

Chapter 1

Plasma Reactor Characterization

1.1 Introduction

Plasma is often referred to as the fourth state of matter. It is highly reactive making it useful for a number of chemical processing applications. Plasma is created when a neutral gas is given sufficient energy from an electronic discharge source to create new product ions and radicals. The source of free electrons is generally a high energy glow discharge such as a high voltage electrode. This resulting collisions of electrons and gas molecules result in a net energy transfer to the molecules producing metastable fragments and energized ions. The resulting product is a mixture of highly excited ions consisting of fragmented portions of the parent molecule. Plasma generated from an oxygen (O_2) carrier gas typically consists of O^+ , O^- , O_2^+ and O_3^+ ions for example. The plasma particles are extremely unstable and their energetic states cause them to be highly reactive with particles or surfaces that they contact.¹ Plasma is generally produced in a low pressure environment using a high vacuum system to promote stability of ionic radicals formed. This low pressure stability is achieved by effectively increasing the mean free path between the active components. Plasma may also be produced in an environment near atmospheric pressure without the need for maintaining an expensive vacuum system.²

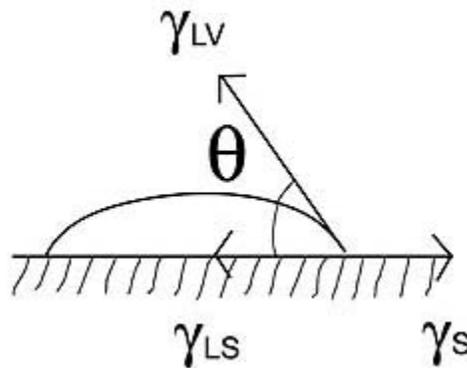
Plasma processes provide a cost effective and environmentally friendly alternative to many important industrial processes because the method produces no unwanted waste products and in most cases exposes operators to no significant hazards. Plasma pretreatment is a vital process used for improving lamination, printing, and adhesion. Plasma promotes adhesion by increasing the effective surface area of the metals for example. This roughening in turn promotes more intimate molecular contact between the metal and the adhesive allowing for stronger bonds to occur.³ The highly reactive ions found in plasma make the processing a valuable tool in surface cleaning. Additionally plasma etching is a tool used in the semiconductor industry to create tunnels on surfaces. Plasma etching achieves this by creating a highly reactive plasma phase which contacts

and volatilizes the solid portion of the material to be etched. The volatilized material can then be removed by desorption from the substrate in gaseous form.⁴

A variety of carrier gases can be used in plasma processing. Oxygen and argon are two examples of carrier gases that can be used to modify surfaces. When plasma is utilized in a controlled vacuum environment, a chemically modified surface can be attained for use in subsequent applications. Oxygen is a commonly used carrier gas because of its reactivity. Oxygen plasma is often used to react with low energy organic contaminants to provide clean, high energy surfaces for chemical applications. The term “plasma etching” refers to the selective removal of material and it is now widely used in industry for a number of applications.⁵ The term more commonly refers to the process of pathway formation on semiconductor surfaces using plasma processes.

Surface energy provides a key measure for gauging the effectiveness of plasma modification on polymers. Plasma treatment improves wettability by creating higher energy surfaces. These high energy surfaces allow water to spread over a solid surface upon contact. The angle at which this solid-liquid contact occur can be measured with a goniometer and studied as an quantification of how much surface modification was induced by the plasma process. This angle is a result of the surface free energy of the solid in equilibrium with the saturated vapor of the liquid (γ_s), the solid-liquid interface free energy (γ_{ls}), and the liquid surface tension in equilibrium with the solid (γ_{lv}).

$$(\gamma_s - \gamma_{ls}) / \gamma_{lv} = \cos \theta \quad \text{Equation 1.1}$$



A liquid which spreads completely on a surface would have a contact angle near 0°. A liquid that displayed extremely poor wettability on a substrate would have a contact angle

approaching 180°. A droplet having a 180° contact angle would appear as a perfectly shaped ball sitting on a table top with no observable spreading occurring at its base in contact with the table.

Surface energy reflects contributions from two distinct components. The polar component (γ_p) of surface energy represents tension related to polar interactions and hydrogen bonding. The dispersive component (γ_d) of surface energy encompasses interactions caused by van der Waals and weaker intermolecular forces. The total surface energy is attained from the sum of these two individual components. To account for both components of the surface energy, contact angle (θ) data is often used from two fluids where both surface energy components are known in each fluid. The total surface energy of the substrate can then be calculated from the harmonic mean in which two equations (Equations 1.1 and 1.2) are solved for polar and dispersive components, γ_p and γ_d .⁶

$$(1 + \cos \theta_1) \gamma_1 / 4 = [\gamma_{1d} \gamma_d / (\gamma_{1d} + \gamma_d)] + [(\gamma_{1p} \gamma_p / (\gamma_{1p} + \gamma_p))] \quad (1.1)$$

$$(1 + \cos \theta_2) \gamma_2 / 4 = [\gamma_{2d} \gamma_d / (\gamma_{2d} + \gamma_d)] + [(\gamma_{2p} \gamma_p / (\gamma_{2p} + \gamma_p))] \quad (1.2)$$

The total surface energy is then calculated from the sum of the polar and dispersive components.

$$\gamma = \gamma_p + \gamma_d \quad (1.3)$$

Corona treatment is a commonly used industrial process for increasing the surface energy of polymer substrates and enhance wettability. It has also been utilized to induce wettability gradients across polymer surfaces for mechanical and biological applications.⁷ Corona discharge utilizes a high potential electrode to ionize gases in the discharge path. The fragmented gas ions are highly reactive and act to modify the polymer surface. The electrical discharge from the corona occurs at a threshold voltage. At voltages less than the threshold voltage, no discharge occurs. When the threshold voltage is exceeded, electrons are emitted from the discharge electrode and move to the lower potential electrode ionizing the gaseous medium in its path. As reactive radicals recombine and undergo relaxation, radiation is given off in the form of visible light yielding a corona

glow. Excessive voltage across the electrode is detrimental to the modification process and produces unwanted arcing between the electrodes.⁸

Polymer surface modification by corona discharge is an unstable process and wetting effects produced by the reactive ions are transient. Effects of corona discharge modification on polyethylene surfaces after five minutes of corona treatment in air disappear and are no longer observable by XPS analysis two days after treatment.⁹ XPS analysis quantifies chemical species on the surface of a sample. All elements and bonding states are identified with this analytical technique with the exceptions of hydrogen and helium. The instrument utilizes x-rays to emit photoelectrons from the sample surface. The photoelectrons emitted are separated by an energy analyzer based on kinetic energy. The photoelectron intensity is then plotted against binding energy to produce the XPS spectrum.

The gradual disappearance of surface modification occurs primarily for two reasons. First, ionic fragments and other contaminants from the surrounding air may imbed in the modified surface reducing the wettability of the polymer. The polymer itself may also be subject to a relaxation in which polar functional groups of the chain are overturned into the bulk of the polymer.^{9,10} Secondly,⁸ the nature of the surface modification induces high energy functional groups which may rearrange to form lower energy species. Therefore it is crucial that further processing of a corona modified surface take place soon after corona exposure. The nature of corona modification produces functional groups on the surface of the polymer which may be utilized in a chemical reaction to produce a sustainable wetting surface.^{11,12} Surfactants may also be used on a corona modified polymer surface to sustain wettability for an extended period of time.

Extensive XPS analysis has been performed on corona treated polystyrene surfaces in air. Greenwood et al have shown corona treatment of polystyrene at atmospheric pressure resulted in a dramatic increase in oxygen character on the surface of the polymer from zero percent to 30.9% carbon-oxygen functionalities. Approximately one third of these oxygen functional groups were carboxylic acid.¹³ The other functional groups were comprised primarily of carbonyl derivatives (-C=O). Hydroxyl groups have been shown to be present in air corona treatment as well.

Literature has also shown that corona discharge and other plasma treatments introduce a significant amount of surface degradation onto the polymer by imparting pit-like structures onto the polymer surface. The amount of surface degradation appears to be dependant upon the pressure of the plasma process being used. High pressure plasma processes induce larger pit-like structures typically on the order of 400-500 nm in diameter. Low pressure plasma processes are much less destructive to the substrate and cause smaller amount of surface degradation.¹³

1.2 Experimental

A plasma reactor was constructed for the purpose of ionizing gases above a polymer substrate placed on a grounded sample holder. The chamber consisted of a 11" x 8" x 8" lexan case built with two inlet ports for gas flow. A 50 kV corona discharge coil with a variable voltage control was mounted through the top of the chamber and sealed. The unit utilized a variable voltage control that allowed voltages of up to 50 kV. Inlet ports were installed at the base of the chamber to allow gases to flow into and out of the chamber. In addition to these features, a 3 inch by 3 inch square sample platform was installed with position adjustment controls to enable the sample holder to be adjusted vertically or horizontally.

Water vapor was first used in characterizing the effects of water plasma on polystyrene surfaces. Silicon surfaces were first cleaned by immersion in xylene for a minimum of three hours. Silicon surfaces were then transferred to ethanol for a minimum of six hours before applying polymer. An 10% by weight solution of polystyrene in xylene was then spun on the cleaned silicon surfaces and baked for 3 hours at 120°C. Water vapor was passed through the chamber by bubbling clean air into water within an enclosed vessel. Tubing at the top of vessel was connected to the inlet of the plasma reactor to allow water vapor to circulate within the chamber as the carrier gas. Humidity levels within the chamber were measured using a Zellweger Analytical Zephyr II+ humidity meter. Humidity levels were found to quickly reach an equilibrium within the chamber at atmospheric pressure of approximately 88% after 10 minutes of air circulation at 40 cc/min.

Polystyrene thin films on silicon were then placed on the sample holder to characterize contact wetting angles as a function of discharge voltage, height below the discharge, and discharge time. Advancing contact angles were measured by removing the film substrates from the chamber and pipetting a 10 μ l water droplet onto each modified surface. A second 10 μ l droplet was then pipetted on top of the first drop and the contact angle of the resulting water mass was measured using a Rame-Hart tilting base model 100-06 goniometer. In the first study, polystyrene films were placed on the sample holder 30 mm below the discharge wire of the corona unit at a voltage of 37 kV and exposure

time of one minute. Contact angle data was taken at additional discharge heights of 35, 40, 50, and 65 mm above the substrate at the same exposure time and voltage. A contact angle curve was graphed as a function of varying discharge height. This characterization study was repeated for discharge voltages of 32 kV, 42 kV, and 47 kV.

A second contact angle study was performed in which the 37 kV discharge height was maintained at a constant value of 30 mm and the exposure time was varied. The 18% solution of polystyrene in NMP was again spun onto cleaned silicon surfaces and exposed to water plasma at time intervals of 10, 20, 30, 45, 60, and 120 seconds. Polybutadiene was used as a second polymer to generate a contact angle series versus time at a discharge voltage of 37 kV and height of 30 mm for comparison.

To calculate surface energy effect resulting from the plasma chamber, two additional series of contact angle data were taken with formamide droplets on polystyrene surfaces. The first data series was taken at exposure heights of 30, 35, 40, 50, and 65 mm discharge height at fixed exposure time of one minute and with a constant discharge voltage of 37 kV. The second data series was taken at exposure times of 0, 10, 20, 30, 45, 60, and 120 seconds at a fixed discharge height of 30 mm and a constant discharge voltage of 37 kV. This data was utilized with parallel data from water droplets in calculations of polystyrene surface energy using the harmonic mean method.

Contact angle characterization was also performed as a function of discharge time and position on the sample platform perpendicular to the linear corona discharge electrode wire. To perform these studies, 5 mm x 8 mm silicon pieces were cut and polystyrene was spuncast onto each cleaned piece from a solution of 10% by weight polystyrene in xylene. The pieces were baked for one hour at 120°C to remove residual xylene from the surfaces. For time characterization of plasma exposure time, polystyrene coated silicon pieces were individually exposed to water vapor plasma at discharge times of 10, 20, 30, 45, 60, and 120 seconds. 10 ml deionized water drops were then pipetted onto each polymer surface. A second drop was then pipetted on top of the initial drop and the advancing contact angle was measured and recorded. Advancing contact angles were measured four times and averaged. Contact angle characterization by sample platform position was achieved by placing polystyrene coated silicon pieces at 0.25 cm intervals across the 3 inch by 3 inch sample platform perpendicular to the discharge wire. Pieces

were staggered in two adjacent, individual rows. Samples were simultaneously exposed to water vapor plasma at 37 kV for 1 minute exposure time at 37 kV and 3 cm depth below the wire. Deionized water was immediately pipetted in 10 ml drops onto each polystyrene film to minimize surface energy losses. Advancing contact angle measurements were then taken for at each position four times and averaged.

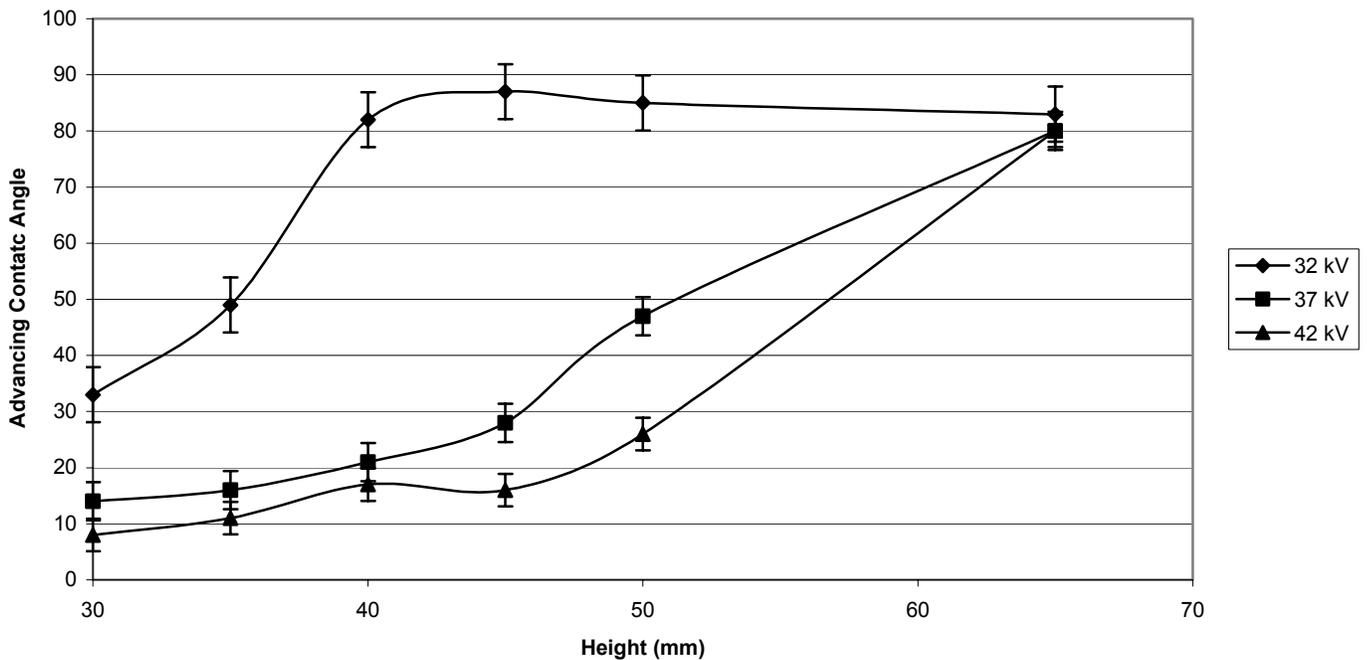
Ammonia hydroxide was used to produce amine functional groups on the polystyrene surface in additional studies performed at a discharge voltage of 37 kV and height of 30 mm. The ammonia carrier gas was produced by bubbling nitrogen gas through ammonia hydroxide at a rate of 40 cc/min. The resulting ammonia rich vapor was then fed into the inlet of the plasma chamber. Advancing contact angle curves were generated for this process as a function of exposure time within the plasma reactor. XPS analysis was also performed to quantify the degree of amine functionalization produced by the ammonia plasma process.

A 2% solution by weight of polybutadiene in xylene was spun cast onto cleaned silicon surfaces and baked for 30 minutes at 40°C. Characterization studies were performed on this polymer as a function of discharge height and exposure time for comparative purposes with polystyrene. Contact angle data was taken at discharge heights of 30, 35, 40, 60, and 65 mm at two voltages of 37 kV and 42 kV. Contact angle data on polybutadiene was taken at a discharge voltage of 37 kV for discharge times of 19, 29, 39, 45, 60, and 120 seconds.

1.3 Results and Discussion

Figure 1.1 shows advancing contact angles measured as a function of distance from the discharge source. Each curve on the plot represents a different source voltage for thirty second plasma exposure time. The curves show that increases in voltage have a significant effect in lowering the contact angle and increasing the surface energy of the polystyrene. Thirty seconds of plasma exposure at conditions of 32 kV do not induce enough modification to produce a fully wetting surface as shown by Figure 1.1. Contact angle data at the same height with voltages of 37 kV and 42 kV generate highly wetting surfaces with contact angles less than 15 degrees. It is also observed that small changes in height greatly affect the degree of surface modification yielded at a voltage of 32 kV. This suggests that voltages of at least 37 kV should be used to produce effective surface modification at thirty second water plasma exposure times.

Figure 1.1: Contact Angle vs. Discharge Height For Water on Polystyrene After a 30 Second Water Plasma Exposure



Similar studies were performed for one and two minute exposure times. Exposure for one minute at 42 kV again yielded the strongest degree of surface modification. Contact angle data at 32 kV however was much closer to the data given at 37 kV when the exposure time was extended to one minute. Figure 1.3 shows contact angle data obtained at the same voltages after an exposure time of two minutes. Contact angle data at 37 kV approaches the values given at 42 kV when the exposure time is increased to two minutes. The data at 32 kV shows significantly less modification than 37 kV and 42 kV conditions at discharge distance greater than 35 mm. Collectively, this contact angle data demonstrates that a maximal degree of surface modification can be achieved by optimizing time, height, and voltage parameters without using large time exposure or voltage conditions.

Figure 1.2: Contact Angle vs. Discharge Height for Water On Polystyrene After a One Minute Water Plasma Exposure

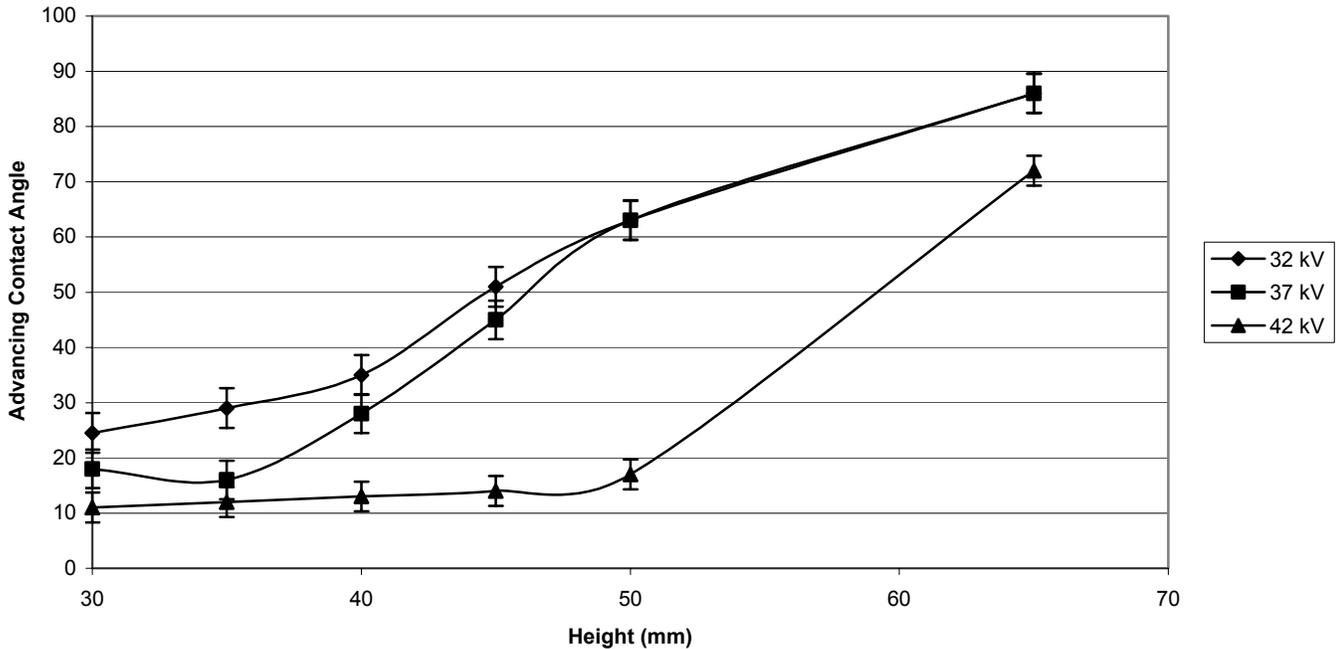
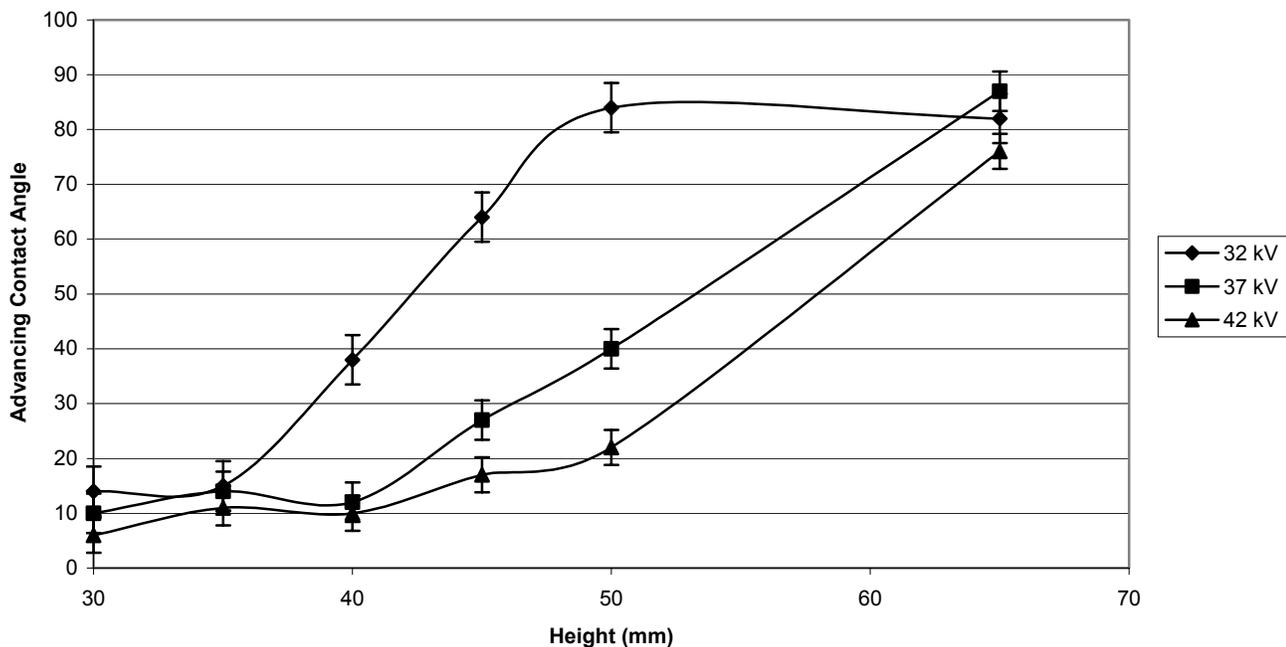


Figure 1.3: Contact Angle vs. Discharge Height For Water on Polystyrene After a Two Minute Water Plasma Exposure



Error bars on contact angle graphs represent the average standard deviation of contact angle data points for each voltage curve. It should be noted however that the spread in measured contact angle data appeared to consistently increase with higher measured values of contact angles. Average advancing contact angle data less than 25° in all cases demonstrated significantly less spread in individual data points than contact angle averages measured on more hydrophobic surfaces with higher values. The 37 kV curve on Figure 1.3 shows an average contact angle value of 10° at a height of 30 mm and a value of 87° at 65 mm. The measured values for the 10° average were 9° , 10° , 10° , and 13° . The measured values for the 87° average were 79° , 85° , 91° , and 94° . This increase in variation with increasing contact angle measurements was likely inherent in the process because the plasma modification was more influenced by small variations in voltage, height, and exposure time when the modification had not reached a maximum. This observed variation was present in all contact angle data taken.

Standard corona conditions were initially selected to use in surface modification of polymer films based on these results. Contact angle results show that better surface modification is achieved with higher voltages. During these experiments it should be noted that some arcing from the discharge wire to the sample platform was observed at larger voltages. Mild arcing was occasionally observed at 42 kV and 3 cm height. Strong arcing appeared more consistently at higher voltages greater than 45 kV. Because arcing has a very destructive effect on the capacitor within the corona power supply it must be avoided. Therefore a voltage of 37 kV was selected as a standard voltage to use unless other power requirements were needed.

Arcing was also a primary consideration in selecting a standard discharge height in plasma experiments. Contact angle curves showed that surface modification of polystyrene films was improved at smaller discharge heights above the sample. However, lowering the discharge wire within 3 cm of the sample platform at 37 kV also produced significant arcing. Therefore a standard experimental height of 3 cm was chosen for later experiments unless other conditions were specifically needed. At the selected conditions of 37 kV and 3 cm height, Figure 1.4 shows that maximum surface modification occurs after approximately 45 seconds of water plasma exposure. Based on this curve, a standard exposure time of one minute was selected for experiments performed at these height and voltage conditions.

Figure 1.4: Contact Angle Data for Water Plasma on Polystyrene After Varying Plasma Exposure Times

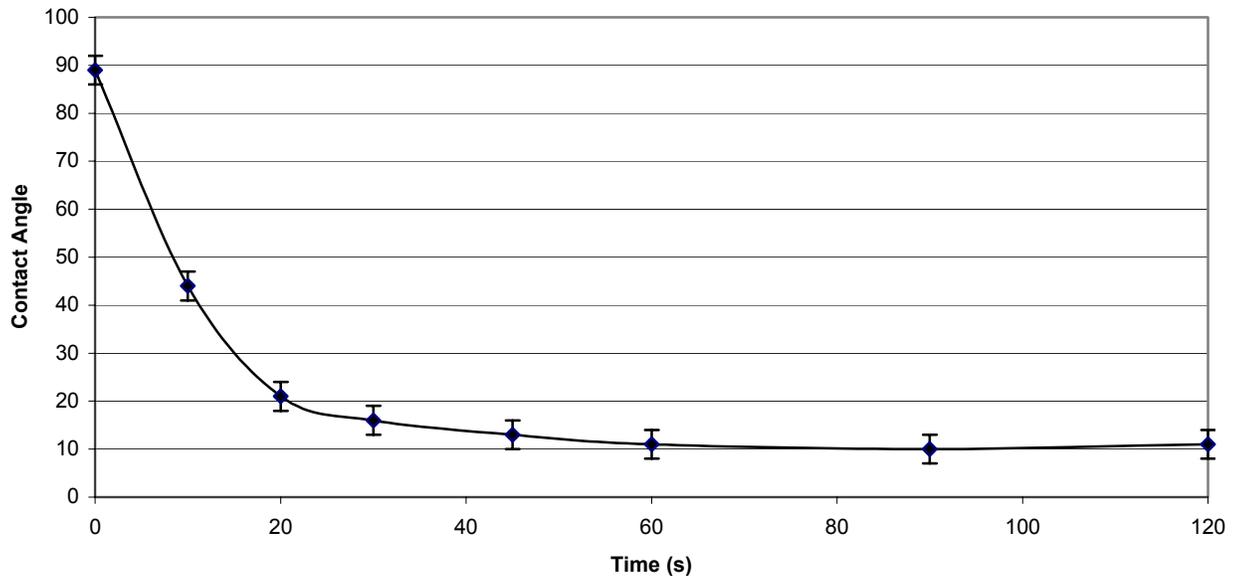


Figure 1.4 depicts contact angle data at plasma conditions of 30 mm discharge height and 37 kV at varying discharge times. The contact angle of water on unmodified polystyrene surfaces was determined to have an average contact angle value of approximately 87 degrees. After twenty seconds of water plasma exposure at these conditions, polystyrene contact angle values reached a plateau value of approximately 16 degrees. This implies that a maximum degree of polystyrene surface modification is achieved with very limited exposure time at these conditions.

Surface energy calculations were performed using the harmonic mean method to quantify the degree of surface modification occurring within the plasma chamber. Matlab was used to solve groups of simultaneous equations (1.1 and 1.2) and each set of conditions. The change in surface energy with discharge height at 37 kV and 1 minute exposure times is shown Figure 1.5. Unmodified polystyrene surfaces have a surface energy of 25.1 dyn/cm. Water vapor plasma surface modification shows a nearly two hundred percent increase in surface energy to 70 dyn/cm at a discharge height of 30 mm. Surface energy effects from the plasma process begin to diminish rapidly as the discharge height is increased above 40 mm. Figure 1.6 shows a rapid increase in polystyrene

surface energy during the first twenty seconds of modification. Surface energy then appears to plateau at 70 dyn/cm with longer exposure times.

Figure 1.5: Surface Energy of Polystyrene vs. Corona Discharge Height at 37 kV and 1 Minute Exposure Time

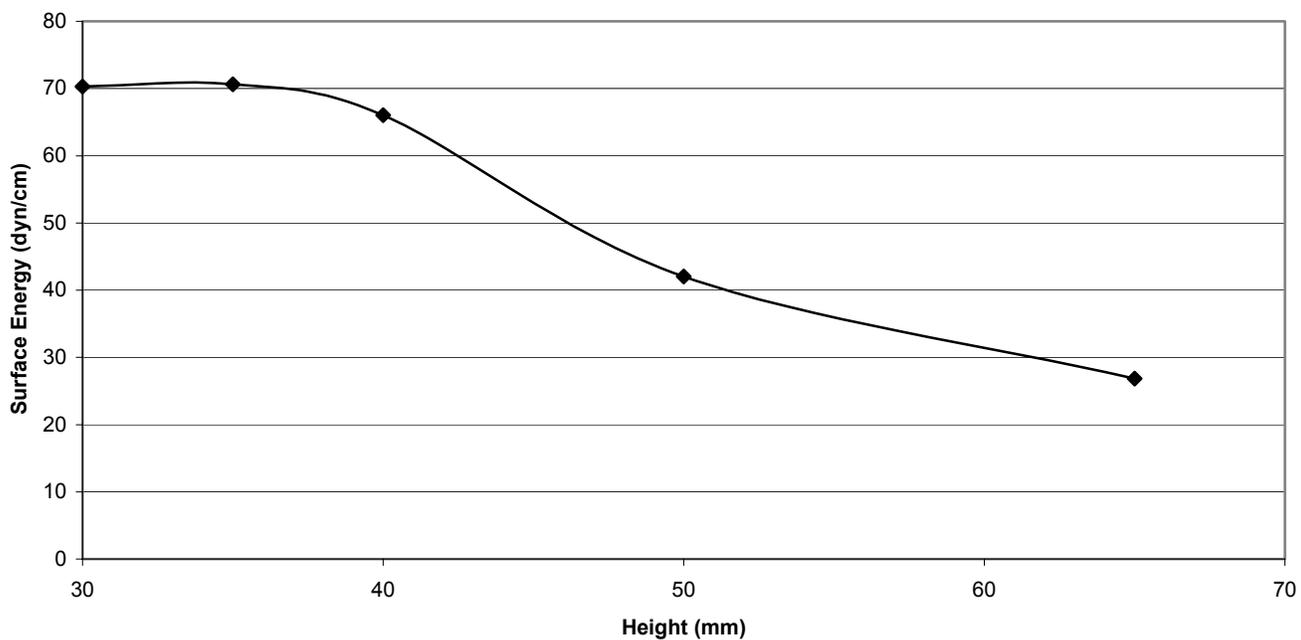
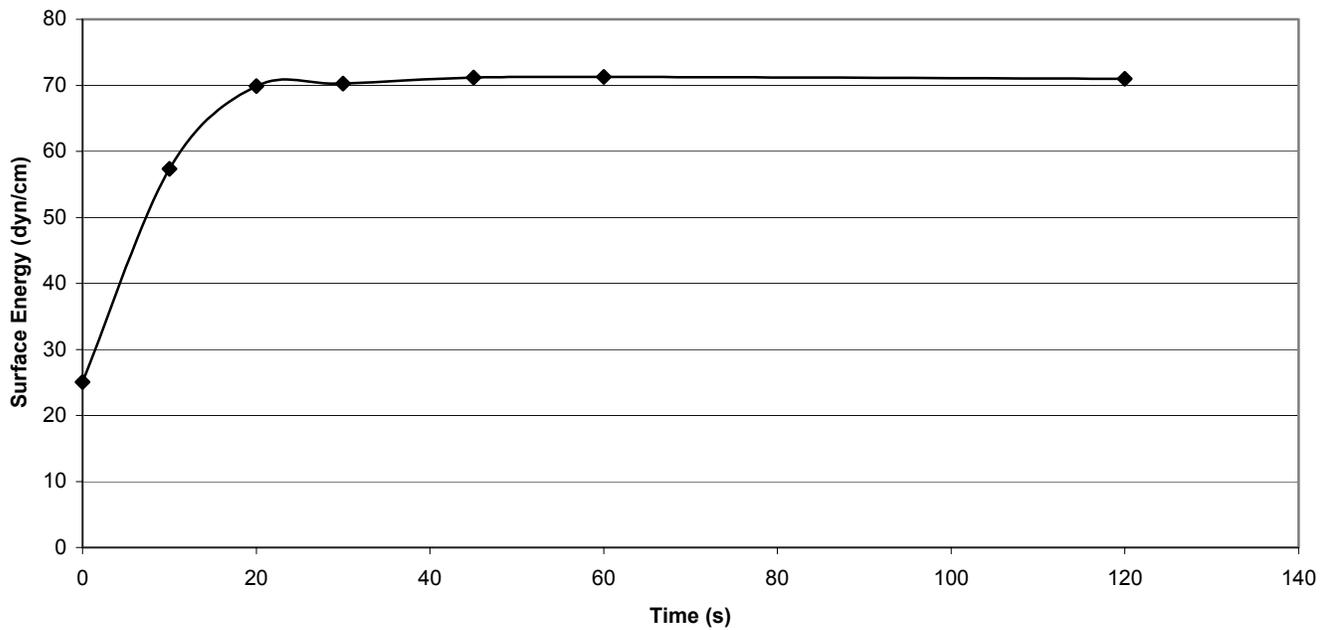
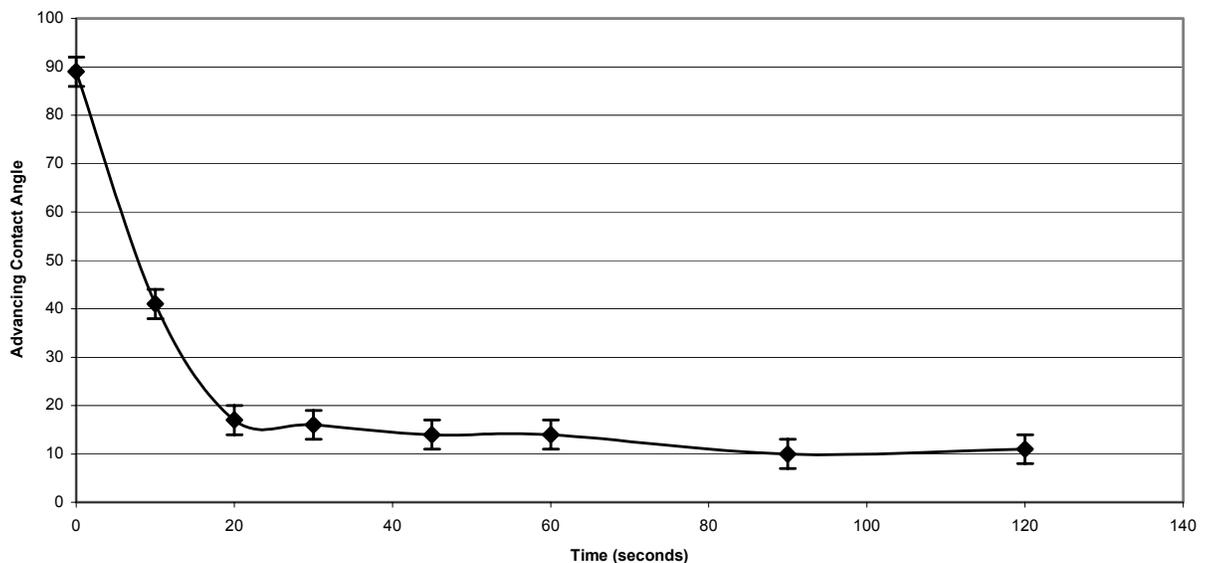


Figure 1.6: Surface Energy of Polystyrene vs. Water Plasma Exposure Time at 37 kV and 3 cm Discharge Height



XPS analysis was used for a chemical analysis of polystyrene surfaces before and after ammonia plasma modification. A carbon (C1s), oxygen (O1s), and nitrogen (N1s) analysis of unmodified polystyrene yielded surface concentrations of 98.01%, 1.76%, and 0.23% respectively. This analysis likely represented atoms down to a depth of approximately 50 angstroms in the sample. Thus XPS analysis does not give a true accounting of the surface composition alone but it does identify increases in amine surface functionalization. The presence of oxygen in the unmodified polystyrene suggests the presence of contamination on the film surface. XPS analysis performed after one minute of water plasma exposure at 37 kV and 30 mm discharge height showed significantly higher levels of surface amine groups as well as an increase in oxygen. Composition molar percentages for the ammonia modified surface were 77.34% carbon (C1s), 17.90% oxygen (O1s), and 4.76% nitrogen (N1s). Contact angle characterization was also performed as a function of time for the ammonia plasma process. Results in Figure 1.7 show a similar plateau is quickly reached after twenty seconds of exposure time. Contact angle values after twenty seconds exposure typically fluctuate between 10° and 15°.

Figure 1.7: Contact Angle Data For Ammonia Plasma on Polystyrene After Varying Plasma Exposure Times



Polybutadiene was used as a second polymer to test the effects of surface modification within the chamber. Figure 1.8 shows contact angle data for water plasma exposure at on Polybutadiene at 1 minute plasma exposure times with voltages of 37 kV and 42 kV. A voltage of 42 kV was only able to produce a contact angle of 20 degrees after a full minute of water plasma exposure. The films resistance to modification may be due to the cross linked nature of the polymer. This result suggests that combinations of polymers that undergo differing levels of surface modification within the chamber can be combined for use in applications where selective modification is required. This hypothesis is further verified by results shown in Figure 1.9 where polybutadiene does not modify with water plasma exposure time. A modification time of 45 seconds on this polymer produced an average contact angle of 44°. This result is significantly higher than the 13° angle observed after 45 seconds of plasma exposure on polystyrene and suggests some form of degradation of the polymer occurs.

Figure 1.8: Corona Height vs. Advancing Contact Angle For Water Plasma on Polybutadiene (1 Minute Exposure)

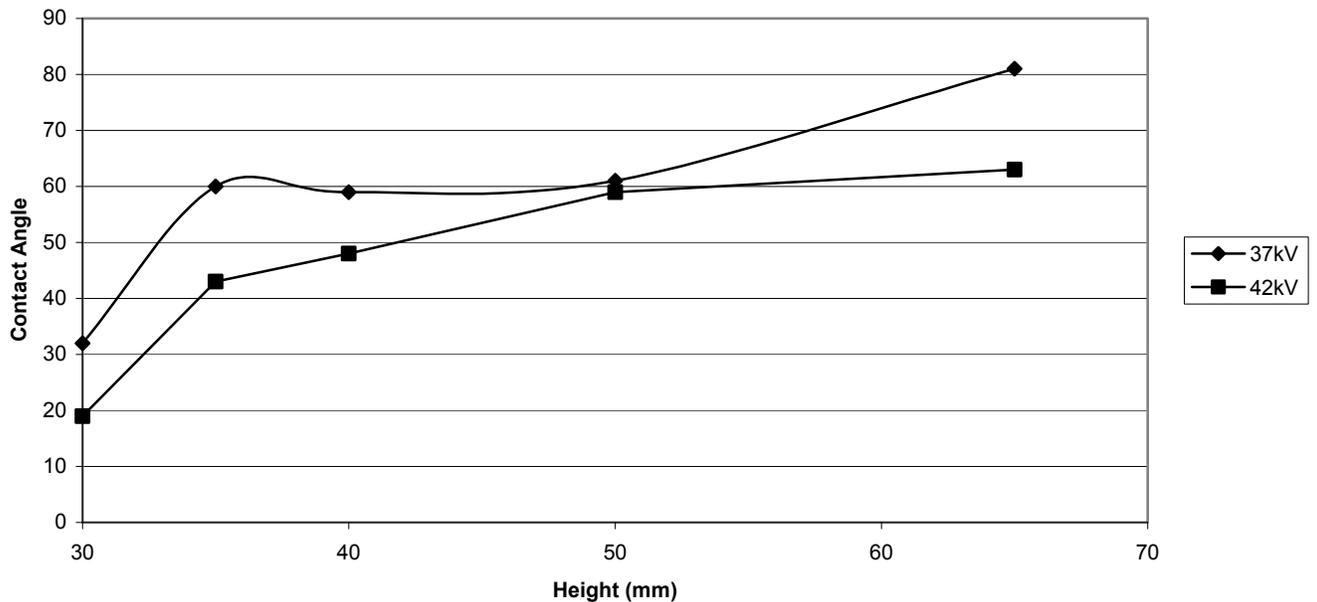
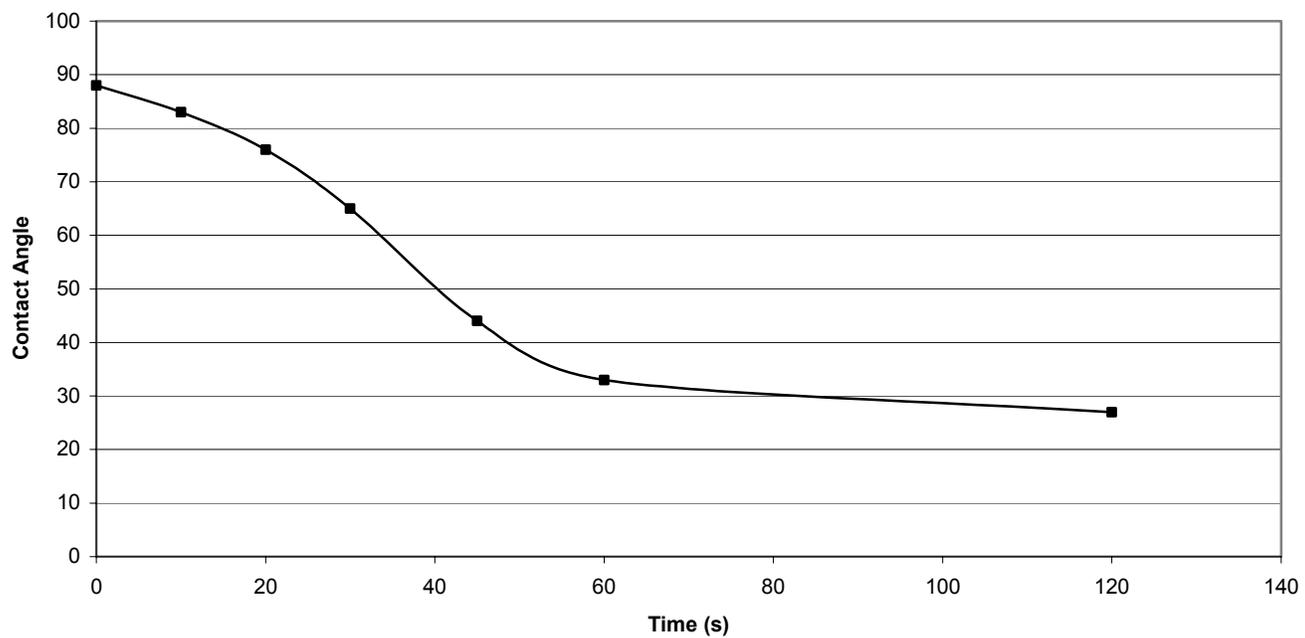


Figure 1.9: Contact Angle of Water on Polybutadiene After Varying Water Plasma Exposure Times



1.4 Conclusions

A plasma chamber can be effectively constructed utilizing a 50 kV corona discharge unit and selected carrier gases. The degree of surface modification will be greatly affected by the distance the polymer film is maintained from the discharge unit as well as the plasma exposure time. Polystyrene samples placed closest to the discharge electrode and exposed for the greatest amount of time will yield the highest degree of surface modification. These conditions will also produce the greatest increase in surface energy as suggested by contact angle data. Discharge voltage, height, and time may be optimized to produce a maximal level of polymer surface modification and prevent arcing without using high voltages which may be detrimental to the corona power supply.

1.4 References

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Chapter 2

Quantification of Surface Modification

2.1 Introduction

Photoluminescence is a phenomenon in which light is emitted from a material excited by another light source of higher energy. The photons from the source must have enough energy to cause excitation for photoluminescence. In this excited state, electrons transition from their valence electron states to a higher energy conductance band. The resulting excited transition state is unstable and the electrons quickly fall back to their original ground states. As the electrons return to ground state, photoluminescent radiation is emitted. This relaxation occurs on the order of nanoseconds and the radiation given in returning to ground state can be collected by a fluorescence spectrometer for analysis. Photoluminescent radiation provides a unique insight into the material properties and electronic energy states of the sample.¹

Photoluminescence analysis is a valuable tool because it provides a wealth of information on the electronic properties of a substance with limited degrading of the sample being tested. Unlike many other methods of optical analysis, photoluminescence is relatively insensitive to issues of excitation beam alignment and surface imperfections of the sample being tested.² The primary requirement for utilizing photoluminescence analysis is that the sample being studied must contain a gap between conductance and valence bands allowing for emissions due to the relaxation of excited electrons. This band gap may be inherent in the material or artificially induced by secondary impurity materials. Samples that do not contain prohibitively large band gaps or contain very small energy band gaps will not produce luminescence in the visible wavelength range without the addition of impurities.

Photoluminescent tagging dyes are often used as staining agents in biological applications to label and sort cells in tissue samples. They are also widely used as molecular probes to label the presence of specific functional groups and molecules. Tagging agents are useful in these applications because they form covalent bonds with

specific functional groups. After attachment the tagging agents absorb light of a specific excitation wavelength. The excited electrons resulting from this absorption in turn emit light of a specific wavelength which can be detected by fluorescence spectrometry. Bryhan et al. have shown fluorescent dyes are useful in tagging oxidized groups on polymers after surface modification with corona discharge.³ Fluorescence intensity has also been used to estimate the concentration of DNA in hybridization reactions by inducing ethidium bromide (EtBr).⁴ Photoluminescent tagging agents are available in a broad range of excitation and emission wavelengths.

O-phthaldialdehyde (OPA) is a photoluminescent tagging agent used extensively as a molecular probe for amine functional groups in biological applications. The two aldehyde groups on the aromatic ring are very reactive with amine functional groups and enable the formation of strong covalent bonds between amine containing molecules on surfaces and the OPA molecules.⁵ Once the chemical attachment has been established, fluorescence spectroscopy can be used to verify the presence of the amine functional groups. When OPA is excited by energy of wavelength of 360 nm and an emission wavelength near 450 nm can be detected.⁶

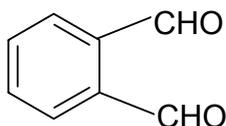


Figure 2.1: O-phthaldialdehyde molecule

7-amino-4-methylcoumarin (AMCA) is a second photoluminescent tagging agent with applications in surface modification. AMCA however is used to probe the presence of carboxylic acid functional groups. The dye is primarily used in biological applications as a fluorescent tagging agent for cellular antibodies and immunological assays.⁷ The dye forms strong covalent bonds with carboxylic acid groups by attachment with its extended amine structure. When AMCA is excited by energy of wavelength 360 nm, a blue photoluminescent emission is given off around 440 nm.⁸

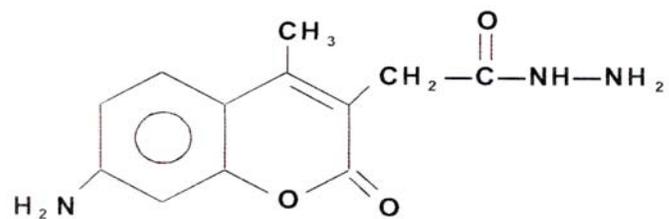


Figure 2.2: 7-amino-4-methylcoumarin chemical structure

2.2 Experimental

Two photoluminescent dyes were used as a basis to verify surface modification by the presence of specific functional groups. A 5 ml solution of AMCA was prepared by dissolving 1 mg of AMCA reagent into 1 ml of dimethylformamide (DMF). The solution was then diluted with the addition of 4 ml of water yielding a base solution with a concentration of 0.81 mmol/L in a total volume of 5 mL. This solution served as a basis from which all other AMCA experiments were performed. OPA was received directly from Pierce Endogen in solution with a molar concentration of 5.96 mmol/L .

The second stage of preparation for this experimental series required the generation of calibration curves for AMCA and OPA for the purpose of estimating the carboxyl and amine surface concentrations from photoluminescent intensity data. Each calibration curve was prepared by using the maximum photoluminescent intensity near the emission wavelength of each dye solution. These peak intensities were then taken for a series of dilutions for each solution and plotted as a function of concentration. All surfaces were prepared by spincoating 10% polystyrene by weight in xylene onto clean silicon substrates. Polymer films were baked for one hour at 120°C to remove residual xylene left over from the spinning process.

AMCA was first used to verify the presence of carboxyl groups on modified polystyrene surfaces during the water vapor plasma process. Polystyrene surface modification was then achieved by corona treatment using deionized water vapor as the carrier gas at 37 kV, 3 cm discharge height, and one minute plasma exposure time. 50 µl of the prepared AMCA dilute solution were pipetted onto the surface immediately after plasma modification. The solution remained on the surface for a period of 10 minutes before the surface was rinsed in deionized water and dried with an air gun. Photoluminescence emission spectra were then taken using the Hitachi F4500 Fluorescence Spectrometer at an excitation wavelength of 360 and a scanning rate 240 nm/min. A resulting emission around 450 nm would indicate the presence of carboxyl functional groups.

The same process was repeated to verify the presence of amine functional groups on polystyrene after ammonia plasma modification. In this process however, the

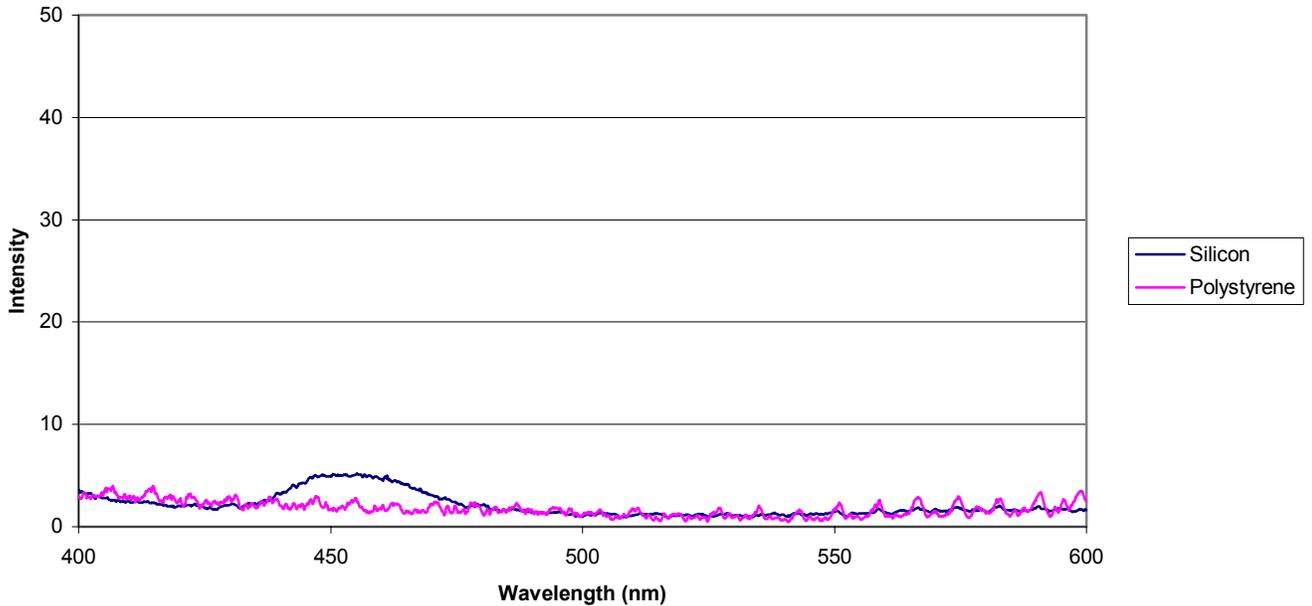
premixed solution of OPA was used as the photoluminescent tag in place of the AMCA reagent. Additional studies were also performed in which AMCA was used in the amine plasma process and OPA was used in the water vapor plasma process.

Photoluminescent tags were also used as a tool to characterize ion current distribution within the plasma chamber. Polystyrene was again spun onto 5 mm x 8 mm rectangular pieces of clean silicon and baked for 30 minutes at 120°C. These pieces were then placed at 0.25 cm intervals across the 3 inch by 3 inch sample platform perpendicular to the discharge wire. Pieces were staggered in two individual rows because the 5 mm width of each sample prohibited placement of the pieces at 0.25 cm intervals in a single row. Samples were exposed to water vapor plasma at 37 kV for 1 minute exposure time at 37 kV and 3 cm depth below the wire. After plasma exposure, the samples were removed and 50 uL of AMCA solution was pipetted onto each polymer film. AMCA remained on each film for 10 minutes before rinsing in deionized water and air gun drying. Photoluminescence spectra were taken of each piece and the maximum intensity was graphed as a function of perpendicular distance from the discharge wire center line (e.g. 0.25 cm, 0.5 cm, 0.75 cm, etc.). AMCA calibration curves were used to estimate relative carboxylic acid concentration per unit area implied by the photoluminescence intensity at each position.

2.3 Results and Discussion

A fluorescence spectrometer was used to obtain photoluminescence spectra of the silicon substrates. Polystyrene films were used to verify that background interference was minimized. Figure 2.3 shows photoluminescence spectra of a silicon surface cleaned with xylene yielding a very small, broad emission peak centered around 455 nm when the surface receives excitation energy of wavelength 360 nm. This excitation wavelength was chosen because this is the key excitation wavelength used by the photoluminescent tagging agents, AMCA and OPA. The figure also shows that the small luminescence signal given by silicon is completely masked and unobservable when the silicon surface is covered by a thin film of polystyrene. The masking of the peak most likely occurs because the incident excitation energy is absorbed by the polystyrene. Polystyrene is known to photoluminesce at an emission wavelength of 333 nm.

Figure 2.3: Photoluminescence Spectra of Clean Silicon and Polystyrene on Silicon at an Excitation Wavelength of 360 nm



Figures 2.4 and 2.5 illustrate the change in intensity as a function of the concentration of the photoluminescing tags in solution. The calibration curve for AMCA was observed to be nonlinear with a concentration of 2×10^{-7} M yielding a photoluminescence intensity peak of approximately 200 units. At concentrations lower than this value, the calibration curve is approximately linear. As the concentration increases above 2×10^{-7} M, the calibration curve becomes more parabolic in nature where increases in concentration do not produce as a significant an effect on photoluminescence intensity. The calibration curve for OPA is also somewhat linear up to a concentration of 0.0002 M. At stronger concentration curve becomes parabolic. These curves were used to estimate carboxylic acid and amine functional group concentrations based on photoluminescence intensities. Because the curves were much more linear for dilute concentrations having intensities of less than 200 units, it was assumed that reasonable estimates of surface moieties could be attained given identical detector conditions.

Figure 2.4: AMCA Photoluminescence Intensity vs. Concentration

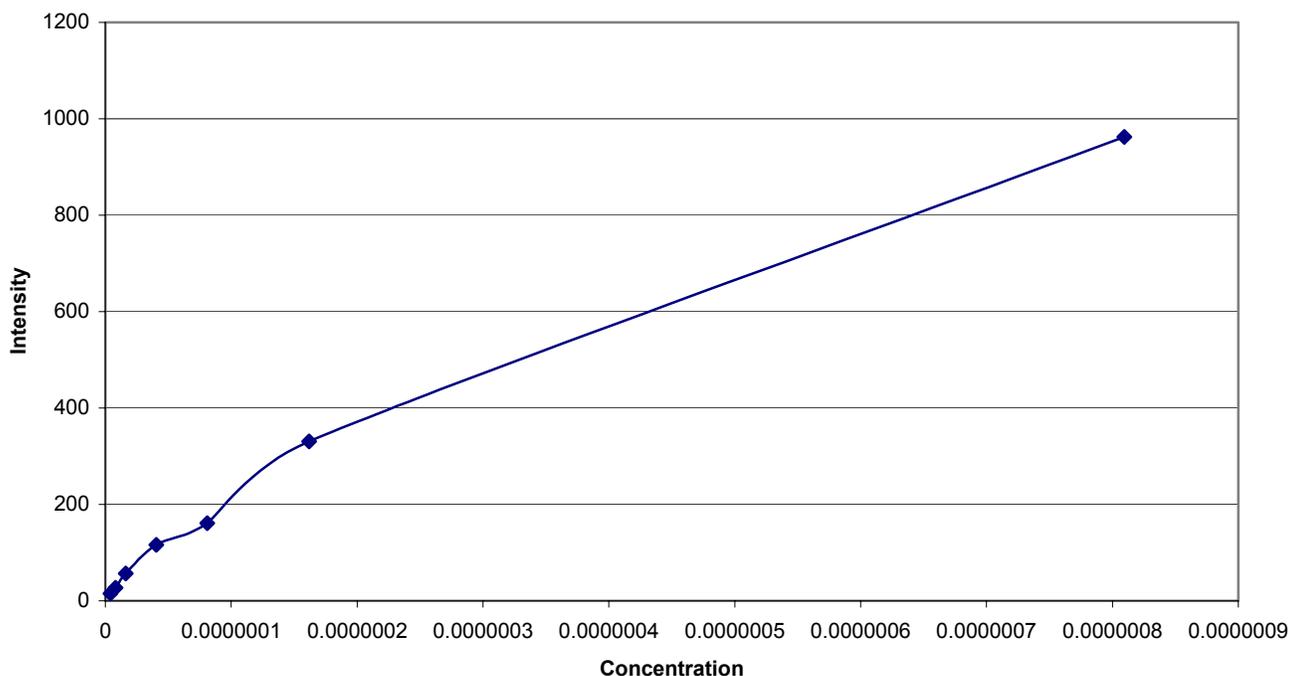
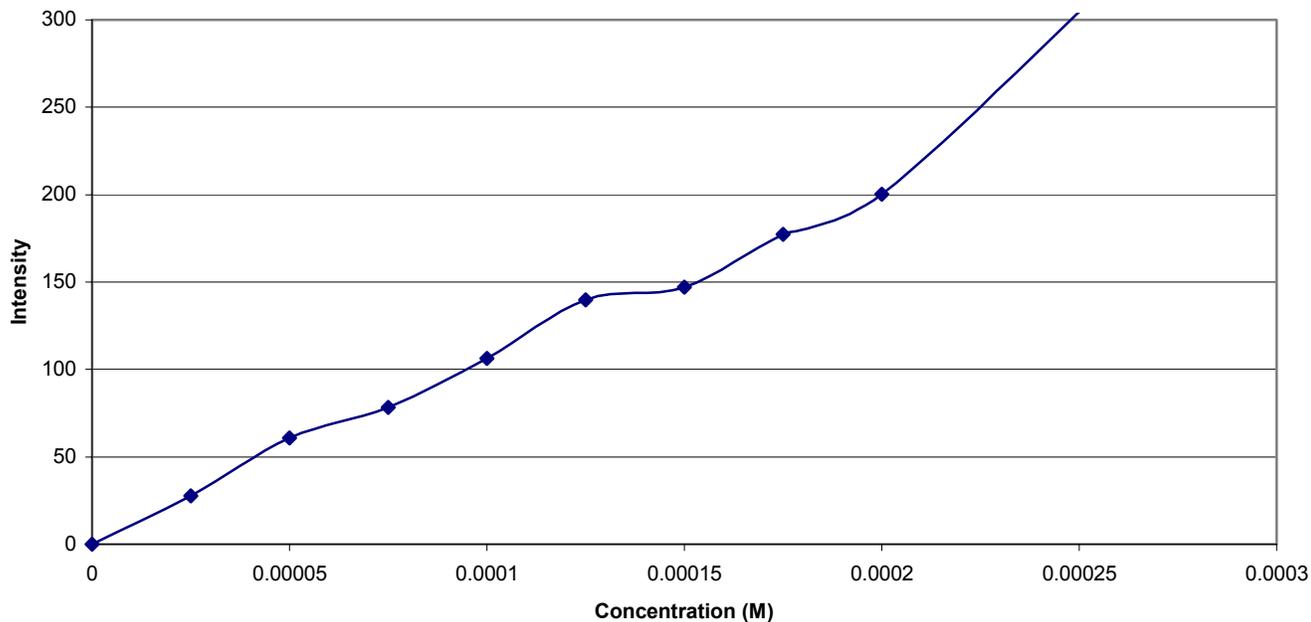


Figure 2.5: O-Phthaldialdehyde (OPA) Photoluminescence Intensity vs. Concentration



Initial experiments of AMCA and OPA on plasma modified surfaces demonstrated that polystyrene could be successfully modified with water plasma and amine plasma using the designed chamber. AMCA was successfully attached to water plasma modified polystyrene and OPA was successfully attached to amine plasma modified surfaces. Additional experiments also showed that OPA would not attach directly to a water plasma modified polystyrene surface. AMCA however does attach to ammonia modified films. This effect is most likely observed because the chamber is not evacuated during the ammonia plasma process allowing atmospheric water vapor and oxygen in the chamber to be ionized and in the process form some carboxylic acid groups. Collectively, the results demonstrate that photoluminescent tagging is an effective method of verifying the presence of specific functional groups in the plasma process.

With AMCA and OPA, further characterization of the plasma chamber was performed by modifying polystyrene surfaces over a series of exposure times. Figure 2.6

illustrates the degree of carboxyl modification as a function of time. Peak intensity is observed after approximately thirty seconds of water plasma modification. The intensity resulting from AMCA begins to diminish from this peak at exposure times longer than thirty seconds. A similar effect is also seen when ammonia plasma is used to graft OPA onto amine modified polystyrene surface. Peak intensity is again observed from OPA after thirty seconds of plasma exposure. This data suggests that the desired functional groups may in some way be destroyed or that the polymer surface may undergo some degradation with plasma exposure times greater than thirty seconds at 37 kV. Although contact angle data suggests a plateau in the degree of modification after twenty seconds exposure time no diminishing effects on the surface energy, the photoluminescent dye data suggests that continued modification after thirty seconds may lead to loss of desired functional groups.

Figure 2.6: Maximum Photoluminescence Intensity of AMCA on PS on Silicon vs. Water Plasma Exposure Time

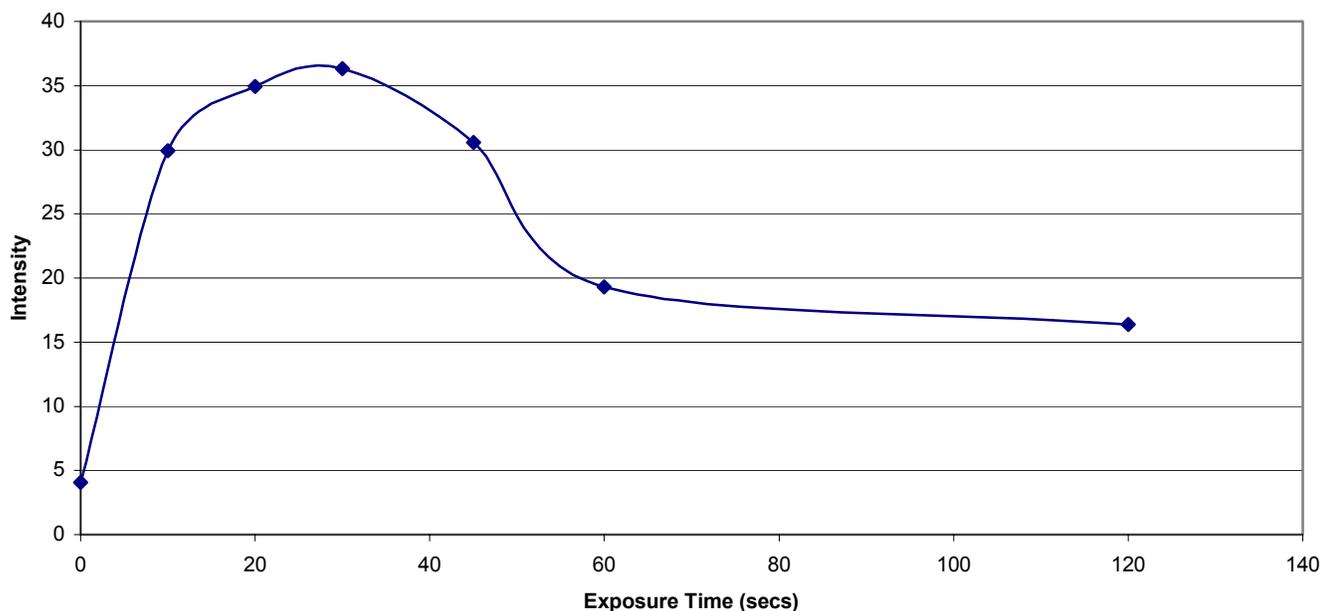
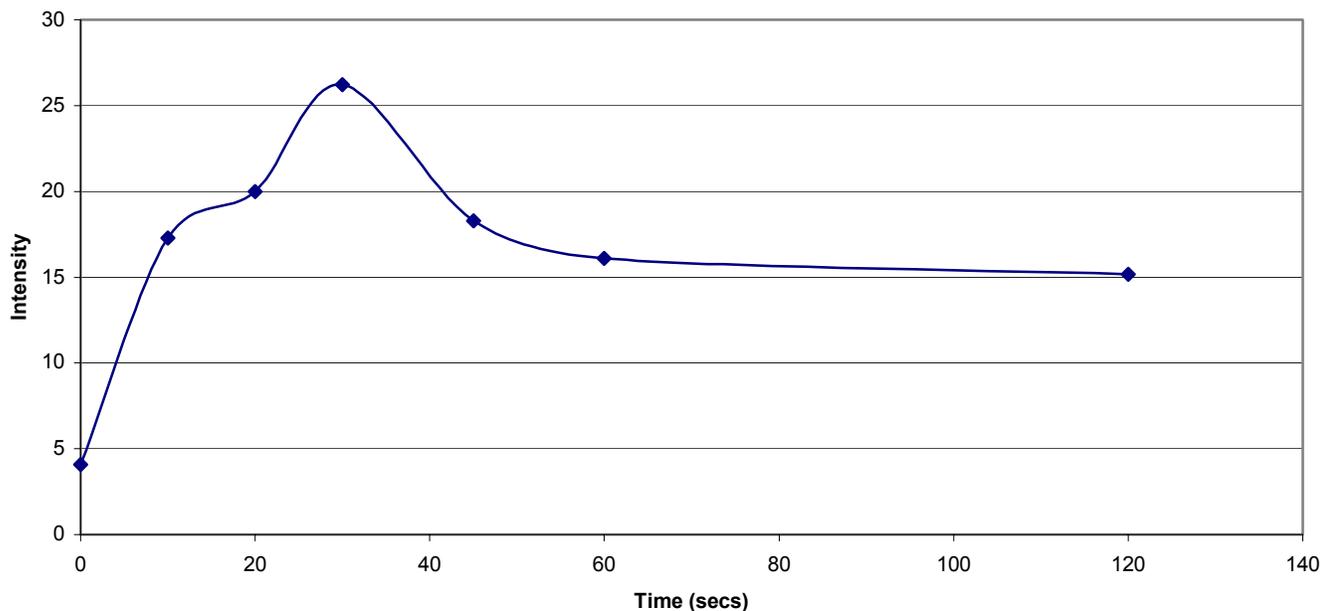
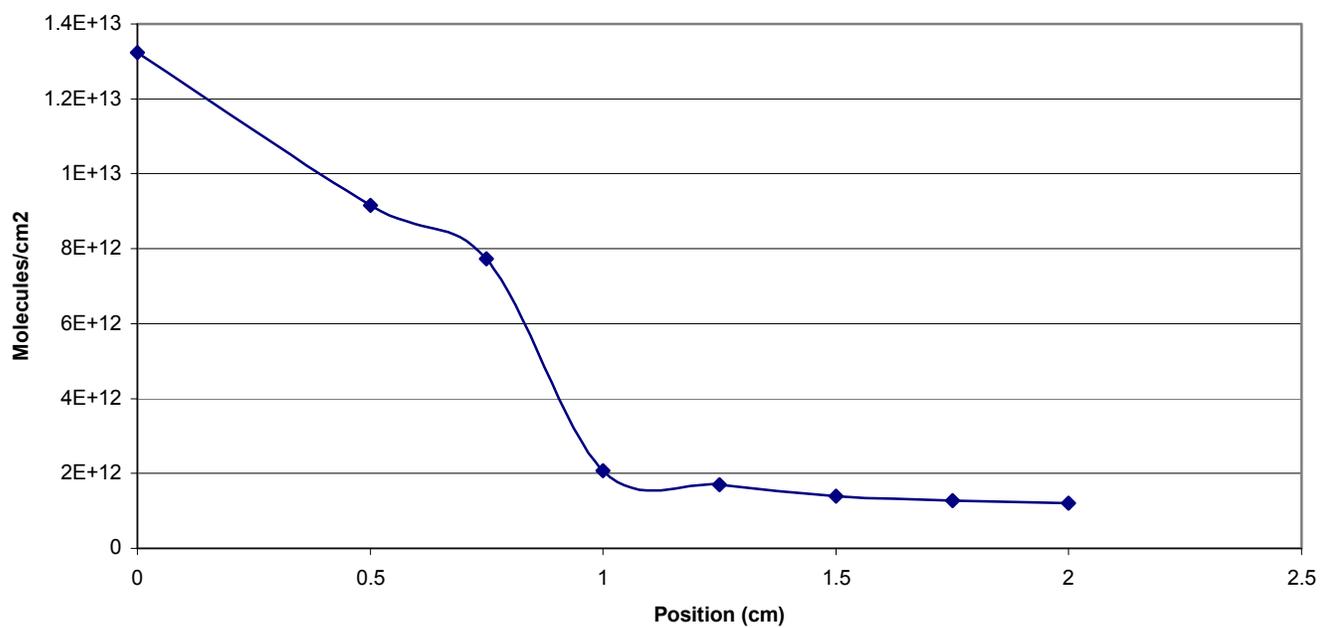


Figure 2.7: Maximum Photoluminescence Intensity of OPA at Varying Amine Plasma Exposure Times



AMCA was also used to quantify the amount of carboxylic acid modification as a function of position on the sample platform using chamber conditions of 37 kV, 30 mm electrode height, and one minute water plasma exposure times. In Figure 2.8, the intensity produced by AMCA begins to quickly diminish at small distances from the electrode centerline on the sample platform. At positions of 7.5 mm or more away from the centerline, the carboxyl concentration is estimated to be negligible. These results show that ion current density of corona is at a maximum at the centerline as observed by surface modification.

Figure 2.8: Estimated Carboxyl Concentration vs. Position From Electrode at 37 kV and 3 cm



2.4 Conclusions

Photoluminescent dyes validated surface modification using the ammonia and water plasma processes. Although photoluminescence does not enable exact quantification of concentrations of functional groups on surfaces to be determined, estimates of functional surface coverage could be made using photoluminescence versus solution concentration calibration curves for the dyes. A maximum degree of modification with the carboxyl and amine functional groups appears after thirty seconds of plasma exposure in both cases. This data suggests that a change in the nature of the surface modification occurs between twenty seconds and thirty seconds of plasma exposure that is not well represented by the contact angle data alone.

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Chapter 3

Applications of Surface Modification

3.1 Introduction

The ability to chemically modify a surface by plasma treatment has important implications in bioengineering applications. Its significance is derived from the ability of deoxyribonucleic acid (DNA) and protein groups to be covalently bonded to surfaces containing carboxylic acid, and amine functional groups, respectively. DNA is composed of deoxyribose sugar, phosphate groups, and four base pairs known as adenine, cytosine, guanine, and thymine.¹ However it is the presence of phosphate groups on DNA structures which enable covalent bonding of the DNA onto carboxyl functionalized surfaces by way of a conjugation reaction with carbodiimide coupling agents. Water soluble ethylcarbodiimide hydrochloride is most commonly used as a coupling agent to assist in these binding reactions. Zammatteo et al and others have shown covalent binding of DNA to amine functionalized surfaces with this process.² Surface attachment of DNA provides a means for additional biochemical study to take place in a stabilized environment. Zhang et al for example have demonstrated hybridization of a DNA single strand to a synthetic complement attached to a thin film of polyethylene-co-acrylic acid by partial penetration into the film.³ They also show that fluorescence spectrometry may be used to verify the presence of single-stranded DNA with an excitation of 265 nm which absorbs maximally at this wavelength. The reduction of absorbance properties of DNA with hybridization make fluorescence spectrometry a valuable tool in measuring hybridization rates in DNA reactions.⁴

Polystyrene is a commonly used substrate for these types of biochemical studies because it is a durable and inexpensive polymer which lends itself well to surface modification by a variety of processes.⁵ Surface modification processes on polystyrene for these applications are tailored to amine and carboxyl functional groups because these groups form the basis for the bonding of numerous biomaterials.⁶ Chemical and plasma pretreatment of polymers are methods used to introduce carboxyl and hydroxyl groups

onto polystyrene. Gamma radiation, chemical pretreatment, and plasma treatment are commonly used to introduce amine groups onto polystyrene.^{7,8}

The ability to cost-effectively produce amine and carboxyl functionalized surfaces is also valuable in the surface attachment of proteins. Proteins are comprised of chains of amino acids. They are like polymers in that they may be composed of as many as sixty or more amino acid units. The presence of carboxyl functional groups make proteins highly reactive with amine groups for surface binding.⁹ There is currently much interest in the attachment of proteins onto amine terminated self-assembled alkanethiol chains for use in DNA sequencing and biomolecular adsorption sensors.^{10,11}

The ability to functionalize polymer thin films in a cost effective manner for reactions of carboxylic acid and amine groups would clearly prove to be a valuable tool for biochemical applications. However, the application of this process would not be limited to bioengineering. The incorporation of semiconductors into thin polymer films is widely used in the fabrication of electronic display devices. The implantation of zinc sulfide in polymer films is a common tool for the production of color behind pixels in electronic display units.

Zinc sulfide is a direct band gap semiconductor compound possessing unique electronic and photoluminescence properties. As a semiconducting compound, zinc sulfide contains an accessible energy band gap allowing electrons with sufficient energy to escape the electron rich valence band and enter its antibonding conductance band.

It is the accessibility of valence electrons to crossing the energy band gap which distinguishes semiconductors from insulating and conducting compounds.¹² Insulators inhibit the flow of electrons through its media because the energy required for electrons to cross the band gap is very large. Similarly, conductive materials like metallic solids have no band gaps where electrons to appear in shared clouds around the atoms in the molecular lattice.¹³ This narrow band gap in essence allows electrons to move freely between the constituent atoms.

The presence of impurities in the compound and its semiconductor band gap give zinc sulfide unique luminescence properties when combined with various doping agents. Zinc sulfide has an energy band gap of 3.68 eV.¹⁴ When radiation of sufficient energy to enable valence band electrons to overcome this band gap is imparted onto zinc sulfide,

the electrons absorb the energy and make the transition across the energy gap. The excited nature of these transitioning electrons make them highly active and the electrons fall back from the conductance band. As the electrons fall back from the conductance band to the valence band, energy is given off in the form of blue light at a wavelength of 420 nm. The energy band gap for zinc sulfide however suggests that radiation should be emitted at 337 nm. The emission at 420 nm results from defects in the material.

The introduction of impurities into the zinc sulfide lattice can greatly alter the optoelectric properties of zinc sulfide. Copper and manganese ions are commonly used as doping agents to change the electronic configurations of zinc sulfide and in turn change the band gap. With the change in the energy band gap comes a new set of luminescent properties for the compound. As the electrons fall back toward their valence band, the dopant allows the electron to undergo the transition in a stepwise manner by falling back to the impurity energy level first. The electrons then undergo a second transition in falling from the dopant energy level to the valence band. Zinc sulfide doped with manganese (Mn^{2+}) impurities yields visible light at a wavelength of 585 nm and appears yellow.¹⁵ Doping with copper however produces an entirely different electronic configuration and zinc sulfide with this impurity produces visible light at a wavelength of 525 nm and appears green.¹⁶

These properties make zinc sulfide a widely used and critical compound fabricating electroluminescent microelectronic devices. Zinc sulfide is most commonly used in thin films synthesized by vapor deposition, chemical vapor deposition, or plasma sputtering. Chemical vapor deposition uses gaseous precursors to form thin films of the semiconductor on the desired substrate at very high temperatures. The deposition process is a costly manufacturing method due to high temperature requirements and waste disposal of unwanted desorbed products.¹⁷ The high vacuum process enables control of deposition on the thickness of a single molecular layer and achieves these objectives with virtually no contamination. The process is again very expensive because of the costs associated with maintaining the high vacuum.

Zinc sulfide is most recognized for its application in thin film electroluminescent displays. They are most commonly used in flat panel displays for computers and laptops. At the heart of each display unit is zinc sulfide and other photoluminescing phosphors

encased in a thin polymer film. The films are typically deposited by plasma sputtering or other high vacuum techniques. When zinc sulfide is used in this capacity, it is usually doped with a manganese impurity to emit yellow light upon excitation. Combinations of other phosphors and dopants are used to generate different colors of light such as red and green. The polymer imbedded phosphors are then layered between two conducting surfaces which provide a source of excitation to trigger the luminescence.

3.2.1 Experimental Procedure: Zinc Sulfide Synthesis in Polystyrene

Using the experimental methods previously documented in the first two chapters, polystyrene films were spun cast onto clean silicon surfaces using an 18% solution by weight of the polymer in 1-methyl-2-pyrrolidinone (NMP). Surfaces were baked for a period of three hours at 120°C to remove unwanted NMP solvent. Films were surface modified with the water plasma process at a distance of 30 mm below the discharge sources at 37 kV. Modified films were then immersed in a 20% solution by weight of zinc acetate in deionized water for a period of four hours to allow zinc to react onto the carboxyl modified surface. Films were removed from the solution, rinsed in deionized water and blown dry with pressurized air. Zinc was imbedded into the polystyrene film by an annealing process in which the films were baked in a vacuum oven for three hours at 120°C under a nitrogen blanket. This annealing process enabled the zinc to settle into the interior of the polymer film creating a hydrophobic surface. Film surfaces were tested for wettability to verify that the annealing process was successful.

After annealing, films were placed in a pressure vessel and hydrogen sulfide gas was pumped over the zinc imbedded films to a pressure of 6 psi. This pressure was maintained for a period of 10 minutes. Films were removed from the pressure vessel and pressurized air was blown across each surface in a fume hood to remove any residual hydrogen sulfide.

Photoluminescence analysis was performed on the films to verify the presence of zinc sulfide. An excitation wavelength of 332 nm was used in photoluminescence analysis at a scanning rate of 240 nm/min with emission and excitation slits width settings of 5 nm.

Additional studies were performed to determine the optimal water plasma exposure time and as well as the optimal immersion time for modified polystyrene slides in the zinc acetate solution. A series of polystyrene films were modified with water plasma at varying exposure times at 37 kV and 30 mm discharge height. The series of six films were treated with water plasma at times of 10, 30, 45, 60, 90, and 120 seconds. The films were then annealed and the zinc acetate was reacted with hydrogen sulfide gas at 6 psi for 10 minutes. Photoluminescence spectra were taken of each sample at an excitation

wavelength of 332 nm. A second study was performed in which five films were modified at the same voltage and height conditions for one minute with water plasma. The films were then placed in the 20% zinc acetate solution for immersion times of 20 minutes, one hour, two hours, four hours, and ten hours. Films were removed and annealed at 120°C. Zinc acetate imbedded in the film surfaces was then reacted with hydrogen sulfide gas to produce zinc sulfide particles. Fluorescence spectroscopy was again performed on the films with an excitation wavelength of 332 nm.

Atomic force microscopy (AFM) was performed on film samples containing zinc sulfide to develop an image of the particles.

3.2.2: Experimental Procedure: DNA Binding to Polystyrene

Silicon surfaces were cleaned by immersion in xylene for a period of six hours. Polystyrene films were then spun cast onto the cleaned silicon substrates from a 1% solution of polystyrene in toluene. Films were baked for 10 minutes at 120°C under a nitrogen blanket to prevent contamination.

Carbodiimide buffer solution was premixed by adding 0.767g of (1-[3-(Dimethylamino) propyl]-3-ethylcarbodiimide hydrochloride (EDC) to 2 mL of deionized water. This solution served as a conjugation agent for reacting amine groups from the DNA to the carboxyl functional groups produced during surface modification.¹⁸ The mixture was shaken to dissolve the EDC. DNA was prepared for surface attachment by mixing 2.2 µL of 27 base pair DNA synthesized by Ransom-Hill Biosciences, Inc. with 200 µL of deionized water. Washing solution consisted of 0.1 N NaOH and 0.25% SDS (dodecyl sulfate sodium salt) in deionized water. This solution was used to wash residual unbound DNA and buffer solution from the surface before further instrumental analysis was performed.

Surface modification of the polystyrene films was achieved by plasma treatment with water vapor carrier gas. A 37 kV discharge voltage was used at one minute exposure times 3 cm above each polymer surface. 50 µL of carbodiimide buffer solution was then applied to the wetting area on each substrate. 10 µL of DNA solution was then pipetted onto the buffer solution on the modified polystyrene surface.

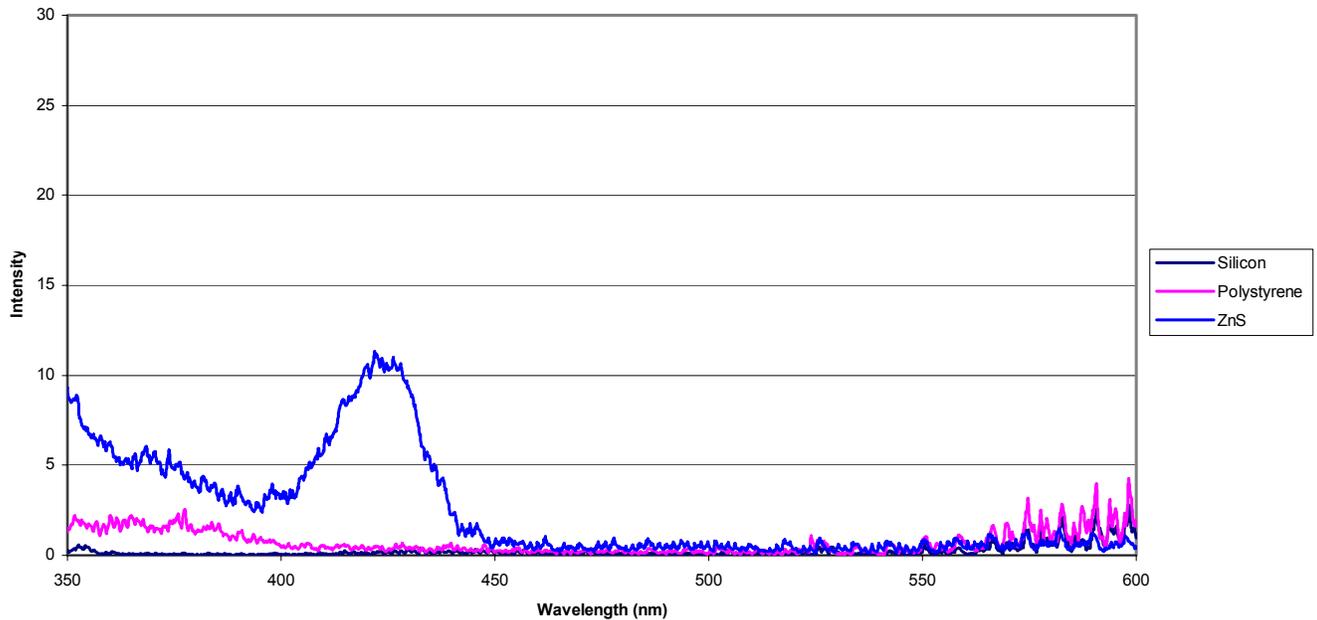
After DNA application, the surfaces with buffered DNA were placed atop a glass slide stationed above a warm water bath for 5 hours at 50°C. After this incubation period, surfaces were rinsed three times in beakers of washing solution that were preheated to 50°C. Surfaces were blown dry with an airgun after the third washing in preparation for fluorescence spectrometry and XPS analysis.

Absorption analysis was performed using a Hitachi F-4500 Fluorescence Spectrometer. Ultra-violet excitation energy was used at a wavelength of 265 nm. Photoluminescence analysis was performed on plasma treated polystyrene surfaces and on DNA binded surfaces. XPS analysis was also performed to probe for the presence of phosphorus on the treated surfaces.

3.3 Results and Discussion

A clean photoluminescence spectrum is shown in Figure 3.1 for silicon substrates used to produce zinc sulfide. At a wavelength of 420 nm, no distinguishable peak was observable. A similar spectrum was produced for polystyrene thin films spun cast on cleaned silicon surfaces from an 18% solution of the polymer in 1-methyl-2-pyrrolidinone (NMP). A clean photoluminescence background is again observed in Figure 3.1. These background spectra provided verification that the photoluminescence peaks observed in near the 420 nm region were generated only from zinc sulfide surface chemistry.

Figure 3.3: Photoluminescence Spectra of Zinc Sulfide in Polystyrene at an Excitation Wavelength of 332 nm



Annealing of the polystyrene films was performed to bring zinc acetate into the polystyrene film. Heating the film at a temperature of 120°C above its glass transition temperature of 100°C enables zinc to slowly imbibe into each thin film. Verification that the annealing process was successful was achieved by wetting tests. Well-annealed polystyrene films with attached zinc produced contact angles greater than 75°. Plasma

modified surfaces containing chemically attached zinc would remain wetting almost indefinitely (at least four months) without the annealing process. This result suggests that a surfactant could be used to produce stable wetting polymer surfaces for an extended period of time after plasma treatment.

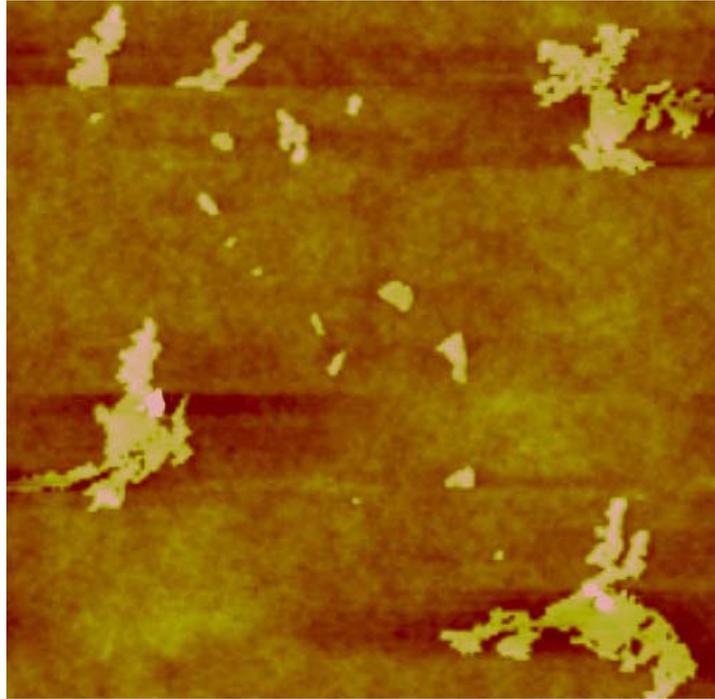


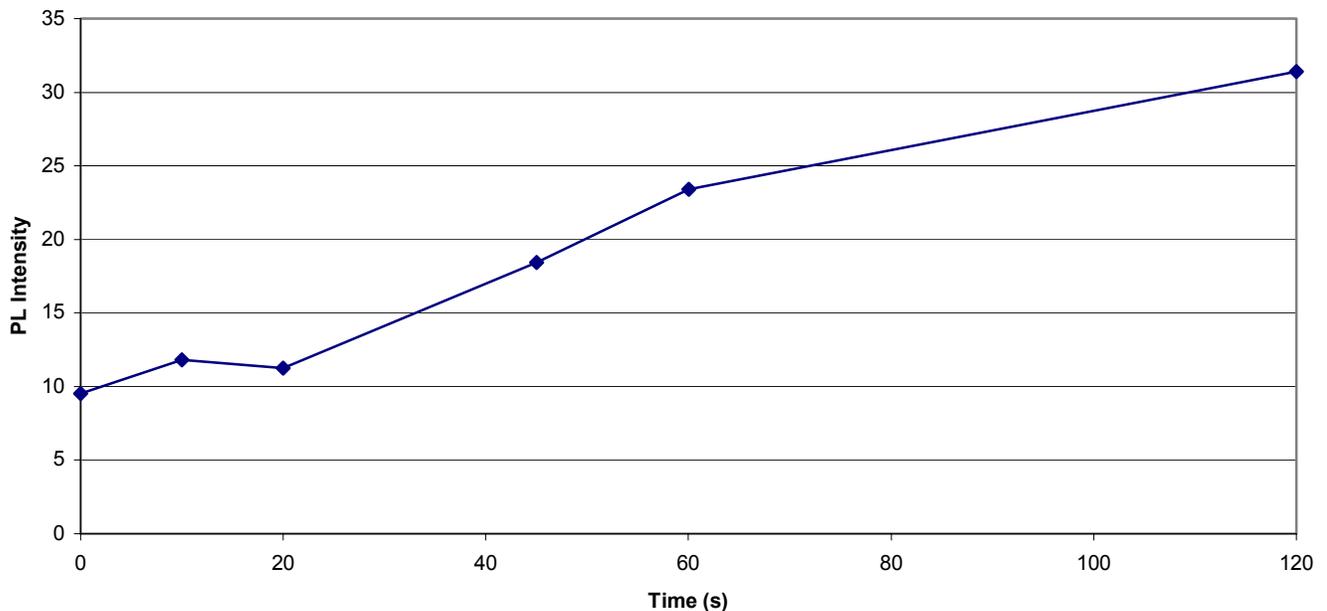
Figure 3.2: A 1 x 1 μm AFM image of zinc sulfide on polystyrene

After the hydrogen sulfide reaction, the presence of zinc sulfide was demonstrated by fluorescence spectrometry. The photoluminescence peak at 420 nm in Figure 3.1 confirms the formation of zinc sulfide in the polystyrene thin film. An AFM image was used to estimate particle sizes formed in the polymer ranging from 50 nm to 350 nm as seen in Figure 3.2.¹⁹

Zinc sulfide reactions were also used as a tool to understand water plasma modification effects on polystyrene. Figure 3.3 illustrates that the water plasma exposure time before immersion in the zinc acetate bath clearly improves zinc sulfide yield without the detrimental effects suggested by data from the photoluminescent tagging study in Chapter 2. This result is more consistent with the contact angle data which shows no increase in wetting angle with increased exposure times above twenty seconds. Contact

angle data does however suggest that the largest degree of surface modification occurs after this initial twenty second period with almost insignificant improvements in surface energy occurring after this exposure time. Data in Figure 3.3 shows a strong correlation between plasma exposure time and zinc sulfide formation with the greatest yield produced after two minutes of plasma exposure. Zinc acetate may also be reactive with other functional groups generated during the plasma process. These groups may contribute to increases in the surface energy of the polymer film but may not be reactive with AMCA.

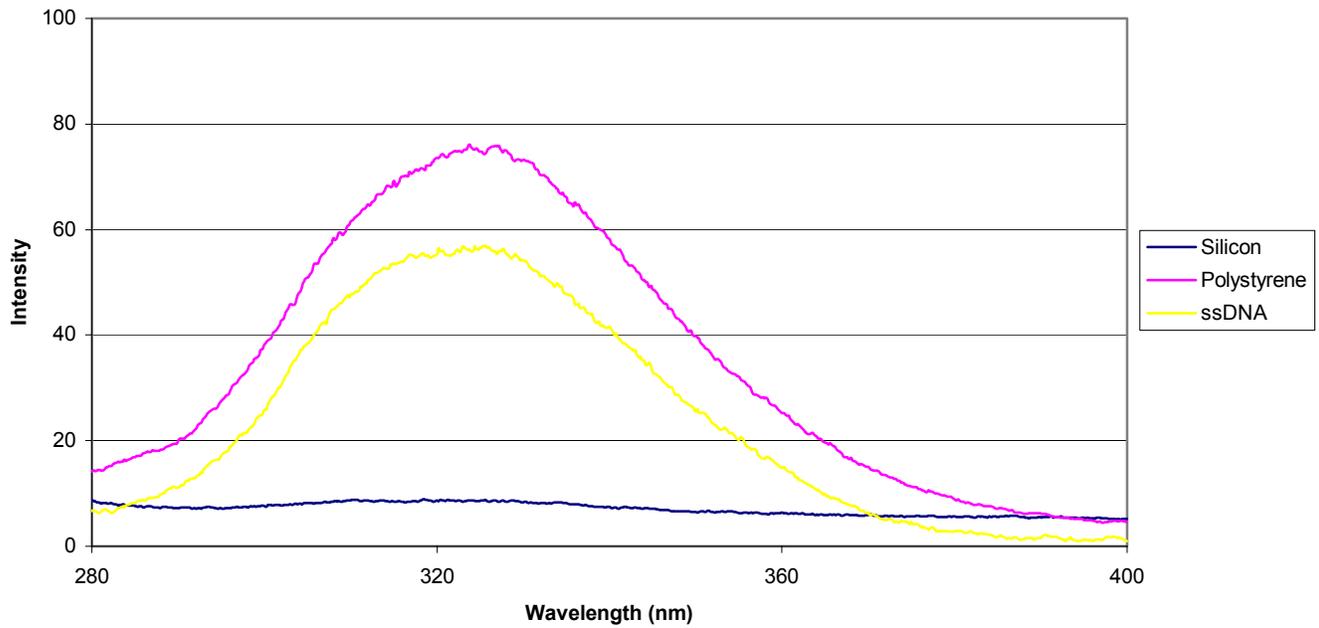
Figure 3.3: Zinc Sulfide Photoluminescence Intensity at 420 nm as a Function of Water Plasma Exposure Time Study



Evidence of successful DNA grafting onto surface modified polystyrene is observed in both photoluminescence and XPS data. A reduction in photoluminescence intensity of polystyrene is observed in Figure 3.4. The film of polystyrene from the 1% toluene solution produces a photoluminescence intensity peak at 333 nm of 76 (arbitrary units). After DNA grafting occurred, the photoluminescence intensity dropped by about 26% from a maximum intensity of 76 to 56. This result may be attributable to strong

absorption properties of single strand DNA. XPS analysis also confirmed the presence of phosphorus on the polymer surface indicating the presence of successfully binded DNA. Results showed an increase in atomic surface percentage of phosphorus to 0.51% from 0%.

Figure 3.4: Photoluminescence Spectra of Single Strand DNA Binded to Polystyrene Film on Silicon Substrate



3.4 Conclusions

Surface modification of polystyrene thin films with atmospheric pressure water plasma provides a means to generate zinc sulfide particles. The presence of zinc sulfide can be confirmed with fluorescence spectrometry. Increasing the water plasma exposure time of polystyrene films clearly improves zinc sulfide yield after the hydrogen sulfide reaction. Zinc sulfide agglomerations formed in this process have a size of approximately 40 nm. Surfactants may be used on plasma modified polymer films to produce long lasting wetting surfaces. Atmospheric pressure water plasma was also utilized to successfully attach single strand DNA to polystyrene surfaces.

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19. AFM images taken by Sanjun Niu from images from samples produced by Jeff Ward.

Path Forward

The characterization of the plasma chamber detailed in this thesis provides a basis for a number of interesting applications to explore in future research endeavors. It has been shown that differences in wettability across a polymer surface can be imparted by careful regulation of height, exposure time, and voltage parameters. Using these controls a fluid could be made to flow across a surface driven by these differences in surface energy. This idea was initiated during AMCA ion modeling studies in which water was observed to problematically flow across adjacent silicon pieces with polystyrene films. These surface energy differences were caused by the location of the silicon pieces at different positions perpendicular to the discharge electrode on the sample platform. The surface modification is transient however and further investigation into the use of surfactants to stabilize these surface energy changes should be performed to make this idea feasible for practical applications.

Polybutadiene experiments proved that different polymers require differing degrees of polymer modification to achieve wettability. This observation could be utilized in conjunction with self-assembling block copolymers to achieve selective surface modification. This modification process could allow structures to be chemically created from specific sites on the copolymer surface using the newly attached functional groups.

Further investigation should also be made into impurity doping of the zinc sulfide generated from the plasma process in Chapter 3. The incorporation of manganese or copper into the semiconductor lattice would create much more usable groups of compounds with a wide-range of photoluminescing applications.