Surface Modification of Polycarbonate by Low Pressure RF Discharge

D P SUBEDI[1*], L ZAJICKOVA[2], V BURSIKOVA[2] and J JANCA[2]
[1.] *Department of Natural Sciences, Kathmandu University, Dhulikhel, Kavre, Nepal*
[2]. *Department of Physical Electronics, Masaryk University, Brno, Czech Republic*

E-mail: deepaksubedi2001@yahoo.com

Abstract

This paper reports the effect of low pressure radio frequency (rf) discharge on the surface properties of lexane type polycarbonate. Discharge was produced in argon and oxygen gases at low pressure in the range of 2-40 Pa. The modified surface was characterized by X-ray Photoelectron Spectroscopy, Atomic Force Microscopy and Contact Angle analysis. Oxygen-to-carbon (O/C) ratio in the composition of PC was found to increase after treatment. An appreciable increase in surface roughness was observed after treatment in oxygen discharge. Contact angle analysis showed that surface free energy of the sample increased from the original value of 35 mJ/m^2 to 63-74 mJ/m^2. Effect of treatment time and applied power on the wettability was studied after the treatment in argon and oxygen discharge.

1. Introduction

In recent years, polycarbonates have become very attractive business article. The world production of polycarbonates increases every year by 8-10% and nowadays it is more than 1.35 million tonnes/yr [1]. Polycarbonates (PCs) have been able to replace more traditional materials like glass and metals in many products, such as automobile headlamps and stoplight lenses, corrective lenses, safety shields in windows, architectural glazing and the like. They can be applied to plastics vessels, parts of machines and in optical grades for compact discs (CDs, CD-ROMs and DVDs), optical fibers etc.

However, the low hardness, low scratch resistance and degradation by ultraviolet radiation make a modification of PC surface properties necessary. The low surface energy of polycarbonate results in poor adhesion of additional coatings which have created numerous important technical challenges to be overcome by manufacturers [2]. Therefore, in many applications (e.g. in industry, technology, biology and medicine) it is necessary to change or improve some of the surface properties of polycarbonate without altering its bulk properties. Several techniques have been developed to modify the polymer surfaces for improved adhesion, wettability, printability and other technologically important characteristics. The common methods of surface modification include mechanical or chemical treatment; and exposure to flames, photons and ion beams. But these methods are found to have problems such as: poor reproducibility and controllability. Moreover, they use a huge amount of toxic liquids during the process which are labeled as environmentally harmful. Among all the methods of modifying polymer surfaces to improve wettability and adhesion, low pressure plasma treatment has proved to be one of the most effective, ensuring uniformity as well as being non-polluting.

This paper presents the modification of polycarbonate surface using a low pressure RF discharge produced in argon and oxygen gases. The modified surface has been characterized by measuring contact angle and subsequent calculation of surface energy. The changes in chemical composition have been studied by XPS analysis.

2. Experimental

Polycarbonate (Lexane type) specimens of the size 50 *mm* × 50 *mm* and 60 *mm* × 20 *mm* were used for investigation. The samples were cleaned in isopropyl alcohol and dried before inserting into the reactor. Plasma treatments of samples (PC) were carried out in capacitively coupled rf glow discharge produced in Argon and Oxygen gases. The details of the plasma treatment system can be found elsewhere [3-4].

The surface free energy of the PC specimens was determined from the contact angles of water and glycerine with the sample surface using Owens-Wendt-Kaelble two-liquid method as represented by Equation (1) [5].

$$\gamma_l(1+\cos\theta) = 2\left(\gamma_l{}^d \gamma_s{}^d\right)^{\frac{1}{2}} + 2\left(\gamma_l{}^p \gamma_s{}^p\right)^{\frac{1}{2}} \quad (1)$$

where γ_l, γ_l^p, γ_l^d are the total surface energy, polar component and dispersion components of the surface free energy of the liquid respectively. Similarly, γ_s, γ_s^p, γ_s^d are the values for solid under investigation. θ is the contact angle between the sample and the liquid. Contact angles with two test liquids were measured in order to determine the two components of surface energy.

The XPS measurements were carried out on an ultra-high-vacuum surface analytical system equipped with Omicron EA 125 hemispherical analyzer working in regime of multi-channel detection. The analyser was operated in the retarding-field mode using a pass energy of 20 *eV*. *Mg Kα* was used for excitation. The electron take-off angle was 90° and the analyzed area 6 mm in diameter. The standard fitting procedure was used to determine the core-level peak position and spectral intensities.

Atomic Force Microscopy (AFM) has been used to study the surface roughness of the PC specimens using an Accurex Topometrix~II~L system in a contact mode.

3. Results and Discussion

3.1 Surface energy measurement

Surface energy of untreated sample and the samples treated in argon and oxygen discharges are summarized in Table 1. The study was made for two different powers. After treatment the surface energy increased from the original value of 35 mJ/m^2 to about 65-74 mJ/m^2. This increase in surface energy is an indication of physico-chemical changes in the surface of the sample. The changes in chemical and physical structures of the sample were also observed from XPS and AFM analysis.

Table 1: Summarized values of surface energies of untreated and plasma treated polycarbonate. The treatments were made for 5 min under a pressure of 1.5 Pa and gas flow of 5.7 sccm.

Power	**Gas**	**Surface Energy**		
		γ	**γ^p**	**γ^d**
Untreated	-	35±9	18±4	17±5
100 W	Ar	65±8	48±5	17±3
400 W	Ar	72±0	56±0	16±0
100 W	O_2	71±5	55±3	16±2
400 W	O_2	73 ±0.3	56±0.4	17±0.2

The values of surface free energy and its polar and dispersion components as a function of treatment time in argon discharge are shown in Fig 1. Significant increase in the total surface energy with the treatment time was observed up to 10 minute of the treatment. For higher treatment times the saturation of the surface energy was observed. It is a sign of equilibrium between the surface modification and the removal of modified surface layer. The sputtering rate as determined by measuring the weight of PC specimens after 45 min of treatment was 1.6×10^{-8} g cm^{-2} s^{-1}. The increase in total surface energy was associated with the increase in its polar component.

In the case of argon plasma the direct and radiative energy transfer processes cause the surface modification. The direct energy transfer corresponds to the ion bombardment of the surface, which is particularly important in the case of PC specimens placed on the dc-biased capacitively-coupled rf electrode. Another important factor for the modification mechanism is the UV (VUV) radiation emitted by the plasma [6]

Unlike argon plasma, the oxygen plasma produces a variety of new functional groups including C–O, C=O, O–C=O, C–O–O that increase hydrophilicity of the sample.

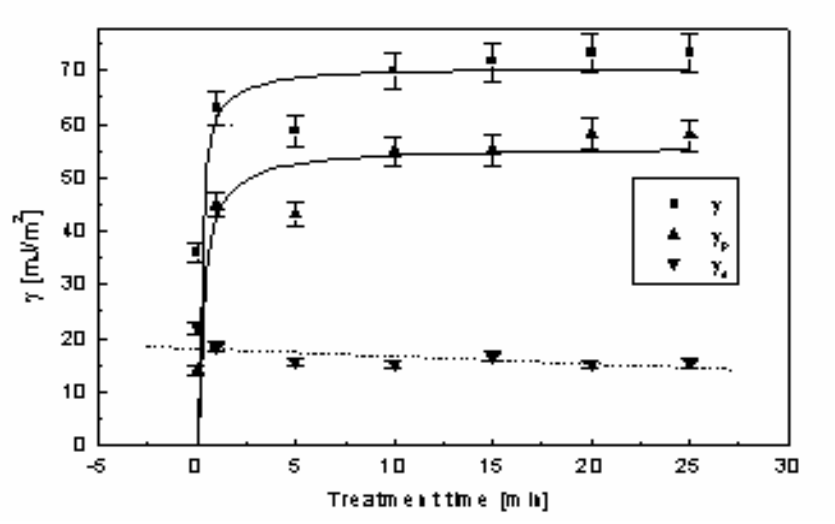

Figure 1. Surface energy and its polar and dispersion components as a function of treatment time in argon discharge. The gas flow rate was 5.7 sccm, pressure 1.5 Pa and rf power 100 W.

3.2 XPS Analysis

Further information about the changes induced by argon and oxygen plasma treatment was obtained from the XPS measurement. The atomic compositions of the PC surface before and after the treatment are compared in Table 2. The treatments produced a reduction in the carbon concentration on the PC surface. On the other hand oxygen content increased and a small amount of nitrogen and silicon also appeared. The increase in oxygen concentration is responsible for the increased hydrophilicity of the sample. The nitrogen impurity found on the sample after the treatment could be the nitrogen incorporated during the plasma treatment as a result of some nitrogen traces in the feed gas as well as after the exposure of the treated surface to the atmosphere. The impurity of the silicon is caused by the fact that the reactor was also used for the deposition of silicon oxide. Although the reactor was cleaned mechanically as well as in oxygen and argon discharge before the treatment of PC, there was probably some residual silica that appeared in the PC surface.

Table 2 Atomic concentrations of carbon, oxygen and nitrogen measured by XPS for untreated and plasma treated polycarbonate. Plasma treatments were performed for 5 min at a pressure of 1.5 Pa and a gas flow rate 5.7 sccm.

Gas	**Power**	**Atomic Concentration (%)**			
		C	**O**	**Si**	**N**
Untreated	–	84.3	15.7	0	0
Ar	100	76.4	20.3	0.4	2.2
O2	100	74.0	24	0.4	1.7

3.3 AFM analysis

AFM micrographs of untreated and plasma treated PC are depicted in Fig. 2(a) – 2(c) It was observed that roughness of the sample after oxygen plasma treatment was higher than that of the argon plasma treatment. This is possibly due to the etching of the sample in reactive oxygen discharge compared to the inert argon discharge. This increased roughness can also contribute to the increased wettability as well as adhesion to other materials which have great technological importance.

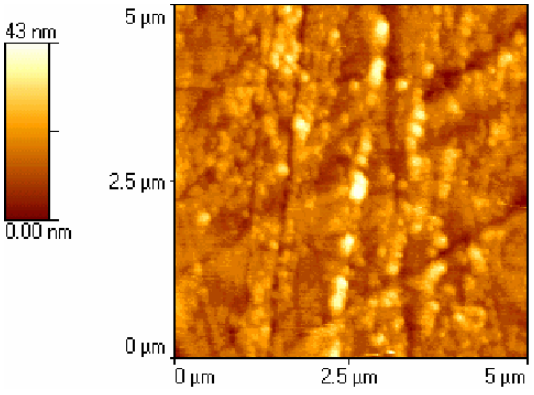

Fig 2a: AFM image (5.04 µm x 5.04 µ m) of untreated PC

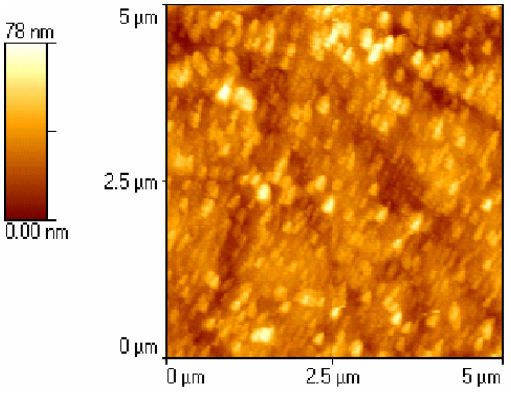

Fig 2b: Dependence of the etch rate on the applied rf power and the negative self bias voltage at 45 sccm of oxygen flow.

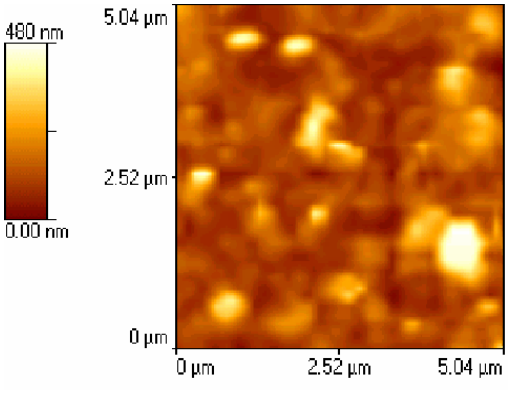

Fig 2c : AFM image (5.04 µm x 5.04 µ m) of PC treated on oxygen plasma for 45 min at rf power 450W and gas flow rate 80 sccm.

4. Conclusion

Surface treatment of polycarbonate sample in low pressure plasma of argon and oxygen resulted in a remarkable improvement in surface properties of PC. After the treatment in argon plasma, a significant rearrangement of the surface structure was induced by the kinetic energy of argon ions and fast neutrals as well as by UV radiation from the discharge. Surprisingly, the O/C ratio increased after the treatment i.e. an oxidation of the PC surface was induced. A steep increase in surface energy was observed for the treatment time up to 10 min. For longer treatment duration the changes were almost saturated due to reaching an equilibrium between the surface modification and removal of the modified surface layer. AFM analysis showed a higher roughness after treatment in oxygen discharge compared to that of argon discharge.

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