Modification of polycarbonate surface in oxidizing plasma

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Abstract. The properties of the surface of the film polycarbonate Lexan 8010 were experimentally studied after treatment in a DC discharge plasma in oxygen and air at pressures of 50-300 Pa and a discharge current of 80 mA. The contact angles of wetting and surface energies are measured. The topography of the surface was investigated by atomic force microscopy. The chemical composition of the surface was determined from the FT-IR spectroscopy data in the variant of total internal reflection, as well as X-ray photoelectron spectroscopy. Treatment in the oxidizing plasma leads to a change in morphology (average roughness increases), an increase in the surface energy, and the concentration of oxygen-containing groups (hydroxyl groups, carbonyl groups in ketones or aldehydes and in oxyketones) on the surface of the polymer. Possible reasons for the difference in surface properties of polymer under the action of oxygen and air plasma on it are discussed.

1. Introduction

The surface of polymers generally has low surface tension and high chemical inertness, and usually not the best adhesion properties and wettability. Consequently, modification of the surface of polymers plays an important role in improving such processes as: wettability and adhesion to coatings during staining and printing, when working with biomaterials and certain types of composite materials. Therefore, the main methods for modifying the surface of polymers are: plasma treatment, ultraviolet irradiation, laser and chemical oxidation, introduction into the flame, and a number of others [1]. Processing in plasma provides ample opportunities for modifying the polymer surface. A lot of works are devoted to the improvement of polymer-polymer and metal-polymer adhesion, as well as to dyeing and printing on polymers [2, 3]. Polycarbonates (PCs) have become widespread in the industry due to their excellent transparency, high strength and resistance to high temperatures.

2. Experimental setup

For the experiment we used the setup described in [4]. Samples of film polycarbonate (PC) of the brand Lexan 8010 were placed along a generatrix on a thermostated wall of a cylindrical glass reactor 3 cm in diameter in the zone of the positive column. The pressure range of the plasma-forming gas is 50 - 300 Pa. The linear velocity of the gas flow was 30 cm / s. The discharge current is 80 mA. The processing time for the polymer is 180 s.

To determine the surface energy, the "neutral drop" method was used, consisting in placing two drops of different liquids (water and glycerin) with a known surface tension on the surface of the material under study. The contact angle of wetting was determined by digital photography.

The topography of the PC surface was investigated by atomic force microscopy using a "Solver 47 Pro" microscope. The scanning was carried out in a semi-contact mode.
The surface of the polymer was investigated by ATR-FTIR spectroscopy. A Nicolet type spectrophotometer of the Avatar-360 type was used. The ATR element was a zinc selenide crystal, the angle of incidence of the ray was 42 °, with a single reflection, a signal accumulation mode was used based on the results of 32 scans, and the resolution was 2 cm⁻¹. The chemical composition of the polycarbonate surface was determined by X-ray photoelectron spectroscopy (XPS). The source was AlKα (with energy 1486.6 eV) with a multichannel chemospheric electrostatic analyzer Phoibos 100. The obtained spectra were corrected for aliphatic carbon at 285 eV.

3. Results and discussion

Processing of polycarbonate films in plasma leads to an increase in the wettability of the surface: the contact angles of polymer wetting with water and glycerin decrease, the surface energy (σ) increases. The increase in the surface energy of the sample is due to an increase in its polar component (σ^p). The dispersion component (σ^d) changes insignificantly as a result of the action of the plasma (Table 1). Processing in oxygen plasma allows to achieve a better effect.

| Treatment conditions | Contact angles, degree | Surface energy, mJ/m² |
|----------------------|------------------------|-----------------------|
|                      | θ (H₂O) | θ (glycerol) | σ^d | σ^p | σ |
| Initial              | 81      | 70          | 20.3 | 10.2 | 30.5 |
| Air, 100 Pa          | 36      | 47          | 10.5 | 48.2 | 58.7 |
| Oxygen, 100 Pa       | 30      | 45          | 10.1 | 52.0 | 62.1 |

The study of samples by ATR-FTIR spectroscopy showed that as a result of processing in plasma, the greatest changes occur in the range of stretching vibrations of the O-H bond (3200-3500 cm⁻¹) and the stretching vibrations of the C = O bond in various functional groups (1625-1860 cm⁻¹) (figure 1).

![Figure 1](image1.png)

**Figure 1.** IR spectrum of polycarbonate films. 1 - initial sample; 2-air processed in plasma; 3 - oxygen treated in plasma. The gas pressure is 100 Pa. a) -O-H (3200-3500 cm⁻¹), b) -C = O (1625-1860 cm⁻¹).

The effect of oxygen and air plasma leads to a decrease in the optical density at the maximum of the C = O bond absorption band in the carbonate bridge (1770 cm⁻¹) and to an increase in absorption due to O-H bond vibrations (3220 cm⁻¹), C = O bond vibrations of ketones or aldehydes (1695 cm⁻¹) and in oxyketones (1650 cm⁻¹) [5]. A similar change in the IR spectrum of polycarbonate during thermal-oxidative degradation is reported in [6]. Changes in the spectrum in the region of 1660 cm⁻¹ are attributed to the possible formation of quinoid carbonyl groups. The paper presents possible mechanisms for the formation of ketone and aldehyde groups, which are represented as a chain process initiated by the detachment of the hydrogen atom in the methyl group.
Figure 2 (a, b) shows the results of measurements of optical densities at the indicated wave numbers assigned to the optical density at a wave number of 1500 cm\(^{-1}\), corresponding to the maximum of the absorption band of the C-C bond vibrations in the aromatic ring, and reduced to the untreated sample.

![Graph A](image1)

**Figure 2.** Dependence of the optical density on the gas pressure in the air and oxygen plasma. (a) 1 - 1650 cm\(^{-1}\), air plasma; 2 - 1650 cm\(^{-1}\), oxygen plasma; 3 - 1770 cm\(^{-1}\), air plasma; 4 - 1770 cm\(^{-1}\), oxygen plasma. (b) - 3220 cm\(^{-1}\), air plasma; 2 - 3220 cm\(^{-1}\), oxygen plasma; 3 - 1695 cm\(^{-1}\), air plasma; 4 - 1695 cm\(^{-1}\), oxygen plasma.

The decrease in the optical density at the wave number of 1770 cm\(^{-1}\) is due to the destruction of the carbonyl groups that make up elementary unit of the polymer. When exposed to air plasma, the decrease is more significant than when processed in oxygen plasma. In the latter case, there is also a higher optical density, and, consequently, the concentration of hydroxyl groups and carbonyl groups in oxyketones (1650 cm\(^{-1}\)), but the concentration of carbonyl groups in ketones or aldehydes (1695 cm\(^{-1}\)) is lower than in air plasma.

The effect of gas pressure on the change in the concentration of the functional groups depends on the type of plasma-forming gas. For a plasma of oxygen, non-monotonic dependences with an extremum at 100-150 Pa are characteristic. In the air plasma, there are increasing dependences, except for the concentration of carbonyl groups in the carbonate bridge, which decreases with increasing pressure.

The results of IR spectroscopy as a whole are consistent with the results of the surface investigation by the XPS method, which also show the destruction of some functional groups of the polymer and the formation of others (figure 3 and Table 2). The concentration of functional groups on the polymer surface is determined by the ratio of the rates of their formation and destruction. It was shown earlier [4] that in the interaction of an oxygen-containing plasma with polymers, the main active plasma factor reacting with the sample is O(\(^{3}\)P) oxygen atoms. These particles initiate the polymer plasmolysis process, which, like the thermal oxidative degradation process, is radical-chain. The fluxes of O(\(^{3}\)P) atoms to the polymer surface in the oxygen plasma are almost three times higher than in the air plasma. This leads, on the one hand, to a higher rate of rupture of the initial bonds in the polymer and the formation of free radicals. On the other hand, these radicals in the oxygen plasma with higher reaction rates with atoms and oxygen molecules, forming both oxygen-containing groups existing in the sample, and new ones. As a result, under the influence of oxygen plasma, the concentration of the carbonyl groups of the carbonate bridge with respect to the initial sample decreases to a lesser degree than in the air plasma. The concentration of newly formed groups in the oxygen plasma as a whole is
also higher. As a result, the degree of oxidation of the polymer surface under the action of oxygen plasma is greater than in the air plasma.

![Diagrams of X-ray photoelectron spectroscopy spectra](image)

**Figure 3.** X-ray photoelectron spectroscopy spectra of C\(_1\)s for untreated (a), air-treated (b) and oxygen-treated (c) polycarbonate. The gas pressure is 100 Pa.

**Table 2.** Change in the composition of the surface of polycarbonate after treatment in air and oxygen plasma

| Sample             | Concentration of main groups, % | Concentration of atoms, % |
|--------------------|---------------------------------|---------------------------|
|                    | \(\pi - \pi^*\) | C-C/ C-H | C-O-C | C=O | O-C=O | CO\(_3\) | COOH | C   | O   |
| Untreated          | 0,5                                            | 75,3          | 15,7  | 4,3  | 4,2   | 0       | 0    | 81,50 | 18,50 |
| Air plasma         | 0,2                                            | 70,9          | 24,7  | 4,2  | 3,1   | 0,1    | 0    | 82,60 | 17,40 |
| Oxygen plasma      | 0                                               | 65            | 23,4  | 1,8  | 1,6   | 1,8    | 6,4  | 76,20 | 23,80 |

Different character of the absorbance dependences (concentration of functional groups) on the gas pressure at the modification of polycarbonate in an oxygen plasma and air, and also different ratio of concentrations of carbonyl groups in various groupings suggests that, despite the similarity of mechanisms plasma-oxidative degradation of the polymer in an oxygen plasma, the common stage of initiation of the radical chain process, the further development of the chain in the oxygen and air plasma can proceed with various ways.

An increase in the content of polar functional groups on the surface of the polymer as a result of the action of plasma leads to an increase in the polar component of the surface energy and an improvement in the wetting of the sample.

Treatment in plasma leads not only to a change in the chemical composition, but also to the micro relief of the surface layer of the polymer (figure 4). Surface study by the AFM method showed that the average roughness increases from 3.36 nm for the original sample to 19.85 nm and 6.06 nm when exposed to oxygen and air plasma, respectively. A similar situation is observed in [7]. More significant changes in the topology of the surface under the action of oxygen plasma are due to higher polymer etching rates compared to air plasma. An increase in the surface roughness, as well as its oxidation, leads to a decrease in the contact angle of wetting.
Figure 4. Images of the surface of polycarbonate obtained by atomic force microscopy: (a) - an untreated sample, (b) - processed in air plasma, (c) - processed in oxygen plasma. The gas pressure is 100 Pa.

4. Conclusion
Treatment of polycarbonate in the oxidizing plasma leads to a change in morphology (average roughness increases), an increase in the surface energy, and the concentration of oxygen-containing groups (hydroxyl groups, carbonyl groups in ketones or aldehydes and in oxyketones) on the surface of the polymer. Similarity of mechanisms plasma-oxidative degradation of the polycarbonate in an oxygen and air plasma, the common stage of initiation of the radical chain process, the further development of the chain in the oxygen and air plasma can proceed with various ways.

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