Plasma Treatment of Polymer Films

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ABSTRACT

Plasma treatment is widely used for the treatment of inorganic and organic surfaces, deposition of thin films and processing of materials. Surface modification of polymer films by plasma is the most effective way of uniform and controlled treatment. The surface energy of the films is controlled to enhance the wettability and adhesion of coatings by plasma treatment at different processing conditions. Sigma Technologies has been producing plasma treatment equipment and has been intensively investigating plasma processes related to surface treatment and modification of various films. In this paper, results of recent work at Sigma Technologies in the area of polymer surface treatment using plasma processing are presented. Results of plasma treatment incorporating different variables that include gas pressure, gas mixtures, polymer films, and electrode geometries will be discussed.

INTRODUCTION

Polymer surfaces are chemically inert with low surface energies. Polymer films, for converting and laminating industries, are commonly treated by corona discharge or flame to enhance their surface energies leading to improvement in wettability, printability and adhesion. Surface modification of polymer films by plasma is superior to corona or flame treatment in terms of uniformity and homogenity. Corona discharges produce locally concentrated discharges known as streamers. These streamers lead to some non-uniformity in the treatment of the film surfaces and the concentrated energy of the streamers can also damage the film surface. Furthermore corona treatment can produce backside treatment which is undesirable in many applications. Plasma treatment is an effective method of treating polymer surfaces to increase the surface energy leading to enhanced wettability and adhesion between various materials. Sigma Technologies designs and manufactures innovative plasma treatment systems for functionalizing material surfaces, including polymer films, metal, fabric and paper. Plasma systems are run at low pressures. Vacuum chambers and pumps are needed to operate these plasma systems. Sigma Technologies has developed a novel atmospheric plasma treatment process that has unique advantages over the existing technologies for surface treatment. This plasma treatment apparatus does not require a vacuum system, produces high density plasma, and the treatment of various surfaces can be performed at low temperatures and at atmospheric pressure.

PLASMA TREATMENT

Plasma is an ionized form of gas and can be obtained using AC or DC power input and ionizing a gas medium. A plasma, commonly referred to as the fourth state of matter, is an ensemble of randomly moving charged particles with a sufficient particle density to remain, on average, electrically neutral. Plasmas are used in a very diverse range of processing applications ranging from manufacturing integrated circuits used in the microelectronics industry to treating polymer films and for the destruction of toxic waste [1-3]. Plasma processes can be grouped into two classes, low and high density, and are often displayed in an electron temperature versus density phase-space plot (Figure 1). Low-density direct-current and radio-frequency glow discharges are usually nonequilibrium, i.e. the electron and heavy particle (ions, neutral) temperatures are not equal. Low-density plasmas have hot electrons ($T_e > 10^4$ K) with cold ions and neutrals. Energetic electrons collide with and dissociate and ionize low-temperature neutrals, creating highly reactive free radicals and ions. These reactive species enable many chemical processes to occur with low-temperature feed stock and substrates. Low density plasmas are usually associated with low material-throughput processes such as surface modification. In high-density, thermal plasmas such as atmospheric-pressure arcs and torches, electron temperature is equal to heavy particle temperature, and this provides an effective source of concentrated enthalpy which can be used in areas such as melting and vaporization of materials.

Low density (or glow discharge) plasmas are used in a variety of processes such as: surface treatment, physical sputtering, plasma etching, reactive ion etching, sputter deposition, plasma-enhanced chemical vapor deposition, ashing, ion plating, reactive sputter deposition, and a range of ion beam-based techniques, which all rely on the formation and properties of plasmas. The types of plasmas encountered in surface treatment processing techniques and systems are typically formed by partially ionizing a gas at a pressure well below atmosphere. For the most part, these plasmas are weakly ionized, with an ionization fraction of 10^{-5} to 10^{-1}. Electron cyclotron resonance (ECR) plasmas can have higher ionization at high pow-

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ers [4]. Low density plasmas can be established by AC or DC power input and these systems can have many different type of geometries depending upon the application.

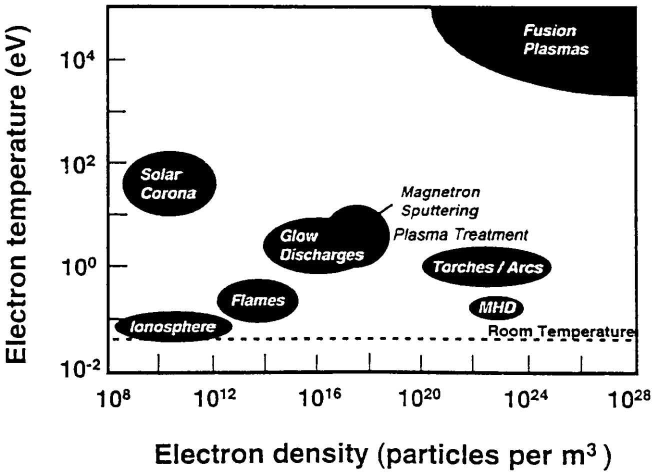

Figure 1. Classification of plasma, ev versus electron density.

Plasma treatment of polymer films on a moving web removes the contaminants from the surface and functionalizes the polymer surface by introducing functional groups such as: hydroxyl (-OH), carbonyl (-C=O), carboxyl group (-COOH), or amino groups (NH_x). This functionalization leads to better wettability, and improved adhesion or bondability between polymer surfaces and other materials deposited on these surfaces. Numerous researchers have discussed various aspects of plasma treatment of polymer substrates [5-7]. The main parameters for plasma treatment are as follows:

- Input power
- Plasma density
- Pressure
- Gas composition and flow rate
- System geometry

Sigma Technologies designs and manufactures innovative plasma treatment systems for functionalizing material surfaces, including polymer films, metal, fabric and paper. Sigma's patented surface treatment and coating technology has been successfully working in four continents over the globe. Sigma's vacuum plasma treater combines hollow cathode and magnets. The hollow cathodes are positioned on one side of the moving web, while the magnets are placed on the other side of the moving web. By doing so, a high intensity plasma is generated in the immediate vicinity of the web to be treated. In this configuration, during the negative part of the cycle, the hollow cathode creates intense plasma zones that are directed towards the film surface. During the positive cycle, the web becomes part of the sputtering cathode, and in addition to the treatment it is actually sputtered by the bombardment of the reactive and/or with inert positive ions. This configuration provides a superior level of surface treatment. A picture of the Sigma's vacuum plasma treater is shown in Figure 2.

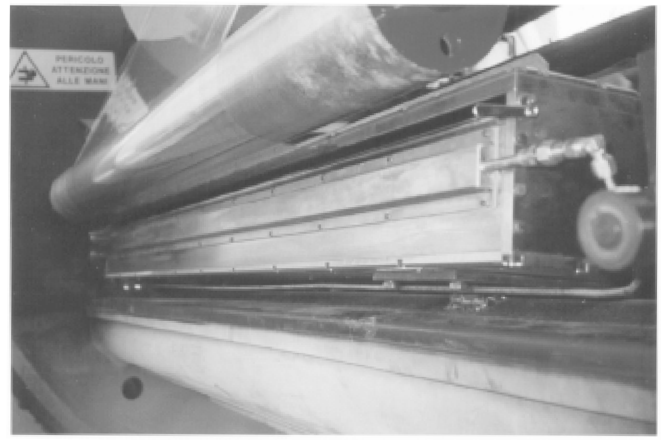

Figure 2. Sigma's vacuum plasma treater.

Polypropylene (PP) film was treated using Sigma's vacuum plasma treater and metallized with aluminum. Barrier testing such as moisture vapor transmission test (MVTR) and oxygen transmission rate (OTR) was performed on these films. Results of MVTR and OTR testing are presented in Tables 1&2 subsequently. As shown in these results, plasma treated films have better barrier properties. MVTR and OTR results were obtained by Sigma clients using industry standard techniques and equipment.

Table 1. MVTR barrier test results.

	MVTR (cc/100in^2/day)	
	PP, Type A	**PP, Type B**
Control Metallization	0.021	0.0315
Plasma Treatment and Metallization	0.0112	0.0197

Type A—Homopolymer-monoweb
Type B—Homopolymer with controlled molecular wt. range

Table 2. OTR barrier test results.

Normally Non-Metallizable Films		OTR cc/100in^2/day
Type A	Controlled Metallization	105.4
	Plasma Treatment	34.54
Type B	Control Metallization	52.5
	Plasma Treatment	10.96
Type C	Control Metallization	22.42
	Plasma Treatment	1.92
Metallizable Films		
Type A*	Control Metallization	2.58
	Plasma Treatment	0.99
Type B*	Control Metallization	1.96
	Plasma Treatment	0.66

Type A—Homopolymer -monoweb
Type B—Homopolymer with controlled molecular wt. range
Type C—Homopolymer with moderately good skin
Type A*—Homopolymer with good skin
Type B*—Homopolymer with very good skin

ATMOSPHERIC PLASMA TREATMENT PROCESS

Sigma Technologies has developed a new atmospheric plasma treatment system (patent pending) for functionalizing polymer films. The newly developed atmospheric plasma treatment (APT) system has unique advantages over the presently used technologies of corona and flame treatment. The APT system allows to create a uniform and homogenous high density plasma at atmospheric pressure and at low temperatures using a broad range of inert and reactive gases and can be used for treating and modifying the surface properties of organic and inorganic materials. APT process treats and functionlizes films in such a manner similar to the vacuum plasma treatment process. Production equipment testing has been successfully performed for the treatment/ functionalization of various polymer films including polytetrafluoroethylene (PTFE), polypropylene (PP), polyethylene (PE), and polyethylene teraphthalate (PET) films on moving webs. The surface energies of the treated films increased substantially (without any backside treatment) thereby enhancing the wettability, printability and the adhesion properties of these films. The attributes of the newly developed plasma process can be summarized as follows:

- Produces uniform and homogenous plasma at atmospheric pressure and low temperatures.
- A variety of process gases can be used
- Ideal for treating polymer films
  - Uniform treatment
  - Enhances surface energy of the films thereby improving wettability, printability and adhesion
  - No backside treatment
- No vacuum chamber and pumps are needed
- Available in all sizes
- Simple and rugged construction
- Automatic control and indicators

In Atmospheric Plasma Treatment (APT) process, plasma is generated at atmospheric pressure and at low temperatures using an AC power source. A proprietary designed electrode, insertion of a dielectric layer between the electrodes, and an appropriate gas mixture as the plasma medium is used in the newly developed APT. Gases such as helium, argon and a mixture of inert gas with nitrogen, oxygen, air, carbon dioxide (CO_2), methane (CH_4), acetylene (C_2H_2), propane (C_3H_8) or ammonia (NH_3) have been used on this treater to sustain a uniform and steady plasma for effective surface functionalization. The electrode is attached to an AC power supply, and the rotating drum is grounded which acts as the other electrode. A general view of the APT treater is shown in Figure 3.

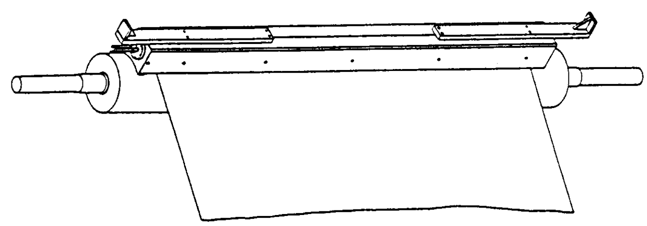

Figure 3. A general overview of the atmospheric plasma treatment apparatus.

Sigma's atmospheric plasma system can be used in the following modes of operation:

- Plasma 'Cold Flame' with controlled chemistry
- Reduced ozone corona
- Corona with controlled gas chemistry

The atmospheric plasma system can be effectively used for functionalization, cleaning and etching of the following substrates:

- Polymer films
- Metallized films
- Fabrics
- Fibers
- Paper

POLYMER FILM TREATMENT USING APT

Several polymer films such as PTFE, OPP, PE, and PET and were treated in the newly developed plasma treater at atmospheric conditions. These films were treated on two webs sized 12 inches and 20 inches in width. Surface energies of the treated films were determined by surface tension test fluids markers (ASTM D-2578) and contact angle measurements. Some samples were tested by x-ray photoelectron spectroscopy (XPS) for surface analysis. Surface energies of these films were substantially enhanced after the plasma treatment. Surface energies of the treated samples were monitored and recorded over a period of time to investigate the aging effect of the treatment. In the following some examples of the treatment of polymer films by Sigma's plasma treater are presented. Experimental variables for the testing are presented in Table 3.

Table 3. Experimental variables.

Variables	
Films	PTFE, OPP, PE, PET
Watt Density, W/(ft^2.min)	0.6 - 3.0
Gases Used	He, Ar, O_2, CO_2, Air, N_2, H_2, CH_4, C_2H_2, NH_3

PTFE is extremely inert, and it is quite challenging to enhance its surface energy using a dry process. PTFE film was treated by the atmospheric plasma system with several gas mixtures such as helium with oxygen, carbon dioxide, nitrogen, and also hydrocarbons such as methane and acetylene. In most of the cases of treating PTFE, the treatment goes away fairly quickly (in hours). Grafting PTFE with acetylene in plasma conditions was found to be very effective. Surface tension of the PTFE film treated in atmospheric plasma with C_2H_2 over some period of time is shown in Figure 4. Contact angle of the treated sample was ~ 25°. Treatment of PTFE with C_2H_2 in atmospheric plasma treater was very effective. As shown in the graph (Figure 3), the treatment effect did not decrease over a period of one month.

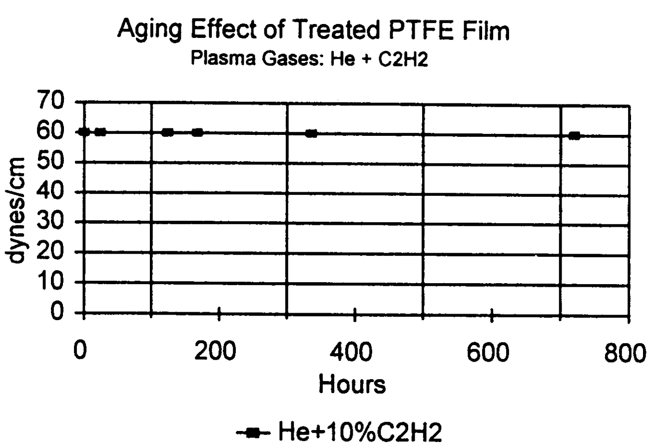

Figure 4. Results of PTFE film treatment with C_2H_2.

X-ray photoelectron spectroscopy (XPS) can be effectively used to determine the functional groups on the treated polymer film surface. It is established by monitoring the bond energy shift in the treated film due to the attachment of different functional groups. XPS was performed on the PTFE sample treated with C_2H_2. Figure 5 shows the survey XPS spectrum of the PTFE plasma treated sample. Figure 6 shows the carbon peaks in the treated sample. The peak on left shows the CF_2 group while the peak on the right represents the CH_2 group. Figure 7 shows the XPS spectrum of untreated PTFE in the similar range of binding energy. It shows only one peak which is for the CF_2 group. These results clearly show the presence of a hydrocarbon group on the plasma treated film. The area under the curves (Figure 6) shows that the CH_2 peak has 3.5 times the area for the CF_2 peak which can be equated to the concentration levels of these species on the surface of the treated samples. Oxygen from atmosphere is also incorporated into the graft.

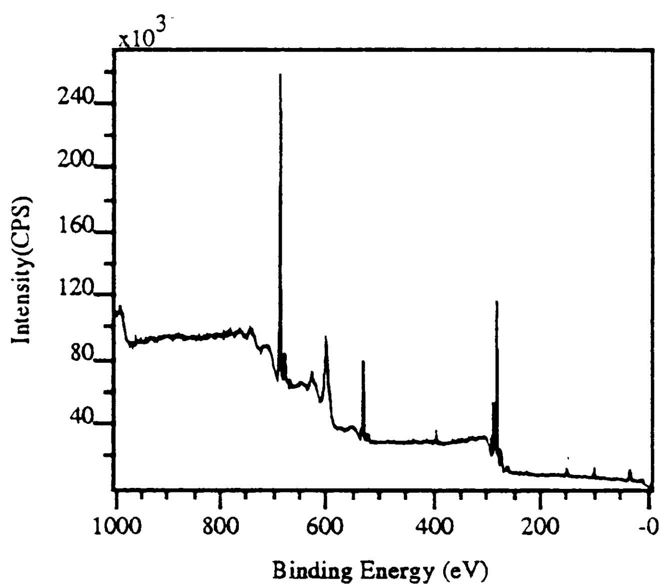

Figure 5. XPS result of PTFE treated sample

Plasma treatment of OPP films were performed using helium and a mixture of helium with carbon dioxide (CO_2), oxygen, nitrogen, and acetylene (C_2H_2). Figure 8 shows the treatment results (surface tension, dynes/cm) and aging of the OPP films treated by atmospheric plasma treater using He and different mixtures of He and CO_2 (surface tension of the film before treatment ~ 30 dynes/cm). In the treatment of OPP with CO_2 and O_2. Hydrogen in the PP structure is possibly substituted by carbonyl (-COO) or carboxyl group (-COOH).

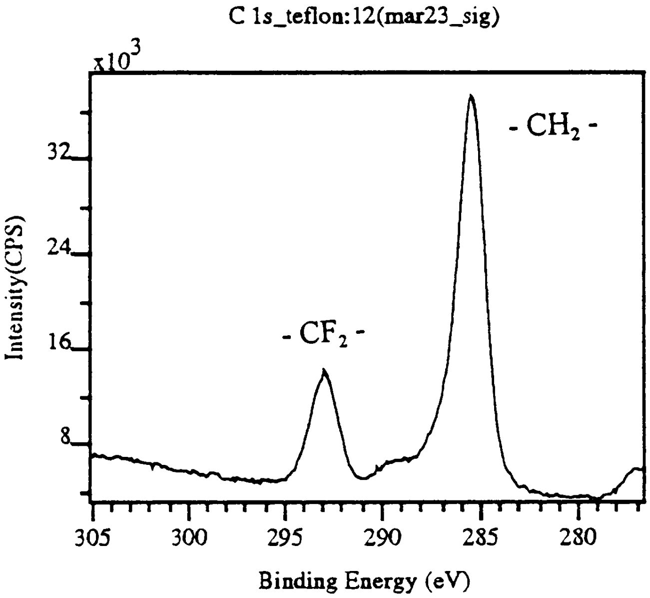

Figure 6. XPS result of PTFE treated sample

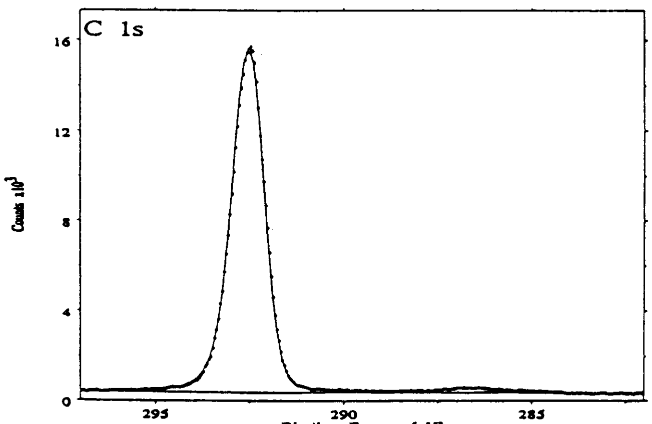

Figure 7. XPS spectrum of untreated PTFE sample

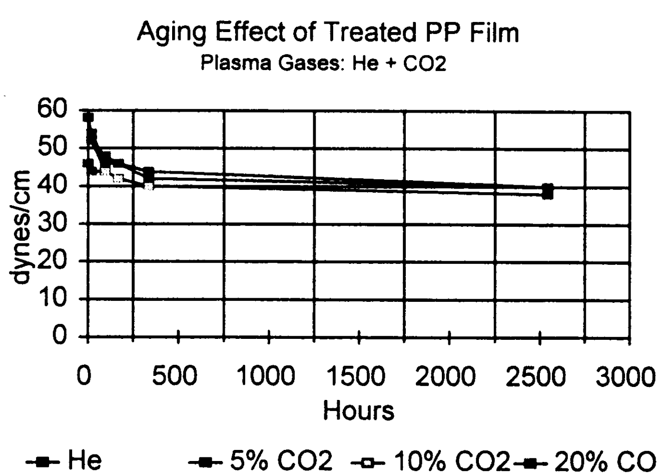

Figure 8. Results of OPP films treatment with CO_2.

XPS was performed on the OPP samples treated with CO_2 and O_2. Figure 9 shows the survey XPS spectrum of the OPP plasma treated sample with CO_2. Figure 10 shows the narrow scan for carbon peak in the treated sample. There is a shift in the carbon peak of 3.3 eVwhich is due to charge buildup in the sample during the XPS measurement.

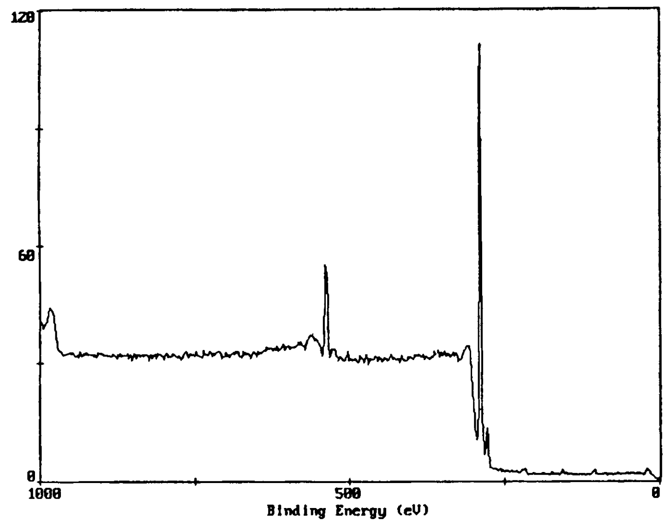

Figure 9. XPS spectrum of OPP treated film.

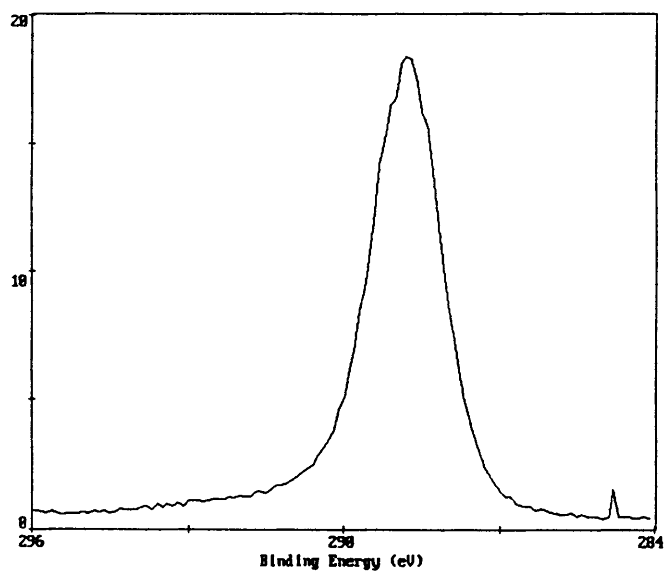

Figure 10. XPS narrow scan spectrum of OPP treated film.

Figure 11 shows the aging effect of OPP films (surface tension vs. time) treated by atmospheric plasma treater using helium and a mixture of helium and acetylene (C_2H_2). Treatment with C_2H_2 is very effective. As shown in the graph, the treatment effect does not change with time.

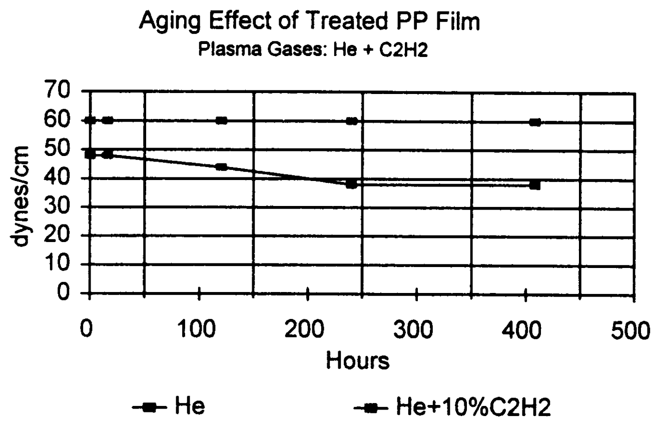

Figure 11. Results of OPP film treatment with C_2H_2.

Plasma treatment of polyethylene (PE) films were performed using helium and a mixture of helium with carbon dioxide (CO_2), oxygen, and acetylene on a 12 inches web. Figure 12 shows the surface tension testing results and aging of the PE films treated by atmospheric plasma treater using helium and different mixtures of helium and carbon dioxide. Figure 13 shows the surface tension testing results and aging of PE films treated using helium and different mixtures of helium and oxygen.

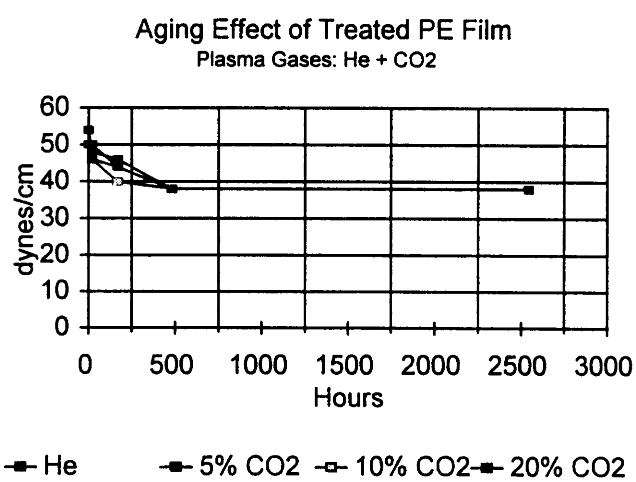

Figure 12. Results of PE films treatment with CO_2.

XPS was performed on PE treated samples with carbon dioxide and oxygen. Carbon to oxygen ratio ($n_{C:O}$)in the PE sample treated with O_2 was 13.4 while the carbon to oxygen ratio in the sample (PE) treated with CO_2 was 17.2.

CONCLUSIONS

- Plasma treatment is a superior method for improving the surface properties of polymer films.

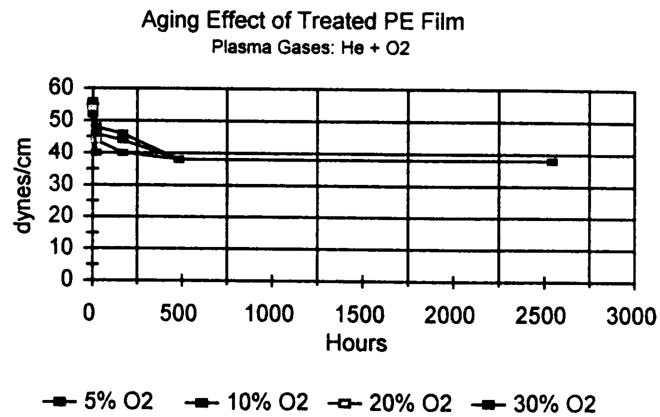

Figure 13. Results of PE films treatment with O_2.

- Sigma's vacuum plasma treaters have been successfully used for surface treatment/functionalization and grafting of polymer films.
- Sigma Technologies has developed a plasma system which can be operated at atmospheric pressure thereby eliminating the need for any vacuum chambers and pumps and has unique advantages over the existing technologies for surface treatment.
- The surface energies of the films treated by the newly developed atmospheric plasma system have been shown to increase substantially thereby enhancing the wettability and adhesion properties of these films. The newly developed system has a flexibility to be used also as a reduced ozone corona system and a corona system with controlled gas chemistry.

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