gamma_1 = 4 \left[\frac{\gamma_1^d \gamma_s^d}{\gamma_1^d + \gamma_s^d} + \frac{\gamma_1^p \gamma_s^p}{\gamma_1^p + \gamma_s^p} \right] \quad \text{Equation 10}$$

$$(1 + \cos \theta_2) \gamma_2 = 4 \left[\frac{\gamma_2^d \gamma_s^d}{\gamma_2^d + \gamma_s^d} + \frac{\gamma_2^p \gamma_s^p}{\gamma_2^p + \gamma_s^p} \right] \quad \text{Equation 11}$$

where subscripts 1 and 2 denote the testing liquids used. γ_1 and γ_2 are known via published values or direct measurement of the liquid surface tension. Contact angles are then measured with two or more test liquids with known γ^d and γ^p . By solving Equations 10 and 11 simultaneously, values of γ_s^p and γ_s^d can be obtained and summing these two components yields γ_s . The harmonic mean method has been shown to accurately predict the surface tension of polymers, with results agreeing well with both the liquid homolog method and polymer melt method [10].

2.3 Plasma

Glow discharge plasma modification of surfaces is an active area of research that attempts to alter surface properties while maintaining the benefits of the bulk material.

Plasma processing treatments are employed to improve wettability, alter adhesion characteristics, and improve flammability. Common examples of products having undergone plasma modification are wool fibers and contact lenses. The depth of surface modification is a function of the power and process gas, but in general modification occurs to a depth of 20-500 Å [11-13].

Plasmas are gaseous uniform collections of ions, neutrals, electrons, radiation, and radicals [12]. Plasma generation can be accomplished in several ways, such as wire/plate electrodes or inductive coils. An illustration of a simple low temperature radio frequency (RF) plasma processing chamber is shown in Figure 4.

Figure 4. A schematic of a simple plasma surface modification chamber.

In general, a substrate is placed between an anode and a cathode, which can be powered by a DC, AC, or microwave voltage source. The chamber is evacuated and some partial pressure of a working gas is introduced at a low flow rate. The working gas serves as a medium for the electrical discharge to be initiated and sustained. Electrons begin to escape from the cathode and gain energy as they travel towards the anode.

These electrons then collide with atoms and molecules in the space between the electrodes, causing excitation, dissociation, and ionization. A glow discharge will be visible in the area between the capacitor plates once a current begins to flow. The plasma species then interact with the chamber and the immersed substrate. Hydrogen gas requires electron energies of 4.5 eV for dissociation and 15.4 eV for ionization [12]. Typical hydrogen gas plasma products are listed in Table I.

Table I. Effects and products of electron collisions with H₂ during plasma generation.

Effect of e ⁻ /H ₂ Collision	Product
Excitation	Photons
Dissociation	H + H
Ionization	H ⁺ , H ₂ ⁺

Plasma modification generally employs “cool” plasmas, where the Boltzmann temperature of the ions and neutrals is close to ambient, while the temperature of the electrons is hundreds to thousands of Kelvin [12]. Ion density is a function of the applied power and the loss of ions to the chamber walls. A charge balance is maintained so that ion densities are equal to electron densities. All reactions are driven by the electron energy distribution, whose function is Maxwellian. Therefore there are a larger number of energetic electrons available for excitation and dissociation, which is between 4-10 eV, than for ionization, which is between 12-25 eV [12].

Ions interact with chamber walls by traversing a sheath that surrounds the plasma. This sheath is caused by the disparity of mass, velocity, and energy between electrons

and ions. Since electrons have greater thermal velocities than ions, they are removed from the plasma at a faster rate. This creates a net positive charge within the plasma. The plasma will then have a positive potential with respect to the chamber wall, creating a sheath potential. In order to maintain a plasma charge balance, ions accelerate from the plasma, through the sheath, into the chamber wall. An electronically isolated substrate placed in the plasma will also form a sheath potential. This phenomenon causes the substrate to be bombarded by ions, radicals, and neutrals in the same manner as the chamber walls, altering the physical and chemical nature of the substrate surface.

RF glow discharge plasmas are typically used in surface modification of polymers because they produce large, uniform, stable volumes of plasma. The typical operating frequency of such plasmas is 13.56 MHz, with discharge pressures ranging from 10^{-3} to 100 torr [13]. Electron/ion densities vary from 10^9 to 10^{11} cm^{-3} for low pressure* systems and may reach 10^{12} cm^{-3} for medium pressure† systems [11].

2.4 Plasma Modification of Polymers

Plasma modification of a polymer surface is a dynamic set of events where a variety of reactions may occur. Energy ranges of plasma species are on the order of 1-20 eV, well above the scission requirement for most single bond polymers [14]. The electromagnetic radiation exhibited in plasma is mostly in the form of the line spectra of the working gas, with UV radiation shown to chemically alter the surface of polymers [15]. Electrons play a major role in plasma excitation, but their effect on

* 10^3 to 1 Torr

† 1 to 100 Torr

polymers has not been verified, although this interaction may be difficult to detect [13,16].

Plasma chemistry changes may occur by various routes, but in general fluorinated surfaces with hydrogen plasmas will undergo the following polymer radical reactions:

The polymer radicals formed then experience radical transfer, chain scission, recombination, oxidation, and disproportionation [10-15]. The result of these polymer radical reactions is the degradation of the polymer surface in the form of crosslinking, oxidation, ablation, and the grafting of functional groups [10-31].

The surface modification of polymers is a dynamic equilibrium of competing functionalization and degradation processes. Chain scission and crosslinking of the polymer surface are a function of the plasma power, working gas, processing time, and the properties of the polymer. Bombardment of the polymer induces small molecule degradation of the chain, lowering the molecular weight through scission, and therefore lowering the glass transition temperature and viscosity of the surface layers. This phenomenon improves bonding/adhesion by creating a layer that accommodates interdiffusion and interfacial flow. The creation of bonding sites through chain scission also allows the formation of surface polar groups and oxidation, which alters surface characteristics by creating localized charge sites and chemical heterogeneity. In the case of PTFE, a non-polar polymer, this may induce adhesion and bonding as a method of

reducing the excess surface free energy and alleviating charge. Recombination of polymer radicals crosslinks chains, increasing the molecular weight of the polymer. An increase in molecular weight will increase γ_s , scaling with Equation 13:

$$\gamma = \gamma_{\infty} - \frac{k_e}{M_n^{2/3}} \quad \text{Equation 12}$$

where γ_{∞} is the surface tension at an infinite molecular weight, k_e is a constant, and M_n is the molecular weight [10].

The incorporation of polar groups and oxidation grafted to polymer radicals is a commonly cited phenomenon [11-14, 26]. This occurs both during plasma treatment and the subsequent exposure to ambient air after processing. Typical polar groups found via X-ray photoelectron spectroscopy (XPS) studies are oxygen groups, such as carbonyls and hydroxyls, and nitrogen groups, such as nitriles and amides [11-14, 26].

CHAPTER THREE

REVIEW OF EXISTING PLASMA SURFACE MODIFICATION THEORIES

In this review of existing PTFE plasma surface modification theories past research has been assembled in order to determine what has been accomplished. There are no general data for the plasma treatment of polymeric materials because the modification effects depend on the plasma equipment and the nature of the plasma [17,18]. The plasma equipment used varies greatly in the studies, from test tubes with inductor coils to commercial plasma systems designed for semiconductor use. Often the experimental parameters are hardly reported and the plasma tool is treated as a researcher's black box. Common plasma parameters such as ion energy, ion flux, sheath potentials, or ion saturation currents are generally not given. This may be due to two reasons, the first being that plasma diagnostic equipment is relatively expensive and requires chamber ports for access to the plasma, such as a Langmuir probe or Faraday cup. Second, voltage and current characteristics of plasmas may not give complete evaluation of plasma used for modification because of radiation effects, mostly UV, which cannot be decoupled and analyzed individually. However, a review of previous research is necessary as it provides a range of process parameters and resulting surface characteristics which can be compared for theoretical justification.

This chapter is a review of existing research on the effect of PTFE plasma surface modification on surface tension, followed by the effects on surface chemistry, and ending with the effects on surface morphology. Specific process conditions and the results obtained from various researchers are included where found.

3.1 Surface Tension

It has been shown by several authors that increased exposure to glow discharge plasmas leads to a decrease in the liquid contact angle of polymers, producing a more hydrophilic surface until some plateau value has been reached [19, 20, 21]. The testing liquid of choice in most studies is DI water, and in some cases phosphate buffered saline solution (PBS). Table II is a summary of past research done in this area, with brief descriptions of the process parameters and the range of water/PTFE contact angles measured by each researcher.

Wilson and coworkers RF plasma treated PTFE with 50 W Argon ions and found that their process significantly increased the wettability of the PTFE surface. They measured an initial water/PTFE contact angle of 108° and, after plasma processing, a contact angle of 62° [22]. Sharma and Hari modified various polymers with glow discharge argon plasma with unknown parameters for a period of 7.5 minutes [23]. They measured a decrease in the DI water contact angle of PTFE from 115° to 82° occurred upon treatment. Hu *et al.* conducted similar research with industrial PTFE and hydrogen plasmas and found a decrease in DI water contact angle from 120° to 81° after a 60 s, 10 W plasma treatment [27].

Table II. Comparison of PTFE plasma processing conditions and results for various authors.

Author	Power (W)	Pressure (Torr)	Time (s)	Gas	Flow Rate (sccm)	Result	Effect of Plasma Treatment, as Measured by DI Water Contact Angle (°)	
							Before	After
Sharma [23]	-	-	450	-	-	Decrease in contact angle	115	81
Chen [24]	110	0.05	45	O ₂ , NH ₃ , (NH ₃ +O ₂)	50	Decrease in contact angle	105	60
Konig [25]	50-500	1.5	5-60	CO ₂ , H ₂ /H ₂ O, H ₂ O (vapor)	-	Decrease in contact angle	110	75
Wilson [22]	3.36	0.007	60	O ₂ , Ar, N ₂ , NH ₃	85	Decrease in contact angle	108	62
Vandencastele [26]	10-90	0.056	0-35 min	N ₂	-	Decrease in contact angle	100	37
Schick [29]	20	0.056	-	Ar	-	Defluorination	-	-
Dai [20]	30-35	-	50- 120	H ₂ O, MeOH, n-Hexane	-	Defluorination	-	-
Kang [21]	28	0.04	5-40	Ar	-	Decrease in contact angle	-	-
Triolo [31]	500	-	5-30	Ar	-	Decrease in contact angle	110	83
Hu [27]	30, 50	0.03, 0.05, 0.07	60	Ar, O ₂ , H ₂	-	Decrease in contact angle	120	81

Plateau values of contact angles were usually obtained after some exposure time. Reported initial and final contact values varied, depending on process, where initial DI water contact angles were found to be 100° to 120° and final contact angles between 37° and 83°. The general observation is that a polymer with an intrinsic hydrophobic nature will become increasingly hydrophilic with prolonged exposure* to RF plasma process [10, 17-27].

3.2 Surface Chemistry

The chemistry of plasma treatments on PTFE have been studied by many authors. Ryan and Badyal verified by X-ray photoelectron spectroscopy (XPS) that plasma treatments lead to defluorination, the production of hydrocarbons, cross-linking, chain scission, and the grafting of oxygen and nitrogen containing groups [28, 29]. Wilson *et al.* also completed work studying the effects of plasma treatment on PTFE where they also concluded that there was significant defluorination and subsequent cross linking [22, 30]. By XPS they measured a peak binding energy of 291.8 eV in the untreated PTFE specimen, correlating to [-CF₂-] bonding, which was greatly reduced in intensity after plasma treatment. The treated samples then exhibited a high intensity value located at 285 eV, correlating to increased [-C-C-] bonding. Chen and coworkers found that XPS results indicated the presence of oxygen and nitrogen containing groups on the plasma treated surfaces [24]. Clark and Hutton also found that hydrogen plasmas lead to rapid defluorination of PTFE to a depth of 20 Å [14]. Triolo and Andrade studied the effect of RF plasma treatment on PTFE sheathed catheters. Their results indicated increases in

* Or increasing power.

oxygen concentration at the surface of the polymers with increased plasma exposure time [31].

3.3 Surface Morphology

Wilson and coworkers determined their argon RF plasma process leads to a 20-50% increase in surface area, but also concluded that increased roughness had little effect on the surface tension [22]. No deep channels or grooves were made during the plasma process. They found this through plasma processing Teflon plumber's tape, which may not be indicative of medical grade PTFE. Teflon sheets supplied to Wilson had a typical roughness in the micron scale and plasma treatments may not have led to any appreciable difference in surface roughness. Plasma modification work completed by Triolo and Andrade found no apparent changes in surface topography via scanning electron microscopy, although it should be noted this was subjective analysis [31].

3.4 Summary

Plasma surface modification in various polymer/gas systems has been shown to:

- a) Decrease the contact angle of DI water
- b) Increase the surface roughness
- c) Alter the chemistry of the surface through crosslinking and the introduction of polar hydrocarbons and other moieties.

While many works have been completed on plasma modification of PTFE, none have used a hydrogen gas/medical grade PTFE combination. Furthermore, a complete evaluation of the surface tension after plasma modification has not been completed in any

of the previous studies, merely DI water contact angle. There is also a lack of surface morphology studies correlating physical alteration, as characterized by surface roughness, to plasma processing and its effect on surface tension.

CHAPTER FOUR

RESEARCH HYPOTHESIS

4.1 Research Hypothesis

Based on the literature review and theoretical considerations the hypothesis of this investigation is that hydrogen plasma surface modification of PTFE will alter the surface tension, surface chemistry, and surface morphology.

4.2 Research Objectives

There do not appear to be any significant studies relating PTFE plasma processing to surface tension. The principle objective of this study was to evaluate changes in the surface tension, surface chemistry, and surface morphology induced by hydrogen plasma treatment. A corollary objective was to define a reproducible protocol for hydrogen plasma surface modification of PTFE to facilitate future biocompatibility testing.

CHAPTER FIVE

EXPERIMENTAL METHODOLOGY

5.1 Experimental Overview

The experimental plan was divided into 4 major categories: initial surface characterization of the as received PTFE, definition of a specimen cleaning protocol, plasma surface modification of PTFE coupons, and surface characterization of the plasma treated PTFE coupons. A flow chart of the experimental procedure is shown in Figure 5. In all cases, surface characterization entailed evaluation of the surface tension via liquid/PTFE contact angle measurement, surface chemistry via XPS analysis, and surface morphology via AFM.

5.2 Materials and Methods

PTFE coupons of 2.54 cm diameter and 0.25 cm thickness were obtained from United States Plastic Corporation (Lima, OH). These coupons were manufactured from raw virgin stock in accordance with US-FDA ISO 10993-1, a standard developed for medical device and dental materials. All coupons were cleaned in an ultrasonic bath of 50% ethanol (EtOH) and 50% DI water for 15 minutes prior to plasma processing. Each coupon was then affixed to a 5 cm² microscope slide with 3M double sided tape. Only one side of each coupon was plasma treated

A Gatan SolarusTM Model 950 plasma chamber was utilized for all PTFE processing. This unit incorporates a variable forward and reflective 13.56 MHz RF power supply, capable of a forward range of 0-65 W and reflective range of 0-50 W.

Figure 5. Flow chart of experimental procedure.

The cylindrical processing chamber measures 8.9 cm diameter and 5.0 cm deep, with ports for both vacuum and process gas, as illustrated in Figure 6. For all experiments, the chamber was evacuated to 5×10^{-3} mTorr and backfilled with 99.995% pure H_2 to 50 mTorr, flowed at 20 sccm. The delivered power was held constant at 25 W. Processing time was the main variable, with times of 1, 3, 10, 20, 40, 80, and 160 s. Directly after plasma treatment the coupons were submitted for contact angle measurement, XPS, or AFM analysis.

Figure 6. Top down and side view of Solarus™ plasma chamber illustrated to show specimen placement within the chamber.

5.3 Characterization

5.3.1 Surface Tension

A Dataphysics Model OCA 20 Contact Angle Meter was utilized for all static sessile drop contact angle measurements which were conducted in a climatized room at 72 F° (22 C°) with controlled humidity of 37%. The PTFE/liquid contact angle was measured using a drop volume of 2 μ L with three different test liquids: dimethyl sulfoxide (DMSO), diiodomethane, and ethylene glycol, obtained from Science Lab (Houston, TX). The surface tension of each liquid (γ_l) was verified via a SITA Science Line T60 bubble tensiometer before contact angle measurements were conducted.

A series of contact angle images were taken at a frame rate of 0.2 s⁻¹ of the corresponding PTFE/test liquid interface, just as the drop touched down. Contact angle measurements were then made of the equilibrium* drop according to Laplace-Young curve fitting, as explained in Appendix A. Four measurements of each test liquid were made across the width of each coupon, with 3 specimens replicated for each plasma treatment time. PTFE coupon surface tension was then calculated using the harmonic mean equation. An example of a harmonic mean calculation is included in Appendix B.

*Equilibrium value reached at the inflection point between advance and receding contact angles

5.3.2 Surface Chemistry

The surface chemistry of the PTFE specimens was assessed utilizing X-ray Photoemission Spectroscopy (XPS). The XPS analysis was carried out in a PHI Quantum 2000 under ultra high vacuum. Spectra were acquired using a monochromated AlK_α anode (1484.6 eV) operating at 93.9 W with acceptance and take-off angles of $\pm 23^\circ$ and 45° respectively. A 1400 x 300 μm area was scanned on each coupon, with wide surveys acquired at 187.85 eV and pass energy. C1s, O1s, N1s, F1s, Si2p, and S2p spectra were acquired with pass energies of 93.9 eV and 23.5 eV.

The data acquisition protocol for each sample was as follows: a 3 minute survey scan; a high resolution scan of the C1s signal only; high resolution scans of C1s, O1s, N1s, F1s, Si2p, and S2p regions; a 20 minute survey scan; and a final 3 minute survey scan. Initial and final survey scans were used to monitor any large changes in elemental composition within the acquisition time. The C1s high resolution scan was taken immediately after the initial 3 minute scan to minimize changes in the C1s region with analysis time.

5.3.3 Surface Topography

Surface topography of the coupons was analyzed before and after plasma treatment with a Digital Instruments Dimension 5000 Atomic Force Microscope (AFM), Model D5-Profilr. A silicon Budget Sensor model BS-TAP300* tapping mode tip was employed for all scans, as this method minimizes the damage to the specimen surface.

* Resonant frequency of 300 kHz, Force constant of 40 N/m

Samples were affixed to glass microscope slides with 3M double sided tape to facilitate sample planarization. Global and local scan areas were acquired in air at $400\text{ }\mu\text{m}^2$ and $25\text{ }\mu\text{m}^2$ respectively, at a frequency of 1 Hz and resolution of 256×256 pixels in a random location on each PTFE coupon. Root mean square (R_{ms}) and average (R_{a}) roughness values were then calculated for each area scan. Three-dimensional topographic reconstructions were also made of each scan to facilitate qualitative assessment.

CHAPTER SIX

EXPERIMENTAL RESULTS

The manufacturing of PTFE creates instances where surface contamination may occur due to the presence of mold release compounds or from handling. Therefore it is necessary to evaluate the as received surface chemistry of the PTFE and also create a cleaning protocol to insure the specimen population is homogeneous. It is also necessary to verify the surface tension of the test liquids used in contact angle measurements, as this will influence measurement accuracy. In this chapter, results of the verification of test liquid surface tension are presented, followed by the evaluation of a cleaning protocol for the as received PTFE specimens. Contact angle and calculated surface tension values of plasma treated and untreated specimens are presented, followed by the results of surface chemistry analysis by XPS. Finally, surface morphology results of plasma treated and untreated specimens, as measured by AFM, are presented.

6.1 Surface Tension

6.1.1 Verification of Test Liquid Surface Tension

The surface tension of each contact angle test liquid (γ_l) was initially verified by bubble tensiometry, with published and measured γ_l for each test liquid listed in Table III. Bubble tensiometer measurements were found to be in very good agreement with published values, with the difference being less than 2%.

Table III. Published and observed surface tensions for various contact angle test liquids.

Liquid	Published γ_l (mN/m)	γ^d (mN/m)	γ^p (mN/m)	Reference	As Measured γ_l (mN/m)
DMSO	43.54	34.86	8.68	[32]	42.73 ± 0.7
Diiodomethane	50.8	50.42	0.38	[33]	50.6 ± 0.35
Ethylene Glycol	48.20	29.29	18.91	[24]	48.39 ± 0.5

6.1.2 Contact Angle Measurements

Images of PTFE/test liquid equilibrium were used to measure the contact angle and also qualitatively assess the phenomenon. Post EtOH bath PTFE surfaces exhibited a highly hydrophobic surface, as can be seen in Figure 7a for $t = 0$ s where a 2 μ L drop of DMSO has just touched down to the PTFE surface. Increased wettability was observed with increased plasma processing time, as depicted in Figures 7b-d. While an initial hydrophobic/non-wetting surface is observed for $t = 0$ s, the surface becomes increasingly wet for increased plasma treatment times, where a treatment time of 160 s almost entirely wets the surface. An increase in wettability is a decrease in contact angle; therefore the qualitative results compare well with the works listed in Table II.

Figure 7. Sequence of images of a 2 μ L drop of DMSO on plasma treated PTFE for times of 0, 3, 40, and 160 s.

A plot of the average PTFE/liquid contact angle as a function of plasma process time for each test liquid can be seen in Figure 8, with raw data found in Appendix C. Each data point represents the average of 4 measurements across the width of a coupon, replicated for 3 coupons, equaling a total of 12 measurements. Best fit trend lines were used to connect data points. Error bars represent the measured contact angle range. All untreated surfaces exhibited a non-wetting/hydrophobic nature as measured by static sessile drop.

Figure 8. A plot of the average PTFE/liquid contact angle versus the plasma process time for DMSO, diiodomethane, and ethylene glycol.

Initial DMSO contact angles averaged 72.9° and quickly fell to 52.3° within 1 s of plasma treatment before asymptotically arriving at 10.4° at a time of 160 s.

Diiodomethane and ethylene glycol also experienced increased wetting with additional plasma processing time. An initial contact angle of 86.5° was observed for diiodomethane, with only a 10% reduction in contact angle in the first 1 s of plasma processing. Contact angles for ethylene glycol began at 96.7° and subsequently fell 23% to 74.8° within 1 s of plasma processing. From Figure 8 it can be seen that a majority of contact angle alteration is accomplished within the first 40 s.

6.1.3 PTFE Surface Tension

PTFE surface tension (γ_s) was calculated using the Harmonic Mean Theory discussed in Chapter 2.2, with results tabulated in Table IV. A plot of γ_s as a function of plasma processing time can be seen in Figure 9. The initial calculated γ_s is 20.5 ± 0.69 mN/m, which compares well to previously published values of 19.1- 23.9 mN/m [10]. Plasma exposure to the PTFE surface led to an increase in γ_s , as can be seen in both Table IV and Figure 9. Again, a majority of the γ_s modification takes place in the first 40 s, increasing nearly 50%. After plasma processing for 160 s γ_s approaches a value of 44.5 mN/m asymptotically.

Table IV. Calculated values of PTFE γ_s , γ^d , and γ^p according to plasma processing time.

Process Time (s)	Surface Tension, γ_s (mN/m)	Dispersive, γ^d (mN/m)	Polar, γ^p (mN/m)
0	20.5 ± 0.7	20	0.5
1	25.9 ± 0.9	21.8	4
3	27.7 ± 0.8	20.2	7.5
10	31.9 ± 0.5	24.4	7.5
20	36.9 ± 0.8	30.4	6.5
40	41.3 ± 0.8	30.2	11.1
80	42.5 ± 0.8	31.6	10.9
160	44.5 ± 0.4	39.9	4.5

Figure 9. A plot of PTFE calculated surface tension as a function of plasma processing time. Also included are the calculated dispersive (γ^d) and polar (γ^p) constituents of γ_s .

Dispersive and polar constituents of γ_s have also been plotted as a function of plasma processing time and are included in Figure 9. As indicated in Chapter Two, the initial surface was found to be essentially non-polar, with a γ^p of 0.5 mN/m; however, plasma processing influenced the polar contribution to a significant degree for the first 40 s of processing time, rising to 11.1 mN/m. After 40 s the polar component decreased to 4.5 mN/m for a processing time of 160 s. The dispersive component increased from 20 mN/m to 30.4 mN/m during the first 20 s of plasma treatment, stayed level from 20 s to 80 s, and finally rose to 39.9 mN/m for a processing time of 160 s. From Figure 9 it can be seen that dispersive forces dominate the initial and final PTFE surface tension.

6.2 Surface Chemistry

6.2.1 Comparison of Specimen Cleaning

Baseline XPS surface chemistry analysis was performed to determine the effectiveness of cleaning samples in a sonicated EtOH bath versus sonicated EtOH bath in addition to autoclaving. One specimen from each cleaning procedure was evaluated. The atomic concentrations of the elements found in the following specimens: “as received” from supplier, after EtOH bath, and after use of EtOH bath + autoclave sterilization* can be found in Table V. A dashed line “-” indicates the element was not detected. A less than symbol “<” indicates accurate quantification could not be made due to weak signal intensity. From Table V it can be seen that the as received specimen contained minor concentrations of O and Si, while the EtOH bath and EtOH bath + autoclave specimens appear free of Si, with a large reduction in O. Therefore, the use of an EtOH bath was determined to be an effective cleaning procedure to remove residual contamination and was employed prior to all plasma treatments.

Table V. Atomic concentrations (in %)[†] of as received and EtOH/autoclaved bathed specimens, as measured by XPS analysis.

Specimen	C	O	F	Si	Cl
As Received	31.7	1.2	66.5	0.6	-
EtOH Bath	31.4	0.3	68.3	-	<0.1
EtOH Bath + Autoclave	31.1	0.2	68.7	-	-

* 121 °C for 20 minutes

[†] Normalized to 100% of the elements detected. XPS does not detect H or He.

6.2.2 Elemental Composition Change

XPS analysis has been observed to cause changes in some polymeric systems, either due to the effect of X-rays or the neutralization process by low energy electrons and argon ions. Brief initial and final survey scans were acquired to monitor any large changes in elemental composition with acquisition time. A comparison of the initial and final survey scans can be seen in Table VI. A large change in composition between the first and final survey scans, with an increase in C and decrease in F was found for specimen t (1). For all other specimens the differences between the two surveys were minimal.

Table VI. Change in atomic concentrations with analysis time (in %)*.

Specimen	C	N	O	F
t (1), initial	35.4	-	2.0	62.6
t (1), final	41.2	-	2.4	56.5
t (3), initial	34.1	-	0.9	65.0
t (3), final	34.7	-	0.6	64.7
t (10), initial	35.6	0.8	2.1	61.5
t (10), final	36.6	0.8	1.8	60.7
t (20), initial	35.5	2.3	3.4	58.8
t (20), final	36.6	1.9	2.6	58.9
t (40), initial	39.3	3.6	5.7	51.3
t (40), final	39.3	3.1	4.7	53.0
t (80), initial	40.0	4.9	7.6	47.5
t (80), final	41.3	4.3	5.8	48.6
t (160), initial	39.1	4.1	7.0	49.8
t (160), final	39.1	4.0	5.8	51.2

* Normalized to 100% of the elements detected. XPS does not detect H or He.

6.2.3 Elemental Composition

Table VII is a summary of the surface atomic concentrations of plasma treated and untreated specimens, as found by XPS spectra, while Figure 10 is a plot of the surface atomic concentration as a function of plasma processing time. Survey spectrographs of each specimen are included in Appendix D. C1s spectrographs annotated to show carbon chemical states can be found in Appendix E and high resolution spectral peaks can be found in Appendix F. For all specimens, F was detected at a binding energy of 689.5 eV to 689.7 eV, which is typical for organic F. Nitrogen was detected at a binding energy typical for an ammonium ion. On the t (1) specimen, Si was detected at a binding energy typical for a silicone and S was detected at a binding energy typical for an oxidized S such as a sulfate. If the t (1) specimen is ignored, the F concentration decreases and the O, N, and C concentrations increase with increased plasma treatment time, for treatment times of 3 seconds through 80 seconds. The t (160) specimen does not follow this trend, with a slightly higher F concentration, slightly lower C concentration, and approximately constant N and O concentrations compared to the t (80) specimen.

Table VII. Atomic concentrations (in %)* of plasma modified specimens.

Specimen	C	N	O	F	Si	S
t (0)	31.4	-	0.3	68.3	-	-
t (1)	38.8	0.2	1.9	58.8	0.2	0.1
t (3)	36.0	0.5	1.0	62.5	-	-
t (10)	34.8	1.2	2.0	61.9	-	-
t (20)	33.4	2.1	3.5	61.1	-	-
t (40)	38.4	3.4	5.3	53.0	-	-
t (80)	40.5	4.9	6.7	47.9	-	-
t (160)	37.2	4.3	6.8	51.7	-	-

Figure 10. Plot of surface atomic concentration as a function of plasma processing time.

* Normalized to 100% of the elements detected. XPS does not detect H or He.

6.2.4 Chemical States of Carbon

A summary of C1s curve fit results are shown in Table VIII. The C1s spectra are complex, with multiple species possible for a given curve fit component. Annotated curve fit spectra are located in Appendix E for all specimens. The assignments were made based on the observed binding energy of the component and selecting a reference structure with the closest binding energy match. Species other than those shown may also be possibilities. In general, a larger plasma treatment time correlates to less fluorinated components. The C1s signal shows lower percentages of CF₂ and higher percentages of less fluorinated carbon species for higher levels of plasma treatment time. Peaks of note are the moieties found at 285.7 eV, 288.5 eV and 290.9 eV, as these increase with increased plasma treatment time.

6.3 Surface Morphology

Tables IX and X contain calculated values of R_a, R_{ms}, and surface area based on local 25 μm² and global 400 μm² AFM scans of plasma treated and untreated PTFE coupons. AFM data were measured on one specimen for each treatment time. The initial local and global R_{ms} surface roughness as measured by AFM was 50.2 nm and 135.6 nm, respectively. AFM of untreated PTFE coupons indicate that a tribological deformation of the surface occurred during manufacturing. Increased plasma treatment led to a decrease in both the local and global roughness, with asymptotic values of 26 nm and 95.8 nm achieved at 160 s, respectively, as can be seen in Figures 11 and 12. Of note is the increase in surface roughness at a plasma process time of 10 s, which is

Table VIII. Carbon chemical states (in %) according to each treated specimen, as measured by XPS*.

Specimen	C-C, C-H 285.0 eV	CH ₂ -CHF C-O 285.7 eV	CH ₂ -CF ₂ C-O 286.5 eV	CH ₂ -CHF C=O 287.9 eV	CHF-CHF O=C-O ⁻ 288.5 eV	CHF-CF ₂ O=C-OR 289.3 eV	CH ₂ -CF ₂ 290.9 eV	CF ₂ -CF ₂ 292.5 eV	CF ₃ 293.9 eV
t(1)	15	-	4	23	-	3	2	71	3
t(3)	-	2	2	3	-	4	3	83	2
t(10)	-	4	5	5	?	8	6	71	2
t(20)	-	3	6	-	6	11	7	64	3
t(40)	-	5	10	-	9	13	9	50	4
t(80)	-	6	11	-	10	14	10	45	4
t(160)	-	6	9	-	9	14	10	48	3

* Normalized to 100% of the elements detected. XPS does not detect H or He.

observed locally but not globally. As with surface tension, a majority of the surface modification took place before 40 s. After 40 s there was little to no change locally, yet globally there was a 20% increase in R_{ms} . Surface area also decreased on both the local and global scale, with a local reduction of 5% from $26.75 \mu\text{m}^2$ to $25.37 \mu\text{m}^2$ and a global reduction of 2% from $414.20 \mu\text{m}^2$ to $404.40 \mu\text{m}^2$.

Table IX. Local calculated AFM average roughness, R_{ms} , and surface area according to plasma processing time.

Plasma Process Time	Ra (nm)	Rms (nm)	Surface Area (μm^2)
t (0)	40.4	50.2	26.75
t (1)	28.2	35.1	26.38
t (3)	23.4	29.2	26.04
t (10)	29.3	37.5	25.57
t (20)	23.5	31.8	25.54
t (40)	19.6	24.9	25.44
t (80)	21.8	27.2	25.79
t (160)	19.7	26	25.37

Table X. Global calculated AFM average roughness, R_{ms} , and surface area according to plasma processing time.

Specimen	Ra (nm)	Rms (nm)	Surface Area (μm^2)
t (0)	108	135.6	414.29
t (1)	112	137.5	412.65
t (3)	105.7	131.7	413.04
t (10)	83.7	100.8	412.37
t (20)	67.1	89.4	407.88
t (40)	65.1	80	404.28
t (80)	74.8	92.8	407.06
t (160)	74.5	95.8	404.40

Figure 11. Plot of local surface roughness, R_{ms} , as a function of plasma process time which indicates that increased plasma processing leads to a smoother coupon.

Figure 12. Plot of global surface roughness, R_{ms} , as a function of plasma process time which indicates that increased processing leads to a smoother PTFE coupon.

Three-dimensional topographic reconstructions were made of local and global AFM scans to qualitatively assess the effect of plasma processing on the surface morphology. As can be seen in Figure 13, apparent local roughness decreases with increased plasma treatment time. Although roughness varies little after 40 s, there is a marked difference in the reconstruction morphology for treatment times above 40 s. A treatment time of 40 s, Figure 13f, appears to have drastic peaks, whereas times of 80 and 160 s, Figures 13g and 13h, have a “smoother” appearance. Similar observations can be made about the global three-dimensional reconstructions in Figure 14.

a) $t = 0$

b) $t = 1$ s

c) $t = 3$ s

d) $t = 10$ s

e) $t = 20$ s

f) $t = 40$ s

g) $t = 80$ s

h) $t = 160$ s

Figure 13. Local 3D topographic AFM reconstructions of plasma treated PTFE for times of 0, 1, 3, 10, 20, 40, 80, and 160 s. Of note is the apparent decrease in roughness for increasing plasma treatment times.

a) $t = 0 \text{ s}$

b) $t = 1 \text{ s}$

c) $t = 3 \text{ s}$

d) $t = 10 \text{ s}$

e) $t = 20 \text{ s}$

f) $t = 40 \text{ s}$

g) $t = 80 \text{ s}$

h) $t = 160 \text{ s}$

Figure 14. Global 3D topographic AFM reconstructions of plasma treated PTFE for times of 0, 1, 3, 10, 20, 40, 80, and 160 s. A trend in decreasing roughness with increasing treatment time can be seen in these images.

CHAPTER SEVEN

DISCUSSION

The principle objective of this study was to evaluate changes in the surface tension, surface chemistry, and surface morphology induced by hydrogen plasma treatment. As seen from Chapter 3, there are a number of authors who have completed similar work, although reporting of experimental setup and protocol is often not properly stated. This is likely due to wide variation in plasma characteristics generated from different chamber geometries. In this chapter, the results presented in Chapter 6 are compared to the established theories of plasma surface modification of PTFE and the calculated surface tensions values are correlated to the physical and chemical modifications. Finally, a discussion is given on the impact this study has on future biocompatibility research.

With the exception of contact angle measurements, there are no population statistics. XPS and AFM analyses were completed on a single specimen for each plasma processing time. Scans were taken to insure a large area was sampled, but replication of specimens was cost prohibitive. However, contact angle data populations show a tight trend in the surface tension of plasma modified PTFE.

7.1 Contact Angle and Surface Tension

Initial DMSO contact angle values are in good agreement with published values by Wu, as seen in Table XI, with a difference of less than 1.3%. Diiodomethane and ethylene glycol measured contact angles are not in agreement with some published data.

Diiodomethane has two published contact angles of 77° and 88° from the same researcher, although in different publications, with 88° being closest to the measured contact angle of 86.5° for this research [10, 34]. The published contact angle of ethylene glycol on PTFE is 86°, 11% smaller than the measured value of 96.7° [34]. This underscores the fact that experimental conditions play a role in measuring contact angle data and direct comparison may not lead to valid conclusions.

Table XI. Comparison of published and observed PTFE/test liquid contact angle data.

Test Liquid	Published Contact Angle (°) [10,34]	Measured Contact Angle (°)
DMSO	72	72.9 ± 1.8
Diiodomethane	77, 88	86.5 ± 0.8
Ethylene Glycol	86	96.7 ± 0.8

All authors observed a decrease in the DI water/PTFE contact angle with exposure to glow discharge plasma, in agreement with the findings of this research. One problem not addressed by most authors is that contact angle data for a PTFE/DI water interface may not be a complete description of the thermodynamic wetting behavior. This is because independent components of γ , γ^d and γ^p , are not evaluated by using a single polar liquid. Also the interaction of a highly polar liquid with a non-polar surface may lead to inconsistent wetting behavior.

A list of published PTFE γ_s in comparison to that calculated for the specimen after EtOH bathing, $t(0)$, can be found in Table XII, where it can be seen the calculated γ_s is within the published range. It can also be seen that the value obtained is dependent on

the method used for calculation. Wu has argued that because the published surface tension value of liquid fluorocarbon oil* has been measured to be 21.5 mN/m, all solid surface tension values must be greater. This is because surface tension increases with increasing molecular weight, as seen in Equation 13. The initial calculated PTFE surface tension of this investigation was 20.5 ± 0.7 mN/m, which is within 8% of the published value of 22.6 mN/m calculated by the Harmonic Mean method [10]. The deviation may be due to surface heterogeneities such as roughness, or possibly experimental error. There are no published error values for Wu's work and it is possible that the calculated values from this investigation may not be statistically different. Direct comparisons of the surface tension of plasma modified PTFE is not possible, as they have yet to be reported.

Table XII. Comparison of published γ_s of PTFE in comparison to those calculated. All values reported in mN/m [10].

Equation of State	Liquid Homolog	Harmonic Mean	Geometric Mean	Zisman's Critical Surface Tension	This Work*
22.6	23.9	22.5	19.1	18	20.5 ± 0.7

* Calculated according to the Harmonic Mean method.

7.2 Chemical Modification

Hydrogen plasma surface modification of PTFE was found to induce chemical changes, such as defluorination and grafting of functional groups, as seen in Tables VII

* $C_{21}F_{44}$

and VIII. These changes were dependent on the plasma processing time, with increased time producing greater alterations. Changes in sample chemistry occurred for all plasma treated specimens, and did not appear to have a plateau value, compared to AFM and surface tension results.

The exposure to air during sample transport led to the sorption of atmospheric water vapor, nitrogen, and oxygen, evident in Table VII and VIII. A possible explanation is that increased plasma treatment times led to increased free radical densities on the surface which facilitated grafting during transport, as these elements were not present in the chamber during treatment.

Crosslinking has been cited as a phenomenon that occurs with plasma treatment, but direct evidence was not found. Wilson *et al.* observed an increase in the -C-C- peak at 285 eV which they attributed to crosslinking [22]. Only specimen t (1) contained such a peak, as shown in Appendix E Figure 34, which has been attributed to surface contamination. This specimen was found to have silicone, single bond carbon, and possibly sulfates on the surface, which are indicative of improper cleaning. All other specimens appeared free of contamination, although another possibility is that plasma treatment times above 1 s are enough to remove residual contamination.

7.3 Morphological Modification

AFM results reported here contradict previous work by Wilson *et al.* where they reported a roughness (R_{ms}) increase of 20-50% with a 1 W plasma system; yet, for this study a local R_{ms} decrease of 50% was measured [22]. This may be due to specimen

morphology heterogeneity between polymer suppliers. Wilson noted that his PTFE sheets were exceptionally rough with an R_{ms} value of 50 nm; therefore he used PTFE plumbers tape as a roughness monitor for fear that he would be unable to detect a measurable difference in the PTFE sheets. Wilson did not report roughness values for plasma treated PTFE sheets, only plumber's tape, which does not compare directly to PTFE. Plumber's tape contains numerous fillers, such as silica, which may influence their findings. This study also used PTFE specimens with an initial roughness of 50.2 nm and found no difficulty in measuring a decrease in roughness. Wilson averaged his roughness from a scan area of $1\ \mu\text{m}^2$, in comparison to the $25\ \mu\text{m}^2$ used in this studies morphology results.

As can be seen in Figure 10, there is a local roughness anomaly for specimen t (10), where the decreasing trend rises sharply. This same behavior was not observed on the global scale, and therefore may be a unique feature. AFM scans were taken without preference and without replication, so it would be of interest to see if other specimens treated for 10 s would have the same behavior.

7.4 Correlation of Physical and Chemical Surface Modification to Surface Tension

As noted in Chapter 6.1.2, a majority of the plasma surface modification takes place in the first 40 s of processing. As can be seen in Figure 15, with the exception of the 10 s specimen, there is direct correlation in the decrease in local roughness with the increase in surface tension. During the time interval 0-40 s there is a decrease in surface area directly beneath the test liquid drop. The decrease in surface area is a reduction in

the excess specific surface free energy, and so γ_s should be decreasing with the reduction in roughness. Therefore, it can be concluded that the decrease in surface area is not a major contributor to the increase in solid surface tension.

A smooth surface has fewer physical barriers to the liquid drop's advancing front, as compared to a rough surface. The equilibrium position of a liquid drop on a smooth surface would therefore have a smaller contact angle, resulting in a higher calculated surface tension. It is likely that the measured 50% reduction in surface roughness contributed to smaller contact angles and led to an increase in the calculated surface tension.

The relationship of chemical surface modification to an increase in γ_s can be seen in Figure 16. The increase in surface atomic concentration of N and O reaches a maximum at a process time of 80 s, whereas the γ_s of PTFE begins to plateau at 40 s. This behavior is also echoed in the increase in carbon moieties found in Table VIII. The increase in surface functional groups containing N and O altered the wetting behavior of both polar and non-polar liquids, increasing the calculated PTFE surface tension.

Figure 15. Comparison of R_{ms} and γ_s of PTFE as a function of plasma process time.

Figure 16. Comparison of the γ_s of PTFE and atomic concentration of N and O as a function of plasma process time.

7.5 Implications for Biocompatibility

The results discussed in Chapter 6 provide the foundation and framework for future biocompatibility testing of hydrogen plasma modified PTFE. Several works have been completed by authors attempting to correlate γ_s to biocompatibility. Lyman and coworkers theorized that the surface tension of the implanted material provides the interaction energy required to induce coagulation [35]. They determined that platelet adhesion was proportional to γ_s of polymers in contact with circulating blood. Lyman *et al.* surmised that polymer surfaces that are hydrophilic should be blood compatible because the vascular walls are themselves hydrophilic and because they measured that hydrophobic surfaces adsorbed larger amounts of blood proteins. Andrade and coworkers postulated that materials which exhibit an interfacial tension of zero would be the most thrombus-resistant because there would be no thermodynamic driving force for protein adsorption, yet no experimental work was done to show this relationship [36].

Baier completed an often referenced work correlating hemocompatibility and surface tension, finding that a theoretical γ_s within the range of 20-30 mN/m may lead to a stable, non-thrombogenic surface [37]. He found that low γ_s equated with poor biological adhesion to synthetic surfaces. Biological components that did adhere were detached by the natural ebbing of blood shear rate. Baier accomplished this by evaluating the coagulation properties of various surfaces in contact with blood, followed by using the Zisman technique for assessing γ_s . He also theorized that surfaces possessing very high γ_s , *e.g.*, greater than 70 mN/m, may also be hemocompatible

because he witnessed that plasma treated Pyrex possessed relatively low coagulation times.

Kaelble and Moacanin found that low polar and high dispersion components correlating to γ_s values of between 40-50 mN/m imply stable adsorption of an albumin protein layer, which they found to be non-thrombogenic [4]. This was accomplished by evaluating several different surfaces. Sharma further evaluated Kaelble and Moacanin's work using several polymers known to have good biocompatibility. He derived different polar and dispersion values that correlate to γ_s of 31 mN/m which exhibit non-thrombogenic properties [38].

Figure 17 is a plot of this work's achievable PTFE surface tension range as compared to the published biocompatible solid surface tension research of several authors. As can be seen in Figure 17, there is little agreement as to an acceptable surface tension for biocompatibility. Included in Figure 17 for reference is low temperature isotropic carbon (LTI carbon), which is a commonly implanted heart valve material. A sufficient range of surface tensions can be realized with the process given in Chapter 5, allowing testing of the hypothesis that surface tension is a major factor in blood coagulation on polymer vascular devices. The design of the plasma processing protocol in Chapter 5 has been shown to be highly repeatable in regards to PTFE surface tension.

Figure 17. A comparison of this work's achievable surface tension range with other biocompatible solid surface tension research [1, 4, 35-38].

CHAPTER EIGHT

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

The exposure of medical grade PTFE to hydrogen plasma has modified the surface tension, surface chemistry, and surface morphology. This is the result of defluorination, grafting of functional groups, and material ablation resulting in a smoother surface. Other chemical modifications observed are the increase in oxygen and nitrogen present at the surface. Surface tension and morphology modification induced by plasma immersion were complete within 40 s of treatment, whereas chemical changes were observed for plasma processing times up to 80 s.

The hydrogen plasma modification process used in this research has been shown to be reproducible, creating a wide range of solid surface tensions which enables future research on PTFE biocompatibility as a function of surface tension. It has also been shown that surface tension calculation is an appropriate method for estimating the thermodynamic behavior of solid surfaces, providing more detailed information than reporting contact angles. An important aspect of this fact is that surface tensions calculated by researchers can be easily compared directly, while contact angles cannot.

Further studies on hydrogen plasma surface modification of PTFE are necessary to determine if larger sample populations follow topography and chemistry trends. It would also be valuable if future experiments measured the radiation and ion/e⁻ bombardment of the specimen and relate them to the physical and chemical modification of the PTFE surface. The verification of plasma induced surface crosslinking via

differential scanning calorimetry or other technique may provide chemical information not obtained through XPS analysis. It would be valuable to determine how plasma treating changes the surface potential because PTFE surfaces are intrinsically electronegative. Also worthy of future research is the effect of aging on plasma treated PTFE, as this would directly relate to the “shelf life” of plasma treated medical implants.

REFERENCES

1. B.D. Ratner, A.S Hoffman, F.J. Schoen and J.E Lemons, Biomaterials Science, An Introduction to Materials in Medicine, (Academic Press, San Diego, 1996), pp. 229-232.
2. S. Kim, R. Lee, H. Oster, D. Coleman, J. Andrade, D. Lentz and D. Olsen, "*Platelet Adhesion to Polymer Surfaces*," Trans. Am. Soc. Artif. Int. Organs, **20**, 449-458 (1974).
3. R. Baier, "*The Role of Surface Energy in Thrombogenesis*," Bull. N.Y. Acad. Med., **48 (2)**, 257-272 (1972).
4. D. Kaelble and J. Moacanin, "*A Surface Energy Analysis of Bioadhesion*," J. Poly. Sci., **18**, 475-482 (1977).
5. H.B. Lee, G. Khang and J.H. Lee, The Biomedical Engineering Handbook: Polymeric Biomaterials, (CRC Press LLC, New York, 2000), pp. 12-18.
6. J. Scheirs, Modern Polymers: High Performance Polymers for Diverse Applications, (John Wiley and Sons, New York, 1997), pp. 2-7.
7. A.W. Adamson and A.P. Gast, Physical Chemistry of Surfaces, 6th Ed. (John Wiley & Sons, New York, 1997), pp. 1-119.
8. S. W. Ip and J. M. Toguri, "*The equivalency of surface tension, surface energy and surface free energy*," J. Mat. Sci., **29 (3)**, 688-692 (1994).
9. Y. Chiang, D. Bernie III and W. Kingery, Physical Ceramics: Principles for Ceramic Science and Engineering, (John Wiley and Sons, New York, 1997), pp. 351-360.
10. S. Wu, Polymer Interface and Adhesion, (Marcel Dekker ,New York, 1982), pp. 178-180.
11. F. Arefi-Khonsari, M. Tatoulian, F. Bretagnol, O. Bouloussa and F. Rondelez, "*Processing of Polymers by Plasma Technology*," Surf. Coat. Tech, **200**, 14-20 (2005).
12. F.K. McTaggart, Plasma Chemistry in Electrical Discharges, (Elsevier, Amsterdam, 1967), pp. 241-268.
13. P.K. Chua, J.Y. Chena, L.P. Wanga and N. Huang, "*Plasma-Surface Modification of Biomaterials*," Mat. Sci. Eng. R, **36**, 143–206 (2002).

14. D.T. Clark and D.R. Hutton, "*Surface modification by plasma techniques. I. The interactions of a hydrogen plasma with fluoropolymer surfaces,*" J. Poly. Sci. Part A, **25 (10)**, 2643-2664 (1987).
15. R.S. Thomas, Techniques and Applications of Plasma Chemistry, edited by J. R. Hollahan and A.T Bell (John Wiley, New York, 1974), pp. 364-397.
16. A.J. Wagner, K. Han, A. Vaught and D.H Fairbrother, "*X-ray Induced Modification of Semifluorinated Organic Thin Films,*" J. Phys. Chem. B., **104**, 3291-3297 (2000).
17. C.M. Chan, T.M. Ko and H. Hiraoka, "*Polymer surface modification by plasmas and photons,*" Surf. Sci. Report, **24**, (1996).
18. J.F. Friedrich, Polymer-Solid Interfaces, edited by J.J. Pireaux, P. Bertrand and J.L. Bredas (Proceedings of First International Conference, IOP Publishing, 1992), pp. 443.
19. Y. Akishev, M. Grushin, A. Napartovich and N. Trushkin, "*Novel AC and DC Non-Thermal Plasma Sources for Cold Surface Treatment of Polymer Films and Fabrics at Atmospheric Pressure,*" Plasmas and Polymers, **7**, 487-495 (2002).
20. L. Dai, H.J. Griesser and A.W. Mau, "*Surface Modification by Plasma Etching and Plasma Patterning,*" J. Phys. Chem. B, **101 (46)**, 9548-9554 (1997).
21. E.T. Kang, K.L. Tan, K. Kato, Y. Uyama, Y. Ikada, "*Surface Modification and Functionalization of Polytetrafluoroethylene Films,*" Macromolecules, **29 (21)**, 6872-6879 (1996).
22. D.J. Wilson, R.L. Williams and R.C. Pond, "*Plasma modification of PTFE surfaces Part I: Surfaces immediately following plasma treatment,*" Surf. Interface Anal., **31**, 385-396 (2001).
23. C.P. Sharma, P.R. Hari, "*Adhesion and Stability of Blood Cells onto Polymer Substrates: Effect of Glow Discharge,*" J. Biomat. Appl., **6**, 73-79 (1991).
24. M. Chen, P. Zamora, P. Som, L.A. Pena and S. Osaki, "*Cell attachment and biocompatibility of PTFE treated with glow-discharge plasma of mixed ammonia and oxygen,*" J. Biomater. Sci. Polymer Edn., **14 (9)**, 917-935 (2003).
25. U. Konig, M. Nitschke, M. Pilz, F. Simon, C. Arnhold and C. Werner, "*Stability and ageing of plasma treated poly(tetrafluoroethylene) surfaces,*" Colloids and Surfaces B: Biointerfaces, **25**, 313-324 (2002).

26. N. Vandencastele and F. Reniers, "Surface characterization of plasma treated PTFE surfaces: an OES, XPS and contact angle study," *Surf. Interface Anal.*, **36**, 1027-1031 (2004).
27. Y.C. Hu, B. Ken, Y. Lid, Y.J. Dui, I. H. Sheen, P. Wen. Ding and W. H. Tao, "*Improvement of bonding properties of PTFE by low pressure plasma treatment*," Int'l Symposium on Electronic Materials and Packaging (2002).
28. M. E. Ryan and J. P. Badyal, "*Surface Texturing of PTFE Film Using Nonequilibrium Plasmas*," *Macromolec.*, **28**, 1377-1385 (1995).
29. C.R. Shick, P.A DePalma and R.K Marcus, "*Radio Frequency Glow Discharge Mass Spectrometry for the Characterization of Bulk Polymers*," *Anal. Chem.*, **68** (13), 2113-2121 (1996).
30. D.J. Wilson, A.J. Eccles, T.A. Steele, R.L. Williams and R.C. Pond, "*Surface Chemsity and Wettability of Plasma Treated PTFE*," *Surf. Interface Anal.* **30**, 36-39 (2000).
31. P. Triolo and J. Andrade, "*Surface modification and evaluation of some commonly used catheter materials. I. Surface properties*," *J. Biomed. Mater. Res.*, **17**, 129-147 (2004).
32. B. Janczuk, W. Wojcik and A. Zdziennicka, "*Determination of the components of the surface tension of some liquids from interfacial liquid-liquid tension measurements*," *J. Coll. Inter Sci.*, **157** (2), 384-393 (1993).
33. F.M. Fowkes, "*Determination of interfacial tensions, contact angles, and dispersion forces in surfaces by assuming additivity of intermolecular interactions in surfaces*," *J. Phys. Chem.*, **66**, 382 (1962).
34. H.W. Fox and W.A. Zisman, "*The Spreading of Liquids on Low Energy Surfaces. I. PTFE*," *J. Coll. Sci.*, **5**, 514-531 (1950).
35. D. Lyman, J. Knutson, B. McNeill and K. Shibatani, "*The Effects of Chemical Structure and Surface Properties of Synthetic Polymers on the Coagulation of Blood*," *Trans. Am. Soc. Artif. Int. Organs*, **21**, pp. 49 (1975).
36. J. D. Andrade, "*Interfacial phenomena and biomaterials*," *Med. Instrum.*, **7**, 110-120 (1973).
37. R. Baier, "*The Role of Surface Energy in Thrombogenesis*," *Bull. N.Y. Acad. Med.*, **48** (2), 257-272 (1972).

38. C. Sharma, "*Possible Contributions of Surface Energy and Interfacial Parameters of Synthetic Polymers to Blood Compatibility*," *Biomat.*, **2**, 57-59 (1981).

APPENDIX A

LAPLACE-YOUNG EQUATION

The Laplace-Young equation is an accurate way of calculating the contact angle of a liquid on a solid substrate. This method takes into account gravitational effects on the geometry of the bubble. The Laplace-Young equation is the relation between the capillary pressure, ΔP , on curved objects, such as drops and bubbles, and the principal radii of curvature, R and R' , as well as the surface or interfacial tension on the phase boundaries γ :

$$\Delta P = \gamma \left(\frac{1}{R} + \frac{1}{R'} \right)$$

The equilibrium of the forces through any horizontal plane is given by:

$$2\pi x \gamma \sin \theta = V(\rho_k - \rho_l)g + \pi x^2 p$$

where P is the pressure exerted on the surface of the drop difference in pressure resulting from the surface curvature, γ is the surface tension, R and R' are the drop's radii, x is the abscissa of the meridian point having z as its ordinate, θ is angle of the tangent, V is the volume of the fluid beneath the plane, ρ_1 and ρ_2 are the density of the fluids or gases, respectively, and g is the gravitational acceleration (ms^{-2}). The measurement of R and R' and subsequent calculation of θ are an operation carried out within the Dataphysics OCA 20 image capturing software.

APPENDIX B

EXAMPLE OF HARMONIC MEAN CALCULATION

Example of Harmonic Mean surface tension calculation using DMSO and ethylene glycol as test liquids on a PTFE substrate:

Measured DMSO contact angle $\theta_1 = 72.5$

Measured ethylene glycol contact angle $\theta_2 = 96.5$

DMSO: $\gamma_1 = 50.8$, $\gamma_1^d = 46.74$, $\gamma_1^p = 4.06$

Ethylene glycol: $\gamma_2 = 48.2$, $\gamma_2^d = 18.91$, $\gamma_2^p = 29.29$

Using Equations 10 and 11:

$$(1 + \cos \theta_1) \gamma_1 = 4 \left[\frac{\gamma_1^d \gamma_s^d}{\gamma_1^d + \gamma_s^d} + \frac{\gamma_1^p \gamma_s^p}{\gamma_1^p + \gamma_s^p} \right] \quad (1 + \cos \theta_2) \gamma_2 = 4 \left[\frac{\gamma_2^d \gamma_s^d}{\gamma_2^d + \gamma_s^d} + \frac{\gamma_2^p \gamma_s^p}{\gamma_2^p + \gamma_s^p} \right]$$

Solving for γ_s^d and γ_s^p :

$$\gamma_s^d = 20$$

$$\gamma_s^p = 0.5$$

Therefore $\gamma_s = \gamma_s^d + \gamma_s^p = 20.5 \text{ mN/m}$

APPENDIX C
CONTACT ANGLE MEASUREMENT RAW DATA

Table XIII. Contact angle measurement raw data.

	Process Time	0	1	3	10	20	40	80	160
Test Liquid	Specimen	Contact Angle (θ)							
DMSO	A	72.5	53.3	50	43.7	33.6	12.5	14.7	10.3
		73.2	51.9	48.7	43.5	32.9	11.8	14.7	11.1
		72.5	51.6	49.4	43.3	32.9	11	14.7	10
		73.8	52.4	50	43	33	11.7	14.7	10.4
	B	72.5	53	49.7	43.6	32.9	12.4	14.7	10
		72	51.5	50	43.5	33	12.6	14.6	10
		72.1	52.1	49.6	43.3	33	11.8	14.5	10.2
		72.3	53	49.6	43.1	33.1	11.9	14.4	10
	C	73.5	52.5	50	43.5	33.4	11.7	14.6	10.7
		73.5	52.3	49	43.4	33.1	11.7	14.5	10.5
		72.2	52	49.5	43.3	33.2	11.6	14.7	10.4
		72.5	52.1	49.6	43.7	32.9	11.4	14.7	10.6
Diiodomethane	A	86.1	79.2	80.3	77.6	68	53.9	47.4	45.6
		86.6	78	80.1	77.9	67.8	51.1	47.8	43.2
		86.5	77.4	78.8	76.3	68.3	50.4	47.9	40.3
		86.9	77.9	80.4	76.8	68	53.2	46.8	42.2
	B	86.5	78.2	79	77	68.1	50.6	47	44
		86.1	78	80.2	77.4	68	50.8	47.2	44.3
		86.9	77.2	80.1	76.8	68.2	53.9	47.4	45
		86.5	77.5	79.9	76.5	67.2	51.1	47.8	43.5
	C	86.6	78.2	79.8	76.7	68	50.4	47.6	43.6
		86.4	78.5	79.4	77	68.2	53.2	47.3	43.7
		86.8	78.2	80.4	77.2	67.9	52	47.8	42.7
		86.5	78	80.1	77.3	67.8	52.1	47.9	43.4
Ethylene Glycol	A	96.8	75.1	69.2	63	50.1	37.5	38.4	43.8
		97	75.4	71.1	63	51.3	35.1	39.7	46.3
		96.6	73.9	71.1	64.4	51.8	36.4	40	42.4
		96.5	75.1	71	64.6	51.9	36.9	39.3	42.9
	B	96.7	74.1	71.2	64.3	50.4	37.1	38.7	43
		96.5	73	71.2	63	51	37.4	39.4	44.3
		96.4	75.4	70	63.2	51.2	36.6	38.9	42
		96.9	73.9	71.1	64.1	50.9	36.7	38.9	42.5
	C	96.2	75.1	71.4	63.5	51.7	36.7	39.4	45.3
		96.5	74.3	70.2	63.8	50.6	36.9	39.6	45.3
		97	75.2	69.3	64.3	50.9	37.1	39.5	42.5
		96.9	73.9	70	64.2	61.2	37.4	40	43.8

APPENDIX D
XPS SURVEY SPECTROGRAPHS

Figure 18. XPS survey spectrograph for as received PTFE coupons. Of note are the Si2s and Si2p peaks, which are consistent with the bonding energy of silicone.

Figure 19. XPS survey spectrograph for EtOH bath coupon.

Figure 20. XPS survey spectrograph for EtOH bath + autoclave specimen.

Figure 21. XPS survey spectrograph for t (0) specimen.

Figure 22. XPS survey spectrograph for t (1) specimen.

Figure 23. XPS survey spectrograph for t (3) specimen.

Figure 24. XPS survey spectrograph for t (10) specimen.

Figure 25. XPS survey spectrograph for t (20) specimen.

Figure 26. XPS survey spectrograph for t (40) specimen.

Figure 27. XPS survey spectrograph for t (80) specimen.

Figure 28. XPS survey spectrograph for t (160) specimen.

APPENDIX E
HIGH RESOLUTION XPS SPECTROGRAPHS

Figure 29. High resolution C1s spectrum for as received specimen.

Figure 30. High resolution C1s spectrum for EtOH bath specimen.

Figure 31. High resolution C1s spectrum for EtOH bath + autoclave specimen.

Figure 32. High resolution F1s spectrum for as received specimen.

Figure 33. High resolution C1s spectrum for t (0) specimen.

Figure 34. High resolution C1s spectrum for t (1) specimen.

Figure 35. High resolution C1s spectrum for t (3) specimen.

Figure 36. High resolution C1s spectrum for t (10) specimen.

Figure 37. High resolution C1s spectrum for t (20) specimen.

Figure 38. High resolution C1s spectrum for t (40) specimen.

Figure 39. High resolution C1s spectrum for t (80) specimen.

Figure 40. High resolution C1s spectrum for t (160) specimen.

APPENDIX F
HIGH RESOLUTION XPS SPECTRA

Figure 41. High resolution C1s, O1s, F1s, and Si2p spectra for as received specimen.

Figure 42. High resolution C1s, O1s, and F1s spectra for EtOH bath specimen.

Figure 43. High resolution C1s, O1s, and F1s spectra for EtOH + autoclave specimen.

Figure 44. High resolution C1s, O1s, and F1s spectra for t (0) specimen.

Figure 45. High resolution O1s, N1s, Si2p, and Si2p spectra for t (1) specimen.

Figure 46. High resolution O1s, N1s, Si2p, and Si2p spectra for t (3) specimen.

Figure 47. High resolution O1s, N1s, Si2p, and Si2p spectra for t (10) specimen.

Figure 48. High resolution O1s, N1s, Si2p, and Si2p spectra for t (20) specimen.

Figure 49. High resolution O1s, N1s, Si2p, and Si2p spectra for t (40) specimen.

Figure 50. High resolution O1s, N1s, Si2p, and Si2p spectra for t (80) specimen.

Figure 51. High resolution O1s, N1s, Si2p, and Si2p spectra for t (160) specimen.