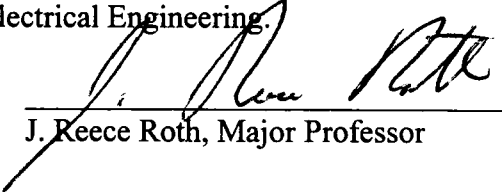


To the Graduate Council:

I am submitting herewith a thesis written by Anna K. Carr entitled "Increase In The Surface Energy of Metal and Polymeric Surfaces Using the One Atmosphere Uniform Glow Discharge (OAUGDP)." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirement for the degree of Master of Science, with a major in Electrical Engineering.


J. Reece Roth, Major Professor

We have read this thesis
and recommend its acceptance:

Marshall Pace

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Associate Vice Chancellor and
Dean of The Graduate School

**INCREASE IN THE SURFACE ENERGY OF METAL AND
POLYMERIC SURFACES USING THE ONE ATMOSPHERE
UNIFORM GLOW DISCHARGE PLASMA (OAUGDP).**

A Thesis
Presented for the
Master of Science Degree
The University of Tennessee, Knoxville

Anna K. Carr

August, 1997

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ACKNOWLEDGMENTS

There are many people to whom I am grateful for making my time at the University of Tennessee so exciting and rewarding. I am grateful to my Thesis Committee, Marshall Pace, Larry Wadsworth, and J. Reece Roth for their support and encouragement. I am specially grateful to my advisor, Dr. Roth, for helping me with a number of revisions and the financial support throughout my graduate program. I would like to thank my friends and family for their constant friendship and support.

Lastly, I want to thank God for this moment.

ABSTRACT

Plasma processed materials are used in our daily lives. Increasing the surface energy of metal and polymeric materials can make possible better coating, printing, bonding, and dyeing of their surfaces. With the patented technology of a One Atmosphere Uniform Glow Discharge Plasma (OAUGDP) reactor developed at the UTK Plasma Sciences Laboratory, one can obtain up to 70 dynes/cm, or erg/cm^2 , in a few seconds of exposure for most materials. The surface energy is measured with a series of mixtures of reagent-grade formamide (HCONH_2) and reagent-grade ethyl cellosolve ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$), which span the range from 30 dynes/cm to 70 dynes/cm. Several polymeric films, including samples made from linear low density polyethylene (LLDPE), low density polyethylene (LDPE), and polyethylene terephthalate (PET) films, as well as metalized paper have been exposed at an RF frequency of 5 kHz and at 6 kV(RMS) for various exposure durations, including 1, 2, 5, 10, 15, 30 and 60 seconds. These samples were exposed in open air to check the aging effect at various times after exposure. The behavior of surface energy with time after exposure shows a wide range of behavior, depending on the specific material under test. Photomicrographs of the surfaces were taken after selected exposure durations, and the morphological characteristics of the surface compared to the surface energy measurements.

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NOMENCLATURE

ΔG^s	Surface Energy
$S_{L/S}$	Spreading Coefficient
W_{SLV}	Work of Adhesion
ESCA	Electron Spectroscopy for Chemical Analysis
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
PET	Polyethylene Terephthalate
SAXS	Small Angle X-Ray Scattering
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XPS	X-Ray Photoelectron Spectroscopy

I. INTRODUCTION

The use of plasma processing for various manufacturing applications has increased dramatically in the past 50 years. Plasma processed materials are all around us. A frequent reason to use plasma in industrial settings is because no comparable method exists to accomplish the same tasks with higher efficiency, or which produces fewer unwanted byproducts. William Crookes described plasma as “the fourth aggregation state of matter” (Penning, 1957). It was first defined by Irving Langmuir in 1928; a recent definition is “An approximately electrically neutral collection of ions and electrons which may or may not contain a background neutral gas, and is also capable of strongly responding to electric and magnetic fields.” (Roth, 1995) The recent development of a One Atmosphere Uniform Glow Discharge Plasma (OAUGDP) at the UTK Plasma Science Laboratory makes it possible to generate a glow discharge plasma at atmospheric pressure and in air. This OAUGDP allows one to expose materials to plasma active species without a vacuum system, and without being restricted to batch processing.

Previous studies show that low pressure glow discharge plasma with gases such as oxygen, nitrogen, inert gases, and other reactive oxidizing and reducing gases can modify the surface of materials (Coates, 1996). Active species from the plasma react with adsorbed monolayers on the surface of materials to change their surface properties either temporarily or permanently. In many industries, extremely high surfaces energy (above 50 dynes/cm) is

required for satisfactory adhesion, printability , and bonding. These products include metals used in the automotive or microelectronics industry, or thin films used in the food packaging industry, all of which can benefit from plasma processing technology.

To obtain a better understanding of the OAUGDP surface interaction, and to measure the changes in surface energy, several techniques can be used. Measuring the surface energy of materials is important because it is closely related to wettability, printability, bondability, and other commercial characteristics. Customary units for measuring surface energy is ergs per square centimeter (erg/cm^2) or dynes per centimeter (dyne/cm); these are identical dimensionally. The corresponding SI units are joules per square meter (J/m^2) or Newton per meter (N/m).

II. REVIEW OF THE LITERATURE

2.1 History of Plasma Surface Treatment

Although thin film formation by glow discharge polymerization can be traced back to 1874, systematic investigation of plasma treatment started in the 1960's due to interest in computer technology, but it was found that many industrial processing technologies can benefit from the use of plasma-cleaned materials (d'Agostino, 1990). Since then, intensive use of plasma surface treatment has developed in microelectronics, medical, textile, and other industries simply because there is no satisfactory alternate way to achieve the high quality results provided by plasma treatment (Kogoma, 1988). Whether the process is deposition, modification, or etching, plasma treatment has made a major contribution to 20th century technology.

An overview of plasma-surface treatment is shown in Figure 2.1. Different samples react differently to plasma exposure. For metal surfaces, plasma treatment can strip off layers of surface oils and contaminants with thicknesses up to several microns. This method allowed applications to cleaning and bonding to grow rapidly. The textile industry has been investigating plasma treatment to make fabrics wettable and to take dyes (Tsai, 1994). Plasma treated thin films have been used in food packaging and other applications. These applications have used three main types of plasma discharge to do surface treatment: low pressure glow discharge, corona, and dielectric barrier discharges.

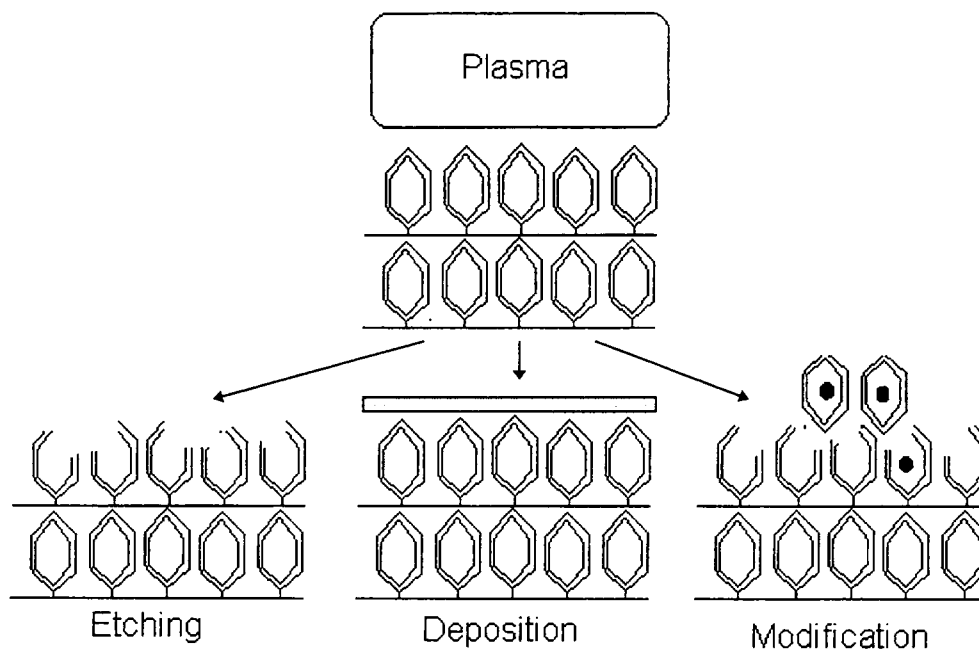


Figure 2.1 Plasma Reactions

2.1.a Low Pressure Glow Discharge Treatment

Low pressure glow discharge treatment has been used in many industries. It is a useful technique to modify the surfaces of polymers and leads to polymerization, grafting, crosslinking, and implantation (Wakida, 1989). Treating fibers in plasma produces free radicals in the polymer matrix, which play an important role in these reactions. The characteristic low-pressure discharge below one atmosphere operates with an RF frequency in the MHz or GHz range.

Plasma processing has become an environmentally favorable alternative for many textile applications (Tsai, 1994). Only 2 minutes of plasma treatment

are needed to enhance the level of shrink resistance of wool fabric, as well as providing a reduction in weight loss compared to the conventional chlorinated polymer treatments during washing (Zuchairah, 1997). Rakowski found that the chlorination process for enhancing the pattern printability of wool toe (raw wool cloth) requires 7 KWH per kilogram of wool, but low pressure plasma treatment requires only 0.3-0.6 KWH per kilogram of wool. Modification of PET (polyethylene terephthalate) fabric with low temperature oxygen plasma combined with pretreatment of dimethylformamide, DMF, has been studied by Wakida (1985). Oxygen plasma treatment leads to the production of a more hydrophilic, low contact angle or wettable, polymer surface (Wakida 1985; Tsutsui 1989).

Plasma cleaning at low pressure has been the best method to achieve the cleanest surface on metals for many applications. Plasma treatment not only cleans unwanted residues on a surface, but it improves the adhesive properties of the surface as well (Korzec et al. 1994; Mittelstadt 1996). Low pressure plasma, however, requires a vacuum chamber and batch processing. The cost of a single vacuum chamber can range up to \$100,000, not to mention high operating and maintenance expenses.

2.1.b Corona Treatment

Corona has many important industrial applications which include electrostatic precipitators, xerography, surface modification, and antistatic

treatment (Ogles 1979). The effect of corona discharge on the surface properties of wool has been researched recently (Wakida 1991; Thomas 1993).

A corona discharge can be used to clean up unwanted gases. It is used to excite, dissociate, and ionize gas molecules to produce radicals such as O, OH[•], and H₂O. These species react with SO₂ and form aerosols which can be dissolved in water (Dhali, 1991).

Air corona discharge has been used to increase the surface energy of polymeric surfaces (Tsutsui, 1989; Menges, 1990). High values of surface energy lasted on the order of minutes due to facile reconstruction of the surface by mobile elastomer chains, but bondability increased with some of the surface-activated elastomers (Lawson, 1987). One recent study of corona versus low pressure plasma treatment of polymers such as PE and PET shows that regardless of the treatment type, the maximum peel force occurred for oxygen concentration in various gases of values between 10~15% (Sapieha, 1993).

2.1.c Dielectric Barrier Discharge

Dielectric Barrier Discharge (DBD) reactors can operate below atmospheric pressure. They are a widely-used source for ozone generation and UV production in the thin film and textile industries. Materials are treated in DBD reactors to increase the surface energy, printability, and adhesive properties of thin films. Various working gases are used, based on the

chemical properties of the materials. Using an applied RF frequency of 13.56 MHz at a pressure of 0.05 Torr, immobilization of glucose oxidase on polyethylene film has been studied by Wang (1993).

The removal of SO_2/NO_x from flue gases, which is of great importance to the utilization of coal as a fuel, can be done with a dielectric barrier discharge (Dhali, 1991).

A dielectric barrier discharge at atmospheric pressure has been used to treat surfaces. With RF frequency of 3000 Hz and a heated bottom electrode, a dielectric barrier discharge was formed at atmospheric pressure and used for deposition on PET (Kogoma, 1991).

2.2 Atmospheric Plasmas

The most common atmospheric plasmas known to man are lightning and the Aurora Borealis. Although they are natural electrical discharges, they are in significant ways opposite extremes. Aurora Borealis or Northern Lights consist of luminous bands or streamers of light that are sometimes visible in the night skies of northern latitudes, and are caused by the ejection of charged particles from the magnetosphere of the earth into the upper atmosphere. Northern Lights occur in the extremely rarefied gas of the uppermost layer of the atmosphere (Penning, 1957).

Lightning, an atmospheric electrical discharge accompanied by thunder, may take place between two parts of the same cloud, between two clouds, or

between a cloud and the earth. lightning may appear as a jagged streak (forked lightning), as a vast flash in the sky (sheet lightning), or, rarely, as a brilliant ball (ball lightning). In 1750 Benjamin Franklin used kites to prove that lightning was not essentially different from electrical sparks. Studying this natural phenomenon established the basis for modern atomic theory.

2.2.a Corona

A corona discharge is a dark discharge which can occur at atmospheric pressure, due to high local electric fields around wires or at sharp points or edges shown in Figure 2.2. The American Heritage dictionary defines corona as a faint glow enveloping the high-field electrode in a corona discharge, often accompanied by streamers directed toward the low-field electrode.

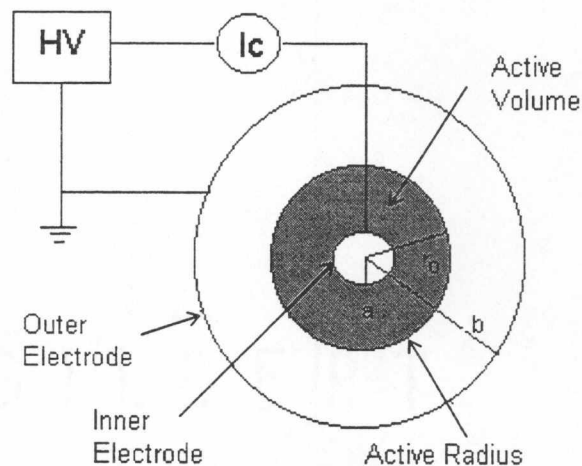


Figure 2.2 Phenomenology of corona generated by a fine wire

The breakdown voltage at standard temperature and pressure in dry air is

$$V_B = 3000d + 1.35 \text{ kV} \quad (\text{kV}), \quad (1)$$

where the breakdown electric field is given by

$$E_B = V_B / d \text{ (kV/m)} \quad (2)$$

and d is the gap spacing (Cobine, 1958). Corona can initiate from sharp points, fine wires, sharp edges, or anything which can create a localized electric field greater than the breakdown electric field of the surrounding gas.

2.2.b Dielectric Barrier Discharge - Filamentary Discharge

The Dielectric Barrier Discharge (DBD), sometimes called the silent discharge, was introduced by Siemens in 1857 for ozonizing air (Siemens, 1857). In 1932 Buss realized that the breakdown of atmospheric air in the presence of a dielectric barrier results in a large number of thin current filaments. The parameters of filamentary discharges or microdischarges were investigated by many people including Kogerlschatz and Samoilovich (Kogerlschatz, 1988).

A dielectric barrier discharge forms when an AC high voltage is applied to two electrodes, at least one of which has an insulator on it, as shown in examples of a dielectric barrier discharge Figure 2.3. The applied high voltage must exceed the Paschen breakdown voltage of the gas. This feature is one of several which distinguish the DBD from the OAUGDP, the latter of which can

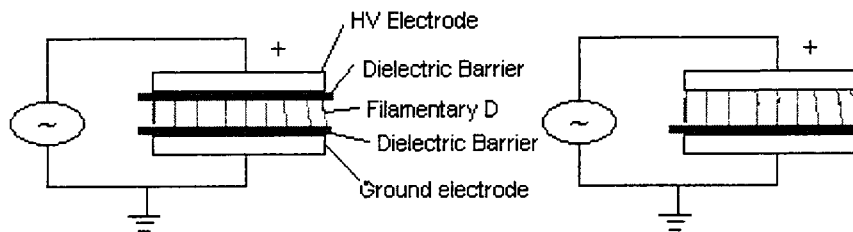


Figure 2.3 Examples of dielectric barrier discharge

operate well below the Paschen minimum voltage. The multitude of current pulses or filaments are randomly distributed in space and time. The discharge generates a large volume of ozone, VUV and UV.

Figure 2.3 shows the parallel plate configuration used for plasma processing purposes, which operates at the relatively high pressure of 0.1 to 10 bar and relatively low frequencies of 50 Hz to 1 MHz. Dielectric barrier discharges can be operated over a wide pressure and frequency range.

Around atmospheric pressure in discharge gaps in the millimeter range, breakdown is regarded as a transient glow discharge. The charge build up at the dielectric reduces the applied electric field within nanoseconds, which causes electron loss mechanisms to dominate electron production in the gas. The current flow is interrupted by electron loss, resulting in a self-arresting discharge. Depending on the insulating properties of the dielectric, this phenomenon occurs independently at many locations (Kogelschatz, 1988). Due to the independence of this arresting action, understanding a single

microdischarge filament is sufficient to understand the properties of the whole parallel plate discharge.

The microdischarge initiates when the ratio E/p is just over its breakdown value. The transported charges will spread over the surface of the dielectric at the discharging location (Eliasson, 1988, 1987). The value of E/p changes depending on the pressure and the gap separation. Also, the charge transported in an individual microdischarge depends on the thickness and the permittivity of the dielectric barriers, in addition to the gap separation. The significant parameters of dielectric barrier discharge operation are gas composition, gap spacing, pressure, temperature, and the dielectric properties of the insulating barriers. Table 1 shows characteristic microdischarge properties (Xu, 1985).

Table 1. Characteristic Microdischarge Properties

Characteristic Microdischarge Properties (Xu, 1985)	
Lifetime	1 - 20 nsec
Filament Radius	100 - 200 μm
Current Density	1 KA/cm^2
Average Electron Energy	1 -20 eV
Electron Density	$10^{14} - 10^{15}/\text{cm}^3$
Gas Temperature	300K

2.2.c Ozonizer

Ozone is used mainly for purification of drinking water and the treatment of waste water. In the early 1900's, ozone generators were installed to purify city water supplies in France and Russia (Kogelschatz, 1988). Ozone, an allotropic form of molecular oxygen, consists of three atoms of oxygen instead of the more common two. Pure ozone is an unstable, faintly bluish gas with a characteristic fresh, penetrating odor. It is the most chemically active form of oxygen. Ozone is formed in the ozone layer of the stratosphere by the action of solar ultraviolet light on oxygen; this layer plays an important role in preventing most ultraviolet radiation, which is harmful to life, from penetrating to the earth's surface. Ozone in the lower atmosphere is a pollutant that can damage lung tissue. It is produced by photochemical processes, or when an electrical discharge, such as lightning or sparking in electric motors, passes through the air. Commercially, ozone is used as a disinfectant and decontaminant for air and water, as a bleaching agent, and in the production of azelaic acid (used in making plastics).

Ozone is manufactured by passing dry air, or depending on the size of the ozone generator, pure oxygen, between two electrodes connected to an alternating high voltage. The generation of ozone by an electrical discharge may be considered one of the most important applications of plasma chemistry. The power requirement of a large ozonizer is in the range of megawatts. Since ozone is not very stable, it cannot be transported or stored, and it must be

produced on site. The most common feed gas is dry air, but pure oxygen is used for larger ozone generating plants.

Ozonizers have been used in the parallel plate configuration in the past, but modern generators use dielectric, cylindrical glass tubes 1-2 meter(s) in length, such as shown schematically in Figure 2.4.

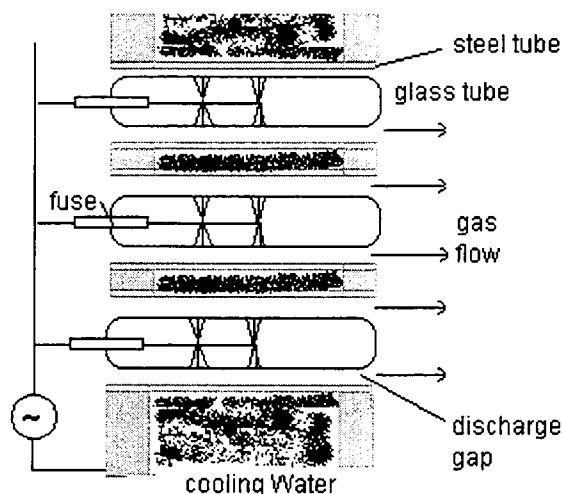


Figure 2.4. Schematic Diagram of Glass and Steel Tubes in O₃ Generator

The traditional ozonizer is operated at line frequency (50 ~ 60 Hz) with a 20 KV step up transformer. The operating pressure ranges from 1 ~ 3 bar. A large ozonizer may use 1 MW, with 1000 discharge tubes each providing 10 kg of ozone per hour. Several types of ozonizer such as transmission-line, parallel-strip-line-with-insulator, and wire-to-cylinder ozonizers are used to achieve the desired performance (Masuda, 1986).

In pure oxygen, about 80% of the electron energy can be utilized for the dissociation of O₂, and the main reactions for ozone formation are the following:



where M is a third collision partner which can be O_2 , O , O_3 or N_2 .

An efficient ozone generator requires a relatively high pressure level to favor the desired three-body reaction (Suzuki, 1952). In order to avoid the oxygen atoms recombining into O_2 , the concentration of oxygen atoms in a microdischarge has to be kept low. Very weak discharges, however, may cause an electron energy loss due to an increase in reactions with ions. A balance of these two requirements are essential to obtain an efficient ozonizer.

In air the ozone producing reaction is more complicated because of the presence of excited nitrogen molecules and nitrogen atom reactions, which are beneficial to ozone formation, in addition to the reactions shown in Equation 3 and 4 (Braun, 1988).



Optimum conditions for these reactions require higher mean electron energies and higher electron densities in the microdischarge channel compared

to pure oxygen (Braun, 1988). This results in different operating conditions for air than those appropriate for pure oxygen. Equations 5 to 8 show that the amount of ozone can be doubled with air compared to pure oxygen, but air as a working gas may cause a catalytic reaction when the NO_x concentration reaches a threshold level. Optimum conditions are those which decrease the NO_x concentration level.

The highest efficiency ozone generator tested in pure oxygen is about 20%, 250 g/KWH, and a characteristic value in dry air is about 8%, 100 g/KWH. Under laboratory conditions, a power efficiency as high as 170g/KWH has been achieved in air (Masuda, 1988).

It is difficult to distinguish the difference between a dielectric barrier discharge and an ozonizer because the dielectric barrier discharge also produces a large volume of ozone. However, the ozonizer favors a weaker microdischarge which corresponds to a high gas density, while the dielectric barrier discharge favors a high current density and thin microdischarge channels, which depend on high pressure and high gas density for their optimum efficiency.

2.2.d A One Atmosphere Uniform Glow Discharge Plasma

The OAUGDP is a recently developed and proprietary (to the University of Tennessee) atmospheric glow discharge plasma which can be operated at one atmosphere, in air and other gases. The operation of this plasma requires

only a RF power supply capable of providing a few tens of kV RMS at a few kilohertz, and no vacuum system. Characteristic areal power densities are a few tens to a few hundred milliwatts per square centimeter. The OAUGDP therefore does not have a power density high enough to damage or degrade most exposed materials, while providing an active species flux greater than corona discharges (Roth, 1995).

The parallel electrode plate configuration of the OAGUDP is shown in Figure 2.5. Two electrodes are driven by a power amplifier capable of operating from 0 to 10 KV rms, with a frequency range from 1 kHz to 100 kHz. Even though helium and argon can break down under relatively low RF electric fields of 2 ~ 3 KV/cm, a high enough RF frequency is required to avoid plasma polarization. An optimum electrode gap spacing, rms voltage, and applied frequency result in the trapping of ions but not electrons between the two plates and produce the desired OAUGDP.

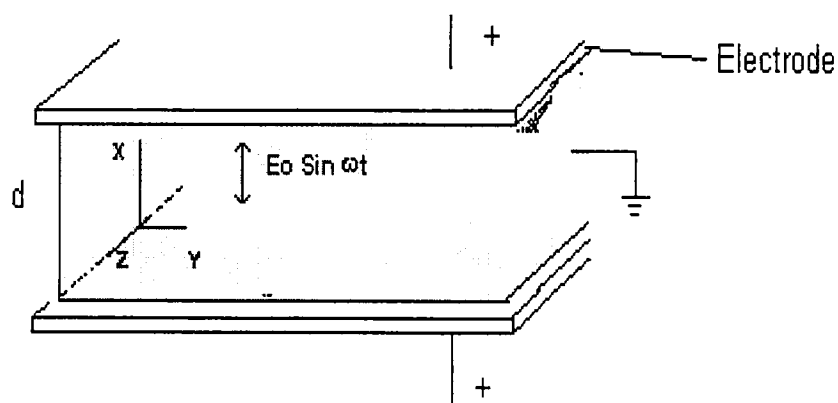


Figure 2.5. Schematic of the OAUGDP (Roth, 1995)

The electric field, E , between the electrodes shown in Figure 2.5 is used to derive the following equations (Roth 1995, Chapter 12.5.2). The distance, d , between the energized electrode and a second grounded electrode is

$$\frac{d}{2} \approx \frac{e V_{rms}}{2\pi m \nu_o \nu_c d^2} \quad (9)$$

The critical frequency is

$$\nu_c \approx \frac{e V_{rms}}{\pi m \nu_o d^2} \quad (\text{Hz}). \quad (10)$$

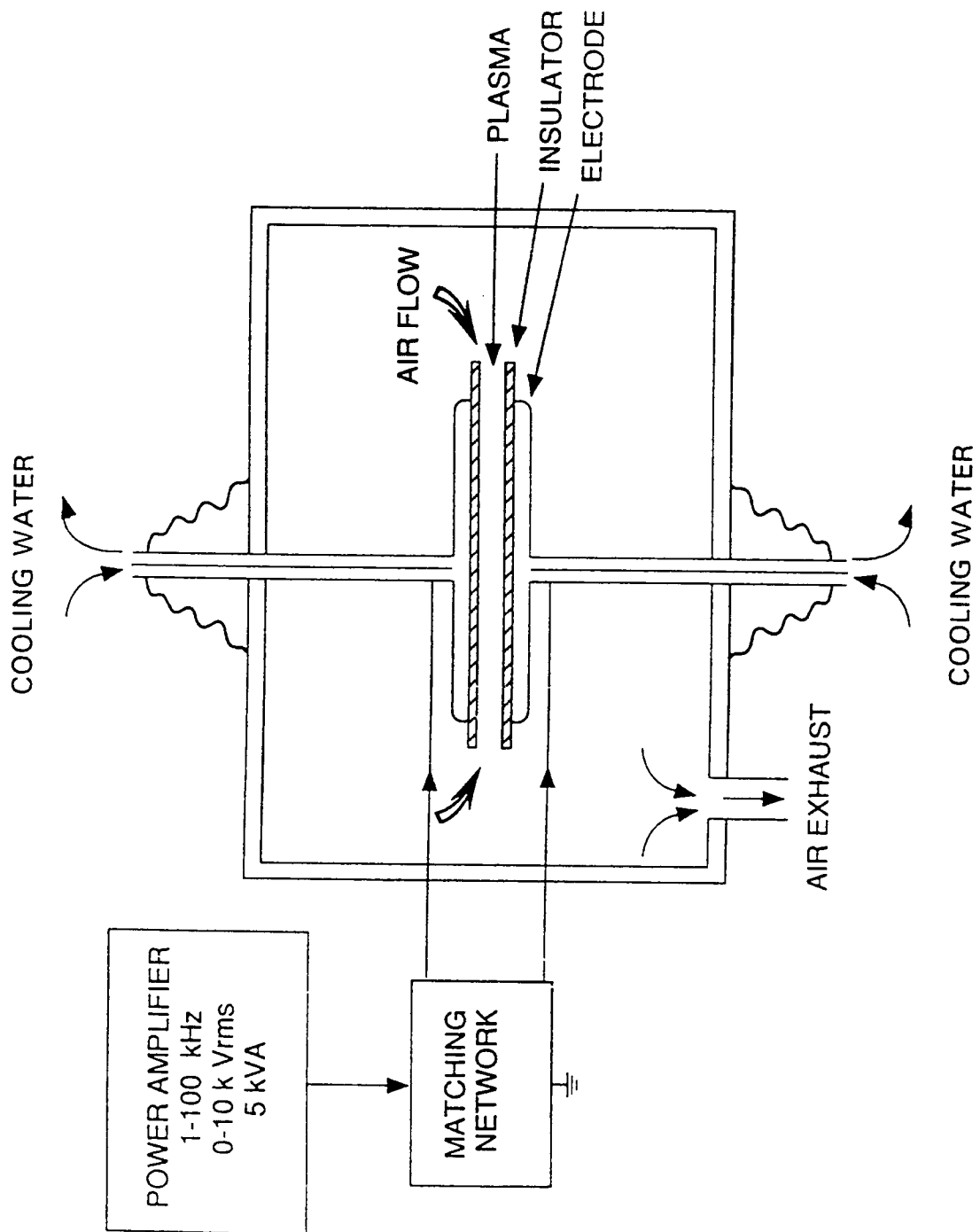
III. EXPERIMENTAL METHODS

3.1 Experimental Apparatus for OAUGDP

Figure 3.1 shows a schematic of the *MOD IV* OAUGDP reactor used for this experiment. The parallel plate configuration of this reactor requires an RF frequency of 4 to 8 kHz with 4 to 6 kV RMS powering the reactor, which is electrically in parallel with a resistive load of 40 k Ω . One or both electrodes may be covered with a quartz sheet of 3.2 mm thickness to prevent the formation of an RF arc. The electrodes are cooled with running water. The electrode gap separation ranges from 2 to 5 mm. The larger gap separation requires the highest voltage of which the power supply is capable. The *Ling* power supply used for the experiment provides a maximum of 6 kV in the given frequency range.

One of the most important requirements to obtain a satisfactory, uniform discharge is the air flow. Enough air flow is required to generate a large volume of active species such as free radicals, UV, ozone, atomic oxygen, ions, and electrons. Without sufficient air flow, an air discharge may break up into an array of thin filaments. These filaments may damage the exposed materials by producing pin-holes, wrinkles, or discoloration. Recirculation of the reactor operating gas causes the active species concentration to build up, and minimizes the number of filaments at the edge of the discharge. Ozone is produced by the plasma, recirculated, then finally exhausted to the outside

Figure 3.1. Schematic of the MOD IV OAUGDP using air. (Dimensions of the reactor: 40 cm x 35 cm x 35 cm, width, height, and depth in respectively.
Surface of the electrode: ~18 cm in diameter.



environment. Table 2 shows characteristic operating parameters for the experiment.

3.1.a Thin Film Samples

Samples are cut into $7 \times 7 \text{ cm}^2$ pieces. Some of the materials are secured to the electrode surface with Scotch® tape, since the air flow can be greater than 5m/s, and they might otherwise be blown away. Figure 3.1 - 3.4 show the sample setup.

3.2 Characteristics of the Samples Treated

The characteristics of thin films treated are summarized in Table 3. Some relevant properties are listed.

Table 2. Characteristic Operating and Plasma Parameters for Surface Cleaning

Characteristic Operating and Plasma Parameters for Surface Cleaning	
RF Frequency:	5 KHz
RMS Voltage:	6 KVRms
RMS Power:	10 ~ 150 watts
RMS electric field:	~10 KV/cm
Approximate plasma number density:	$10^{10}/\text{cm}^3$
Plasma areal power density:	$10 \sim 400 \text{ mW}/\text{cm}^2$
Electrode gap separation:	< 6 mm
Working gas:	Air
Pressure:	760 +15, -5 Torr
Treatment time:	1, 2, 5, 10, 15, 30, 60 s

Figure 3.2. OAUGDP Operating Using Air at 5 kHz and 6 kVrms.
(Safety door opened for the photo purpose only)

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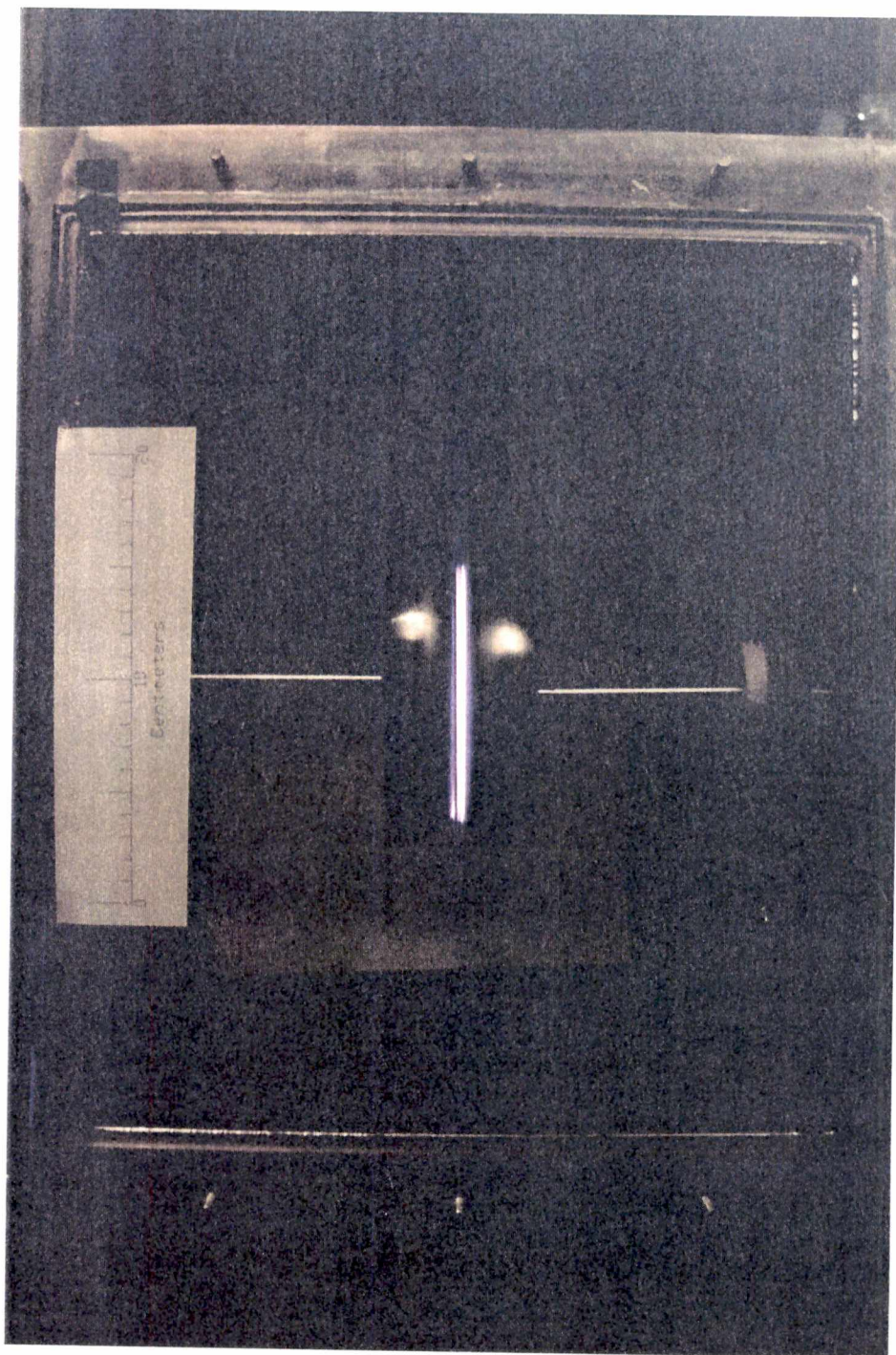


**Figure 3.3. Picture of OAUGDP MOD IV with the Sample and the
Plasma Off.**

(Sample shown is a biological sample)

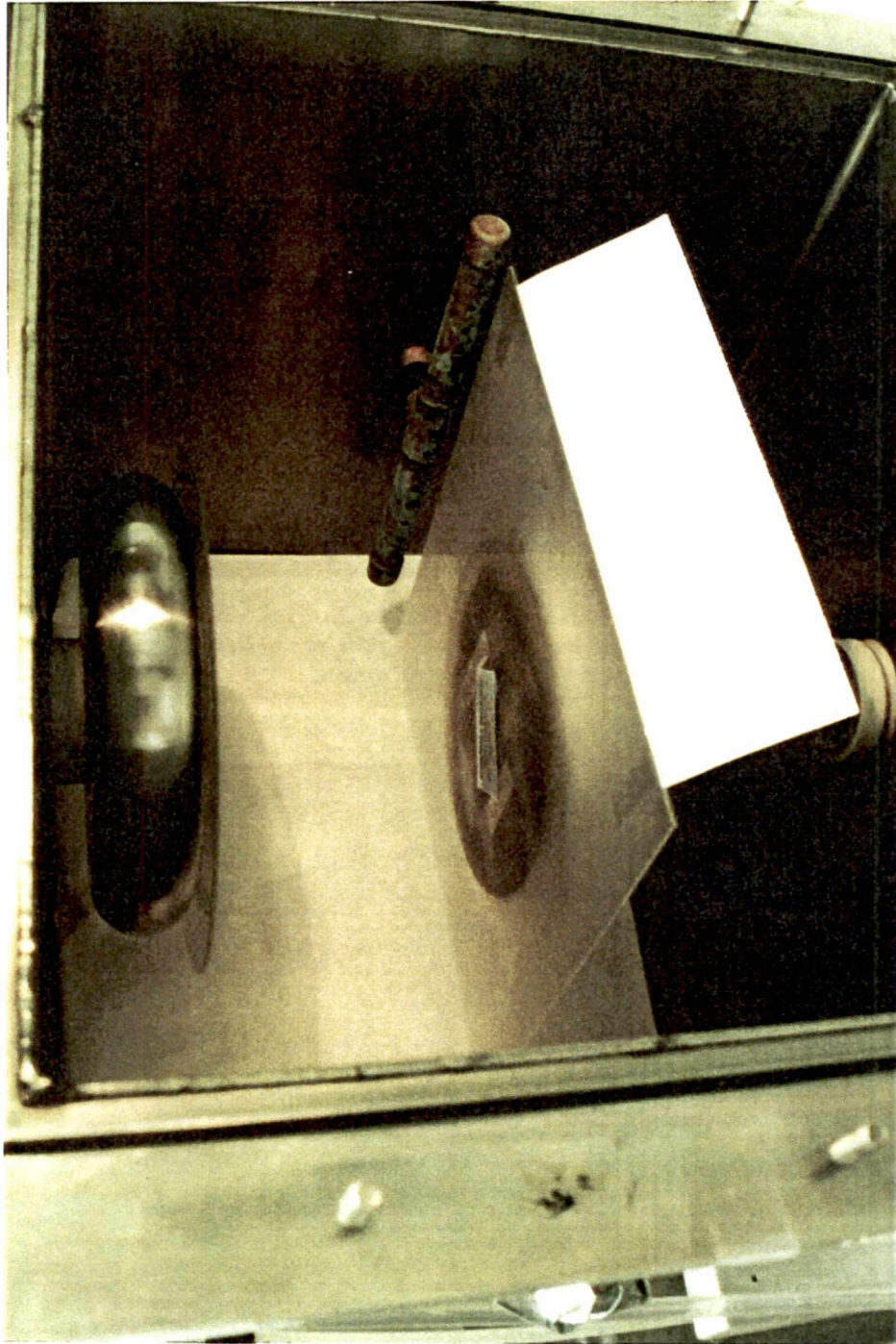


Figure 3.4 Picture of OAUGDP MOD IV Plasma On at 5 kHz, 6 kVrms
(Safety door is closed. Air is recirculated.)

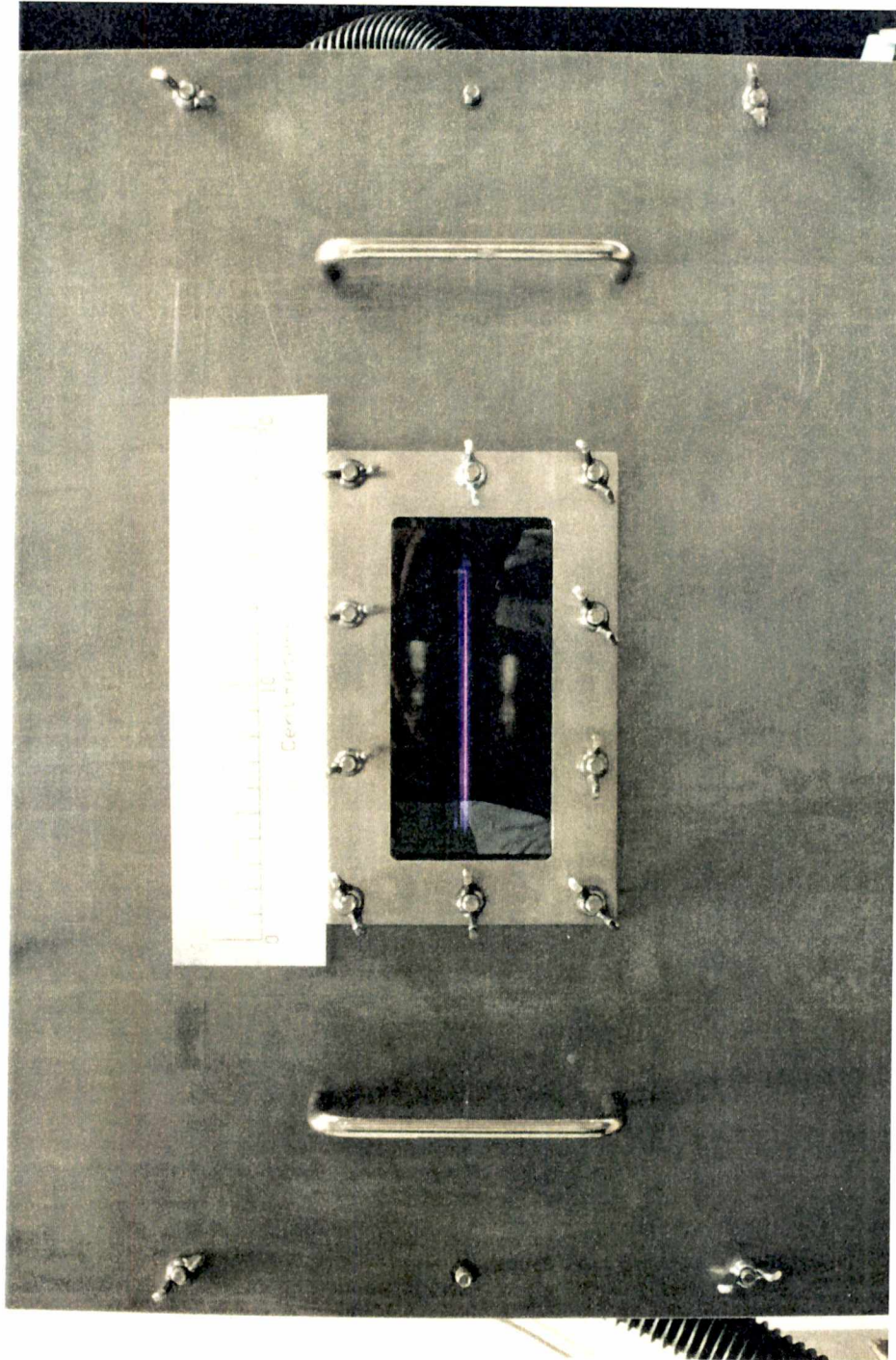


Table 3. Characteristic of Samples provided by TANDEC (Textile and Non-Wovens Development Center, UTK) and Rexam Co.

Name	Also Known	Size	Untreated Surface Energy	Previous Treatment
Malinex 442/142	--	442/142	30 dynes/cm	Not treated
Malinex 442/92	Mylar	442/92	30 dynes/cm	Not treated
Metalized Paper	--		31 dynes/cm	--
Aluminum Foil	--		46 dynes/cm	--
Low Density Polyethylene	LDPE	0.85 mils	31 dynes/cm	No Corona Treated
Linear Low Density Polyethylene	LLDPE	1.1 mils	41 dynes/cm	No Corona Treated
Polyethylene Terephthalate	PET	2.3 mils	30 dynes/cm	Not treated

- Malinex 442/142: This clear thin film was not treated prior to testing, and its surface energy is 30 dynes/cm.
- Malinex 442/92 (aka 'mylar'): This opaque thin mylar was not previously treated, and its surface energy is 30 dynes/cm.
- Aluminum foil.
- Linear low density polyethylene (LLDPE): This white, thin film sample contains titanium dioxide as a color pigment. The surface contains a thin linear grid pattern with no previous corona or other treatment, and its untreated surface energy is 41 dynes/cm. The contact angle is greater than 40°.
- Low density polyethylene (LDPE): This blue transparent thin film was not subject to corona treatment, was the thinnest sample, and had an untreated surface energy of 30 dynes/cm.

- Polyethylene terephthalate (PET): This film is transparent with a small admixture of brown pigment, and was subject to no previous treatment. Its untreated surface energy is 31 dynes/cm.
- Metalized paper: A thin layer of aluminum which is not perfectly uniform is bonded to the paper. Small pin-holes can be seen with an optical microscope of 80X or greater magnification. These samples were subject to a previous proprietary treatment, and their untreated surface energy was 31 dynes/cm.

3.3 Surface Energy Measurement Methods

The surface composition of materials can be determined by *Electron Spectroscopy for Chemical Analysis* (ESCA), sometimes called *X-ray Photoelectron Spectroscopy* (XPS). The surface energy can be determined by contact angle measurement, or wetting the surface with series of a formamide mixtures of variable surface tension. Other methods such as Scanning Electron Microscopy (SEM), *Transmission Electron Microscopy* (TEM), and Small Angle X-ray Scattering (SAXS) can be used to determine the topological features of a surface. In this work, contact angle measurements and a series of fluid mixtures are used to measure the surface energy. To observe the surface topography of the material tested, SEM is used.

3.3.a American Society For Testing And Materials Designation - D2578-67

This method covers measurement of the wetting tension of thin film surfaces in contact with drops of calibrated test solutions in the presence of air using a series of mixtures of formamide and ethyl cellosolve. These water based solutions wet surfaces at surface energies which range from 30 dynes/cm to 70 dynes/cm. The highest measurable surface energy using a water based solution is determined by the surface energy of water, which is 73.2 dynes/cm. Each numbered solution represents the surface energy in dynes per centimeter with uncertainties of less than 5%.

A cotton applicator soaked with one of the mixtures is applied to the surface of a sample with a surface energy above that of the initial testing fluid, over an area of approximately 6.5 cm^2 , which results in a thin film of liquid. It is important to use a minimal amount of liquid, since an excess of liquid might cause shrinkage of the thin liquid film. The mixture is considered to wet the test material when it remains intact as a continuous film of liquid for at least two seconds. If the applied mixture holds its shape for more than two seconds, one proceeds to the next higher surface energy mixture. If the continuous film breaks into droplets in less than two seconds, one proceeds to the next lower surface energy mixture. The critical mixture at which the liquid just wets the surface indicates the surface's approximate surface energy in dynes per centimeter. Shrinking of the liquid film about its periphery does not indicate a

lack of wetting, but breaking up of the liquid film into individual droplets indicates a lack of wetting.

A clean cotton applicator and a clean location on the surface must be used each time to avoid contamination of the solution. The tested location should not be retested because the surface energy is altered by the previously applied reagent. The precision of a single-operator is about ± 0.5 dynes/cm. The single-laboratory, multi-operator precision is ± 1 dynes/cm (Corotex Instruction Manual®, 1997).

3.3.b Contact Angle Measurement

The contact angle is defined as the angle between the solid surface and the tangent of the liquid-vapor interface of a sessile drop (Ried, 1958). The contact angle is related to the surface energy, the wettability, and the adhesion, or bondability. This measurement is affected by as little as one or two monolayers of adsorbed contaminants on the solid surface. The advancing angle, θ_a , is measured when a liquid boundary is advanced over a surface and allowed to come to rest. The receding angle, θ_r , is measured when the liquid boundary recedes over the previously wetted surface before coming to rest. These measurements may differ when contamination is present, or when the surface is anisotropic or rough. The contact angle can be seen through a goniometer eyepiece within a few seconds after a water drop is applied to a surface. When a water drop forms on a hydrophobic surface, a large contact

angle results, indicating a non-wettable surface. A hydrophilic surface produces a small contact angle, indicating a wettable surface.

Using Young's Equation, one can relate these measurements to the surface energy and wettability. The surface free energy, ΔG^s , is related to a small displacement ΔA , in Figure 3.5, of the liquid on a surface by the following equation,

$$\Delta G^s = \Delta A (\gamma_{SL} - \gamma_{SV}) + \Delta A \gamma_{LV} \cos(\theta - \Delta\theta). \quad (11)$$

At equilibrium,

$$\lim_{\Delta A \rightarrow 0} \frac{\Delta G^s}{\Delta A} = 0 \quad (12)$$

$$\gamma_{SL} - \gamma_{SV} + \gamma_{LV} \cos\theta = 0 \quad (13)$$

Equation 13 with the definition of the work of adhesion, becomes the Dupré equation,

$$W_{SLV} = \gamma_{LV} (1 + \cos\theta). \quad (14)$$

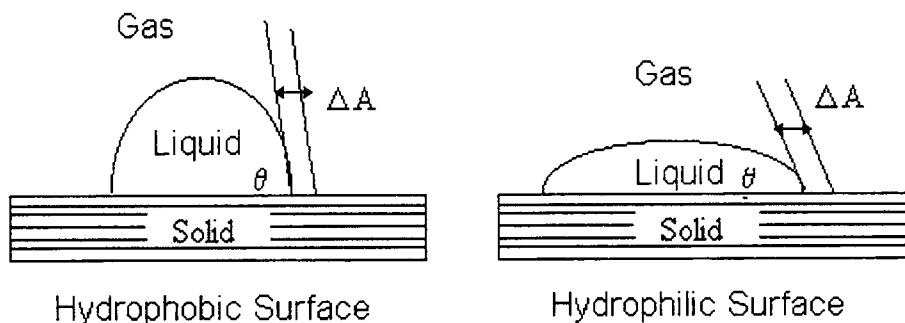


Figure 3.5. The Solid Liquid Interface- Contact Angle

A contact angle greater than 20° is considered to be nonwetting and when it is less, it is considered wetting. For a finite contact angle when $\theta > 0$, the imbalance of surface free energies is given by a spreading coefficient

$$S_{L/S} = \gamma_{SV} - \gamma_{SL} - \gamma_{LV}. \quad (15)$$

Lowering the contact angle represents a higher surface energy. This method is sensitive to the properties of the surface and represents a good wettability test. When comparing contact angle measurements for different liquid or polymer systems, consistency of surface topography should be ensured.

3.3.c Scanning Electron Microscopy (SEM)

Two techniques most widely used to obtain information about the topological appearance of the material down to a few thousand Angstroms are TEM and SEM. The Scanning Electron Microscope has been used to determine the location of fractures in adhesion studies. The surface is scanned by a focused electron beam, and the intensity of secondary electrons is monitored. The output from a secondary electron detector modulates the intensity of a rastered electron beam of a cathode-ray tube scanned in synchronization with the focused electron beam sweeping over the sample. Each point of the raster image corresponds to a point on the sample surface. The intensity of secondary electron production from each of the surface

determines the strength of the image. SEM images can be viewed with a wide contrast in light intensity. This allows the images to have great depth of field.

In this work, samples were cut into small pieces approximately 0.5 cm^2 in area. An adhesive was placed under the samples. The surface of the sample was coated with various coatings. To obtain a high quality of sharpness and clarity, a gold coating was used in a few cases. This allowed the sample to be viewed mostly clearly under the scanning electron microscope. The SEM image gives a good topological view, but one cannot re-examine same point on a sample to compare progressive developments on the surface.

IV RESULTS

4.1 Measurements After Various Durations of Exposure

All samples were treated with the OAUGDP in air. Figures 4.1 ~4.17 illustrate the surface energy as a function of the plasma treatment time and SEM results for the tested materials listed in *Table 3*. Tested samples show no significant physical damage such as pin-holes or discoloration. Figure 4.1 shows that the surface energy of LLDPE increased from 31 dynes/cm to 70 dynes/cm with 1 second of treatment. SEM pictures shown in Figures 4.2, 4.3, and 4.4 show the untreated, the 2 minute treated, and the 5 minute treated surfaces. Growth of the small white bumps shown in the figures, which are grains of titanium dioxide pigment, increases as the treatment time increases. Diameters of these grains of pigment range from 200 nm to 300 nm.

The surface energy of LDPE in Figure 4.5 has increased from 30 dynes/cm to 60 dynes/cm in 1 second of treatment and reached 70 dynes/cm within 30 seconds. The surface morphology has changed significantly after treatment. Figure 4.6, the untreated LDPE surface, and Figure 4.7, a LDPE surface treated for minutes, are totally different from each other. The treated surface almost looks like it has been affected by heat damage, but it has not. Again, erosion of the titanium dioxide coating from the surface results in such morphology. Table 4 contains the comparison of surface energies.

Figure 4.9 shows an untreated PET surface. After 2 minutes of treatment, 50 to 100 nm bumps have formed as shown in Figure 4.10. The

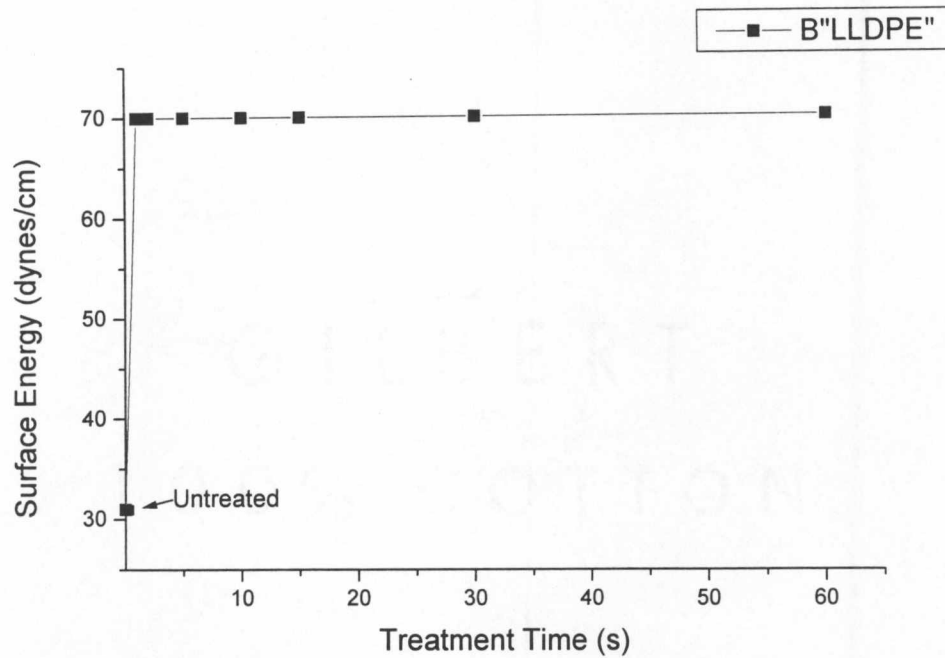


Figure 4.1 Plasma Treatment Effect on LLDPE 5 kHz, 6 kVrms

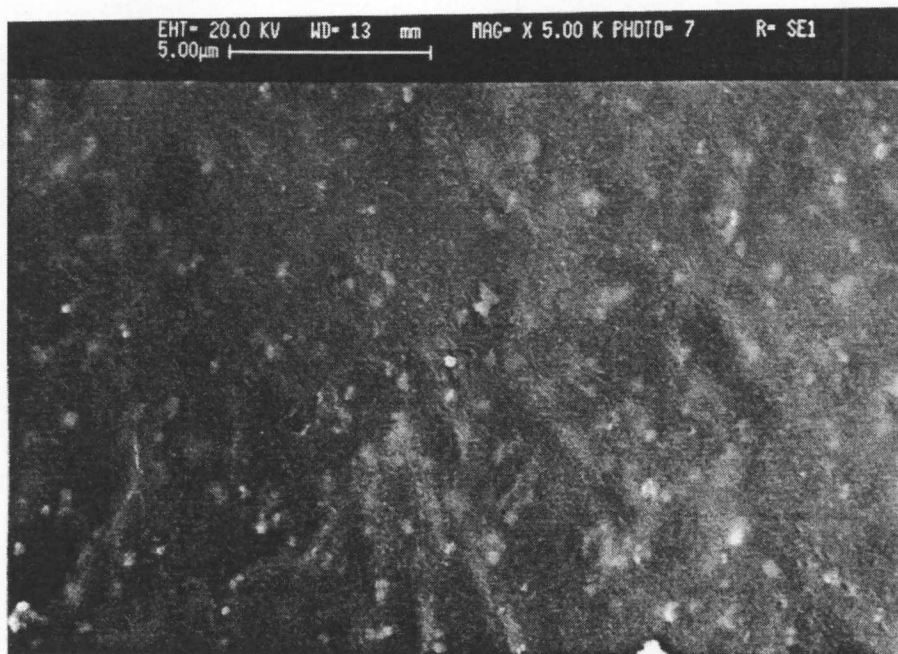


Figure 4.2 Scanning Electron Micrograph of (SEM) Untreated LLDPE

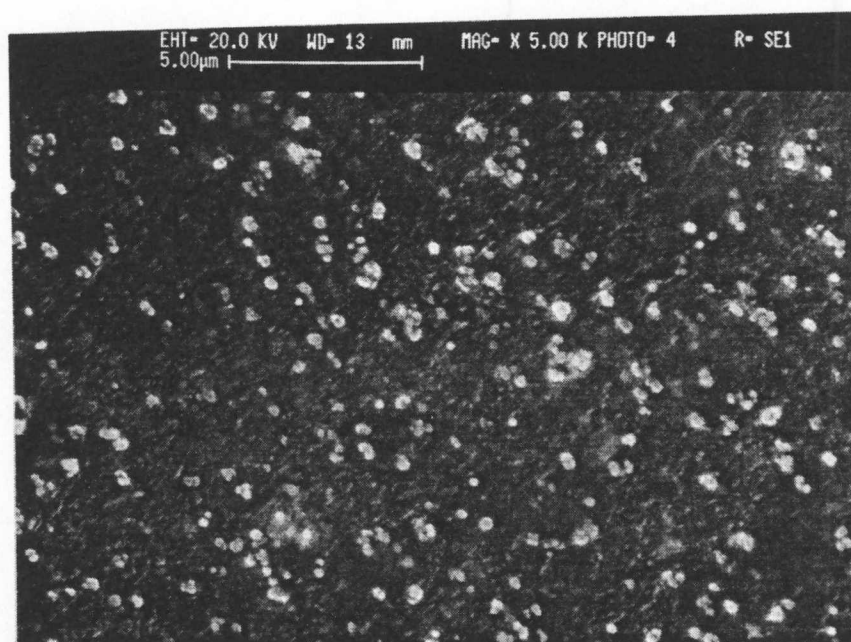


**Figure 4.3 Scanning Electron Micrograph of (SEM) LLDPE Treated 2min,
5 kHz, 6 kVrms**

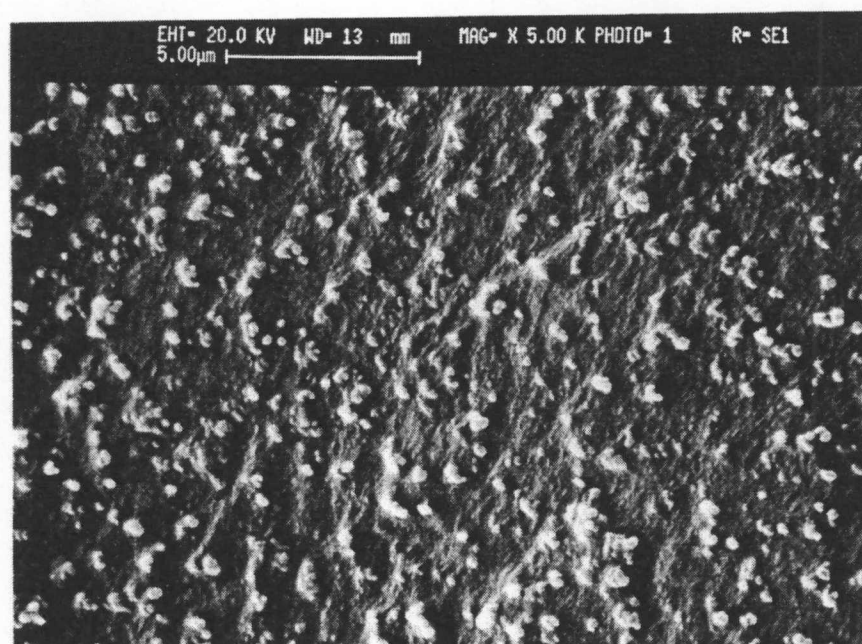


**Figure 4.4 Scanning Electron Micrograph of (SEM) LLDPE Treated, 5min,
5 kHz, 6 kVrms**

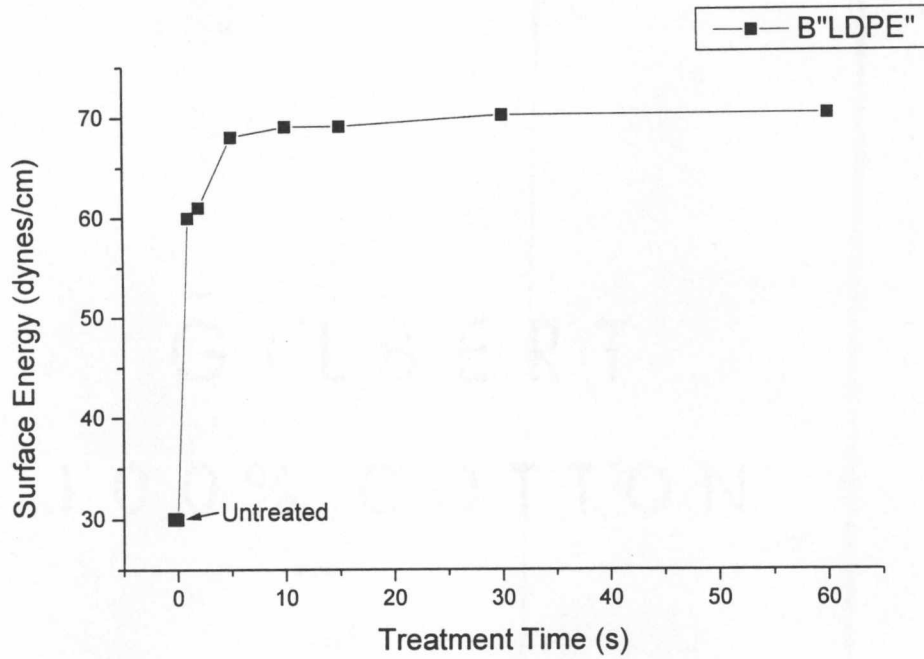


Figure 4.5 Plasma Treatment Effect on LDPE 5 kHz, 6 kVrms



Figure 4.6 Scanning Electron Micrograph of (SEM) Untreated LDPE

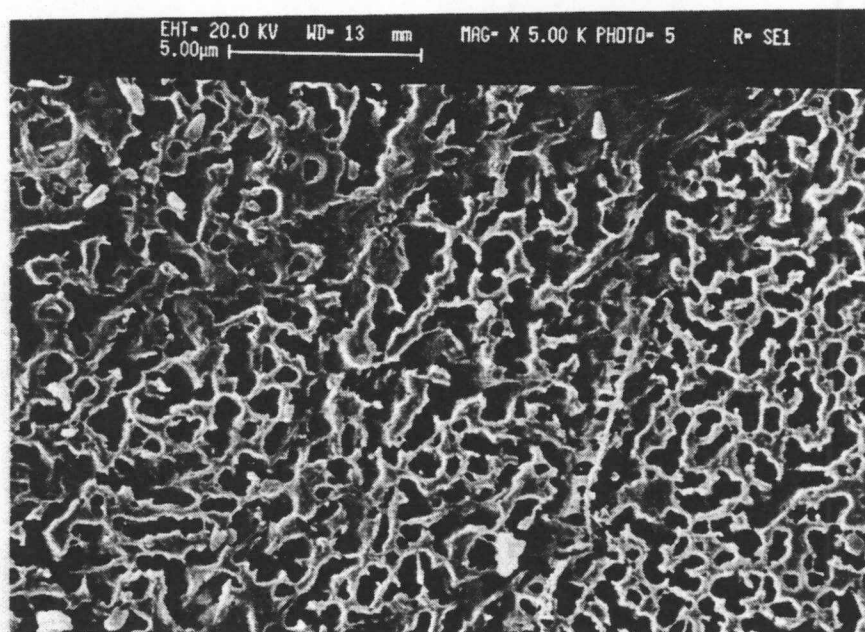


Figure 4.7 Scanning Electron Micrograph of (SEM) LDPE Treated for 3 min., 5 kHz, 6 kVrms

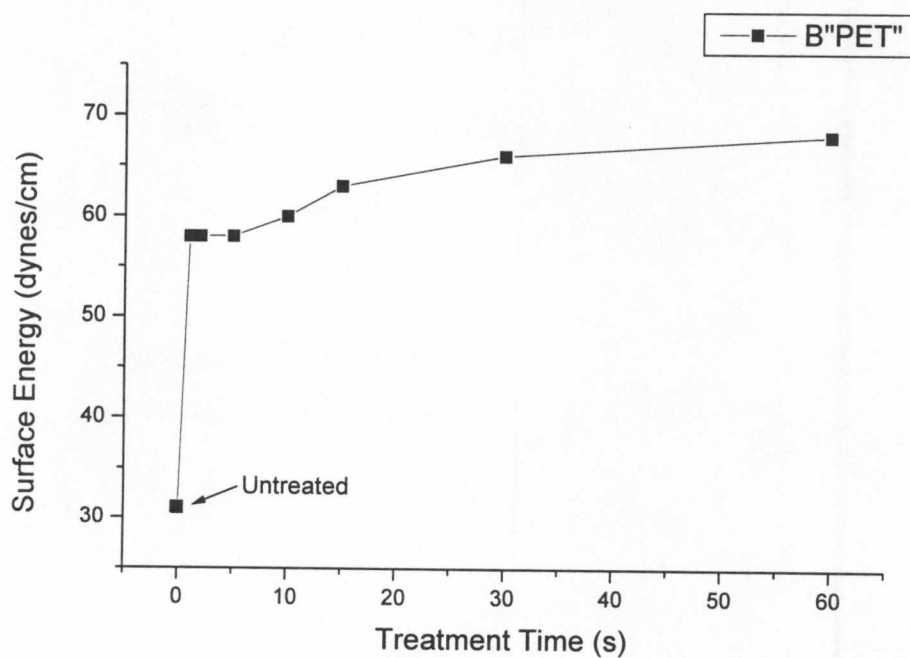


Figure 4.8 Plasma Treatment Effect on PET 5 kHz, 6 kVrms

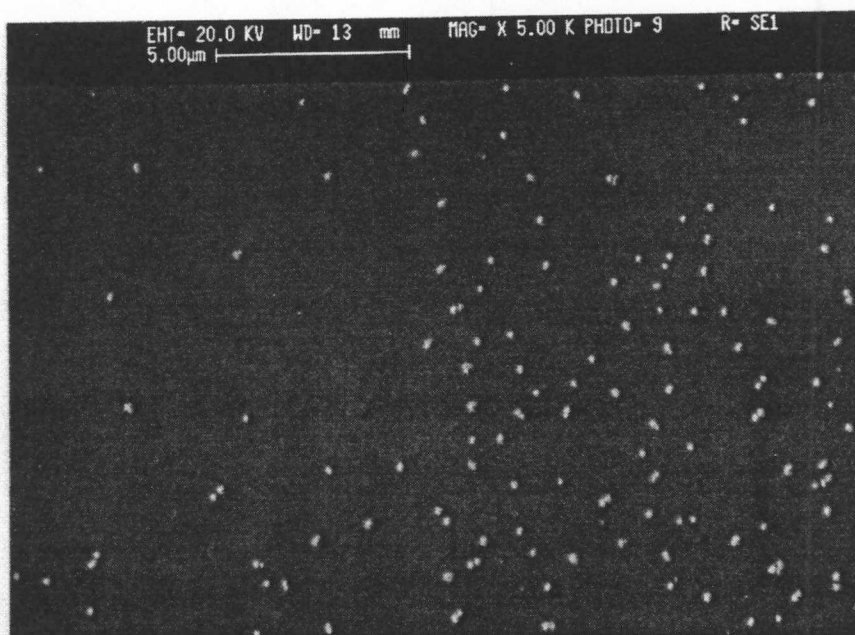


Figure 4.9 Scanning Electron Micrograph of (SEM) Untreated PET

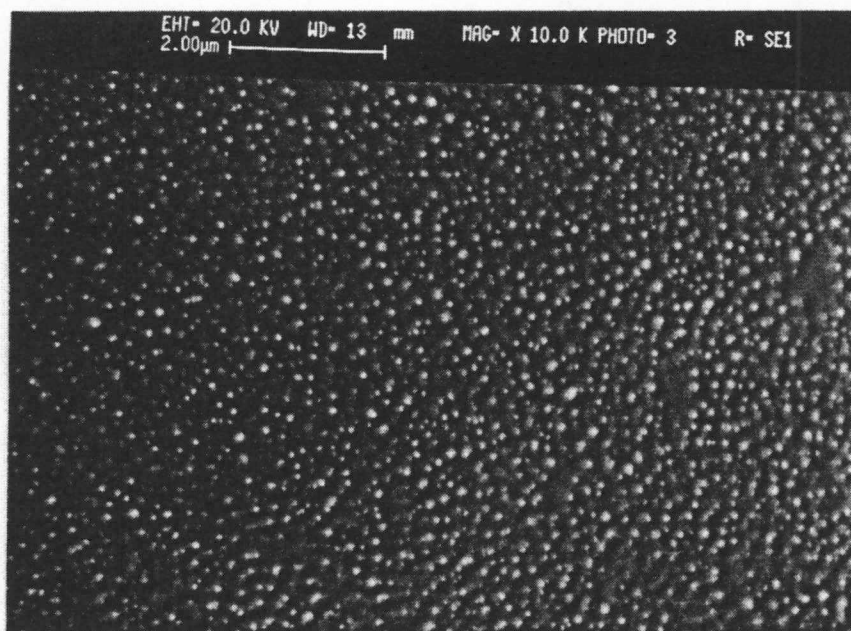


**Figure 4.10 Scanning Electron Micrograph of (SEM) PET Treated 2 min.,
5 kHz, 6 kVrms**

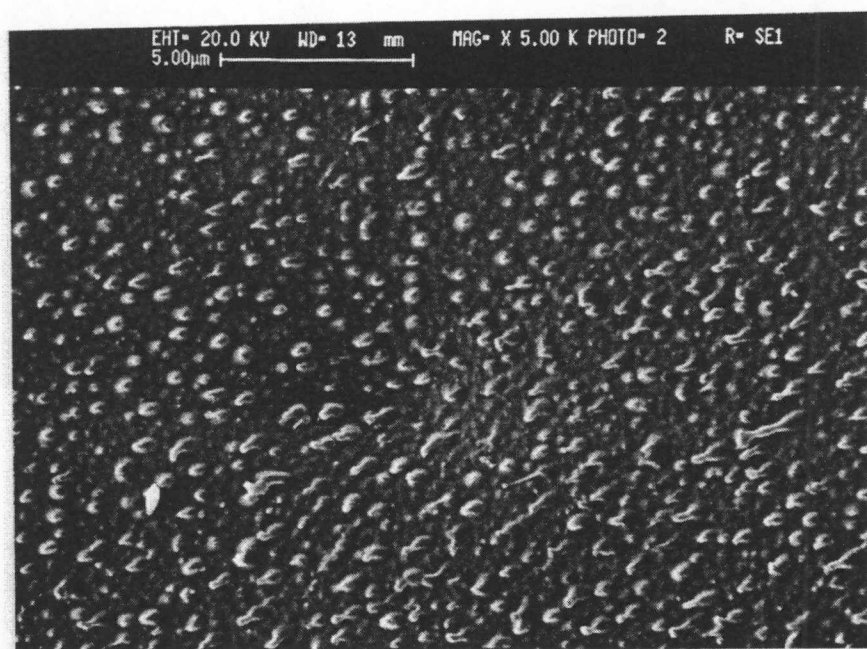


**Figure 4.11 Scanning Electron Micrograph of PET Treated 5 min.,
5 kHz, 6 kVrms**

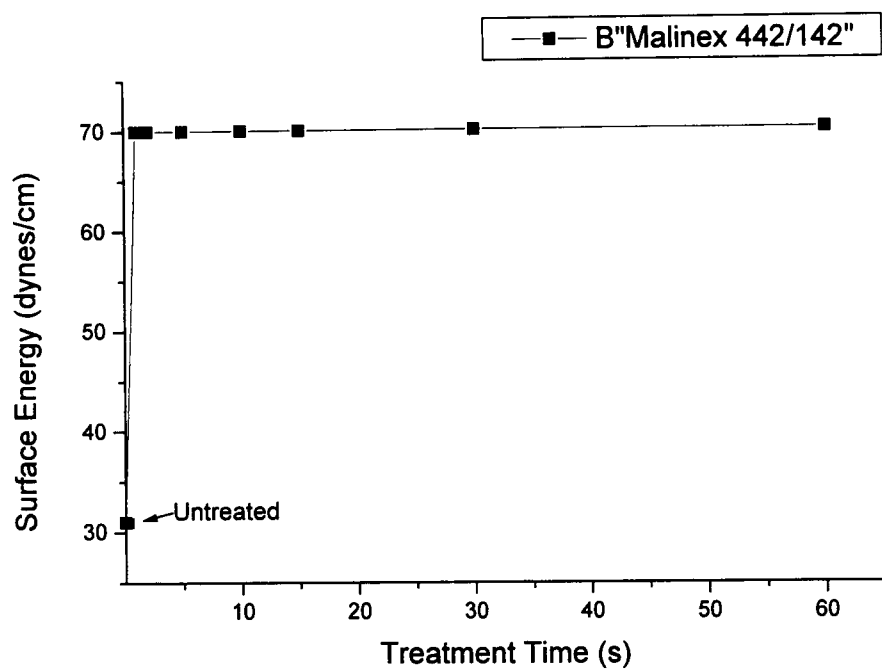


Figure 4.12 Plasma Treatment Effect on Malinex442/142, 5kHz, 6 kVrms

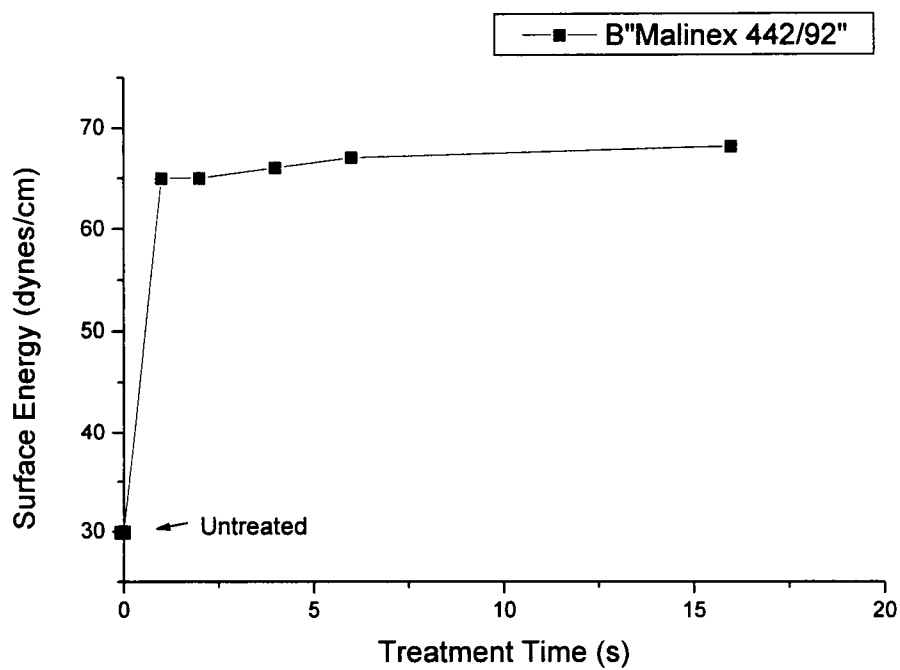


Figure 4.13 Plasma Treatment Effect on Malinex442/92, 5 kHz, 6 kVrms

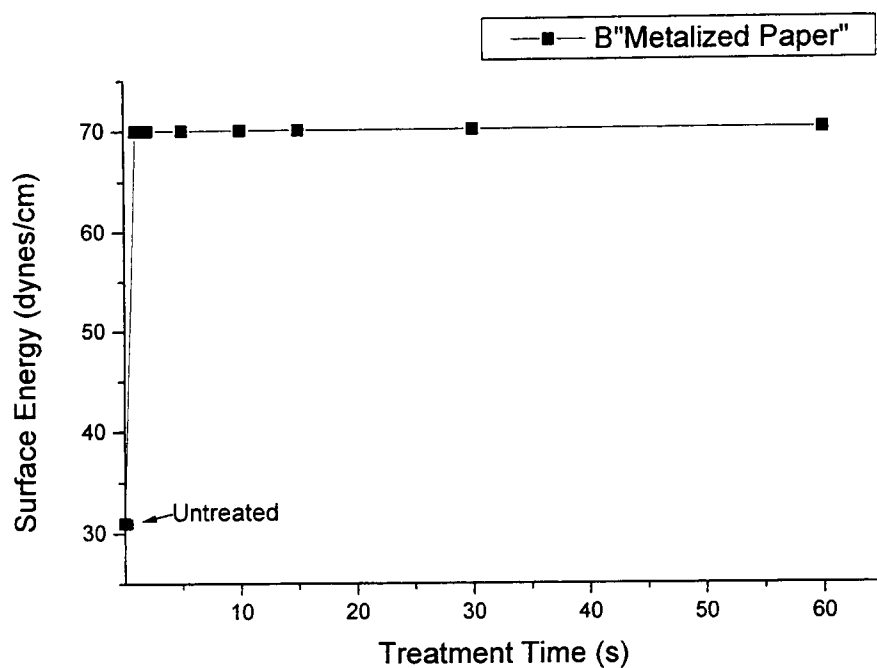


Figure 4.14 Plasma Treatment Effect on Metalized Paper, 5 kHz, 6 kVrms

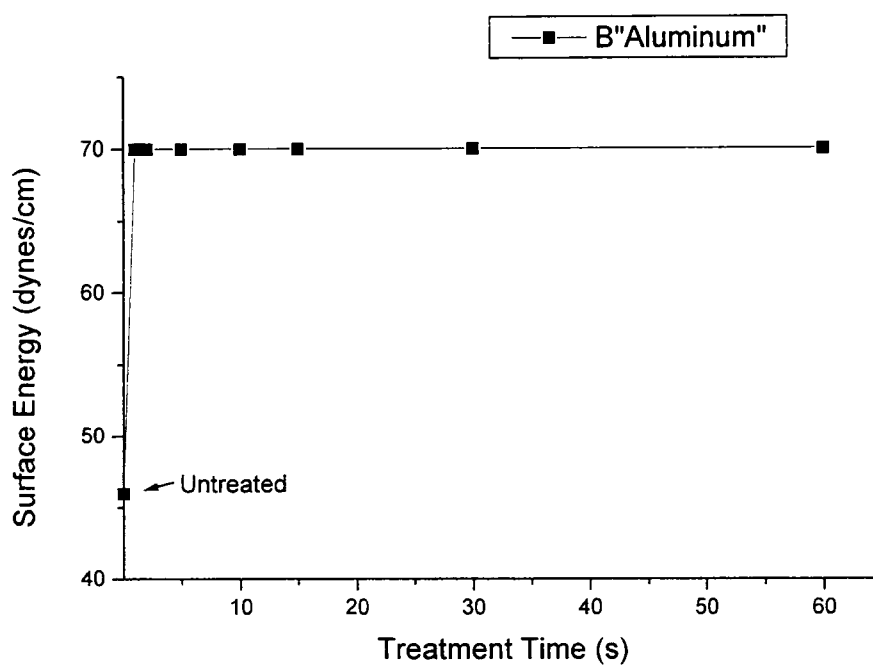


Figure 4.15 Plasma Treatment Effect on Aluminum Foil, 5 kHz, 6 kVrms

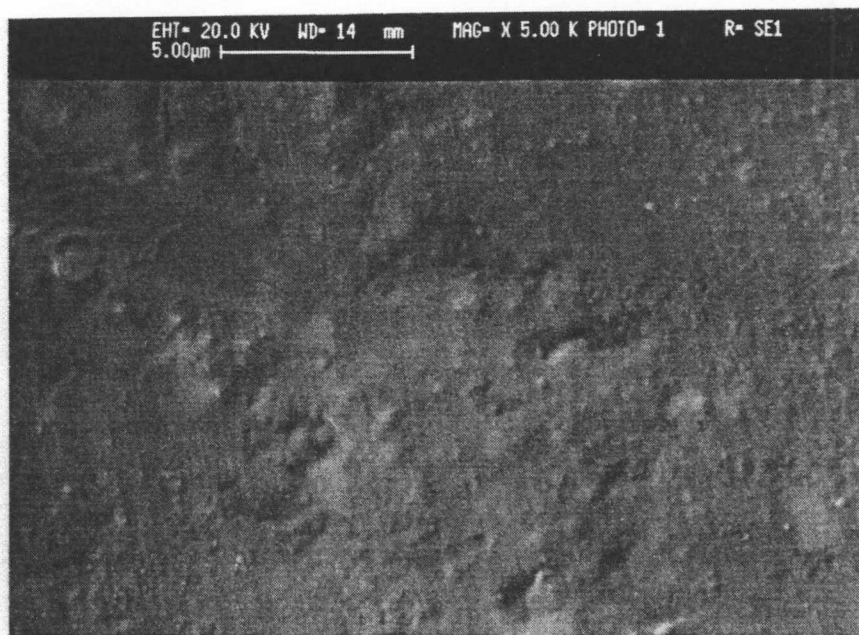


Figure 4.16 Scanning Electron Micrograph of (SEM) Untreated Aluminum Foil

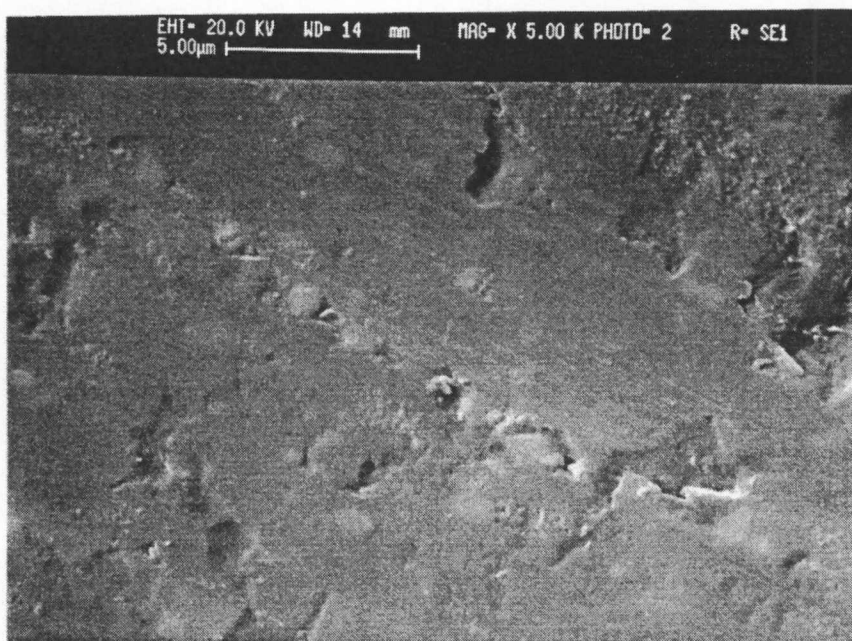


Figure 4.17 Scanning Electron Micrograph of (SEM) Aluminum Foil Treated for 3 min., 5 kHz, 6 kVrms

Table 4 Comparison of Surface Energies

Name	Original Surface Energy (dynes/cm)	Plasma treated Surface Energy (dynes/cm)	Time (s)
Aluminum Foil	46	70	1
Linear Low Density Polyethylene	41	70	1
Low Density Polyethylene	31	70	1
Malinex 442/92	30	65	1
Malinex 442/142	31	70	1
Metalized Paper	30	70	1
Polyethylene Terephthalate	30	58 66	1 30

height of the bumps increased after 5 minutes of plasma treatment, Figure 4.11, to form spire-like structures. Also, an erosion of PET material has occurred at the rate of about 0.5 microns per minute, with diameters of less than 10nm, as shown in Figure 4.11. These thin spires are not evenly formed. As shown in Figure 4.8, the surface energy increased from its untreated value of 31 dynes/cm to 58 dynes/cm in 1 second of treatment, and reached 66 dynes/cm after 60 seconds of treatment.

The effect of OAGUDP treatment on Malinex 442/142 and 442/92 are shown in Figures 4.12 and 4.13 respectively. The surface energy of Malinex 442/142 has increased from 31 dynes/cm to 70 dynes/cm after 1 second of treatment, where as Malinex 442/92 increased from 30dynes/cm to 65 dynes/cm after 1 second, and then gradually increased to 70 dynes/cm after 60 seconds of treatment. No SEM photos are available for these samples.

Both the surface energy of metalized aluminum coated paper and aluminum foil increased to 70 dynes/cm after 1 second of treatment as shown in Figures 4.14 and 4.15. Figure 4.16 and 4.17 show the untreated and 3 minute plasma treated surfaces of aluminum foil. No significant morphological changes have occurred, except possibly for the removal of a surface film by the treatment.

4.2 The Change of Surface Energy After Exposure

The aging effect of LLDPE shown in Figure 4.18 is not a linear power law. The surface energy stayed above 55 dynes/cm for 30 days of exposure time. The surface morphology did not change after 8 days, as shown in Figure 4.19.

Figure 4.20 shows a power law relationship between the surface energy and the exposure time for LDPE. The surface morphology of Figure 4.7 was rechecked in 8 days as shown in Figure 4.21. Figure 4.21 shows a major reformation of the top layer morphology.

Figure 4.22 shows the aging effect of PET. The surface energy has remained above 53 dynes/cm after 30 days of open air exposure time. A linear, log-log, or power law dependence exists between the surface energy and the open air exposure time. No significant changes in morphology were observed from immediate exposure to 8 days after exposure, as shown in Figures 4.11 and 4.23.

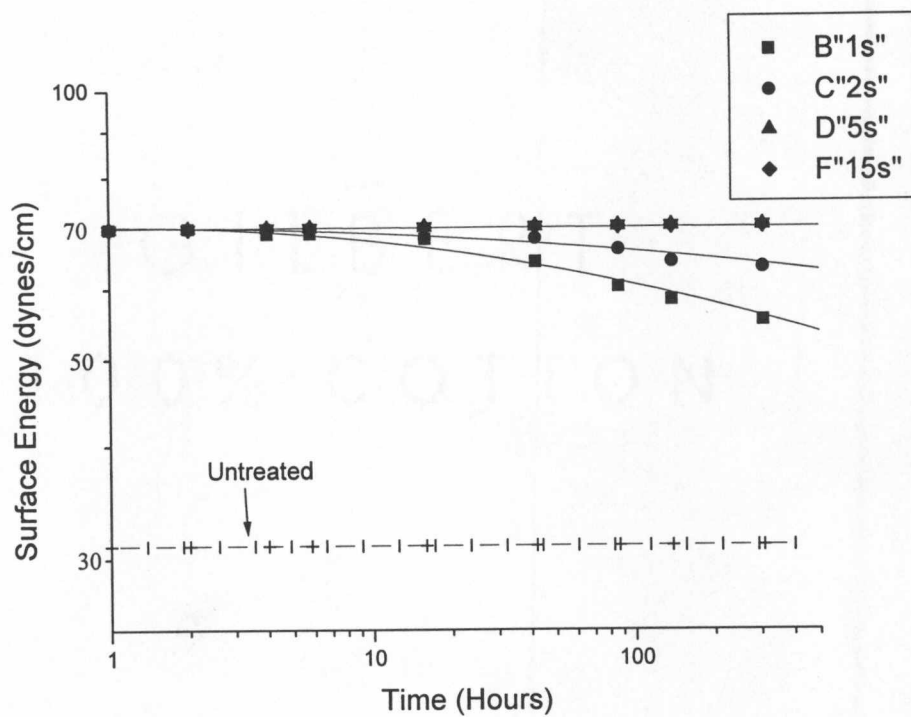


Figure 4.18 LLDPE Aging Effect, 5kHz, 6kVrms

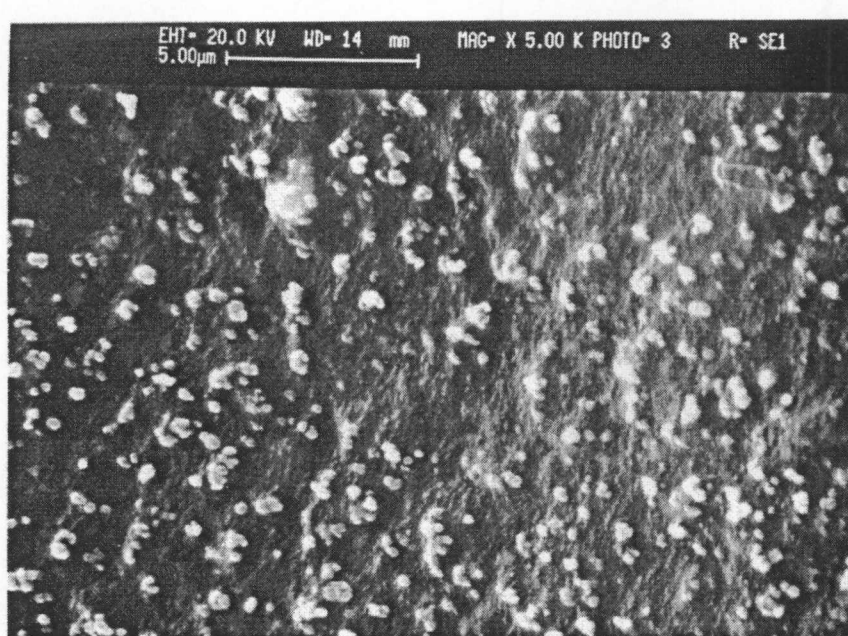


Figure 4.19 Scanning Electron Micrograph of (SEM) LLDPE Treated, 5min, 5kHz, 6kVrms (8 days after)

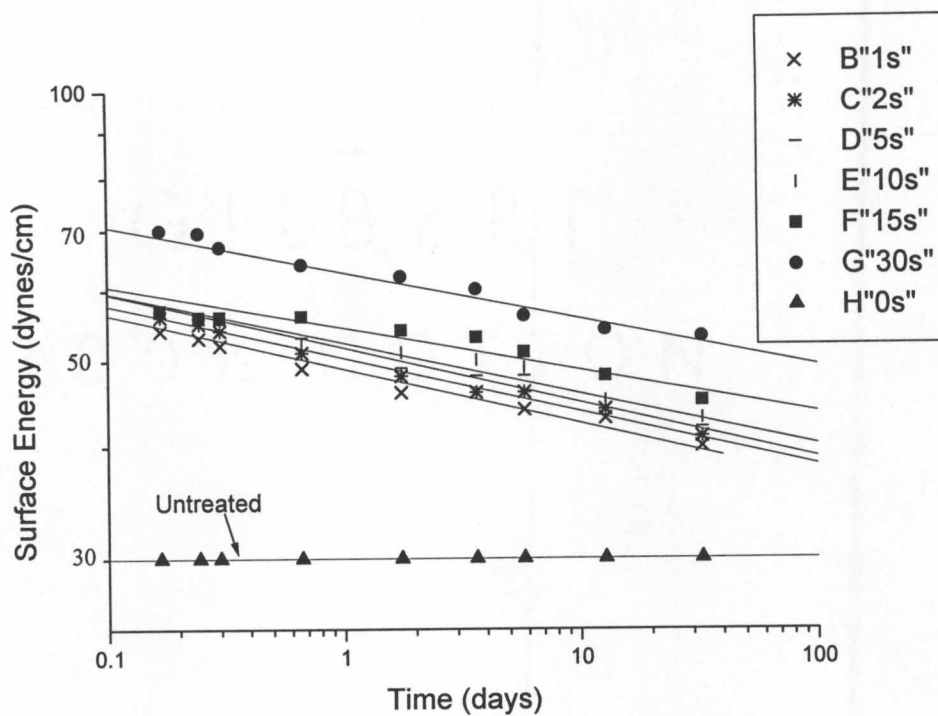


Figure 4.20 LDPE Aging Effect, 5 kHz, 6 kVrms

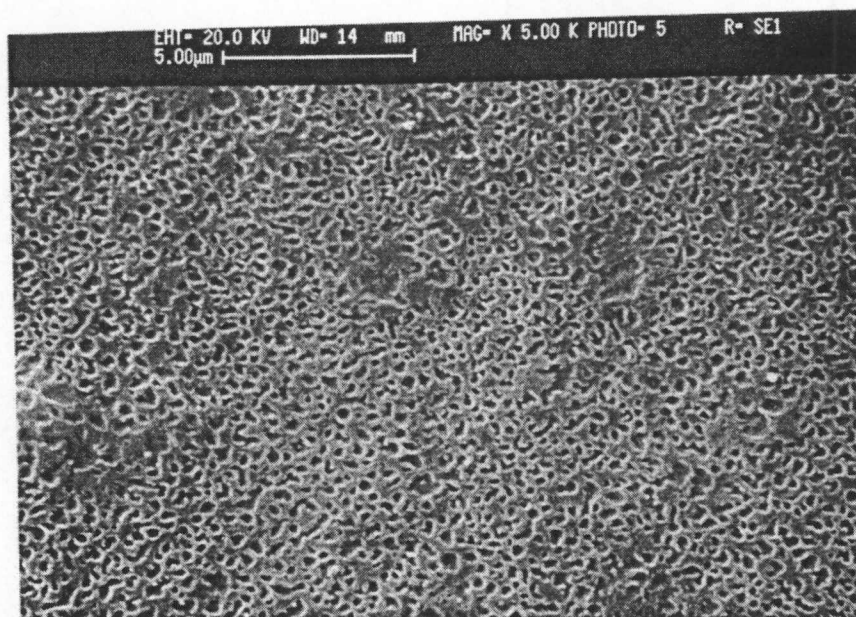


Figure 4.21 Scanning Electron Micrograph of (SEM) LDPE Treated for 3 min., 5 kHz, 6 kVrms (8 days after)

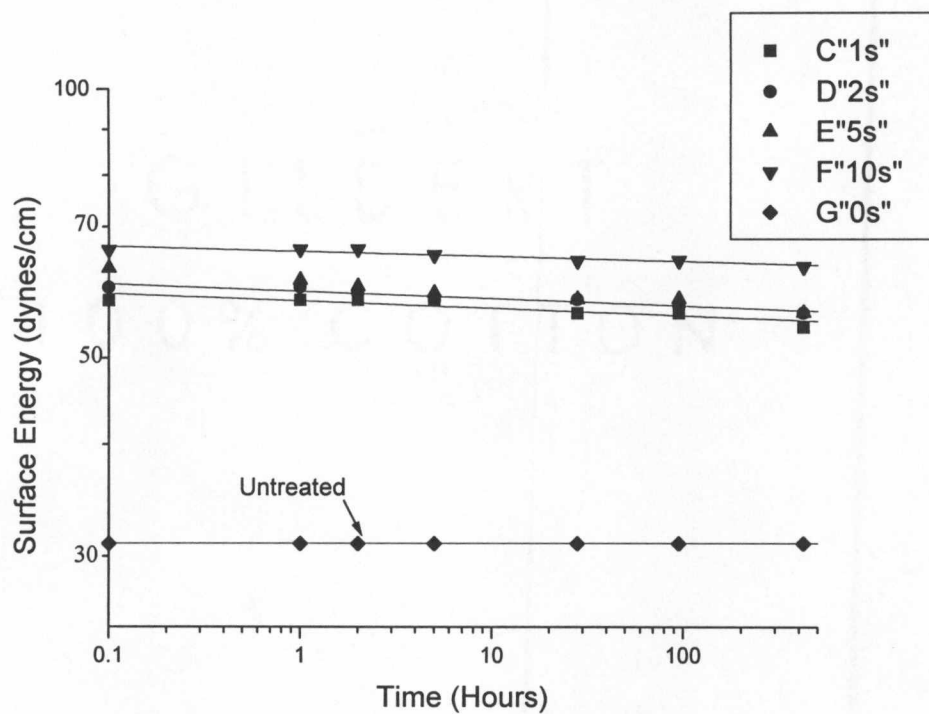


Figure 4.22 PET Aging Effect, 5 kHz, 6 kVrms

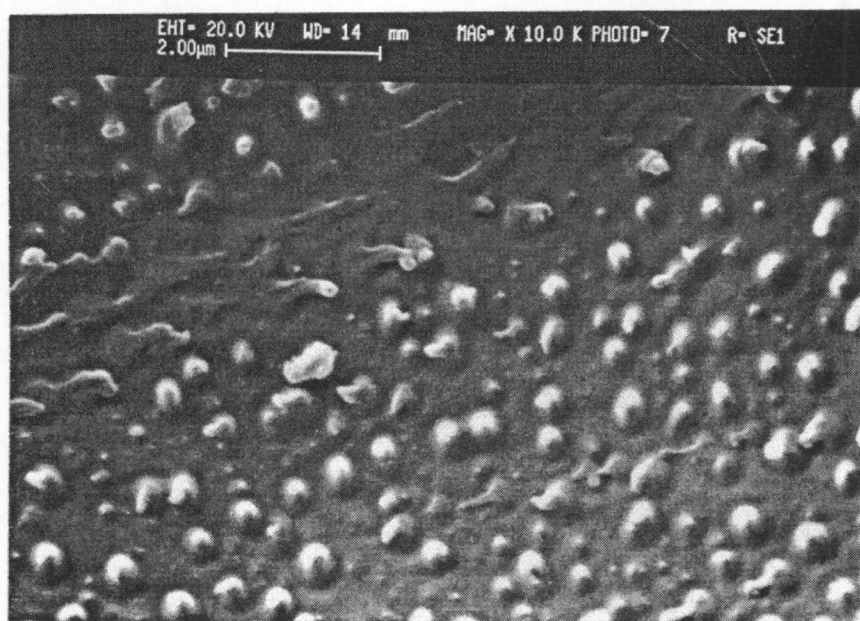


Figure 4.23 Scanning Electron Micrograph of (SEM) PET Treated 5 min., 5 kHz, 6kVrms (8 days after)

Figure 4.24, is a plot of the surface energy as a function of time of Malinex 442/142, which shows a polynomial decay curve. The surface energy has returned to its original value, 30 dynes/cm, after about 2 weeks. The surface energy of Malinex 442/92 shown in Figure 4.25 stayed above 40 dynes/cm two weeks after exposure. A nonlinear, non-power law relationship is shown in Figure 4.25.

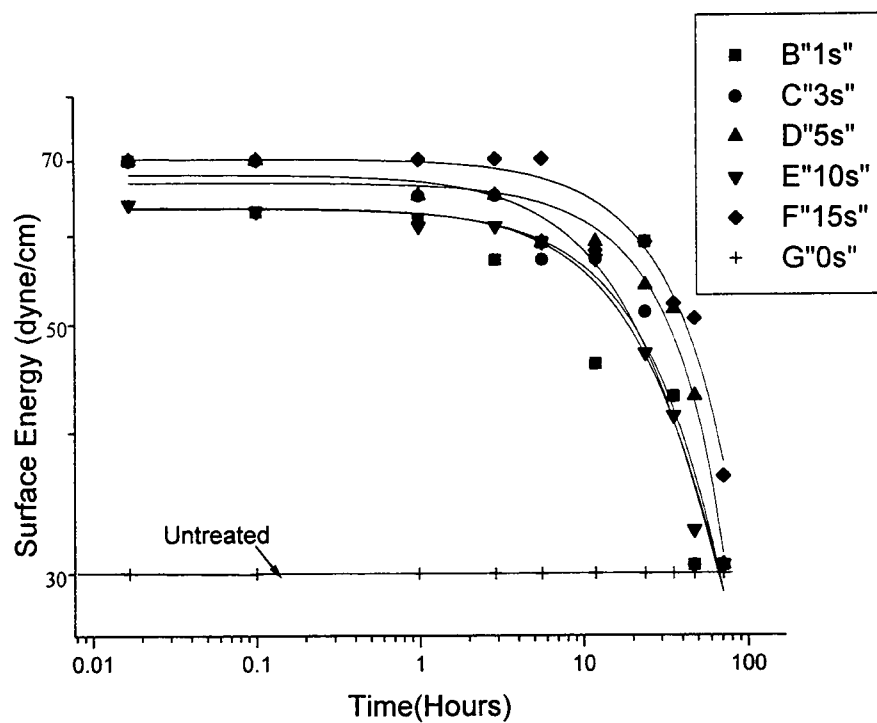


Figure 4.24 Malinex442/142, Aging Effect, 5 kHz, 6 kVrms

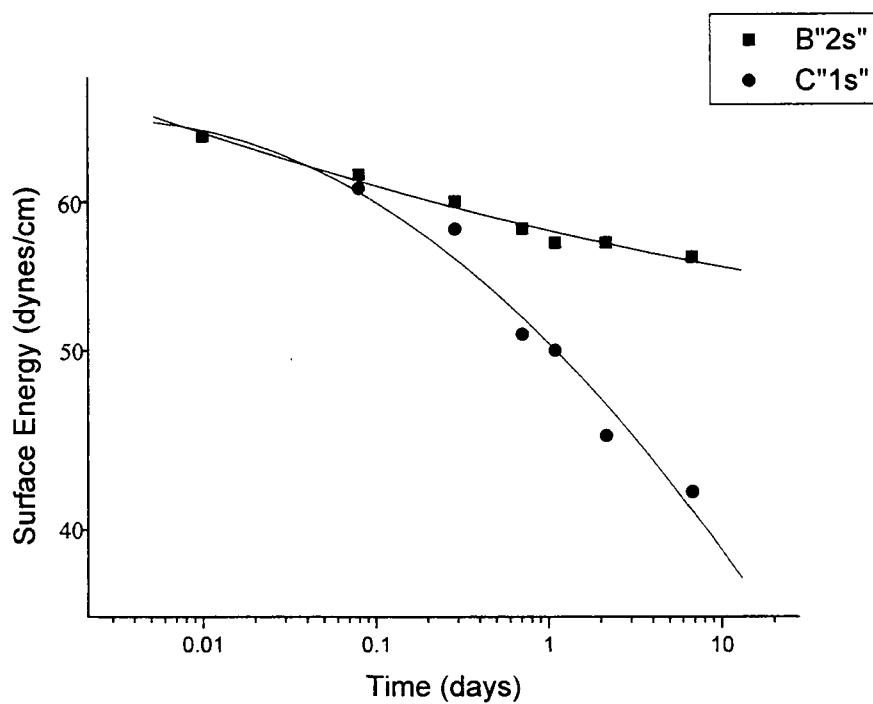


Figure 4.25 Malinex 442/92 Aging Effect, 5kHz, 6kVrms

V. CONCLUSION

OAUGDP exposure allows plasma surface treatment at one atmosphere without a requirement for batch processing. A OAUGDP using air as a working gas provides a variety of active species which raise the surface energy of most materials to values of 70 dynes/cm in less than 60 seconds. Each material had a characteristic appearance and functional dependence of its surface energy decay curve after exposure. The surface energy of some polymeric materials dropped after a few days to 50 to 60 dynes/cm and stayed there; others had a power law relationship; still others had a polynomial dependence before returning to pre-exposure values of 30 ~ 40 dynes/cm after several days or weeks. It was also found that longer exposures to the OAUGDP resulted in higher surface energies for longer times after exposure than did shorter exposure of the samples. SEM results showed that erosion or etching occurred to most of the polymeric materials at a rate of 0.5 microns per minute, while metalized samples showed cleaning of the top layer.

With a OAUGDP in air, one can achieve the industrially satisfactory value for surface energy of 50 dynes/cm, in less than one second of treatment on LLDPE, LDPE, PET, Malinex, metalized paper, and aluminum. SEM results showed that the OAUGDP affected the surface morphology of polymeric materials without heat damage. The graphs of surface energy versus the aging time showed that the dependence varied with the different materials and the treatment times, but the surface energy stayed above 50 dynes/cm for several

hours or days. The results showed that air is a sufficient working gas to increase the surface energy of materials. With the parallel plate configuration, a OAUGDP can be generated on a conveyor belt setup without a vacuum system. With a higher applied voltage, one can shorten the treatment time or enlarge the electrode gap separation.

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