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PLASMA MODIFICATION OF
POLY (P-PHENYLENEBENZOBISTHIAZOLE)

THESIS

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THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology

Air University

In Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Engineering Physics

Patrick E. Godfrey, B.S

First Lieutenant, USAF

December 1989

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Preface

This area of research was chosen for several reasons. Previous work done on the same material as that chosen for this effort promised to provide a benchmark by which my early results could be evaluated. At the same time, that work was sufficiently inconclusive that potentially useful research remained to be done. At the end of this effort, a working plasma treatment facility would be available for further work. Finally, this work would afford me the chance to learn how to operate a number of devices, such as an electron microscope and an XPS spectrometer, that I would not otherwise have the opportunity to use, as well as introduce me to the sometimes frustrating world of high vacuum.

This thesis would not have been completed without the assistance ungrudgingly provided by many people. Materials Laboratory personnel were particularly helpful. Dr. Wade Adams, chief of the polymers branch at the Materials Laboratory, provided some of the gases used in the experiment and allowed his people to take time from their many projects to help me. Capt Cady Coleman provided the equipment needed to clean the film samples, performed the contact angle measurements, and attempted to fill the huge void in my knowledge of chemistry and polymers. She was also kind enough to serve on my committee. Dr. C. Y. Lee provided critical information concerning lap shear tests.

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Gary Price taught me how to use the electron microscope.

Dr. Alan Garscadden, chief of WRDC's Plasma Physics Branch, let me use a laboratory room in his building, and allowed me to utilize the talents of his workers, such as Jimmy Ray, who created a work of art when he made our glass plasma chamber.

Employees of the University of Dayton Research Institute associated with the Materials Lab were also of immense help. Arthur Behme allowed me to use his laboratory to prepare the lap shear test specimens. Dr. Peter John and his assistant Arthur Safriet let me look over their shoulders while they performed the XPS runs and patiently explained all the subtleties involved. David E. Spielvogel, a senior research associate at Becton Dickinson Polymer Research, kindly lent me the use of a contact angle goniometer at his laboratory, after calls to base and university labs failed to turn one up.

I particularly wish to thank Bob Knight, whose patient guidance in all matters related to high vacuum systems helped us to finally get the plasma chamber to work, despite all the problems, roadblocks, and disasters that we discovered, often beset experimental work. Without his fully stocked supply of bolts, flanges and advice, this project would never have gotten off the ground.

I would also like to thank Dr. William Bailey for

serving on my committee and providing valuable advice. Finally, I extend my most sincere appreciation to Capt Pete Haaland, my thesis advisor, whose patience and good cheer knew no bounds.

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Abstract

A plasma treatment chamber was constructed and used to treat samples of poly (p-phenylenebenzobisthiazole) (PBZT), an ordered polymer material. Analysis of scanning electron microscope results showed that exposure to an argon plasma for extended times eroded the surface of the polymer. X-ray photoelectron spectroscopy indicated that oxides were formed on the plasma-treated surfaces upon exposure to air. Treatment using argon, argon/water vapor and nitrogen plasmas was shown to increase the wettability of the polymer surface.

PBZT films bonded between aluminum coupons failed cohesively when shear forces were applied. Plasma treatment improved the shear strength of PBZT films by over 50%. This improvement is attributed to an enhancement of the cohesive strength of the PBZT via crosslinking between polymer chains.

1. Introduction

The Air Force is becoming ever more dependent upon composite materials in its effort to pack more capability into each new aircraft or missile. As new materials are developed and tested, potential uses are discovered that open doors long thought closed by the previously contradictory requirements of strength and lightness. Many of today's systems, such as the B2 Stealth bomber, simply could not be built using the materials available only a few years ago.

The possible uses of new materials, and the processing steps required to achieve these uses, are not always immediately obvious when a material is developed. It is important, therefore, that these materials be subjected to a variety of processing techniques and treatments, in order to determine the optimum methods.

Poly (p-phenylenebenzobisthiazole), known, mercifully, as PBZT is an example of a new class of "ordered" polymer materials whose unique characteristics may one day make them integral components of a large number of systems. The molecules of PBZT are aligned in rows, which makes its properties strongly anisotropic. Layers of the material, with the molecules oriented in different directions, can be combined to produce sheets with material properties tailored for specific uses. Ordered polymer film-based

composite materials have shown potential weight reductions up to 50% over quasi-isotropic graphite/epoxy composites and extended use temperatures greater than 400 degrees Celsius (19:1-1). Ordered polymer films surpass the performance of fiber-reinforced composite materials without suffering from the drawbacks of distinct fiber and matrix phases and will be used in applications demanding low weight, high strength and stiffness, high temperature capability, environmental resistance and radar transparency. The characteristics of PBZT make it particularly amenable to use in spacecraft and impact-resistant structures; some proposed uses include trusses for space stations and telescopes, balloons for the lofting of scientific payloads, cores for high-purity, high-conductivity wires, substrates for printed wire boards for computers, and aircraft structures (19:2-21--2-23).

Since it is new, however, the best ways to utilize PBZT are only now being discovered. One of the more promising areas where PBZT may be used is in the formulation of composite structures such as panels and tubes, processes that require the bonding of thin sheets of PBZT into thicker structures with the desired properties of strength, lightness, temperature resistance, and flexibility. Clearly, the characteristics of these structures will depend not only on the characteristics of

PBZT itself, but also on the strength of the bond between the PBZT and whatever material is used to join the thin films.

The goal of this thesis was to determine the chemical and physical changes in PBZT film due to plasma treatment.

Chapter II of this thesis outlines the history of the use of plasmas to treat polymers and discusses previous efforts to enhance the adhesive properties of PBZT via exposure to various plasmas. Chapter III describes the apparatus and techniques used in this experiment. The conditions obtained within the plasma and the changes that occur in a polymer as a result of the plasma treatment are also discussed. Chapter IV presents the results obtained in the course of this work. These results are discussed in Chapter V. Finally, conclusions and recommendations are presented in Chapter VI.

II. Historical Development and Previous Work

Development of Plasma Treatment

Almost as soon as laboratory discharges became available, chemists began to use them for chemical synthesis (21:58). The first experiments of this type were reported as early as 1796, when four Dutch chemists subjected ethylene to spark discharges and obtained an oily substance. Later, particular attention was focused on high-voltage glow discharges after the discovery that they could be used to prepare atomic hydrogen, oxygen, and nitrogen. Most recently the availability of radio-frequency and microwave generators has focused attention on the use of electrodeless discharges.

A growing interest has arisen over the last thirty years in the use of plasmas to modify the surface structure and composition of solid materials (13:113). This interest has been motivated in part by the ability of plasmas to produce unique surface modifications and by the ease with which the extent of modification can be controlled. This latter property can afford plasma treatment processing an edge over more conventional processes, leading to the increasing prominence of plasma treatment techniques in industrial applications.

Plasmas and Polymers

The principal changes brought about by exposure of a polymer to a plasma occur in a surface layer 1-10 microns in depth. While such properties as the surface wettability, the molecular weight of the surface layer, and the chemical composition of the surface can be changed, the bulk properties of a treated polymer remain unchanged.

The wettability of a polymer surface is an important characteristic which relates to the adherence of dyes, inks, and adhesives to the polymer. Plasma processes which lead to an improved wetting have found application in the packaging, electronics, construction, and clothing industries. To take one example, plasma processes have been used to increase the surface wettability of polymers used as jackets for wires and cables. These polymers tend to be inert and cannot be printed, painted, or dyed. After plasma treatment, however, the jackets can be labeled, and the treatment produces no changes in the bulk properties which led to the use of the polymer originally (13:116). Similarly, plasma treatment has been used to enhance the adhesion of lubricants to Teflon catheters, making insertion of the catheters through the skin much less painful (29).

Another aspect of plasma treatment that has received widespread attention is the improvement in the strength of

bonds between polymers and dissimilar materials. Adhesive bonding of plastic parts to each other or to parts made of other materials often has many advantages over other fastening techniques. However, many of the most widely used plastics cannot be bonded with structural adhesives unless a suitable surface treatment is first applied. Plasma treatment using activated gases is particularly useful since it is easier to control than flame treatment, is applicable to a wider variety of plastic parts than corona discharge, and eliminates the use of corrosive acid baths, which must be renewed when depleted and can be a significant source of heavy metal pollution in plant effluents (33:2).

The effects of treating polyethylene using a plasma were first reported in 1956 (12:2085). Since that time, many polymers have been subjected to such treatment. Schonhorn and Hansen showed in 1966 that exposing polymers to activated inert gases for short intervals resulted in dramatically improved bonding characteristics (27:1461). These improvements were attributed to the replacement of a weak layer of amorphous low molecular weight material by a crosslinked surface layer with higher cohesive strength that was, therefore, ideal for the production of strong adhesive joints. This surface treatment technique became known as CASING (Crosslinking by Activated Species of INert

Gases). When analytic techniques more sensitive to surface effects became available, however, it was shown that the hypothesis that most polymers are covered by a weak boundary layer was untenable, and that other mechanisms must be responsible for the increase in bond strengths (15:138-138). The Army's Picatinny Arsenal has conducted an exhaustive series of tests involving structural plastics being considered for uses in Army materiel (24:1, 33:1). To summarize, the research conducted to date has shown that the adhesive bond strengths of a wide variety of polymer materials can be enhanced by exposure to activated gas plasmas. Typical adhesive-strength improvement for a number of polymers after treatment in a variety of plasmas is shown in Table 1. (1 MPa equals 145.04 psi.)

Prior Work with PBZT

Researchers at the Materials Laboratory of the U.S. Air Force Wright Research and Development Center have pioneered the development of ordered polymers including polymer synthesis, fiber spinning and film processing. Foster-Miller, Inc., under contract to the Materials Lab, has worked to achieve the transition from material development to engineering applications. As part of that effort, the company has investigated a number of surface treatment techniques designed to provide good bonding with tough high temperature adhesives.

Table 1. Typical Lap Shear Adhesive-Strength Improvement After Treatment in a Variety of Plasmas

<u>Polymer</u>	<u>Lap Shear Strength (MPa)</u>	
	<u>Control</u>	<u>After Plasma Treatment</u>
High-density polyethylene	2.17	8.00 to 24.3
Low-density polyethylene	2.57	8.62 to 10.11
Nylon 6	5.83	8.41 to 27.30
Polystyrene	3.90	21.50 to 27.70
Mylar	4.26	8.17 to 8.39
Lexan	2.83	4.58 to 6.40
Polypropylene	2.55	1.38 to 21.20
Acetal copolymer	.81	1.28 to 1.78
PBZT	3.54	3.27 to 5.45

Note: Data from (17:62) except for PBZT (18:3-31)

Work at Foster-Miller has shown that fluoro-carbon and ammonia glow discharge plasma treatments do change the surface properties of PBZT films (18:2-31--3-58). Exposure to a carbon tetrafluoride plasma led to an increase in the percentage by weight of fluorine in the surface layers of the film from 0 to approximately 60%, depending on exposure time. The surface became strongly hydrophobic (hard to wet) after treatment. An ammonia plasma was less effective

in altering the surface composition of the polymer, but did lead to improved adhesive qualities; lap shear joint strengths (Chapter III) were increased by up to 54%. The surface was made strongly hydrophilic (easy to wet) by exposure to the ammonia plasma. Scanning electron microscope analysis showed that little, if any, surface erosion had occurred as a result of exposure to either the fluorocarbon or the ammonia plasmas.

The experiments described in this thesis were intended to build upon these results by considering the effects of other plasmas.

III. Experimental Apparatus and Procedures

Sample Description

Poly (p-phenylenebenzobisthiazole), or PBZT, is, as was mentioned previously, a member of a new class of polymeric materials collectively referred to as ordered polymers. The PBZT repeat unit is shown in Figure 1. As

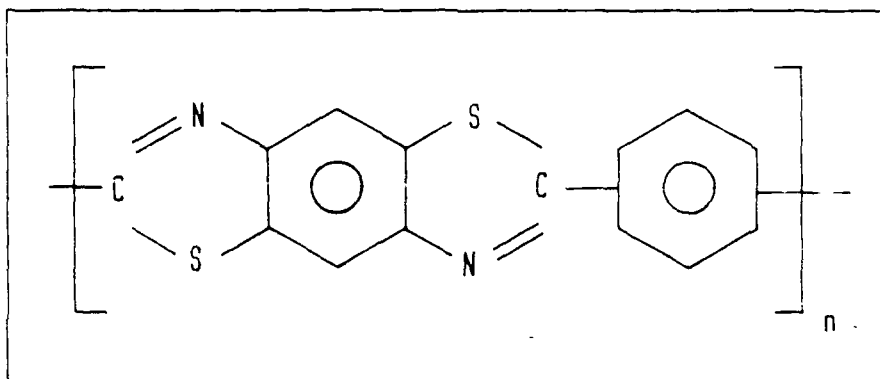


Figure 1. PBZT Repeat Unit

a result of their rigid rod-like molecular structures, these materials form liquid crystalline solutions from which extremely strong, stiff fibers and films have been processed. The fiber and film forming processes involve several steps (19:2-2--2-8). First, an isotropic or unoriented polymeric solution or "dope" is prepared. This dope consists of PBZT in solution with polyphosphoric acid.

Next, drawing, shearing flow or other forces are used to orient the polymer molecules. During this step, the film is shaped to the desired form and can be processed so that the rod-like molecules will lie in the plane of the film, and will be oriented in more than one direction (biaxial orientation). After this, water is used as a coagulant to bring the PBZT out of solution. Coagulation causes the polymer molecules to agglomerate, and "locks in" orientation and shape. The film is finally washed to remove the phosphoric acid, densified to remove the water, and heat treated to improve its mechanical properties.

Sheets of biaxially oriented PBZT film 5 microns thick were supplied by the Foster-Miller Company. The orientation of the molecules in successive layers was 0 and ± 22 degrees.

Sample Cleaning

Before the samples were treated or analyzed, they were repeatedly boiled in methylene chloride (CH_2Cl_2 , also known as dichloromethane), a chlorinated hydrocarbon solvent particularly effective against oil-based impurities. Glass-distilled high pressure liquid chromatography grade methylene chloride supplied by the Aldrich Chemical Company was used. Film samples approximately 5 cm by 7.5 cm were cut from the PBZT sheets, then rinsed and boiled in the methylene chloride; the used solvent was then replaced and

the samples boiled again. This procedure removed gross debris from the film surfaces. Those samples not immediately plasma treated were stored in evacuated glass tubes (Figure 2) to prevent recontamination.

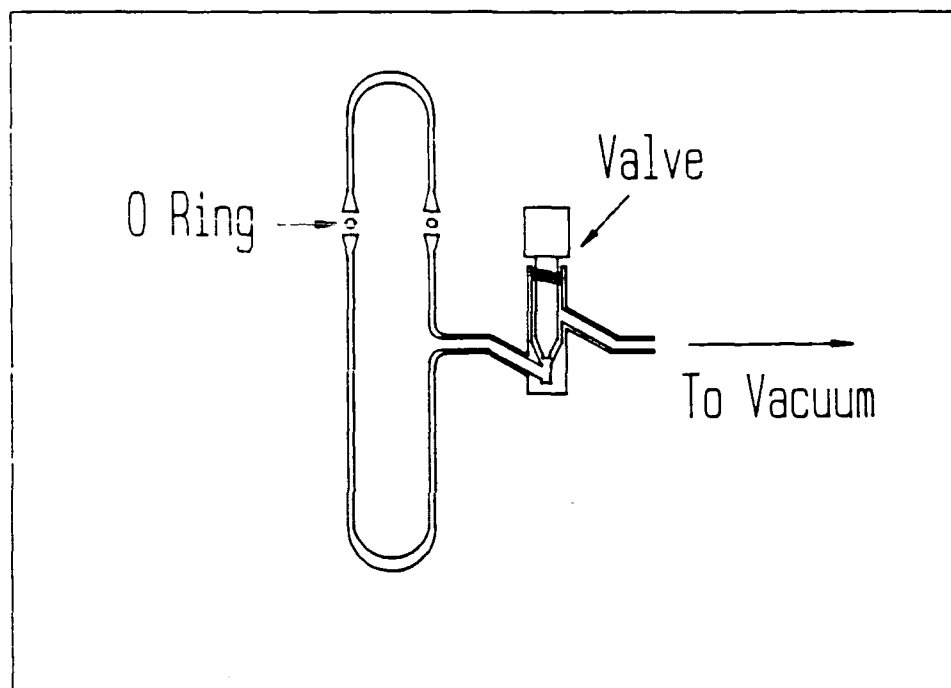


Figure 2. Evacuated Tube Used to Store Samples

Plasma Treatment Equipment and Procedures

A plasma chamber (shown in Figure 3), consisting of a high-voltage dc discharge inside a glass reaction vessel, was designed and constructed. The aluminum electrodes were

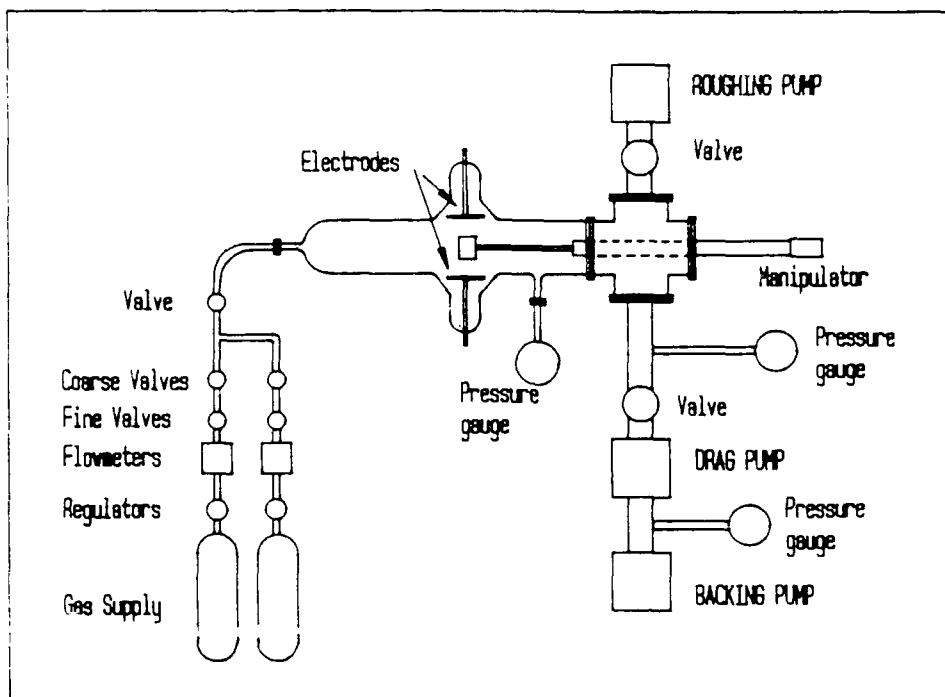


Figure 3. Plasma Treatment Apparatus

discs 2.54 cm in radius spaced 12.5 cm apart. The high voltage was provided by an HP 6525A power supply and a 100k ohm ballast resistor was placed in series with the supply and the discharge. When initiated, the resistance of a discharge is very low; in the absence of a ballast resistor the resulting high currents might burn out the power supply. The current was monitored using a multimeter, and returned to the power supply via ground. The polarity of the discharge could be changed by switching the leads on the electrodes. To minimize the danger of electrocution, care

was taken to ensure that the metal components of the plasma chamber were grounded.

The plasma chamber was attached to a four-way cross. The arm of the cross opposite the chamber was sealed with a flange through which a manipulator passed. This flange was removed to insert or remove samples. A Sargent-Welch roughing pump was attached to the chamber through one of the other arms of the cross; this pump was used to pump out the chamber while samples were being treated. An Alcatel oil-free drag pump (capable of obtaining pressures of 10^{-4} torr) and its associated diaphragm backing pump was connected to the fourth arm of the cross; these pumps were used for the initial pump-down, then isolated from the chamber during sample treatment by a valve. Ultra-high vacuum components were used so that the chamber could be evacuated by the drag pump to a low pressure that would facilitate the outgassing of any contaminants from the polymer samples and the chamber interior. An ionization gauge (Granville Phillips model 270 gauge controller) was used to monitor the low pressures obtained by the drag pump while a compensated capacitance manometer (MKS Baratron PDR-5B power supply/readout) was used at the higher pressures (about .5 torr) observed in the plasma chamber during sample treatment. A Granville Phillips model 275 Convection gauge was used to monitor the pressure at the

drag pump; this pump cannot be started until the pressure is reduced to about 20 torr by its associated diaphragm backing pump.

A gas manifold was assembled that allowed the flow of one or two gases through the discharge while a PBZT sample was being treated; this flow ensured that any materials ejected from the polymer surface would be swept out of the plasma chamber. The flow rates were monitored using Tylan FM 360 mass flowmeters connected to an MKS Baratron Type 254 flow ratio controller. The pressure inside the chamber during sample treatment was regulated by the interplay of the flow rate into the chamber (controlled by needle valves) and the flow rate out of the chamber (controlled by a valve between the chamber and the roughing pump). Typically, flow rates of about 50 standard cubic centimeters per minute (sccm), with the valve on the line to the roughing pump almost fully closed, resulted in chamber pressures near .5 torr. The gauges were monitored during sample treatment and small adjustments made, when necessary, to keep the chamber pressure and flow rates within .002 torr and .2 sccm of their initial values, respectively.

A sample holder was fabricated of glass-covered metal wire. The glass coating prevented the discharge from striking to the holder while the metal wire provided the necessary strength. The sample holder was attached to the

manipulator allowing the sample to be translated along the axis of the tube while a vacuum was maintained. Samples could, therefore, be inserted into or removed from the area between the electrodes while a discharge was going. The exterior handle of the manipulator was electrically isolated from the sample holder, in case the discharge did strike there; with use the glass covering on the wire cracked and allowed this to happen at chamber pressures above about a torr, but no problems were noted at lower pressures.

Most of the samples were treated using argon, but one sample was exposed to a nitrogen plasma. Ultra high purity nitrogen could be obtained, but only technical grade argon was available. A lecture bottle of Freon 14 (carbon tetrafluoride) was also obtained, and a small amount mixed with argon was used to treat one sample.

Two samples were treated using argon mixed with a small amount of water vapor. As shown in Figure 4, a portion of the total argon flow passes through a bubbler containing distilled water picked up water vapor that was subsequently dissociated in the discharge to produce an H_2OH plasma. The percentage of water vapor in the gas flowing into the plasma chamber was estimated based on the assumption that the water vapor in the bubbler was in equilibrium with the liquid phase. The vapor pressure of

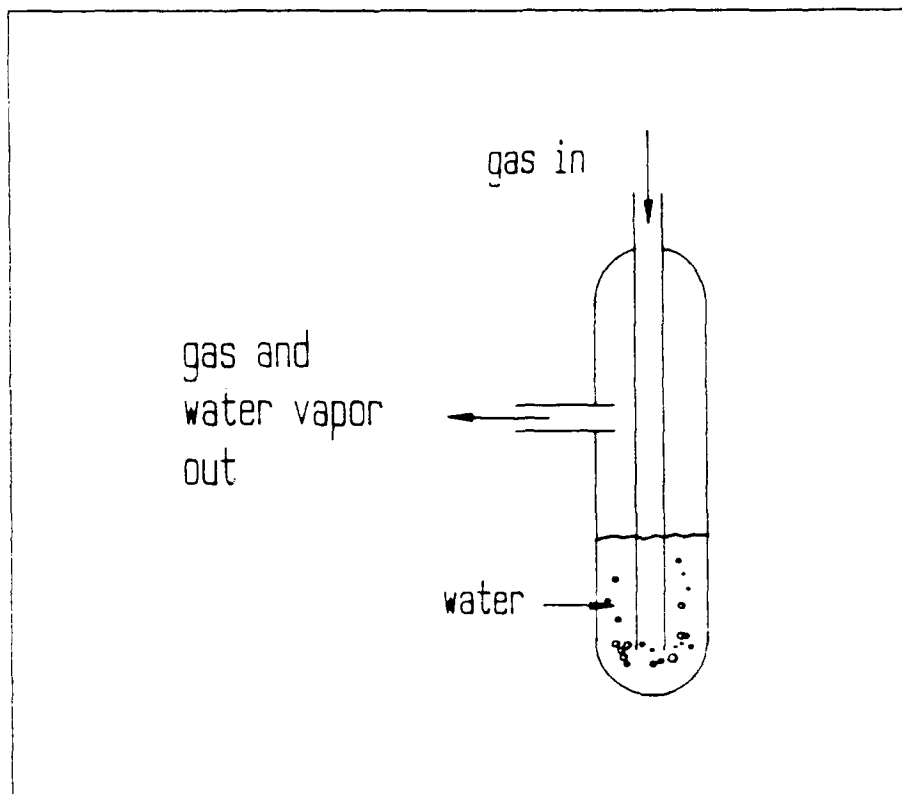


Figure 4. Bubbler Used for OH Plasma Treatment

the water could then be found in the CRC Handbook 9:D-232 and the contribution of the water to the total pressure determined. The argon pressure inside the bubbler was determined using the pressure gauge on the argon tank; this gauge shows the pressure above atmospheric. For instance, for a regulator reading of 2 psi (100 torr) the total pressure inside the bubbler is about 860 torr. The vapor pressure of water at 21 degrees Celsius is 18.65 torr. Therefore water constitutes $(18.65/860) \times 100$, or about 2.2%

of the gas in the bubbler. If the gas flow through the bubbler is 9 sccm and the main argon flow is 51 sccm, the flow through the bubbler is $(9/60) \times 100\%$ or 15% of the total flow. Therefore the water vapor is 2% of 15%, or .3% of the total gas flow into the plasma chamber, and argon makes up the rest.

After a sample was inserted into the plasma chamber, the drag pump was used to lower the pressure to about a millitorr. Samples were allowed to sit in the plasma tube under vacuum overnight before being treated. The pressure inside the tube over this period increased from .001 to about .5 torr due to sample outgassing and residual system leaks. Without a sample in place, the pressure inside the tube increased to about .3 torr over the same period. When a sample could not be left overnight, it was kept in the plasma chamber at about .005 torr for 60 minutes prior to treatment. To begin treatment, the proper flow rates were obtained to achieve the desired chamber pressure. With the sample out of the area between the electrodes, the discharge was struck, usually with the power supply set at 900 volts. Next, the sample was moved into the discharge and any changes in the color or shape of the discharge noted. The current passing through the discharge was also monitored for variations.

After the prescribed time, the polarity of the

discharge was reversed and treatment continued for an equal time to ensure that the two sides of the film were treated equally. The total treatment time, along with chamber pressure and discharge voltage, is used to characterize the runs. Once both sides had been treated, the valve between the plasma chamber and the roughing pump was closed and the pressure inside the chamber allowed to slowly increase to atmospheric, so as to minimize the chance that a rapid pressure build up might shatter the chamber. Initially, the flow of argon was maintained to slowly raise the pressure; once the chamber pressure reached about 10 torr a valve was cracked open to allow air to leak in until atmospheric pressure was achieved. The samples were then removed and kept in the evacuated glass tubes until they could be tested.

Plasma Conditions and Effects

Actual plasma conditions at the sample were not determined, but some order of magnitude estimates are possible. Samples were placed in the positive column of an argon discharge operating in the abnormal glow regime at .1 to .8 torr, with most samples treated at about .5 torr. With the power supply set at 900 volts, the current carried by the discharge was typically 5 to 6 ma and dropped by about .2 ma when a sample was inserted between the electrodes. Assuming a current of 5.2 ma, the voltage drop

across the 100K ohm resistor would be 520 volts and the voltage drop across the discharge would be 380 volts.

Figure 5 is a schematic representation of the numerous interactions which are possible in a gas plasma impinging on a polymeric substrate. The gas in the positive column

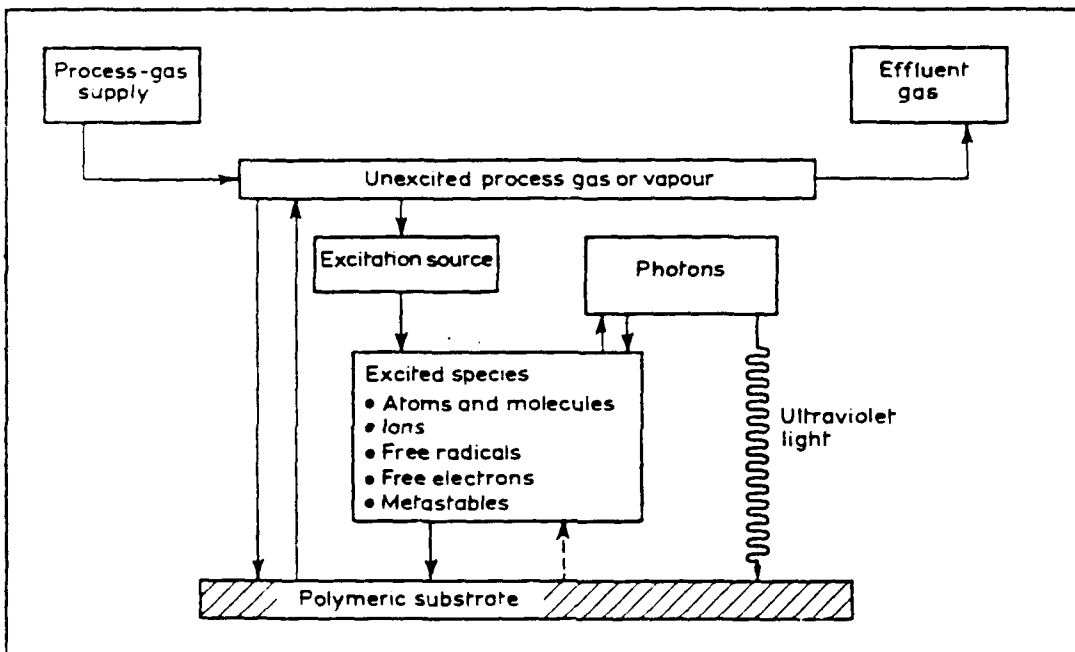


Figure 5. Possible Plasma Interactions

is in a partially ionized state with equal densities of ions and electrons (4:28, 32:132). The ratio of electrons (or ions) to neutral atoms is on the order of 10^{-7} to 10^{-8} . At a pressure of .5 torr, there will be 2×10^{16} neutral

atoms and 10^8 to 10^9 electrons or ions per cubic centimeter. Electron energies will be about 1 eV while ion and neutral temperatures will be much lower at about .025 eV. In addition to the neutral atoms, ions, and electrons, there will be active, or un-ionized but excited, metastable atoms. If the gas contains molecules they can become active or be dissociated to become free radicals. The discharge will also produce ultraviolet radiation. All of the constituents of the plasma can interact with the polymer surface.

Previous work has shown that PBZT is very resistant to electron bombardment and ultraviolet irradiation (11A). The electrons and uv radiation present in the glow discharge used in this experiment, therefore, should not affect the films. Furthermore, the neutral atoms are at thermal equilibrium with the film and chamber at such low energies that no effects due to these constituents of the plasma are expected. Since argon is an inert gas, there will be no chemical reactions between the neutral atoms and the PBZT molecules.

When a nonconducting surface is exposed to a plasma, a negatively charged sheath will form that will slow electrons impinging on the surface and accelerate positively charged ions. The ions will gain kinetic energy equal to the average electron energy in the plasma. When the ions hit the surface, the kinetic energy and

ionization energy can be transferred to the surface. Metastable atoms may couple with the surface, also delivering energy to the polymer atoms. The ions and metastables are responsible for the changes induced in PBZT upon exposure to a plasma.

Given the pressure at which a plasma is operated, the voltage across it, and the current that it carries, the flux of ions onto the surface of the polymer can be estimated. For a glow discharge operated at .55 torr and 380 volts, the cathode fall will be about 140 volts (6A:284). Therefore the electric field in the positive column will be about 240 volts/ 12.5 cm or 19.2 V/cm. This gives a value of 35 V/(cm-torr) for E/N. This number is used to determine the energy of the electrons (32:243). The electron temperature per volt of ionization energy, T_e/V_i , is found from tables to be about 600 degrees Kelvin per volt. With V_i equal to 15.5 volts for argon, T_e is found to be 9300 K or .80 eV, giving an electron drift velocity of about 5×10^7 cm/s. For a current of 5.2 mA and an electrode area of 20 cm^2 , the current density is .26 mA/cm² and the flux of electrons is about 1.5×10^{16} electrons per square centimeter per second. The density of electrons is then $(1.5 \times 10^{16}) / (5 \times 10^7)$ or about 3×10^8 electrons per cubic centimeter. The ion density will be equal. At .55 torr, the density of neutral atoms is about

2×10^{16} , giving a fractional ionization of about 10^{-8} . After being accelerated across the sheath, the ions have a kinetic energy of .80 eV, corresponding to a velocity of 2×10^5 cm/s. The ion flux onto the polymer surface is, therefore, $(3 \times 10^8 \text{ ions/cm}^3) \times (2 \times 10^5 \text{ cm/s})$ or 6×10^{13} ions/cm²-s.

The density of PBZT is 1.5 gm/cc and the average mass of its atoms is about 10 amu or 1.66×10^{-23} grams, so that there are about 10^{23} atoms per cc. Assuming an atomic radius of 1 Angstrom or 10^{-8} cm, there will be approximately 10^{15} atoms per square centimeter at the surface of the PBZT film. The ion flux deposits a equal number of atoms every 10 to 20 seconds.

The ions hitting the surface of the polymer can transfer the sum of their kinetic and ionic energies, 16.3 eV per ion, to the PBZT molecules. Typical bond energies in polymer materials range from 3 to 8 eV (4:34), so the ions are capable of scissioning the PBZT molecules. The energy flux due to the ions is about 10^{15} eV per square centimeter per second, or about 10^{-4} watt/cm².

Each metastable atom hitting the surface will deliver on the order of 9 eV. The kinetic energy of each metastable will be negligible since they will not be accelerated by the sheath. The number of metastable atoms present in the plasma is difficult to estimate, but the metastable contribution to the total energy flux is

expected to be small.

The major effects of plasma treatment can include the following (15:129-131, 23:42-43) and, of course, several may occur simultaneously:

Cleaning. All materials exposed to the environment adsorb oils and other organic materials onto their surfaces. The excited species may have sufficient energy to displace low molecular weight contamination present on the surface. (The displacement process may be proceeded by the plasma degrading, and reducing the molecular weight of, the contamination.) Plasma cleaning leaves little, if any, residue.

Degradation and ablation. The plasma may cause degradation of the surface regions of the polymeric substrate and lead to removal of material from the surface. This process is distinct from cleaning since actual polymer material, not contaminants, may be degraded and removed. Plasmas of air or oxygen have a marked tendency to cause degradation and ablation compared to plasmas of inert gases such as helium and argon. Further, some polymers, such as poly(ethylene terephthalate), are more prone to these effects than others. Ablation can increase the surface area and result in improved mechanical linkages; it is also used for inorganic chemical analysis, photoresist stripping, and the stripping of insulation from fine wires.

Crosslinking. Noble gas plasmas promote crosslinking when used in an atmosphere devoid of oxygen or other free radical scavengers. The free radicals can only react with one another or return to their unexcited state; they can cause crosslinking, recombination, unsaturation, or branching through free radical migration.

Surface activation. The plasma often leads to the introduction of polar groups, such as carbonyl groups, into the surface regions of the substrate. This may occur even when inert gases are employed. In such cases, the oxygen is suggested to arise from traces of oxygen being present in the treatment chamber (e.g. in the gas, on the chamber walls or in the polymeric substrate) or from post-treatment reaction occurring when the polymer is removed from the treatment equipment.

Polymerization and grafting onto the substrate's surface. The plasma may induce the polymerization of a constituent of the gas phase and so cause the deposition of a thin polymeric film onto the substrate. Such a film may be grafted to the underlying substrate. It is possible that some of the gaseous species from cleaning and ablation of the surface may subsequently polymerize and redeposit as a polymeric film on the substrate.

Ion implantation. The plasma may cause foreign atoms to be implanted in the surface regions of the substrate and these atoms may either aid adhesion or adversely affect the joint

strength and durability.

Lap Shear Tests

Single lap shear tests were used to determine the strength of the bond between the PBZT film and an epoxy adhesive. Although single lap shear tests do not measure pure shear (11:43), the test specimens are practical and easy to prepare and the tests provide reproducible, usable results (16:288).

Samples of the film were bonded between aluminum coupons to form the lap shear test specimens, in accord with the procedures outlined in ASTM D 1002-72 (3). Before bonding, the aluminum (2024 T3 alloy) adherends were cleaned with acetone, scoured with metal pads and coated with Pasajel, a gelled sodium disulfate etching agent. The Pasajel was removed after 15 minutes, and the adherends rinsed in distilled water and dried in a circulating air oven for 10 minutes at 60 degrees C. This process removes any surface oxide layers and roughens the surface, thus promoting a good bond between the adhesive and the aluminum (16:53). Since the manufacturer's estimate (10:4) of the shear strength for the aluminum/epoxy bond that results when this process is used is approximately five times higher than the maximum reported failure strength of PBZT, a failure at the adhesive/aluminum bond line is extremely unlikely.

Those adherends not immediately used were sprayed with primer, as recommended by the adhesive manufacturer (10:2), to ensure that the surfaces did not become oxidized again. Primed adherends can be stored up to three weeks without fear of contamination or degradation of the final bond (10:2).

FM 123-2, a modified nitrile epoxy film on a polyester mat, was used to bond the polymer film between the aluminum adherends. This adhesive film, supplied by the Cyanamid Corporation, is .006 mm thick and is designed for structural bonding of metal-to-metal, metal honeycomb sandwich, structural plastic laminates and composite structural plastic sandwiches (10:1). Adhesive film is much easier to use than two-component liquid epoxies and produces a more uniform bond line thickness.

The adherends, 1 inch wide by 4 inches long (2.54 cm by 10.16 cm), were assembled in a jig that provided a 1/2 inch (1.27 cm) overlap and could accomodate five specimens at a time. After the first layer of adherends were placed in the jig, a strip of adhesive, cut slightly larger than the overlap area, was laid across them. Next, the PBZT film was cut into pieces also slightly larger than the overlap area and applied to the adhesive strip. Another piece of adhesive was then placed over the PBZT, followed by the top adherend. The resulting configuration is shown

in Figure 6. Cutting the adhesive and the PBZT slightly larger than the overlap area ensured that the actual overlap area being tested was determined by the jig. Excess adhesive extruded out of the joint has been shown to have little effect on lap shear test results (17).

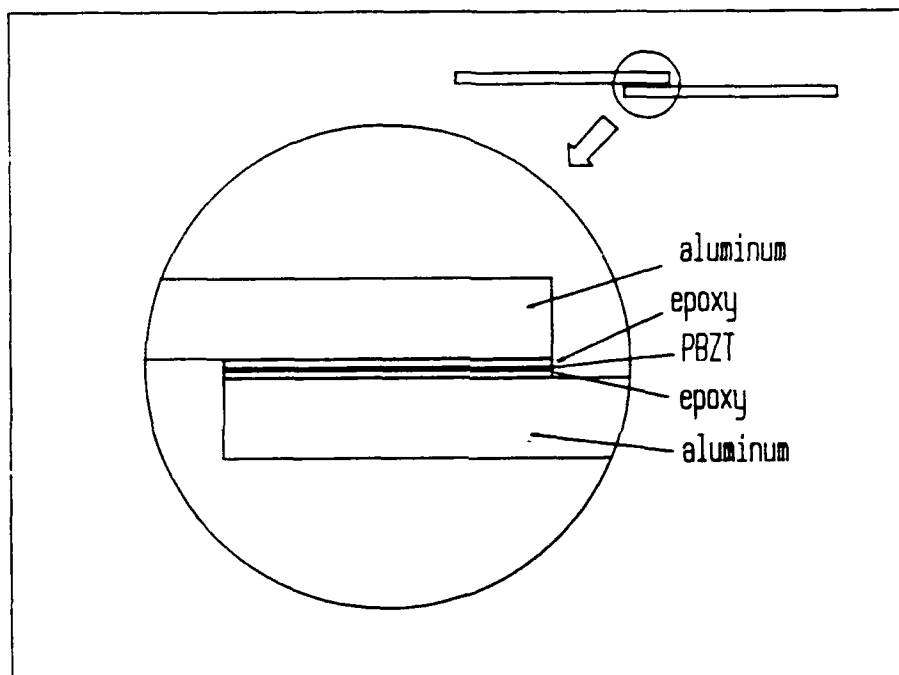


Figure 6. Lap Shear Specimen Cross Section

Aluminum and teflon spacers were used to guarantee proper alignment of the adherends, and a thermcouple was placed near the overlap area to monitor the temperature during the cure cycle. After all the components were in place, a piece of silicon rubber was placed over the bottom

part of the jig and a metal cover set in place, as shown in Figure 7. This cover allowed nitrogen under pressure to be

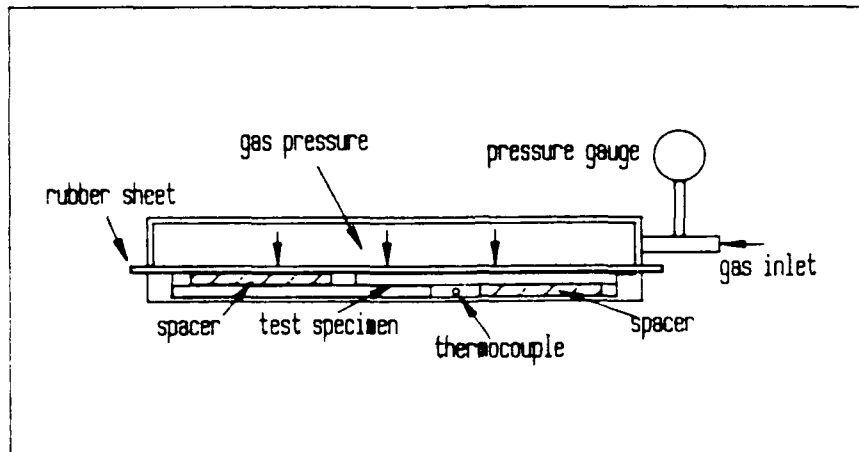


Figure 7. Lap Shear Test Assembly Jig

pumped onto the jig in such a way that the rubber sheet was compressed against the specimens, thus providing .275 MPa of clamping pressure during the curing process. This pressure could be monitored using a gauge attached to the gas inlet; a hole in the metal cover of the jig permitted the discovery of any leaks around the rubber sheet.

The jig was placed in a press that kept the top and bottom halves of the jig closed against the pressure of the nitrogen. Electric heating elements in the top and bottom platens of the press produced the elevated temperatures

required for curing. The cure temperature of 120 degrees C was reached about 30 minutes after the heaters were activated. The nitrogen pressure inside the jig had to be monitored during this period since it increased with rising temperature. The elevated temperature was maintained for one hour, after which the heaters were turned off and the specimens allowed to cool, usually with the aid of a fan. The specimens remained clamped as the jig cooled; the clamping pressure decreased somewhat as the jig cooled but was usually not adjusted. Once a temperature of about 60 degrees Celsius was reached, the samples were removed from the jig and separated from one another. The lap shear tests were normally performed immediately after the cure cycle was finished. The manufacturer of the adhesive recommends a 30 to 60 minute heat-up to a cure temperature of 105 to 120 degrees C followed by a 60 min hold at 120 degrees C and a pressure of .17 to .34 MPa (10:2). No specific cool-down cycle is recommended.

The lap shear tests were performed in accord with ASTM recommendations using a Tinius-Olsen SG machine at a crosshead speed of .05 in/min (1.27 mm/min). The opposite ends of the lap shear specimens are grasped by self-tightening jaws and slowly pulled apart, until failure occurs. The failure can occur at the adhesive/PBZT bond lines (adhesive failure) or within the PBZT itself

(cohesive failure). All tests were performed at ambient temperature, which varied somewhat around 23 degrees Celsius, and ambient relative humidity, which was usually 35 to 45%.

Load at failure, measured in pounds, was recorded and shear at failure determined (shear strength = load/area) assuming that the lap shear overlap area was 1/2 square inch. The results are reported in megapascals (MPa), with 1 MPa equaling 145.04 pounds per square inch. No attempt was made to determine the actual overlap area for each specimen, but use of the jig kept the overlap areas fairly uniform. The results can therefore be compared to obtain relative changes in lap shear strengths.

Contact Angle Determination

The beading of liquids on surfaces is a commonly observed phenomena. The quantitative determination of the angle of contact between the liquid and the surface, a measure of the wettability of the material, provides important information about the forces acting at the surface. It has been recognized for many years that the establishment of intimate molecular contact is a necessary, though sometimes insufficient, requirement for developing strong adhesive joints (15:18). This means that the adhesive needs to be able to spread over the solid surface, and needs to displace air and other contaminants that may

be present on the surface. A thin layer of liquid which completely wets two flat solids can serve as an adhesive; even when complete wetting is not apparent it is nevertheless often still possible to get good adhesive action by merely pressing the solids together until only a thin layer of liquid remains between them (1:171).

Basic to the subject of wettability is Thomas Young's concept of the contact angle formed by a drop of liquid resting on a plane solid surface (6:25). If a drop of liquid does not spread completely a state of equilibrium is reached involving a three phase point of contact between the solid, liquid and vapor phases, as shown in Figure 8. The liquid-vapor interface will form an angle, known as the "contact angle", with the solid surface. The tensions at the contact point are related via Young's equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

where theta is the contact angle and the subscripts SV, LV refer to the solid and liquid phases in equilibrium with the vapor and SL to the solid-liquid interface. The terms represent the surface free energies at the different boundaries or, equivalently, the horizontal components of the surface tension forces (6:25). When the contact angle is greater than zero the liquid is non-spreading, but when theta equals zero the liquid wets the surface completely

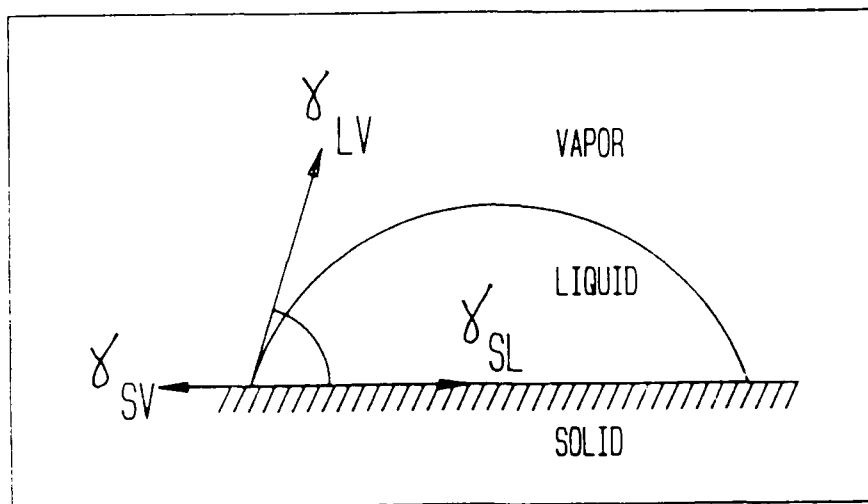


Figure 8. Liquid Droplet Resting on a Surface

and spontaneously spreads freely over the surface at a rate that depends upon such factors as the liquid viscosity and roughness of the solid surface. It is possible to make a liquid spread across a solid surface even when θ is greater than zero, but this requires the application of a pressure or a force to the liquid.

An important consideration when measuring contact angles is the phenomenon of contact angle hysteresis. Angles measured at the edge of a drop which is advancing over a surface may be greater than the values measured when the liquid is receding--usually by only a small amount, but sometimes by as much as 80 degrees (6:31-33).

Contact angle hysteresis arises from solid surfaces seldom being either ideally smooth or chemically homogeneous (14:22). The advancing contact angle is most commonly reported (15:23).

Surface roughness may change the advancing contact angle observed for a given liquid on a rough surface, θ_f , compared to the angle observed on a smooth surface, θ_s . This change in the contact angle may be expressed by:

$$\cos \theta_f = r_f \cos \theta_s$$

where r_f is the roughness factor or the ratio of the actual area to the projected area (15:23). If the contact angle for the smooth surface is less than 90 degrees, then roughening the surface will result in θ_f being even smaller. This will increase the extent of wetting. However, if θ_s is greater than 90 degrees, roughening the surface will increase the contact angle, making the surface harder to wet. The advancing contact angles measured in this experiment were used to determine the roughness factor for each treated sample; this assumes that any change in the contact angle is due to roughening and not to other effects.

A Rame-Hart model 100 telescopic goniometer was used to obtain the contact angles. Distilled, deionized water with a conductivity less than 0.3 micromho was used.

Dynamic advancing and receding measurements were made using a syringe to apply or withdraw the water, as shown in Figure 9. Several measurements were made on each sample,

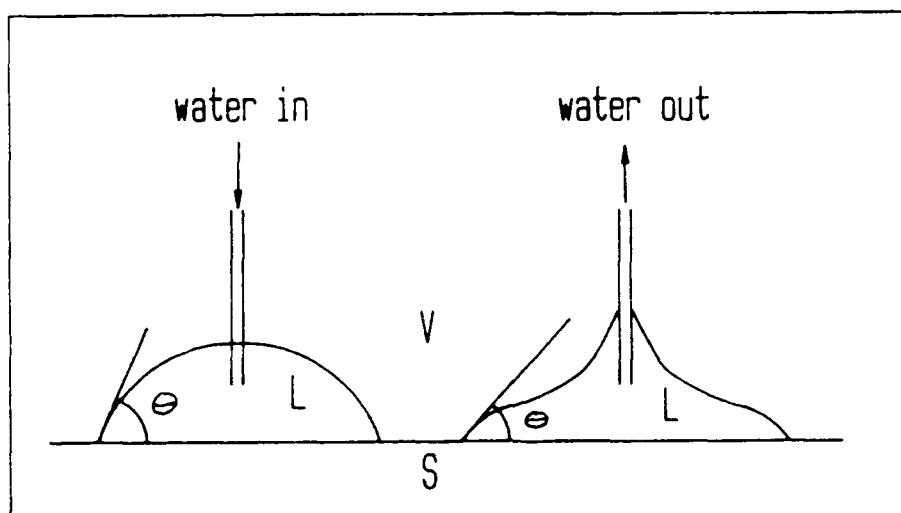


Figure 9. Advancing and Receding Contact Angles

and the average and standard deviation determined. Since PBZT has a tendency to crinkle, the surfaces of the specimens could not be made perfectly flat and some of the angle measurements obviously reflected these tilts; these values were not used to calculate the averages. The measurements were made at ambient temperature and humidity, about 21 degrees Celsius and 35% RH.

X-Ray Photoelectron Spectroscopy

The chemical composition of the treated and untreated films was analyzed using XPS (X-Ray Photoelectron Spectroscopy), a technique also known as ESCA (Electron Spectroscopy for Chemical Analysis). XPS is a non-destructive technique particularly suited to the analysis of surfaces (8:101,8:287).

XPS uses a nearly monoenergetic X-ray beam to excite the photoelectric spectrum of the material under analysis; only core electrons are ejected since the photoelectric cross sections of valence electrons are very small. For this reason, XPS cannot detect hydrogen. The X-ray beam is relatively harmless to most materials, especially when compared to the ion or electron beams used in some other analysis techniques. As the photons travel through the material some are absorbed and their energy is transferred to electrons which can be ejected from the specimen. The spectrum, the electron intensity versus the binding energy of the electron to the atom, is obtained by pulse-counting techniques. However, only electrons originating very near the surface have a high probability of escaping from the surface without losing energy; hence the surface sensitivity of this technique. The depth of investigation is governed by the electron mean free path (MFP) in the material and is typically 40 to 100 Angstroms for polymeric materials (22:104).

XPS shows systematic shifts in emission peak positions resulting from changes in the chemical structure and oxidation state of chemical compounds in the material being analyzed. This "chemical shift effect" is due to a decrease in electron density in the valence region around an atom in a molecule, which produces an increase in the binding energy of core level electrons (22:106). Oxides can often be readily identified via these shifts, and different oxidation states will produce peaks shifted from the main peak by different amounts. The resolution of the spectrometer used in this experiment, however, was not good enough to distinguish the various oxidation peaks.

The ability to obtain detailed chemical information from plastic and organic surfaces is an unparalleled capability of XPS. During X-ray irradiation, however, such nonconductive samples can undergo a change in surface potential. This surface charge is normally positive, and retards the photoejected electrons. This decrease in the kinetic energy of the photoelectrons results in higher apparent binding energies than the true values. All binding energies are shifted by the same amount so that relative energies are unchanged.

The XPS analysis was performed using a Kratos ES300 machine using 1253.6 eV K alpha X-rays from a magnesium source. The pressure inside the spectrometer during

the runs was 10^{-7} torr. Samples of the PBZT film, carefully handled to avoid contamination, were cut into rectangles approximately 1.27 cm by 1.91 cm and stuck to a tantalum mount using double-sided adhesive copper tape. The detector averages the signal over the entire sample, making the analysis of areas smaller than the sample size impossible. A survey spectrum ranging in binding energies from 1000 eV to 0 eV was made first and used to locate potentially interesting peaks. Most of the scans were made with the detector at 45 degrees to the normal. A small number of scans were made at 22 degrees to minimize the depth of investigation; no significant differences were noted. Sample charging produced shifts in the peaks on a few scans of about 5 eV. The data were manually shifted using the locations of peaks from major constituents such as nitrogen and carbon as a guide. Other techniques, such as charge injection or the use of an internal standard, were not available and are not considered necessary for routine spectra. Overall resolution is about 1 eV.

The intensity of the observed ESCA signal is a function of the amount of material present. In addition, however, the intensity depends upon the MFP of the electrons and the efficiency of absorption of the exciting X-rays by the sample material. A fully quantitative analysis of the ESCA spectra is therefore quite difficult. However, the peak intensities, corrected for the differing

photoelectric cross sections of each element, can be used to estimate the relative amounts of different elements present on the surface. This technique produces estimates good to about 20% (22:114).

As an example, assume that an ESCA scan showed peaks from oxygen and carbon, with the oxygen 1s peak 40 units high and the carbon 1s peak 20 units high. Table 1 in reference 22 gives the photoelectric cross sections of the elements relative to that of carbon 1s, for magnesium K alpha X-rays. The cross section for oxygen 1s is 2.85. The corrected oxygen 1s peak height is $40/2.85$ or 14 while the carbon peak height is unchanged. These corrected peak heights are approximately proportional to the number of atoms of each type present in the sample. Therefore, if only carbon and oxygen are present, carbon constitutes $((20/(20 + 14)) \times 100\%$ or 58.8% and oxygen $(14/34) \times 100\%$ or 41.2% of the total number of atoms. These "mole percentages" can be converted to "weight percentages" by considering the atomic weight of each atom. In this case, carbon represents 51.7% by weight and oxygen 48.3%.

When the XPS spectrum of an element shows the shifted peak characteristic of oxidation, the fraction of the element oxidized can be estimated by comparing the heights of the shifted and unshifted peaks. For example, if the shifted peak is 10 units high and the unshifted peak is 20

units high, then $10/(10 + 20) \times 100\%$ or 33% of the atoms are oxidized and $20/30 \times 100\%$ or 67% are not. The total number of atoms of that type present is proportional to the sum of the heights of the two peaks.

Scanning Electron Microscopy

Plasmas have been shown to rapidly erode the surfaces of some plastics while having little or no effect on others. A scanning electron microscope was used to detect any changes in the surfaces of the PBZT films due to plasma treatment.

Scanning electron micrographs were obtained using a JEOL JSM-840 microscope typically operated at 10 kV and a working distance of 16-17 mm. Slivers of the PBZT film were attached to aluminum mounts using conductive carbon paint and coated with a mixture of gold and palladium to a thickness of 10 nm using a Balzers/Union sputterer. Photomicrographs were made at magnifications of 30000, 15000, 5000 and 250 in order to look for changes in the morphology of the film surfaces at a variety of scales.

IV. Experimental Results

Table 2 lists the various treatments used on the PBZT film samples examined in the course of these experiments. Care must be taken when comparing results since samples were treated at different pressures as well as for different times. Samples 1 through 10 were from the same batch of PBZT, while 11 and 12 were from a different batch prepared by Foster-Miller three months later. Each listed treatment time is the sum of equal treatment times at two different discharge polarities. The power supply was set at 900 volts for all runs except number 8, which was run at 1000 volts.

Table 3 lists the tests performed on each sample.

Table 2. Sample Treatment Parameters

<u>Sample</u>	<u>Treatment</u>
1	cleaned with methylene chloride
2	Ar plasma, 20 minutes at .130 torr
3	Ar plasma, 200 minutes at .169 torr
4	Ar with .3% water vapor, 100 minutes at .540 torr
5	Ar plasma, 100 minutes at .762 torr
6	Ar with .3% water vapor, 140 minutes at .600 torr
7	Ar with 1% CF ₄ , 140 minutes at .600 torr
8	N ₂ plasma, 140 min at .758 torr
9	cleaned with methylene chloride
10	Ar plasma, 100 minutes at .510 torr
11	cleaned with methylene chloride
12	Ar plasma, 200 minutes at .588 torr

Table 3. Sample Test Matrix

<u>Sample</u>	<u>Treatment</u>	<u>Lap Shear</u>	<u>XPS</u>	<u>Contact Angle</u>	<u>SEM</u>
1	clean	X			X
2	Ar 20 min	X			X
3	Ar 200 min	X			X
4	OH 100 min	X			X
5	Ar 100 min			X	
6	OH 140 min		X	X	
7	CF4 140 min		X		
8	N2 120 min			X	
9	clean		X	X	
10	Ar 100 min		X		
11	clean	X			
12	Ar 200 min	X			

Table 4 lists the lap shear strengths for all of the specimens tested, along with the average strength and the standard deviation. All failures occurred within the PBZT film.

Table 4. Lap Shear Test Results

Sample	1	2	3	4	11	12
Lap shear strengths	2.37	1.86	3.43	3.19	2.22	3.94
	2.45	1.68	2.53	3.60	2.48	3.94
	2.92	2.74	3.08	3.34	2.52	4.27
	2.22	3.97	3.60	2.72	2.50	3.70
	2.44	3.27	2.95	2.85	2.48	3.89
						3.76
Average	2.48	2.70	3.11	3.14	2.44	3.91
Standard Deviation	.21	.86	.38	.32	.11	.18

Table 5 lists the advancing and receding contact angles determined for four samples. Five to seven measurements were made on each sample and the average and standard deviation determined for each. The roughness factor, calculated using the advancing contact angles, is also presented. The contact angle determined for sample 9 was taken to be the value for a smooth surface.

Table 5. Contact Angles Test Results

Sample	Treatment	Contact Angle (deg)		r_f
		Advancing	Receding	
5	Ar 100 min	54 +/- 3	33 +/- 6	2.3
6	OH 140 min	31 +/- 4	15 +/- 3	3.3
8	N2 120 min	36 +/- 4	15 +/- 3	3.1
9	clean	75 +/- 8	44 +/- 3	1.0

Figure 10 compares the initial survey scans made on the four samples analyzed using XPS. Comparisons of the oxygen, sulfur, nitrogen, carbon and phosphorus peaks are shown in Figures 11 through 15. These plots are not to the same scale and cannot be directly compared. However, all curves presented in any one figure are to the same scale. The top phosphorus peak in Figure 15 is actually a misidentified silicon peak, the argon-treated sample shows no phosphorus in its ESCA spectrum.

Table 6 presents the elemental analysis based on these peaks, in mole percentages and weight percentages. Zero entries indicate that the amount of that element present was below detectable limits. Silicon and tantalum are not included in the weight percentages since these elements are present as test chamber contaminants, not as components of

the PDZT. The sample identified as "FM", cleaned in methylene chloride but otherwise untreated, was analyzed for Foster-Miller (18:3-51).

Table 7 shows the percentage of nitrogen and sulfur atoms oxidized in the four samples tested in this experiment. Results for the Foster-Miller sample were not available.

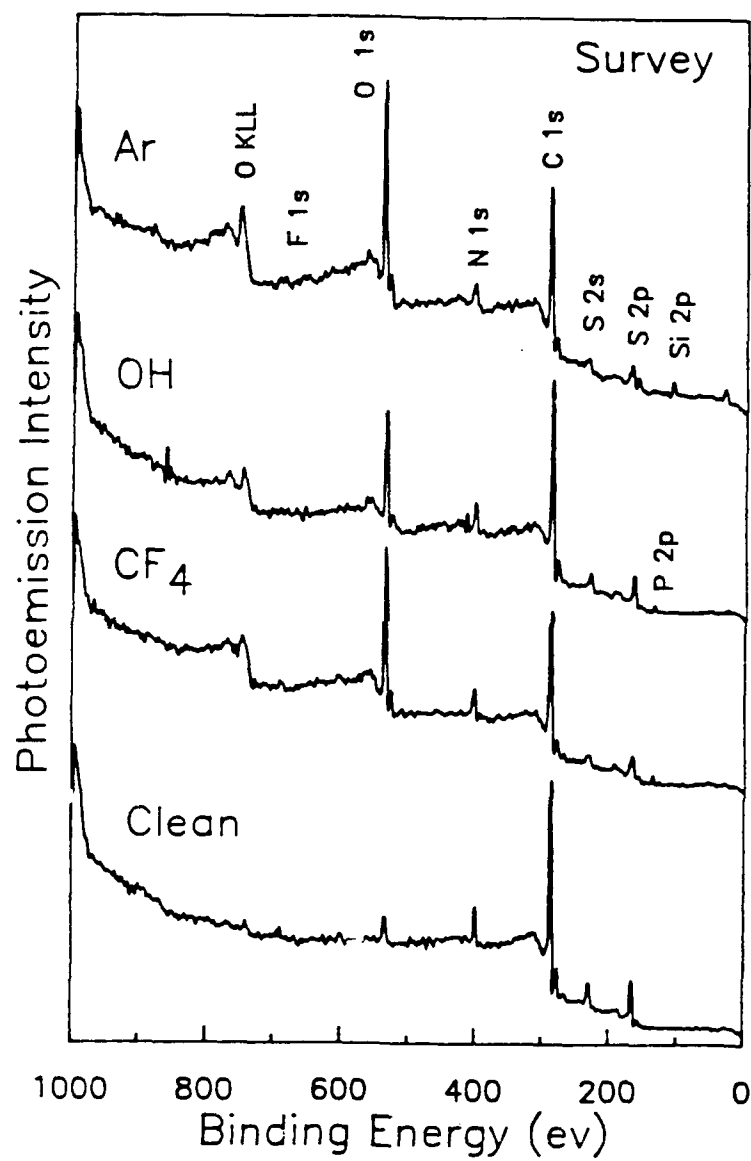


Figure 10. XPS Survey Spectra of PBZT Films

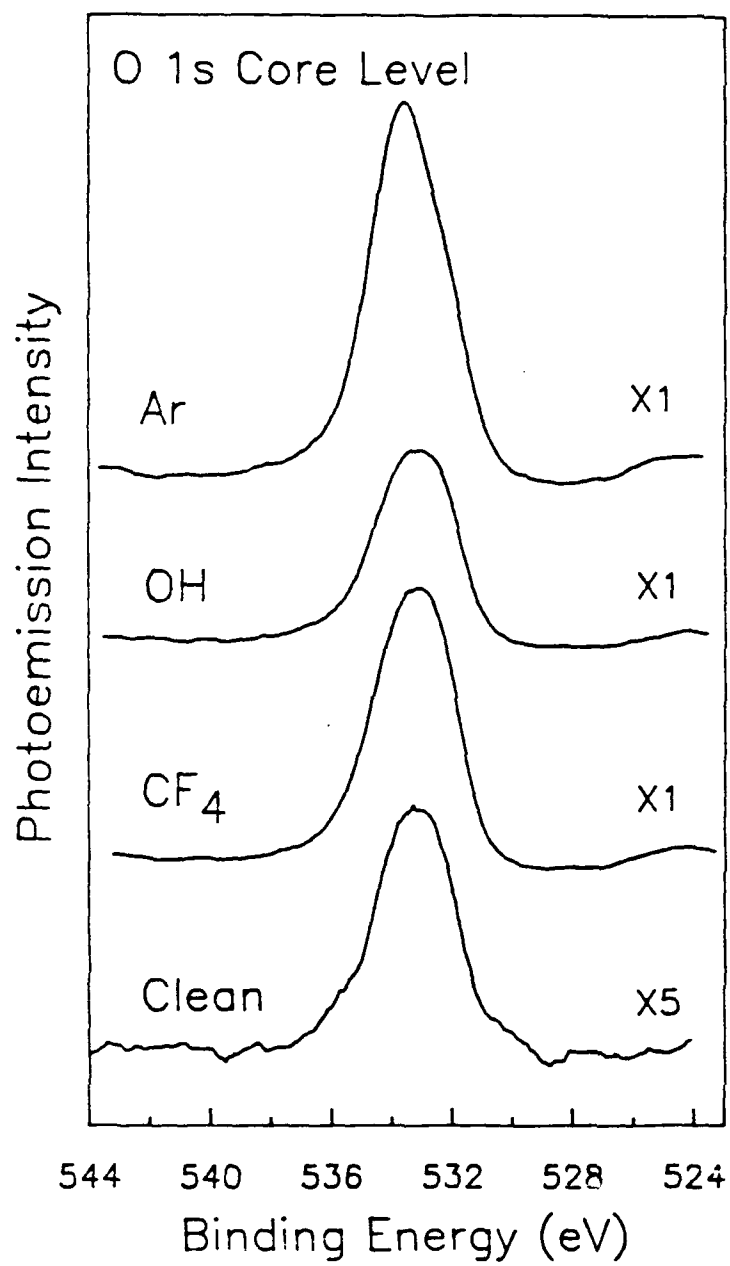


Figure 11. XPS Oxygen 1s Line Spectra

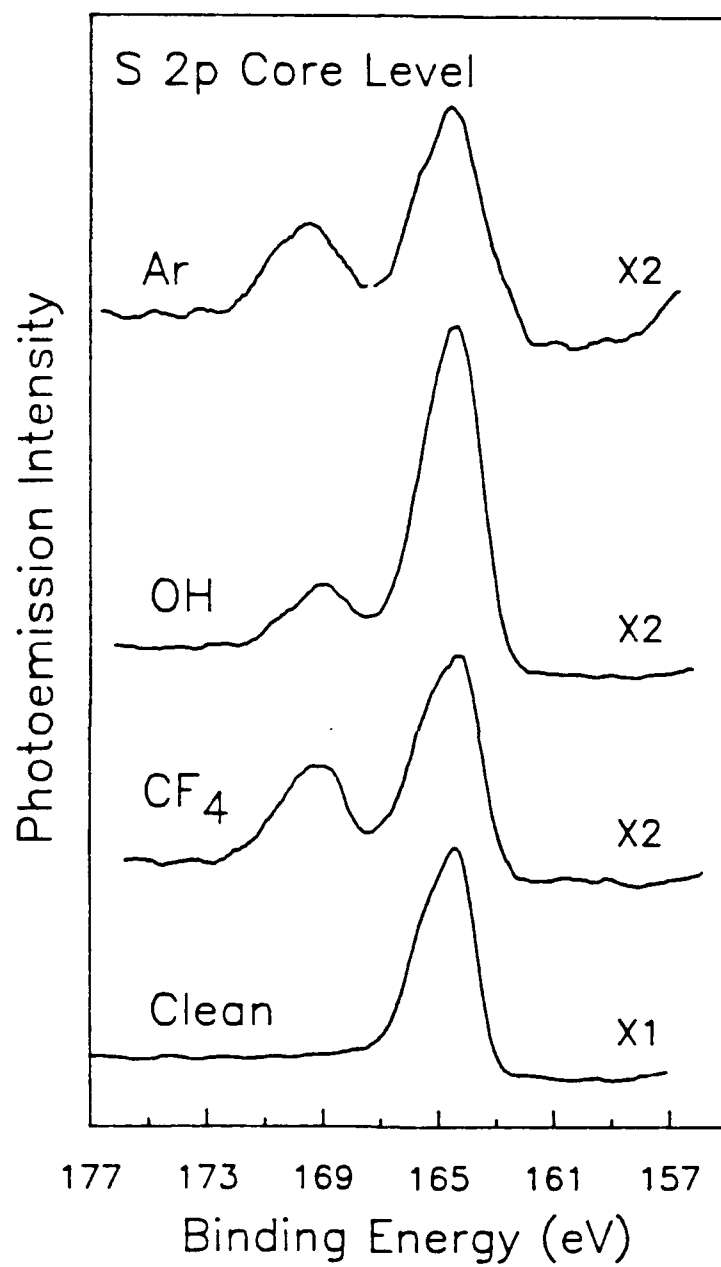


Figure 12. XPS Sulfur 2p Line Spectra

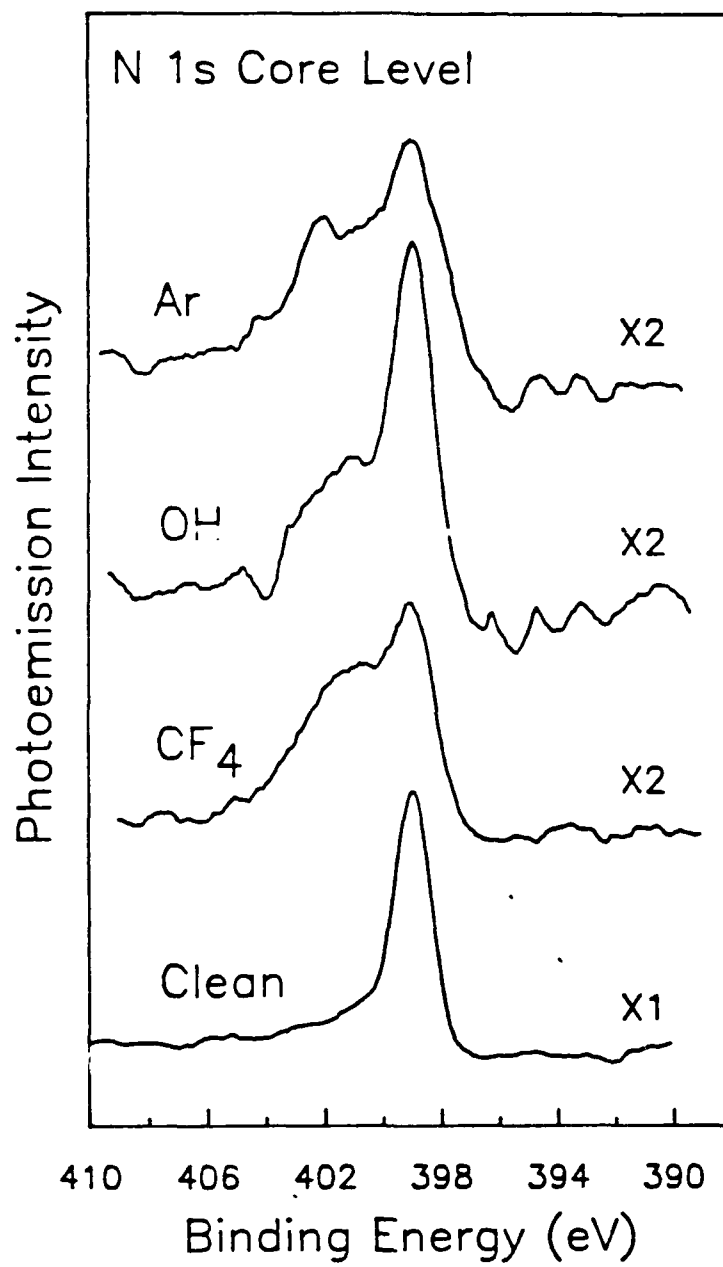


Figure 13. XPS Nitrogen 1s Line Spectra

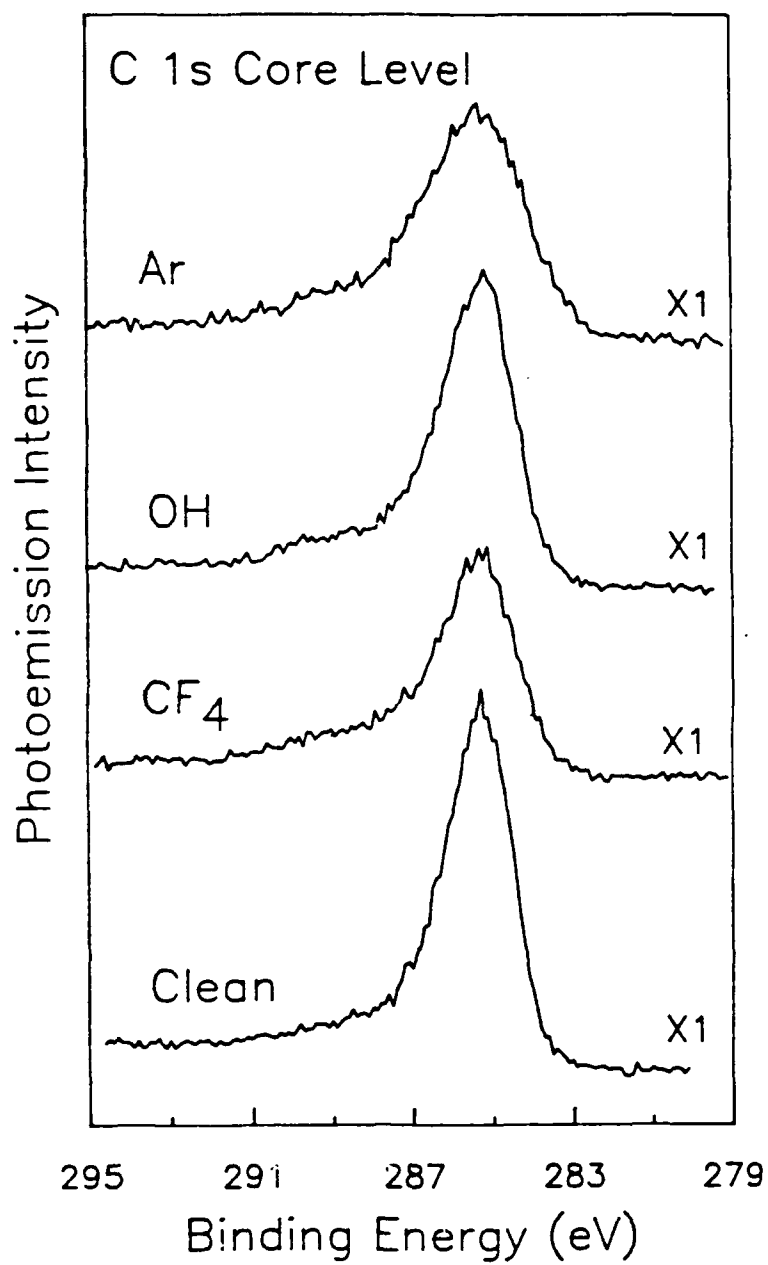


Figure 14. XPS Carbon 1s Line Spectra

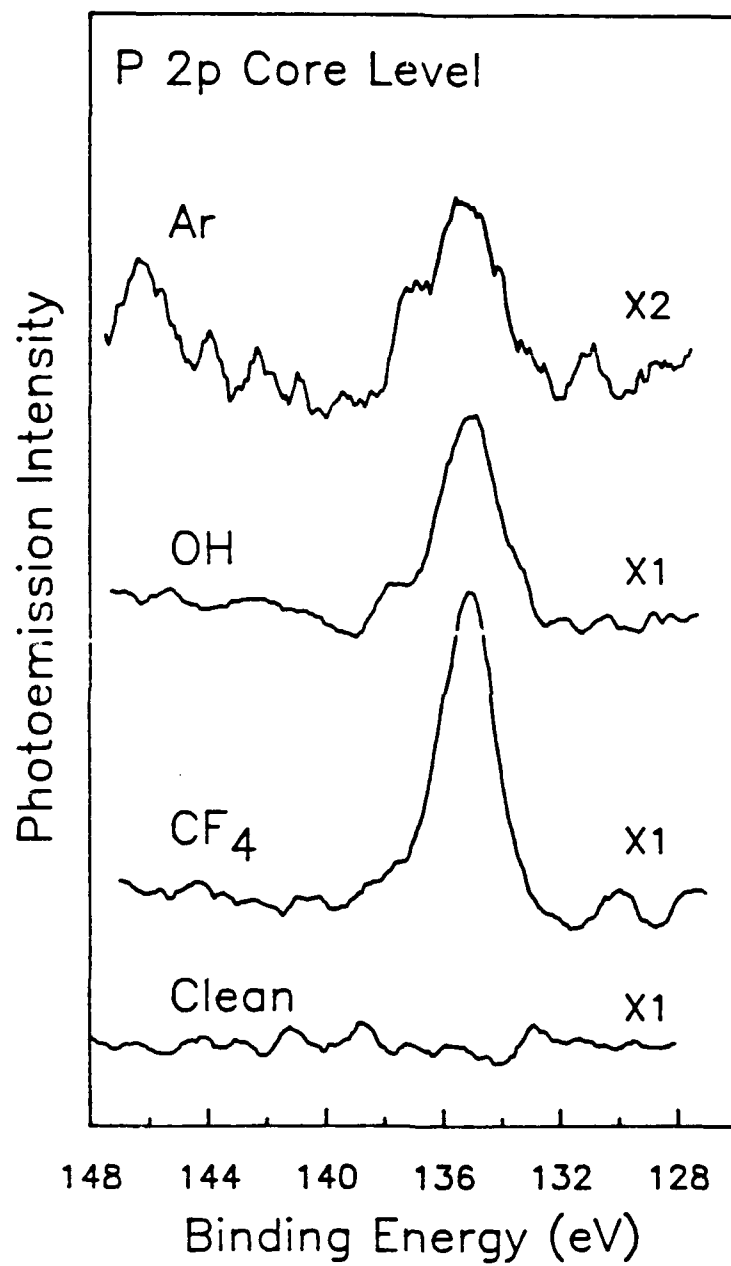


Figure 15. XPS Phosphorus 2p Line Spectra

Table 6. Summary of XPS Results

Sample	6	7	9	10	FM
Treatment	OH 140 min	CF4 140 min	cleaned	Ar 100 min	cleaned

Mole percent					
C	66	55	80	54	71.6
N	9	12	9	8	6.2
S	6	5	7	4	4.1
O	14	23	4	26	17.8
Si	0	0	0	5	.3
Ta	0	0	0	3	0.0
P	5	5	0	0	0.0

Sample	6	7	9	10	FM
Treatment	OH 140 min	CF4 140 min	cleaned	Ar 100 min	cleaned

Weight percent (Si and Ta contaminants not included)					
C	54	44	70	49	62.4
N	9	11	9	9	6.3
S	12	11	16	10	9.5
O	15	24	5	32	20.8
P	10	10	0	0	0.0

Table 7. Percentage of Atoms Oxidized

Sample	6	7	9	10
Treatment	OH	CF ₄	cleaned	Ar
	140 min	140 min		100 min

Percent Oxidized				
N	29	43	<10	39
S	18	31	<10	31
P	13	<10		
C	<5	<5	<5	<5

Figures 16 through 19 are SEM photographs of the cleaned sample, the samples treated for 20 and 200 minutes in argon, and the sample treated for 100 minutes in argon/water vapor.

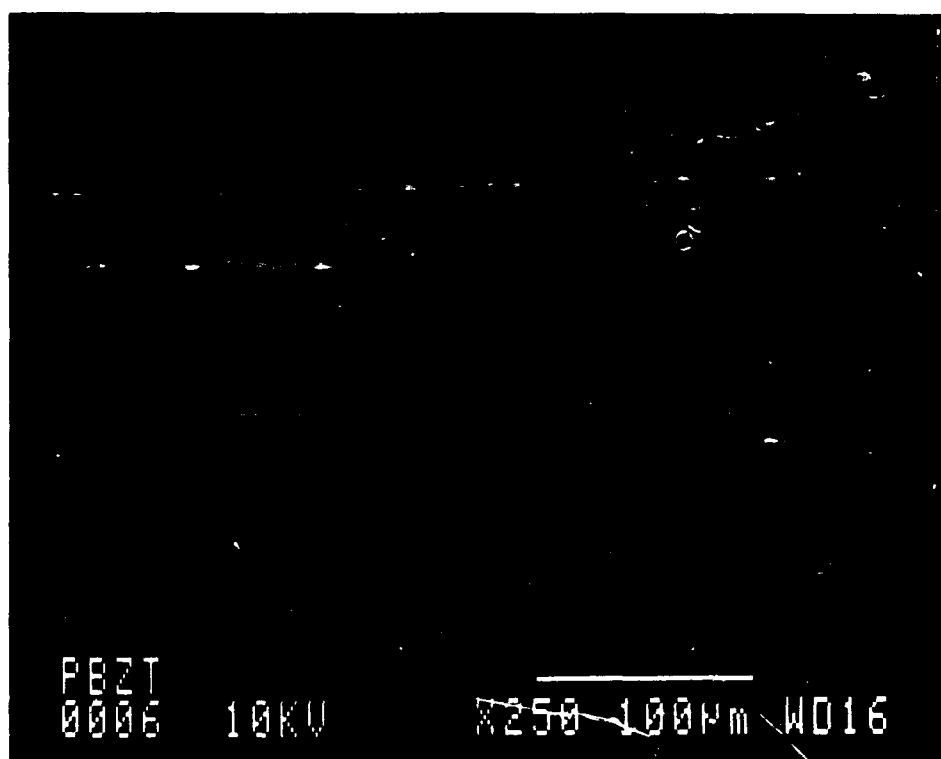
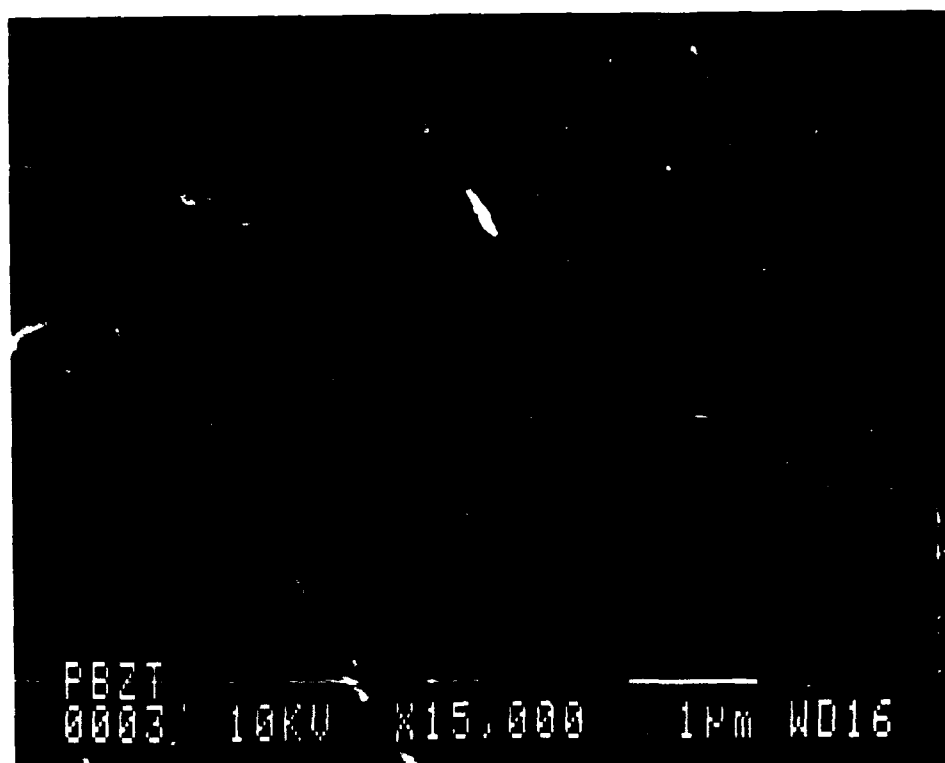


Figure 16. SEM Photographs of Cleaned-Only Sample, Magnificatic 250X and 15000X

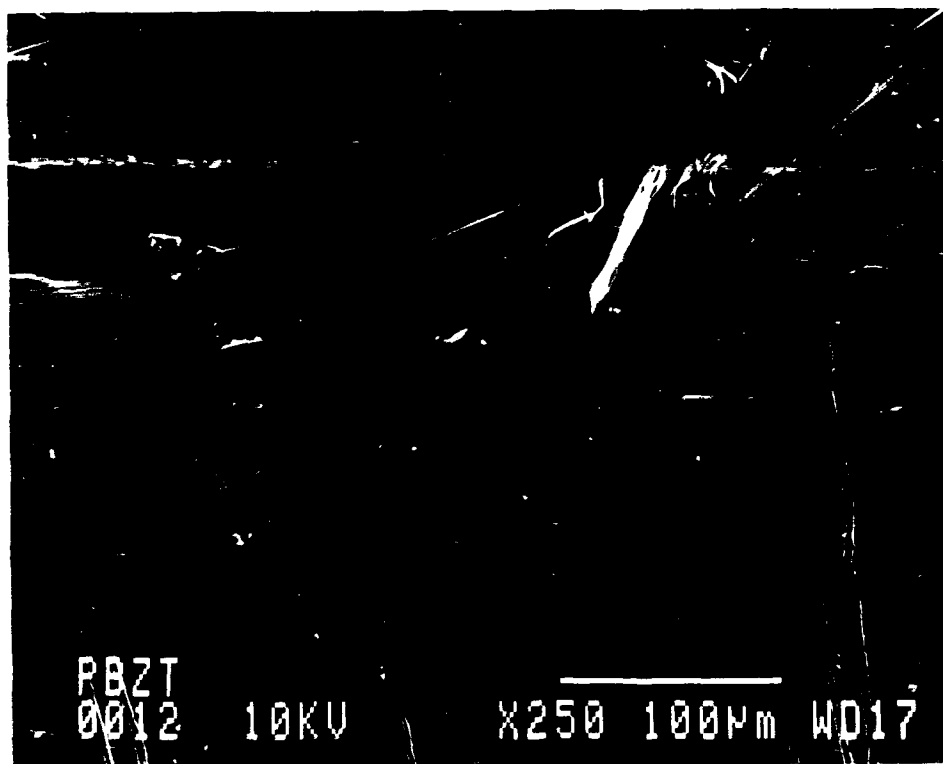
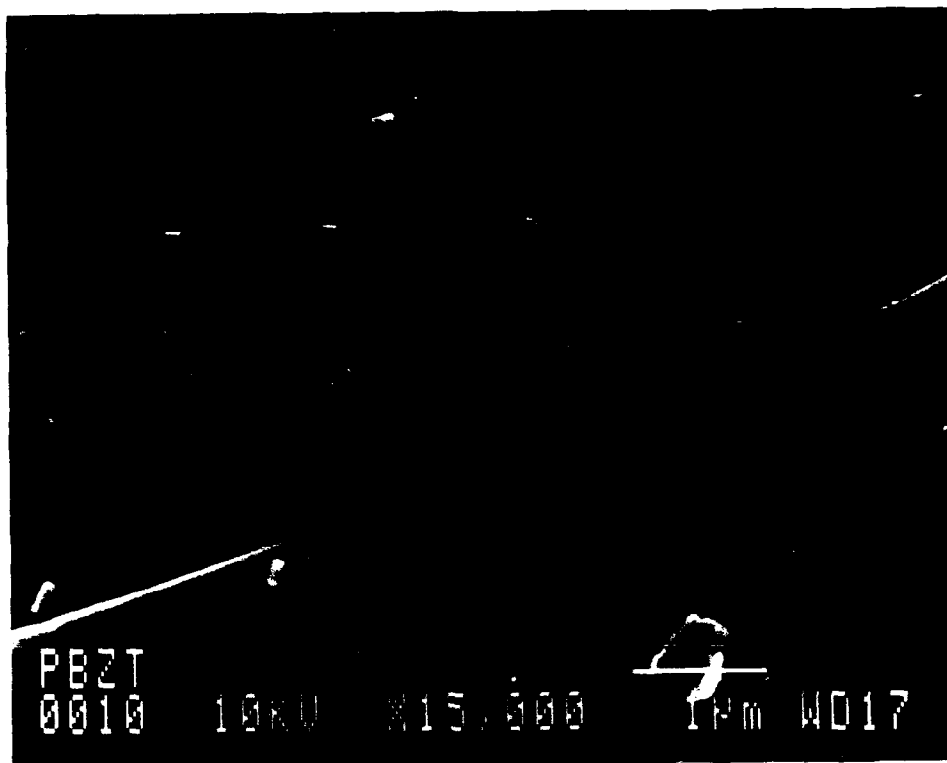


Figure 17. SEM Photographs of Sample Treated in Argon Plasma for 10 Minutes per Side, Magnification 250X and 15000X

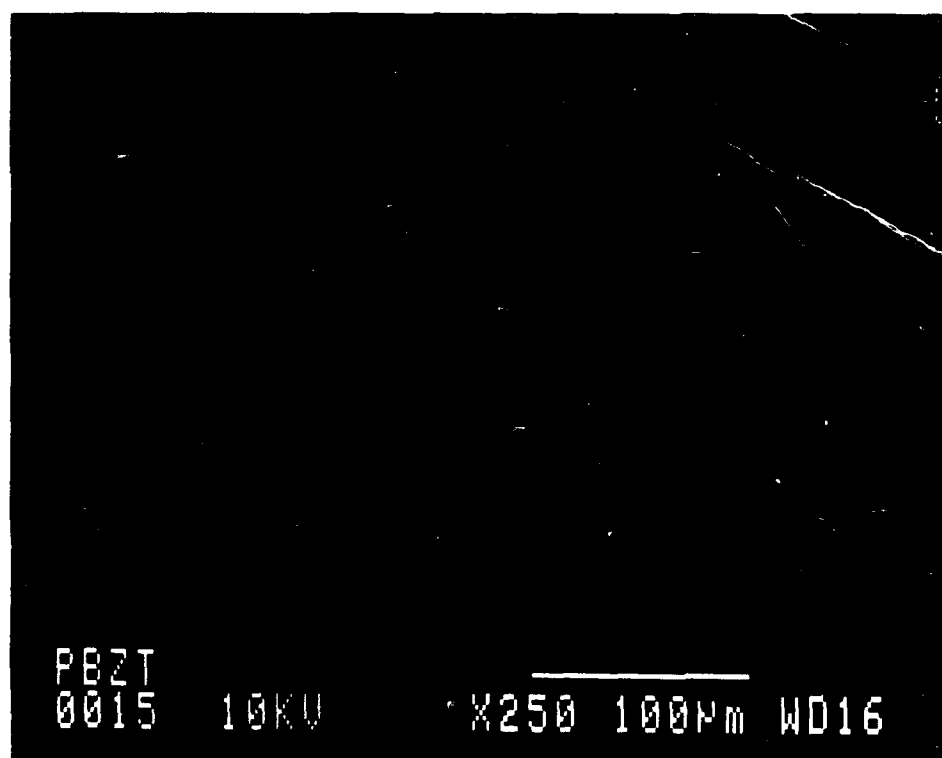
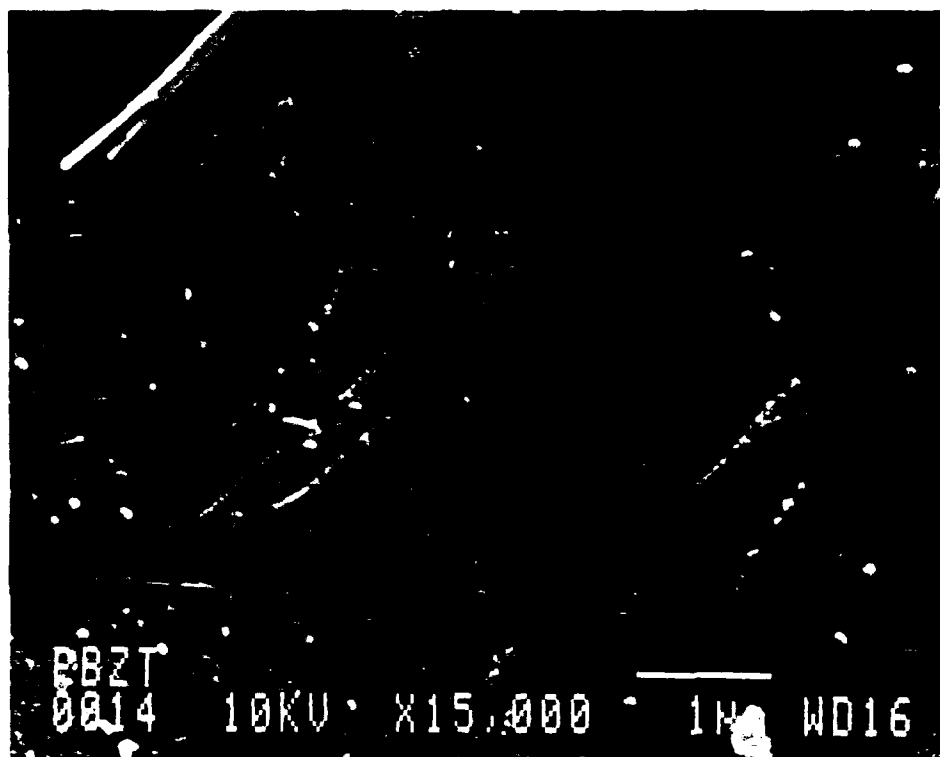


Figure 18. SEM Photographs of Sample Treated in Argon Plasma for 100 Minutes per Side, Magnification 250X and 15000X

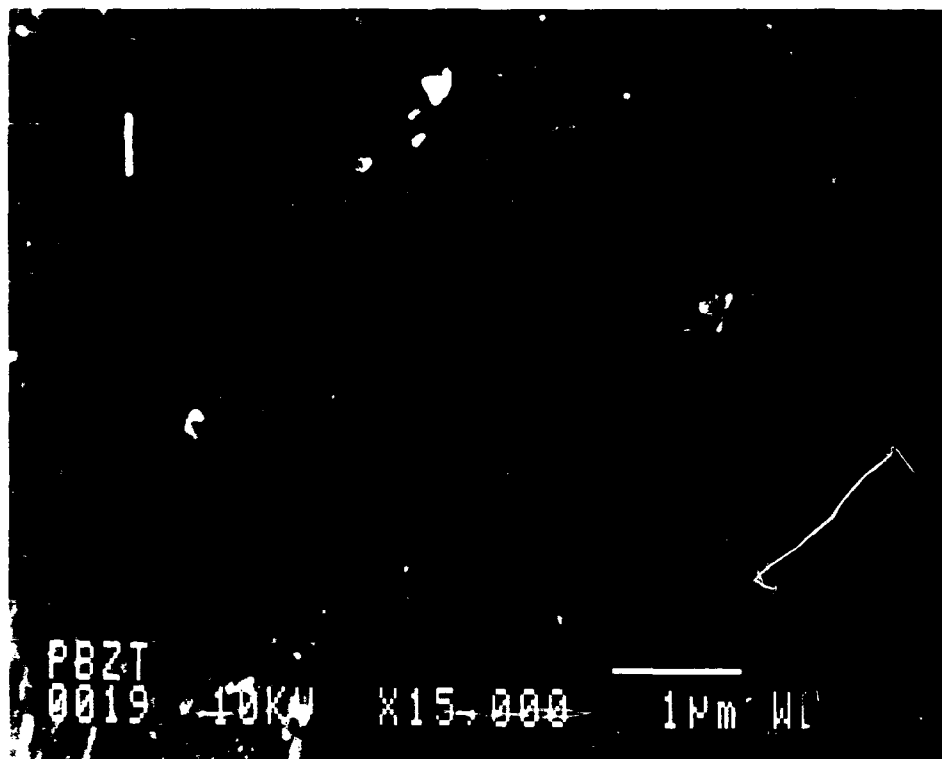


Figure 19. SEM Photographs of Sample Treated in Argon/Water Vapor Plasma for 50 Minutes per Side, Magnification 250X and 15000X

V. Discussion

X-Ray Photoelectron Spectroscopy

The sample treated in the argon-only plasma for 100 minutes shows small silicon and tantalum peaks that are not present in the other spectra. This sample was treated last, after some work had been done on the spectrometer vacuum system, and the silicon is likely due to chamber contamination. The tantalum is from the sample mount.

Except for contaminants, the samples show similar spectra; the most obvious difference is that all the plasma treated samples show strong oxygen lines, while the cleaned, but otherwise untreated, sample shows only weak oxygen lines. The sample treated at the lowest pressure for the shortest time, number 10, shows the highest oxygen content, 32% by weight, while the sample cleaned in methylene chloride shows only 5% oxygen by weight. The large amounts of oxygen present on the surfaces of the plasma treated samples analyzed using XPS could not have come from within the film, since PBZT contains no oxygen. Instead, the oxygen was absorbed onto the reactive surface left after plasma treatment. Although the treated samples were stored in evacuated tubes, they were exposed to atmospheric oxygen during transfers. The origin of the large amount of oxygen in the untreated Foster-Miller is unknown.

The sulfur (Figure 12) and nitrogen (Figure 13) spectra show shifted peaks indicating that oxides of these elements were formed on the surfaces of the treated samples. Comparison of the main and shifted peaks shows that the sample treated in an argon/ CF_4 plasma had the largest fraction of its nitrogen and sulfur atoms oxidized, 43% and 31% respectively. The small amount of oxygen present in the cleaned sample meant that few of its atoms were oxidized. The carbon peaks (Figure 14) are approximately the same in the four samples. There is no evidence for oxidation of the carbon in any of the samples.

The cleaned-only sample shows no evidence of phosphorus (Figure 15), while two of the plasma treated samples display small phosphorus peaks. Apparently, treating the film allowed phosphorus, left in the film due to incomplete washing, to come to the surface where it could be detected using XPS. The small peaks, however, indicate that only minimal amounts were left behind. There are also small chlorine peaks in the spectra, with the cleaned-only sample showing the largest peak, indicating that most of the methylene chloride used to clean the samples prior to treatment evaporated while what little remained was effectively removed by exposure to the plasmas.

The absence of fluorine in the CF_4 treated sample, as

well as the fact that the OH treated sample actually shows less oxygen than the argon treated sample, indicates that the attempts to implant atoms into the surface were unsuccessful. This is probably due to the small concentrations of CF_4 and water vapor (1% and .3%, respectively) used in this experiment. Any fluorine atoms or OH radicals that did impinge on the surface were probably swept away by the much larger number of argon atoms hitting the surface at the same time.

Contact Angle Determination

Exposure to argon, nitrogen and water vapor plasmas all made the surface of the PBZT films more wettable. The mechanism behind this is unclear. The argon and OH treated samples show few differences in their XPS results, yet the OH sample showed an advancing contact angle of 31 degrees while the argon sample showed 54 degrees, compared to the cleaned-only sample value of 75 degrees. Unfortunately, the samples were not treated for equal times (140 minutes vs. 100 minutes), so that the difference may be the result of increased surface roughening due to longer exposure to the plasma. Assuming that the increased wettability is the result only of surface roughening, the sample treated for 100 minutes has a roughening factor of 2.3 while the one treated for 140 minutes has a roughening factor of 3.3. If the effect of different treatment pressures is ignored,

these data indicate that the roughening varies approximately linearly with the exposure time. The sample treated in a nitrogen plasma for 120 minutes showed a contact angle slightly lower than that of the OH sample, but this sample was not examined with either XPS or SEM and little more can be said. However, assuming that nitrogen erodes the PBZT film as efficiently as argon, the roughening factor for the nitrogen-treated sample, 3.1, once again indicates that the roughening is, approximately, proportional to the treatment time.

Scanning Electron Microscopy

The samples show about the same amount of debris on their surfaces, while the 100 minute argon and water vapor samples show signs of surface erosion, including pitting and fissuring. The electron microscope photographs show that the surface of the PBZT is eroded by long exposures (100 to 200 minutes) to a plasma, while shorter exposures (20 minutes) produce little damage. The roughening factor for these surfaces is difficult to estimate using only these photographs, but the values based on the contact angle measurements seem too high, indicating that the increased wettability of the surfaces is not entirely due to surface roughening.

Lap Shear Tests

All of the lap shear specimens failed within the PBZT

film, not at the epoxy/film interface. Even for the untreated sample, the adhesive/film bond was stronger than the interlaminar strength of the film itself. This was very surprising. Previous work by Foster-Miller indicates that the film should be able to take about 5.8 MPa before failing cohesively, yet the untreated films failed at less than half this value. The highest value observed in this experiment was 4.3 MPa, still significantly less than the values reported by Foster Miller. Untreated samples from two batches of the polymer, prepared at different times, failed at essentially the same load, indicating that this phenomenon is not due to differences between batches.

Although all samples failed cohesively, the plasma-treated samples failed at higher loads. The fact that the lap shear strengths were up to 58% higher for samples exposed to argon plasmas indicates that this treatment was able to reach below the surface of these very thin films in order to increase the interlaminar cohesive strength of the material. Longer treatments, at higher pressures, produced larger increases in the cohesive strength.

The improvement in the cohesive strength of the PBZT is probably due to cross-linking between polymer chains from one layer of ordered molecules to another. The material used in these experiments consists of molecules aligned side-by-side. The strength of the material in the

direction along which the molecules are aligned is much higher than the strength in the perpendicular directions. The interlaminar strength is therefore quite low, and is probably made even lower by the shearing process used to produce the balanced biaxial film used in these experiments.

VI. Conclusions and Recommendations

This work resulted in the construction of a plasma treatment chamber and the development of the techniques associated both with its use and with the analysis of sample treated in it. PBZT film was exposed to a variety of plasmas and the resulting changes determined.

Plasma treatment was shown to increase the wettability of PBZT, demonstrated by an decrease in the contact angle of water from 75 degrees for an untreated sample to 31 degrees for a film treated for 140 minutes in an argon plasma. This increased wettability is partly due to increased surface roughness; long exposures to an argon plasma significantly eroded the film surface, as shown in SEM photographs.

Analysis of XPS spectra showed that oxides of nitrogen and sulfur were formed on the surfaces of PBZT films treated in a plasma and subsequently exposed to air. Attempts to implant fluorine atoms and OH radicals, using plasmas formed from mixtures of argon with small amounts of carbon tetrafluoride and water vapor, were unsuccessful.

Single-lap shear tests were performed to determine if exposure to a plasma would improve the adhesive properties of PBZT film. No improvement in adhesion could be shown, however, since all samples failed within the film, not at the film/adhesive interface. The internal cohesive

strength of the film was lower than the strength of the adhesive/film bond, even for untreated samples. However, the lap shear strengths were higher for samples exposed to argon plasmas, indicating that this treatment was able to increase the interlaminar cohesive strength of the material. This improvement is probably due to cross-linking between polymer chains from one layer of ordered molecules to another, and was shown to increase with exposure time.

Techniques such as gel permeation chromatography and attenuated total reflectance infrared spectroscopy should be used to determine the degree and type of cross-linking in order to determine if cross-linking is responsible for the increased cohesive strength of the films treated in plasmas. The effects of argon and other plasmas should be systematically investigated so that the cause of increased wettability can be better defined. Spectroscopic or other techniques could be used to determine the actual plasma conditions at the sample during treatment, and a fuller theoretical treatment should be attempted.

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A plasma treatment chamber was constructed and used to treat samples of poly (p-phenylenebenzobisthiazole) (PBZT), an ordered polymer material. Analysis of scanning electron microscope results showed that exposure to an argon glow discharge plasma for extended times eroded the surface of the polymer. X-ray photoelectron spectroscopy indicated that oxides were formed on the plasma-treated surfaces upon exposure to air. Treatment using argon, argon/water vapor and nitrogen plasmas was shown to make the polymer surfaces more hydrophilic.

PBZT films bonded between aluminum coupons failed cohesively when shear forces were applied. Plasma treatment improved the shear strength of PBZT films by over 50%. This improvement is attributed to an enhancement of the interlaminar strength of the PBZT via crosslinking between polymer chains.

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