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# Stability of atmospheric-pressure plasma induced changes on polycarbonate surfaces

Rajesh Sharma<sup>1</sup>, Edward Holcomb<sup>1</sup>, Steve Trigwell<sup>2</sup>, and Malay Mazumder<sup>1</sup>

<sup>1</sup>Department of Applied Science,  
University of Arkansas at Little Rock,  
2801 S. University Ave., Little Rock, AR 72204  
phone: (1) 501-569-8055; fax: (1) 501-683-7222  
e-mail: rxsharma@ualr.edu

<sup>2</sup>Electrostatics and Surface Physics Laboratory ASRC Aerospace, ASRC-20  
Kennedy Space Center, FL 32899

**Abstract**— Polycarbonate films are subjected to plasma treatment in a number of applications such as improving adhesion between polycarbonate and silicon alloy in protective and optical coatings. The changes in surface chemistry due to plasma treatment have tendency to revert back. Thus stability of the plasma induced changes on polymer surfaces over desired time period is very important. The objective of this study was to examine the effect of ageing on atmospheric-pressure helium-plasma treated polycarbonate (PC) sample as a function of treatment time. The ageing effects were studied over a period of 10 days. The samples were plasma treated for 0.5, 2, 5 and 10 minutes. Contact angle measurements were made to study surface energy changes. Modification of surface chemical structure was examined using X-ray Photoelectron Spectroscopy (XPS). Contact angle measurements on untreated and plasma treated surfaces were made immediately, 24, 48, 72 and 96 hrs after treatment. Contact angle decreased from 93° for untreated sample to 30° for sample plasma treated for 10 minutes. After 10 days the contact angles for the 10 minute plasma treated sample increased to 67°, but it never reverted back to that of untreated surface. Similarly the O/C ratio increased from 0.136 for untreated sample to 0.321 for 10 minute plasma treated sample indicating increase in surface energy.

## INTRODUCTION

Plasma treatment is one of the most versatile techniques in surface modification. It has been widely used to alter the surface properties of materials in a

number of applications such as improving adhesion of coatings to metals and polymers [1], increasing wettability and printability of polymers [2, 3], enhancing biocompatibility of implants [4], and manufacturing of semiconductor devices [5, 6]. Plasma surface modification uses the active species of plasma such as radicals, ions and electrons to alter surface chemistry of polymers. The collision of these energetic active species with the surface results in transferring of their energy to lattice atoms. As a result, some of the substrate bonds break, making the surface more reactive. Depending upon the type of precursor gas used to generate the plasma, certain new functional groups are grafted on the surface. Thus, plasma surface modification can be used to induce a specific surface chemistry without changing the bulk properties of the materials. A large number of studies have shown that plasma treatment of polymers can develop surfaces with controlled and specific surface chemistry [7, 8]. Surface chemistry is tailored by varying the operational parameters such as the processing gas and plasma power.

Plasma surface modification of polycarbonate films is utilized in a number of applications such as enhancing biocompatibility [9] and improving adhesion between polycarbonate and silicon alloy in protective and optical coatings [10]. It has been observed that plasma treated polymers try to revert back to their original surface properties with time. Thus stability of the plasma induced changes on polymer surfaces over desired time period is an important issue. The objective of this study was to examine the effect of ageing on atmospheric-pressure helium-plasma treated polycarbonate sample as a function of treatment time. The ageing effects were studied over a period of 10 days. The samples were plasma treated for 0.5, 2, 5 and 10 minutes. Contact angle measurements were made to study surface energy changes. Modification of surface chemical structure was examined using X-ray Photoelectron Spectroscopy (XPS).

## EXPERIMENTAL PROCEDURE

### *A. Atmospheric Pressure Plasma Reactor*

The atmospheric plasma reactor used in this study, was constructed using a cylindrical Pyrex glass tube (30 mm ID, 90 cm long) with its inlet port connected to a gas flow rate regulator for introducing helium gas to the plasma reactor (11). The outlet of the plasma reactor was connected to the exhaust. A pair of copper electrodes (7.5 cm x 3 cm) was placed across the reactor for coupling the electrical drive to the plasma reactor. The reactor operated at 12

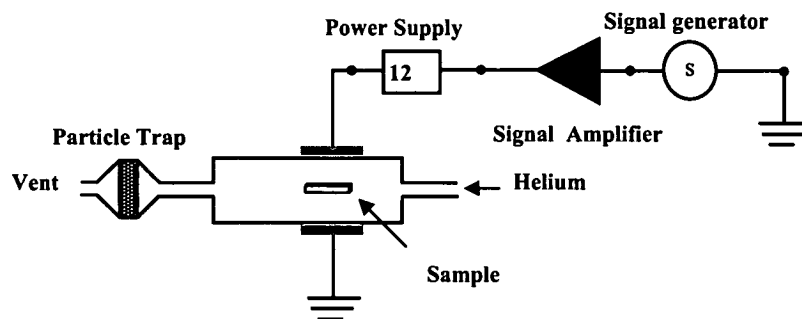


Fig. 1. Atmospheric pressure dielectric barrier discharge plasma reactor kV

(peak-to-peak) at a frequency of 700 Hz, delivering 100 watts of power. Polycarbonate samples (1"x 2") were placed inside the reactor for plasma treatment. Following that, the samples were used for contact angle measurement and surface chemistry analysis.

#### B. Surface Chemistry Analysis

X-ray Photoelectron Spectroscopy (XPS) was used to analyze the surface chemistry of the untreated and plasma-treated polycarbonate surfaces. The XPS data were obtained using a Kratos XSAM800 ESCA Spectrometer using a Mg K $\alpha$  ( $h\nu = 1253.6$  eV) x-ray radiation source. The x-ray beam used was 150W, with a spot size of 1 mm in diameter. The experimental data were referenced to the Au4f peak at  $84.0 \pm 0.05$  eV and the C1s peak to 284.6 eV. The high-resolution scans of the C1s peak were acquired at a pass energy of 40 eV, in 0.2 eV steps with a 300 ms dwell time. The individual element spectra were converted to ASCII format and imported to a computer where the peak curve fitting was performed using Thermo VG Scientific Eclipse V3.0 XPS data reducing software. The relative concentrations of the C1s peak components were determined by measuring the area under each fitted peak and normalizing the total to 100% to get relative percentage concentrations. Detection limits for XPS are approximately 0.05 to 1.0 atomic % depending upon the sensitivity of the elements.

#### C. Contact Angle Measurements

Changes in surface energy can be evaluated using contact angle measurements. To assess the effect of plasma treatment, contact angle measurements on untreated and plasma treated polycarbonate films were made using de-

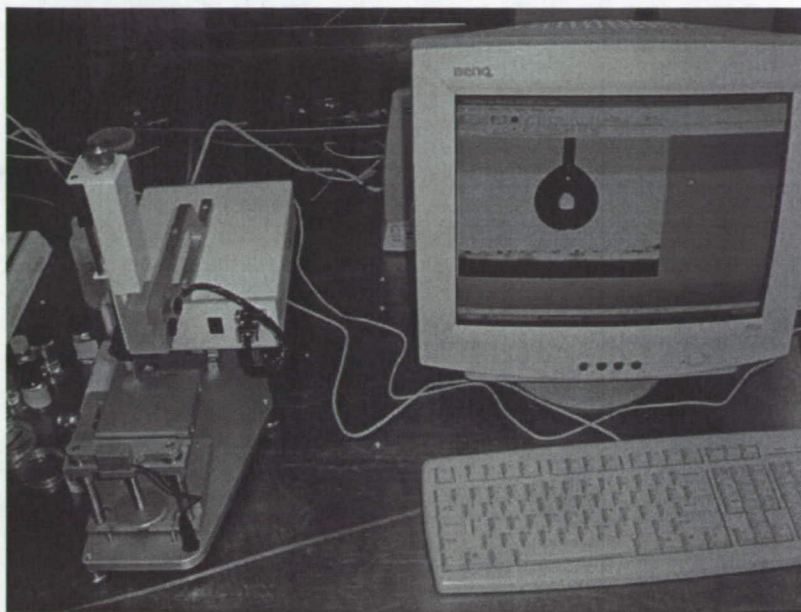


Fig. 2. VCA Optima surface analysis system for measuring contact angles

ionized water. A VCA-optima Surface Analysis System (AST Products, Inc., MA) was used to measure contact angle (Figure 2). All the experiments were carried out under ambient conditions (50% RH,  $\sim 23^{\circ}\text{C}$ ).

#### RESULTS AND DISCUSSION

The polycarbonate samples were plasma treated for 30, 120, 300 and 600 seconds. Five sets of samples were plasma treated for each treatment time. Contact angle measurements were made on one set of samples immediately following the plasma treatment. Measurements were made on other four sets of samples 1, 2, 3 and 10 days after plasma treatment. Contact angle was also measured for an untreated sample. The contact angle for an untreated sample was found to be  $93^{\circ}$ . It decreased to  $40^{\circ}$  after 30 seconds exposure to plasma (Figure 3). There was no significant decrease in contact angle with further increase in plasma treatment time. The contact angle for 600 second plasma treated sample was  $30^{\circ}$ .

The contact angle measurements made on samples 1, 2, 3 and 10 days after the treatment showed an increase for all the samples as compared to that of the samples analyzed immediately after plasma treatment (Figure 4). For a 30 second plasma treated sample the contact angle changed from  $39^{\circ}$



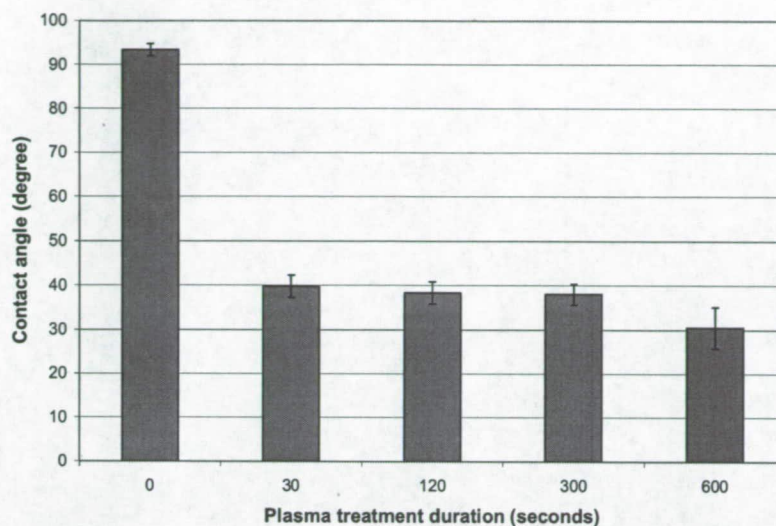


Fig. 3. Effect of plasma treatment duration on wettability of polycarbonate sample. Contact angle measurement represents wettability of a surface.

immediately after plasma treatment to  $51^\circ$  one day after plasma treatment. It further increased to  $79^\circ$  after 2 days. There was no significant change in contact angle beyond that. Similarly for 120 and 300 s plasma treated samples the contact angle increased from  $38^\circ$  immediately after plasma treatment to  $54^\circ$  and  $53^\circ$  respectively one day after plasma treatment. The 600 second plasma treated sample showed a trend similar to 30 second treated sample where contact angle increased one and two days after treatment but there were no significant changes subsequently.

The XPS analysis showed an increase in O/C ratio with increase in plasma treatment time up to 300 seconds (Figure 5). This increase in O:C ratio is indicative of the increase in oxygen containing polar functional groups on the surface. Increase in polar moieties on the surface increases surface free energy making surface hydrophilic [3, 8]. This explains the decrease in contact angle with increase in plasma treatment time as shown in figure 3. Further increase in plasma treatment time caused a decrease in O:C ratio. The overall drop for the 600 seconds data suggest that the treatment time was past optimum for oxidation. This could be due to breakup of oxygen functional groups and increased crosslinking. Table 1 shows the summary of the relative concentration of the carbon peak components. Increased oxygen concentration with plasma treatment is evident from the increase in C-O functional group. A decrease in C-C/C-H ratio with increase in plasma treatment time suggests increased crosslinking. The phenomenon of cross linking occurs when

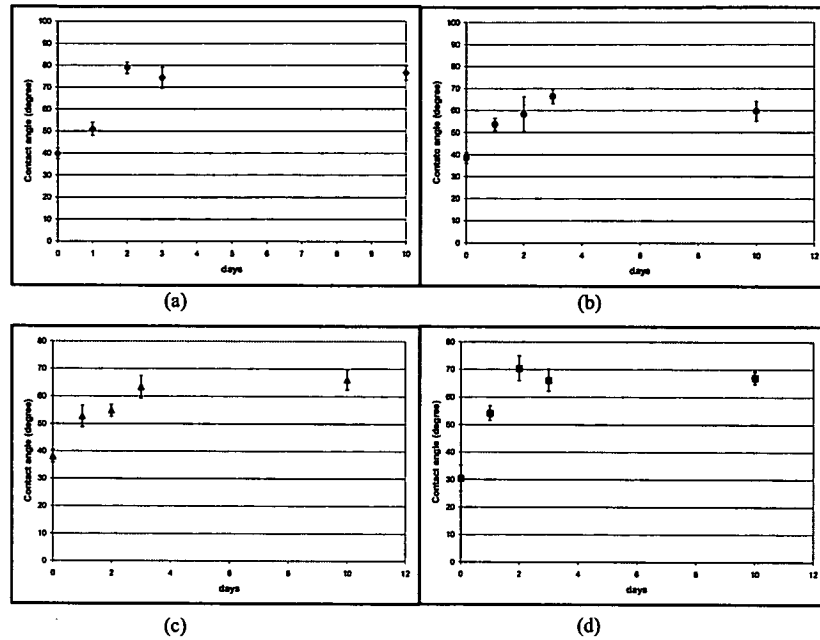


Fig. 4. Effect of ageing on wettability of polycarbonate surface plasma treated for (a) 30 seconds, (b) 120 seconds, (c) 300 seconds, and (d) 600 seconds

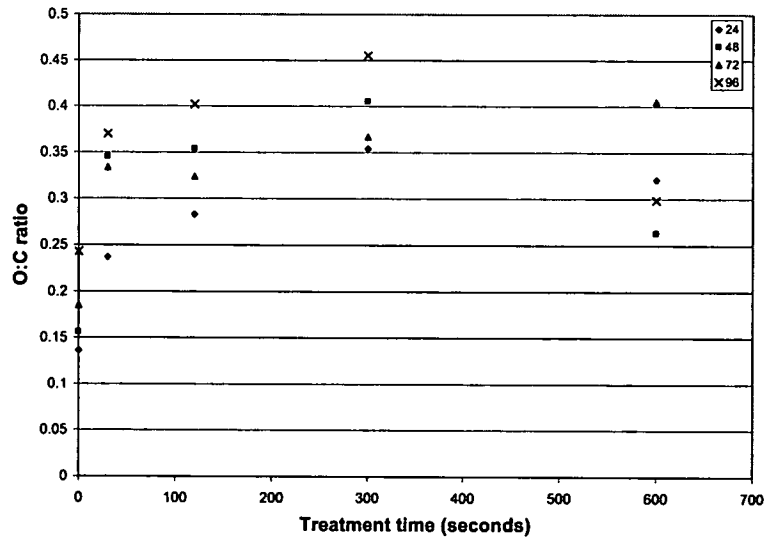


Fig. 5. Effect of plasma treatment time on O:C ratio

TABLE 1. Surface functional groups concentration (%) on untreated and plasma treated polycarbonate surfaces as determined by XPS

Sample	treatment time	C-C/C-H	C-O	C=O	O-C=O	$\pi$ - $\pi$ *
24 hrs	0	90	7.1	0.7	2.2	0.3
	30 seconds	82	12	3.8	2.2	-
	120 seconds	86	12	2.1	0.5	-
	300 seconds	80	12	3.3	3.0	2.1
	600 seconds	75	18	2.4	4.1	0.5
48 hrs	0	91	6.0	-	1.2	1.7
	30 seconds	76	16	2.0	4.7	1.6
	120 seconds	77	13	3.4	3.2	3.2
	300 seconds	78	14	2.3	4.3	1.4
	600 seconds	81	13	0.7	3.2	2.0
72 hrs	0	91	6.0	-	2.0	1.6
	30 seconds	78	16	2.3	3.4	1.3
	120 seconds	76	16	1.1	3.9	3.4
	300 seconds	76	14	2.0	3.7	4.0
	600 seconds	79	14	2.3	4.6	0.8
96 hrs	0	90	2.7	1.1	0.3	5.9
	30 seconds	80	10	3.6	2.1	4.8
	120 seconds	78	14	2.2	2.4	3.9
	300 seconds	71	15	4.2	5.6	4.6
	600 seconds	79	12	1.8	3.3	4.0

plasma species (typically inert plasma) interact with polymer surface to break C-C or C-H bonds resulting in recombination, unsaturation or branching of polymer chains [12].

However, it was found that O:C ratio increased with time after plasma treatment. This indicates a multitude of prolonged post plasma reactions. Free radicals formed at or below the surface during plasma treated have been found to be stable for long durations [1]. Thus they have opportunity to react with atmospheric oxygen or water vapor. This explains the increase in O:C up to 72 hrs after plasma treatment. After 72 hrs there was a decrease in O:C, suggesting a depletion in free radicals on the surface which in turn prevented introduction of any more oxygen containing functional groups. The decrease in O:C beyond 72 hrs could also be due to ageing of the surface. The ageing of plasma-treated polymer surface has been described by Liston et al. [1] as a combination of processes including reorientation of polar functional groups from surface to sub-surface as governed by thermodynamics, diffusion of mobile additives from bulk to surface and reaction of free radicals. This also ex-



plains the decreased wettability or increase in contact angles on samples 1, 2, 3 and 10 days after plasma treatment.

#### CONCLUSION

Atmospheric-pressure helium plasma was used to modify a polycarbonate surface. The stability of plasma induced changes on surface chemistry and wettability was studied. It was found that plasma treatment increased the wettability of the surface as indicated by decreasing contact angle. The contact angle decreased from 93° for untreated sample to 30° for a 600 second plasma treated sample. The plasma-treated surface became less wettable with time due to ageing. The O:C ratio increased with increase in plasma treatment time. The post-plasma reactions continued to increase oxygen component on the surface till 72 hrs after plasma treatment.

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