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## Treatment of polycarbonate by dielectric barrier discharge (DBD) at atmospheric pressure

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**Abstract.** Generally most plastic materials are intrinsically hydrophobic, low surface energy materials, and thus do not adhere well to other substances. Surface treatment of polymers by discharge plasmas is of great and increasing industrial application because it can uniformly modify the surface of sample without changing the material bulk properties and is environmentally friendly. The plasma processes that can be conducted under ambient pressure and temperature conditions have attracted special attention because of their easy implementation in industrial processing. Present work deals with surface modification of polycarbonate (PC) by a dielectric barrier discharge (DBD) at atmospheric pressure. The treatment was performed in a parallel plate reactor driven by a 60Hz power supply. The DBD plasmas at atmospheric pressure were generated in air and nitrogen. Material characterization was carried out by contact angle measurements, and X-ray photoelectron spectroscopy (XPS). The surface energy of the polymer surface was calculated from contact angle data by Owens-Wendt method using distilled water and diiodomethane as test liquids. The plasma-induced chemical modifications are associated with incorporation of polar oxygen and nitrogen containing groups on the polymer surface. Due to these surface modifications the DBD-treated polymers become more hydrophilic. Aging behavior of the treated samples revealed that the polymer surfaces were prone to hydrophobic recovery although they did not completely recover their original wetting properties.

### 1. Introduction

Polymers are frequently applied in modern industry owing to their high performance, relatively low cost and easy recycling. Among these materials, polycarbonate (PC) has high creep resistance, high toughness and excellent optical transparency, making it an attractive polymer material. PC is used in variety of applications as viable substitute for glass e.g. automobile headlamps, corrective lenses, plastic vessels, and compact discs. However, the low hardness, low scratch resistance and degradation by ultraviolet (UV) radiation of PC have restricted his application. To remedy these limitations, attempts of producing hard protective coatings on PC have been tested [1]. However the adhesive strength between the deposited film and the PC substrate is poor due to the low surface energy of the polymer. As a matter of fact, many polymers commonly used in industry have disadvantageous surface properties with regards to gluing, printing, painting, inking or coating because of their low surface energy [2]. Therefore, to enhance the surface energy of polymers, their surface should be activated by some kind of chemical or plasma treatment [3].

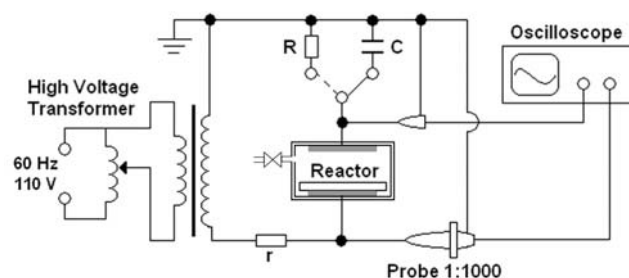


Plasma treatment is one of the most versatile techniques in surface modification, which can alter the outmost surface layers of polymer without changing its advantageous bulk properties [4]. The plasma is usually generated by ionization of a feed gas that produces positive and negative ions, energetic electrons, UV photons, along with active free radicals. The effect of plasma treatment of polymeric surfaces can range from branching and crosslinking to etching and fictionalization of surface groups. The extent of these effects depends mostly on the processing parameters such as the treatment time, gas pressure, kind of feed gas, discharge power, frequency and so on. The chemical effect of plasma treatment consists of reactions between the plasma species and polymer surface can form different polar groups, such as, -OH, C-O, C-OH, C=O etc. These polar groups cause increasing of the surface energy and an enhancement of the material wetting properties [4, 5]. Atmospheric plasma treatments are especially attractive due to the elimination of expensive vacuum equipment, easier handling of the samples and simple scalability for industrial in-line processing. Therefore, in resent years, a lot of effort has been directed into the development of non-thermal plasma reactors working at (or near) atmospheric pressure. One promising technology for producing atmospheric plasmas is based on the use of dielectric barrier discharge (DBD) [6]. Here, a dielectric barrier covers one or both of the reactor electrodes leaving a small gas gap between them. The DBD discharge can produce large volumes of non-thermal plasma at atmospheric pressure. The mean electron energy is in the range of 1–10 eV, while the chemical binding energy of polymers is less than 10 eV [7]. Therefore, energetic particles in DBD can easily break the chemical bonds of polymers and active radicals abundant in the plasma can react with the surface, modifying its properties. Since plasmas modify the chemical and physical nature of the surfaces, the wettability of polymers is therefore normally altered by the plasma treatment [4,5, 8]. Some authors have investigated the enhancement of PC scratching resistance as well as improvement of polymer wetting properties by low-pressure plasma treatment [9, 10]. More recently atmospheric pressure plasma treatments, such as an air plasma torch [11], a DBD in helium [12] and a homogeneous DBD in nitrogen [8] were used for modification of PC surface properties.

This work describes the surface modification of PC polymer by atmospheric pressure filamentary DBD and compares the efficiency of the treatment in atmosphere of air and nitrogen. The samples utilized in this study were cut from commercially available PC used for protective glasses. Material characterization was carried out by contact angle measurements, surface energy assessments and X-ray photoelectron spectroscopy (XPS).

## 2. Experimental

The experimental arrangement used to generate DBD discharge at atmospheric pressure is sketched in figure 1.



**Figure 1:** Experimental set-up

The DBD discharge is generated between two 9.5-cm-diam parallel aluminum electrodes enclosed within a 150-mm-diam cylindrical chamber made from Delrin®. A glass layer with 2.0 mm thickness completely covered the bottom reactor electrode. The upper electrode was grounded and the lower one was employed as high-voltage electrode. The distance between the two electrodes was kept constant

during the DBD treatment at 3 mm. The cylindrical chamber was connected to a flow regulator for introducing gas precursor into the plasma reactor. The reactor outlet was connected to an exhaust. Before starting the plasma processing the samples (10x15 mm<sup>2</sup>), cut from 0.5-mm-thick commercial polycarbonate film, were placed on the lower electrode. After introduction of the samples into the reactor it is flushed with the discharge gas at a rate of 5.0 slm for 5 min. This purging step is performed in attempt to remove the residual air from the reactor. Subsequently the feed gas flux into reactor chamber is maintained at 2.4 slm using a rotameter. In this work two different feed gases (Air Liquid, Brazil) are used: dry air and nitrogen.

Prior the DBD treatment, the samples were ultrasonically cleaned in distilled water and detergent for half an hour. The samples were washed by rinsing in isopropyl alcohol for 10 min to remove organic contaminants from the surface and after that dried at room temperature. The high-voltage power supply is consisted of a step-up high-voltage transformer (110/20000V of  $V_{rms}$ , 60Hz) driven by an autotransformer Variac. The AC voltage applied to the reactor lower plate is measured by using a 1000:1 high-voltage probe (Tektronix P6015A, 75MHz) and displayed on a digital oscilloscope (Tektronix TDS 2024B, 200MHz). For each feeding gas all plasma treatments were carried out at a fixed voltage of 30kV<sub>p-p</sub> and gas flux of 2.4 slm while the treatment time was varying. Following the plasma treatment, the samples were subjected to contact angle measurements and surface chemistry analysis.

The contact angle (CA) was obtained by the sessile drop method on a standard Rame-Hart goniometer, model 300 using the DROPImage software. The measurements were carried out at room temperature in controlled environment kept at relative humidity of 60%. The volume of each liquid drop was 2 µl and two different test liquids: de-ionized water and diiodomethane were used. At least five different drops were deposited on the polymer surface to obtain the average value of the contact angles. The maximum error in the contact angle assessments did not exceed 3%. Surface energies were calculated by using the Owens-Wendt method on which polar and non-polar (dispersive) contributions are considered to explain the interaction between the liquid and the solid phases. The geometric-mean method was used to determine the surface energy and its polar and dispersive components using the equation system:

$$\gamma_L(1 - \cos \theta_i) = 2\sqrt{\gamma^p \gamma_L^p} + 2\sqrt{\gamma^d \gamma_L^d}$$

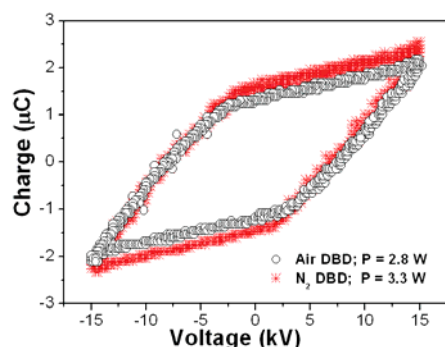
where  $\theta_i$  stands for the contact angle of each test liquid.

Surface chemical characterization was carried out by X-ray photoelectron spectroscopy using a Kratos XSAM HS system. The base pressure in the analyzing chamber was kept below 10<sup>-7</sup> mbar. As excitation source the Mg K<sub>α</sub> line (hν = 1253.6eV) was employed with the emission voltage and current of the source set to 6.0 kV and 5.0 mA, respectively. The obtained spectra were processed by the code provided by the apparatus manufacturer using the Shirley method for background subtraction. All peaks were fitted using Gaussian curves. The value of 284.8 eV of the hydrocarbon C1s core level was used for calibration of the energy scale.

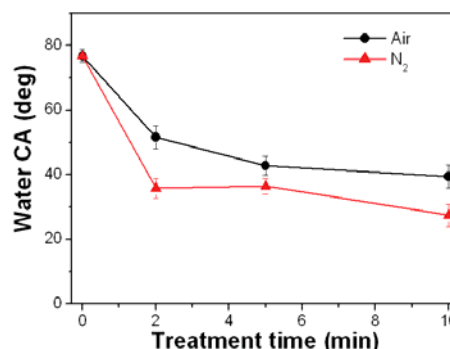
### 3. Results and discussion

The DBD discharge used for PC treatment operates in filamentary mode i.e. it is constituted by many tiny streamers distributed over entire area of the dielectric barrier. The discharge current consists of large number of short micro-pulses typical for the DBD discharges. To calculate the discharge power of the DBD, the current measuring resistor was replaced by a capacitor C = 0.91 µF. The charge  $Q(t)$  stored on the electrodes is represented as a function of  $V_p(t)$  for one period to form so-called Lissajous figure. In case of filamentary DBD driven by a sinusoidal power source the typical shape of its  $Q$ - $V$  curve is a parallelogram [6]. The area enclosed by the Lissajous figure gives the electrical energy consumed for voltage cycle. The discharge power  $P$  is then calculated by multiplying the electrical energy by the frequency of the applied voltage (60 Hz). Figure 2 represents the  $Q$ - $V$  figures of DBD in different gases. As can be seen in figure 2 the shape of the Lissajous figures depends on the kind of feeding gas however the discharge energy per cycle, represented by Lissajous's figure area in both

cases is almost the same. The mean discharge power measured for DBD in nitrogen and air gas precursors was 3.3 W, and 2.8 W, respectively.

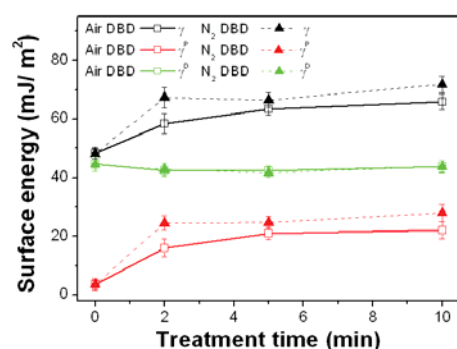


**Figure 2:** Q-V diagrams for DBD in air and nitrogen.

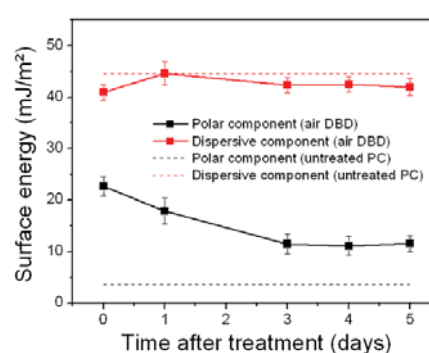


**Figure 3:** Water CA of PC samples measured soon after the treatment.

To investigate how surface wetting properties of PC are affected by the plasma exposure PC samples were treated for 2, 5 and 10 min using different feed gases. The PC water contact angle measured soon after the DBD is shown in figure 3. As expected all plasma treatments lower the water CA with respect to the untreated PC sample. The initial CA of pristine PC (76°) was reduced to about 40° after 10 min air plasma treatment. No significant changes in the contact angle with further increase of the plasma exposure time were detected. The DBD treatment in N<sub>2</sub> seems to be more efficient in reducing water CA of PC, reaching saturation value of about 30° after 10-min N<sub>2</sub> plasma exposure.



**Figure 4:** Variation of PC surface energy and its polar and dispersive components.



**Figure 5:** Evolution of SE polar and dispersive components.

Figure 4 shows the variation of surface energy as well as its polar and dispersive components of PC samples treated with air and N<sub>2</sub> DBD. The surface energy of pristine PC was 48.2 mJ/m<sup>2</sup> with dispersive and polar components of 44.6 mJ/m<sup>2</sup> and 3.6 mJ/m<sup>2</sup>, respectively. After 10 min of plasma treatment the surface energy of PC samples increased up to 71.8 mJ/m<sup>2</sup> and 66.0 mJ/m<sup>2</sup> for N<sub>2</sub> and air plasma, respectively. As can be seen in figure 4 the increase of polymer surface energy is mainly associated with the increase of its polar component. They increase with the treatment time reaching saturation values beyond 5 min of treatment. Generally, for most polymeric materials the DBD treatment results in no or little variation of the dispersive component of surface energy [5]. Based on this it can be concluded that the polar component plays an important role in the improvement of surface energy of DBD treated polymers. This enhancement of the surface energy polar component is

due to the oxygenation of the polymer surface by the plasma. Reactions between the plasma species and the polymer chain introduce polar oxygen groups (C-O, C-OH, C=O, O-C-O, O-C=O) on the surface, which results in enhancement of polar component of the surface energy [8]. Nitrogen plasma turns out to be more efficient in promoting enhancement of the surface energy polar component, which results in better wetting properties of PC surface DBD. This finding will be further discussed when presenting results from XPS analysis.

It is known that the polymer surfaces treated by plasma and left in ambient conditions tend to partially recover their original wetting properties [13]. This process is referred to as hydrophobic recovery. Contact angle measurements with both test liquids were made immediately following the plasma treatment and after 1, 2, 3, 4 and 5 days of storage at controlled ambient (temperature of 21°C and 60% relative humidity).

The evolution of both components of PC surface energy can be observed in figure 5. This surface aging effect is attributed to the orientation of polar groups located on the surface into the bulk of the material and diffusion of nonpolar groups from the volume to the surface [13]. Both processes result in a partial reduction of the surface energy polar component while the dispersive component remains practically unchanged (see figure 5). The process of hydrophobic recovery predominantly occurs during the first couple of days after the treatment and further aging seems to be less important.

Table 1. Atomic composition of PC samples

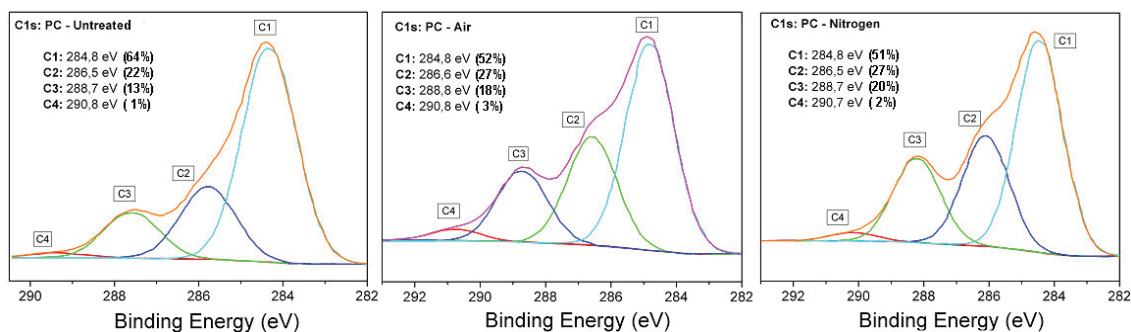
	C (%)	O (%)	N (%)	O/C	N/C
<b>Untreated PC</b>	80.51	19.49	-	0.24	-
<b>Air plasma</b>	70.68	28.03	1.29	0.40	0.02
<b>N<sub>2</sub> plasma</b>	69.25	27.18	3.57	0.39	0.05

When polymers are exposed to plasma the plasma energetic species (electrons and UV photon) preferentially break the weaker C-C and C-H bonds on the surface. Atmospheric plasmas are abundant of reactive oxygen atoms which react with the dangling bonds on the polymer surface forming different species such as mono-oxidized C-O, C-OH carbons, bi-oxidized C=O or O-C-O carbons and tri-oxidized O-C=O carbons [5]. These oxygen-related polar groups are responsible for the enhanced hydrophilicity of the DBD treated polymers [8]. Surface atomic composition of the plasma-modified polymers, determined by XPS analysis, is shown in table 1. The measurements were performed at least 2 weeks after the DBD treatment therefore the XPS analysis presents the atomic composition of polymeric surfaces when they had already underwent the process of hydrophobic recovery and the surface chemical composition reached a state-state. As can be seen in table 1 both plasma treatments lead to increase of polymer O/C ratio to about the same extend. Since our experiment is conducted in an open environment it is impossible to ensure DBD discharge in pure N<sub>2</sub> atmosphere. Due to residual air trapped in the reactor chamber there are always some oxygen impurities in the discharge. Even in little quantity as in case of N<sub>2</sub> DBD, the oxygen atoms are very reactive and they are incorporated onto the polymer surface. Also, after the treatment all samples are kept in ambient conditions where unsaturated bonds on the polymer surface can be subjected to reactions with the atmospheric oxygen. That is why the oxygen content on the surface of polymers treated in different discharge gases is about the same. Nevertheless the O/C ratio is almost the same for both treatments the DBD in N<sub>2</sub> gas shows higher efficiency in reducing water CA as shown in figure 3. This finding may be explained by the fact that the DBD in nitrogen plasma added more N atoms on the PC surface (see Table 1).

The characteristic photoelectron C1s peak obtained by XPS for PC before and after the DBD treatments is shown in figure 6. All peaks were resolved into 4 components C1 (C-C/C-H), C2 (C-O), C3 (C=O or C(=O)-N) and C4 (O-C(=O)-O). The peaks binding energies and relative areas are shown in figure 6. For both DBD-treated PC samples the intensity of C1 component decreases while the intensity of the other three components increases as observed by other authors [8-10]. As can be seen in figure 6 the composition of the oxidized carbons species on the surface of PC samples DBD treated in air and N<sub>2</sub> is practically the same. For the N<sub>2</sub> DBD in the originally empty N 1s region appears a new



peak at 399.8 eV which is assigned to the amide group C(=O)-N. Similarly for air DBD a new N 1s peak develops that can be decomposed into two components N1 at 399.7 (amide group, area 72%) and a smaller component at 401.7 eV with 28% relative area assigned to the protonated amine [3].



**Figure 6:** Deconvolution of C1s peak of PC samples.

#### 4. Conclusions

Polycarbonate samples were subjected to atmospheric pressure DBD plasma in air and nitrogen. Both treatments result in incorporation of polar oxygen and nitrogen groups on PC surface which leads to enhancement of material wetting properties. The DBD process in nitrogen turns out to be more efficient probably due to the higher amount of N atoms added on the surface. After the treatment the samples were stored in air at ambient temperature to study the aging behaviour of plasma-modified samples. The polymer surfaces are prone to hydrophobic recovery however after 5 days of storage they only partially restore their original wetting properties.

#### Acknowledgments

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