

# Surface modification of polycarbonate (bisphenol A) by low pressure rf plasma

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Effects of low pressure radio frequency (rf) plasma treatment on the surface properties of polycarbonate are presented in this paper. Results obtained from the surface energy measurement after different conditions of treatment are compared. After treatment the surface free energy increased from the original value of 35 mJ/m<sup>2</sup> to 63-74 mJ/m<sup>2</sup>. X-ray photoelectron spectroscopy measurements showed an increase in oxygen to carbon ratio after the treatment indicating an increase of oxygen-containing functional groups on the polycarbonate surface. A study of the stability of the modified surface property has been made on the basis of surface free energy. To study the improvement of adhesion between the polycarbonate and thin coatings, organosilicon thin films were deposited on the untreated and plasma treated polycarbonate. The adhesion of film to substrate was quantitatively analysed by 'cross-hatch peel test'.

**Key words:** Polycarbonate, surface modification, rf plasma, ageing, surface energy

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## Introduction

Polymers have been applied successfully in fields such as adhesion, biomaterials, protective coatings, friction and wear-resistant composites, microelectronic devices and thin film technology. Polymeric materials have been able to replace traditional engineering materials like metals and glass because of their high strength to weight ratio, resistance to corrosion, possibility of recycling and their relatively low cost. However, the low surface energy of polymers and resulting poor adhesion of additional coatings have also created numerous important technical challenges which have to be overcome by manufacturers (Michael et al. 1999). Polycarbonates (PCs) are synthetic polymers with a very wide field of applications due to their excellent breakage resistance, good transparency, low inflammability and good workability.

In recent years, polycarbonate has become a very attractive business article. The world production of PC increases every year by 8-10% and nowadays it is more than 1.35 million tonnes/year (Mapleston 1999). The most important types are the PCs based on bisphenol A (business labels Diflon<sup>®</sup>, Macrolon<sup>®</sup>, Lexan<sup>®</sup>, and so on). PCs can be used for plastic vessels and machine parts; optical grades can be used for compact discs (CDs, CD-ROMs and DVDs), optical fibres, etc. But the low hardness, low scratch resistance and degradation by UV radiation require modification of surface properties by means of additional coating.

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 the polymers without altering the 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, ion beams, and other types of radiation (Pasco and Everest 1978). Mechanical treatment alone has limited effectiveness, and

chemical treatments with solvents, oxidants such as chromates and permanganates, strong acids or bases, and sodium-liquid ammonia treatments for fluoropolymers are becoming increasingly unacceptable because of environmental and safety considerations. Furthermore, wet chemical treatments tend to entail inherent problems of uniformity and reproducibility. 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.

In general, the surface modification techniques can be divided into three categories: (i) cleaning and etching by removal of material from the surface; (ii) surface reactions producing functional groups and cross linking (these entail little or no removal or addition of material); and (iii) deposition of thin films on the surface (Yasuda et al. 1990, d'Agostino et al. 1990). An important objective of any such treatment is to remove loosely bonded surface contamination, thus providing intimate contact between interacting materials on the molecular scale.

This paper discusses the surface modification of PCs utilising a low pressure rf glow discharge produced in argon, oxygen and ammonia gases. However, detailed study of the modified surface has been undertaken after argon and oxygen plasma treatment only. The modified surface has been characterised by measuring the contact angles and calculating the surface free energy. The changes in chemical composition have been studied by X-ray photoelectron spectroscopy. The results of adhesion test are also presented.

## Materials and methods

Plasma treatment and film deposition

The major part of the research work consists of plasma treatment and film deposition performed at the plasma chemical laboratory of Masaryk University, Czech Republic. Plasma treatments were carried out in rf capacitively coupled glow discharge. The bisphenol

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A PC samples of sizes 50 by 60 mm<sup>2</sup> were cleaned in isopropyl alcohol and dried before inserting into the reactor. The samples were placed on the powered bottom electrode, which was capacitively coupled to the rf generator PG 501 working at the frequency of 13.56 MHz. The effect of treatment time and rf power on the wettability of PC was investigated. The rf power was varied from 100 to 400 W, and the DC negative self bias voltage varied from -10 to -270 V depending on the rf power and the pressure inside the reactor. The gas flow was controlled by electronic massflow controller. All the treatments were carried out in flow regime. The reactor chamber was pumped by a diffusion pump backed by a rotary pump.

The SiO<sub>2</sub> films were deposited from the hexamethyldisiloxane/oxygen (HMDSO/O<sub>2</sub>) feeds 4 hours after the treatment in argon discharge (Q<sub>Ar</sub> = 5.7 sccm, p = 1.5 Pa, P = 100 W, U<sub>bias</sub> = -35 V, t = 5 min). The gases were fed into the reactor through the showerhead electrode to ensure uniform deposition. The distance between the electrodes was 55 mm. For film deposition, 4 sccm of HMDSO was diluted with two different oxygen flow rates, namely 45 sccm and 10 sccm. The rf powers were 100 and 400 W respectively.

TABLE 1. Surface free energy and its polar and dispersion components of water and glycerine used to determine the surface energy of PC

Liquid	Total surface energy (mJ/m <sup>2</sup> )	Polar component (mJ/m <sup>2</sup> )	Dispersion component (mJ/m <sup>2</sup> )
Water	72.8	51	21.8
Glycerine	63.4	29.7	33.6

Source: Correia et al. 1997

TABLE 2. Atomic concentration 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 gas flow rate 5.7 sccm

Gas	Power(W)	Atomic concentration (%)			
		C	O	Si	N
Untreated	-	84.3	15.7	0	0
Ar	100	76.4	20.3	0.4	2.2
O <sub>2</sub>	100	74.0	24	0.4	1.7

TABLE 3. Results of adhesion measurements of silica films deposited on PC after an argon plasma treatment carried out at different rf powers and treatment times

Gas	Power (W)	Treatment time (min)	Film thickness (nm)	Adhesion (%)
Untreated	-	-	490	10
Ar	100	5	459	90
Ar	400	5	545	96
Ar	100	10	472	94
Ar	400	10	523	99

### Surface characterisation

Over the years a large number of techniques have been developed to probe the different aspects of the physics and chemistry of surfaces; however, only a few have found wide application in basic surface science and applied surface analysis. Among these methods, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy are used to study the surface chemical composition. Similarly, scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to investigate the surface morphology of the material at the atomic scale. These methods require relatively expensive equipments, skilled technicians and quite sophisticated techniques to interpret the data. A good understanding of the surface properties of a solid may be obtained relatively inexpensively from the measurement of the surface free energy. Therefore contact angle measurement has been used in the study of surface free energy, wettability and adhesion of low surface energy materials. The surface free energy of a solid is an important parameter, playing a vital role in the phenomena that occur at solid-liquid and solid-gas interfaces. Hence, knowledge of this parameter is useful in studies of adsorption and wettability processes which play important role in many industrial applications of the material (Zimon 1974, Leja 1982). Measurement of contact angle of liquid with the solid surface permits a rapid and qualitative evaluation of surface free energy of polymers. In the present paper, analysis of the surface free energy of PCs has been made on the basis of dispersive and non-dispersive components. Surface free energy ( $\gamma_s$ ) and its polar ( $\gamma_s^p$ ) and dispersion ( $\gamma_s^d$ ) components of the sample were determined from two sets of contact angles (water and glycerine) according to Owens-Wendt-Kaelble equation (Owens and Wendt 1969).

$$\gamma_l(1 + \cos\theta) = 2[\gamma_l^d \gamma_s^d]^{\frac{1}{2}} + 2[\gamma_l^p \gamma_s^p]^{\frac{1}{2}}$$

where,  $\gamma_l$ ,  $\gamma_l^p$  and  $\gamma_l^d$  are the total surface free energy, the polar component and the dispersion component of the surface free energy of the liquid, respectively. The values of the surface free energies of the test liquids obtained from the literature are given in Table 1.

The changes in the chemical composition of the samples after the plasma treatments were analysed by XPS measurements. The measurements were carried out on an ultra-high-vacuum (lower than 10<sup>-8</sup> mm Hg) surface analytical system equipped with Omicron EA 125 hemispherical analyser working in multi-channel detection regime. The analyser was operated in the retarding field mode using pass energy of 20 eV. MgK $\alpha$  was used for excitation. The electron take-off angle was 90° and the analysed area 6 mm in diameter. Standard fitting procedure was used to determine the core level-peak position and spectral intensities. The charging was evaluated and corrected after the fitting of the C1s signal from the position of C-H peak, which is characterised by binding energy of 284.6 ± 0.2 eV.

The improvement made by the argon plasma treatment in the adhesive property of PC to thin coating of silica was studied using the cross-hatch peel test method. SiO<sub>2</sub> films of about half mm thickness were deposited by plasma enhanced chemical vapour deposition (PECVD) on the untreated and plasma treated PC. The deposited films were cut into 384 2.5 by 2.5 mm<sup>2</sup>; adhesive tape (3M No. 369) was then applied to the film and pulled swiftly. The numbers of the squares adhering to the PC was counted and the ratio of the adhering film area to the total area of the film under the applied tape was determined. The percentage adhesion of the films after different conditions of argon plasma pre-treatment was determined.

Results and discussion

Surface free energy measurement

The values of surface free energy and its components before and after the treatment in argon, oxygen and ammonia plasmas are compared in **Figure 1**. The surface energy corresponds to the contact angles measured within 10 min of the plasma treatment. It shows that all three types of treatment can produce significant increase in the surface free energy. The treatment carried out in argon and oxygen plasma resulted a higher value of total surface energy compared to ammonia plasma. Argon plasma treatment produces purely physical surface modification; no new functional groups are incorporated on the polymer surface. The direct and radiative energy transfer processes cause the surface modification in all types of inert gas plasma treatments. The direct energy transfer corresponds to the ion bombardment of the surface, which is particularly important in the case of the 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 (Chan et al. 1996). The exposure of the sample to the argon discharge is sufficient to break chemical bonds (C-C, C-H), leaving free radicals at or near the surface. These radicals can react only with other surface radicals or by chain-transfer reactions. If the polymer chain is flexible, or if the radicals can migrate along it, then recombination, unsaturation, branching, or cross-linking can occur. Moreover, the plasma removes low molecular weight species or converts them to high molecular weight species by crosslinking reactions. In summation, the argon plasma treatment causes the crosslinking of the PC surface as well as the sputtering of the material.

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 polymer wettability. In general, two processes may occur simultaneously during the oxygen plasma treatment: (i) etching of the polymer surface through the reactions of atomic oxygen with the surface carbon atoms, yielding volatile products, and (ii) the formation of oxygen functional groups at the polymer surface through reactions between the active species from the plasma and the surface atoms. Hence, for oxygen plasma, the reactive oxygen atoms play an important role in the surface modification of the sample.

The mechanism of surface modification in the case of ammonia plasma treatment is somewhat similar to that of oxygen plasma. Ammonia plasma treatment incorporates hydrophilic functional groups such as amine (N-H), imine (N=C), nitrile (N≡C) and amide (N-C=O) on the surface of PC. Moreover, the additional oxygen functional groups can be incorporated after the ammonia plasma treatment because free radicals created on the surface react with oxygen when the surface is exposed to the atmosphere (Hudis 1974).

For untreated PC the values of polar and dispersion components of surface free energies are almost the same. But there is a substantial increase in the polar component after all treatments, whereas no any remarkable change in the dispersion component was observed. The ratio of polar component to the total surface free energy is also regarded as the polarity of the material. An important information obtained from the surface energy measurement is that the polar component increases, corresponding to the formation of covalent bonds. The formation of covalent bonds plays an important role in adhesion at the interface.

XPS Analysis

Further information about the changes induced by argon and oxygen plasma treatment was obtained from the XPS measurements. The atomic compositions of the PC surface before and after the treatment are compared (**Table 2**). The treatments

produced a decrease in the carbon concentration on the PC surface. On the other hand the oxygen content increased and a small amount of silicon and nitrogen appeared. The impurity of the silicon is caused by the fact that the reactor was also used for the deposition of silicon oxides. Although, before the PC treatment experiments the reactor was cleaned mechanically as well as in argon and oxygen discharges there was probably still some residual silica that appeared on the PC surface. 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.

Adhesion measurement

The percentage adhesion of the SiO<sub>2</sub> films deposited on PC with and without pre-treatment is presented in **Table 3**. A significant improvement in the relative adhesivity of the film to substrate is achieved by argon plasma treatment made before deposition of the film. A five-minute argon plasma treatment was sufficient to increase the relative adhesivity from 10% to as high as 96%. The argon plasma pre-treatments were made with two different rf

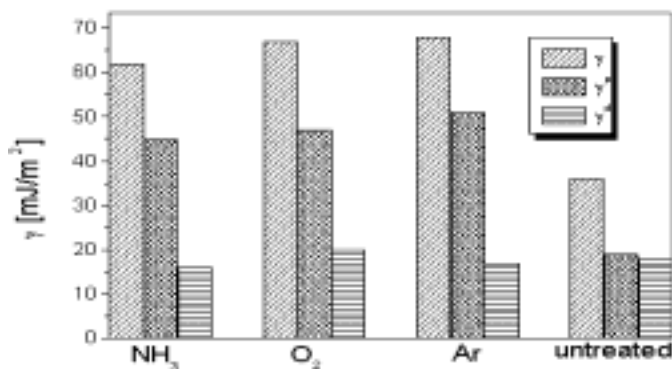


FIGURE1. Comparison of surface free energy and its components before and after the treatment in Ar, NH<sub>3</sub> and O<sub>2</sub> discharges. The domain represents the types of the sample. The treatment conditions were P = 100W, Q = 52 sccm, p= 36.5 Pa, and exposure time t = 10 min. The bias voltages U<sub>bias</sub> were -20, -25, -30 V for ammonia, oxygen and argon discharges respectively.

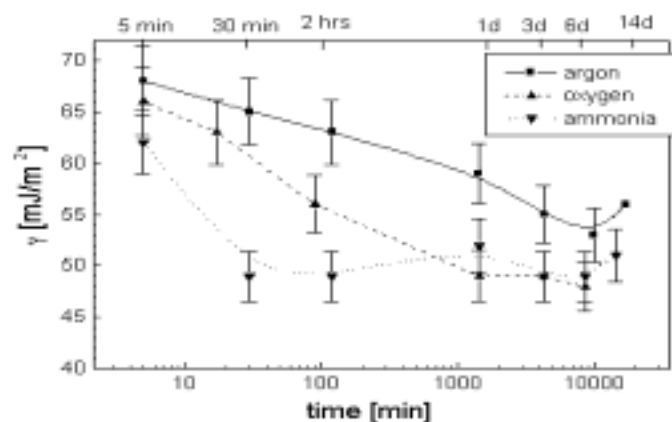


FIGURE 2. Ageing of surface free energy of PC after treatment in Ar, NH<sub>3</sub> and O<sub>2</sub> plasmas. The treatment conditions were P =100 W, U<sub>bias</sub> = -25 V, Q = 52 sccm, p = 36.5 Pa. and treatment time t = 10 min. The bars in the graph correspond to standard deviation.

powers and treatment time in order to observe the influence of these parameters on the adhesivity. However, the difference in the results for the treatments at different rf powers and with different treatment times was within the limit of experimental error.

The adhesion or bondability between polymer surfaces and other materials deposited onto them can often be related to wettability as determined from the contact angle measurements. Plasma treatment can improve adhesion to polymers via surface cleaning, cross-linking, or formation of chemical bonds. The increased adhesivity produced by argon plasma treatment is well supported by our contact angle measurements. From these we observed that argon plasma treatment under the conditions as used before the film deposition produces significant increase in wettability of PC, which can be correlated with the increased adhesivity. A previous study of the adhesivity of SiO<sub>2</sub> film to PC has reported that a Si-O-C bond must be formed in order to produce the strong adhesivity of the film to the substrate. The unsaturated bonds opened by the treatment in argon plasma can help the formation of such bond and hence increase the adhesion.

A scratch test performed on PC showed that SiO<sub>2</sub> films deposited without pre-treatment were almost completely delaminated from the surface, whereas there was negligible delamination of the film deposited on PC after argon plasma pre-treatment. The characteristics of thin SiO<sub>2</sub> films deposited on PC by PECVD have also been discussed in our previous paper (Zajickova et al. 2001).

We also studied the dependence of the surface free energy of the sample on time after treatment. For that purpose, surface energy of PC was measured for several days after the treatment in Ar, O<sub>2</sub> and NH<sub>3</sub> plasma by storing the samples in a dust-free environment. The results are shown in **Figure 2**. It indicates that the most stable modification of PC surface was produced by argon plasma treatment. On the other hand, ammonia plasma resulted in the least stable modification of the surface.

This effect, commonly known as 'ageing', is important from the point of view of industrial application. It has been reported that ageing is due to (i) thermodynamically driven reorientation of polar species away from the surface to the subsurface, (ii) diffusion of mobile additives from the polymer bulk to the surface, and (iii) the reaction of residual free radicals with the ambient (Spell and Christenson 1979). The more stable surface free energy after argon plasma treatment is due to the cross-linking effect. The uses of cross-linking process via inert gas plasma treatments to obtain better surface properties are discussed in detail elsewhere (Michael

et al. 1999, Sheu et al. 1992, Vallon et al. 1996). The result clearly indicates the different effects of treatment in inert and reactive plasmas.

### Conclusion

The effects of argon, oxygen and ammonia plasma treatments on PC are discussed in the paper. The result of surface energy measurement and its dependence on time after treatment are summarised. All types of treatment resulted an appreciable increase in the wettability of the sample. However, the improved wettability decreased with time. Results of XPS analysis revealed an increase in O/C ratio of the sample after the treatment. The peel tape test showed that a significant improvement in adhesivity of deposited protective film to PC can be achieved by performing a treatment of the sample before the deposition of the film. ■

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