RF PLASMA TREATMENT OF POLYCARBONATE SUBSTRATES✤

S. Kitova*, M. Minchev, G. Danev

Central Laboratory of Photoprocesses "Acad. J .Malinowski", Bulgarian Academy
of Sciences, Acad. G. Bonchev str., bl.109, 1113 Sofia, Bulgaria

The effect of Ar, Ar/C_2H_5OH, O_2 and Ar/O_2 RF (13.56 MHz) plasma treatments on surface free energy and morphology, optical properties and adhesion of polycarbonate (PC) substrates has been studied. Changes in the surface properties were followed as a function of the plasma treatment time. The polar and dispersion components of the polymer free surface energy were determined on the basis of the theory of Owens, Wendt, Kaelble and Uy. It was found that all RF plasma treatments led to an increase in the polar component of PC, mainly due to an increased hydrogen bonding ability. The increase in surface free energy reached its maximum at short plasma treatment with 3:1 gas mixture of Ar/O_2. This treatment also led to pronounced improvement of the adhesion of thin SiO_2 films plasma deposited on modified PC substrates, while the treatments with pure oxygen or Ar/ethanol plasma had negative effect on the adhesion.

1. Introduction

In recent years organic polymers are frequently able to replace traditional engineering materials such as metals, glasses and ceramics because of their many desirable physical and chemical characteristics [1]. Polycarbonate is well known commercially available optical polymer used in a variety of optical applications due to its combination of chemical stability, optical and mechanical properties. However, its desirable bulk properties are compromised by its unfavourable surface characteristics, such as low hardness, low resistance to abrasion and scratching, and low surface energy, which generally leads to low wettability and poor adhesion of the films deposited directly on it [1, 2].

Over the years several methods have been developed to modify polymer surfaces for improved wettability, adhesion, etc. [3-12]. They include mechanical or wet chemical treatment, exposure to flames, corona discharges and glow discharge plasmas. Modification of polymer surface by plasma treatment, both corona and low pressure glow discharge presents many important advantages and overcomes the drawbacks of the other process mentioned above. Corona discharge is the longest established and most widely used in plasma process [4]. It has the advantage of operating at atmosphere pressure, the reagent gas usually being ambient air. However, this circumstance is important limitation for the chemical effects achievable with reagent gases other than air. These restrictions are largely absent in the case of low pressure glow discharge treatment (for review see [3]). In a low pressure (<1Torr) high frequency (>1 MHz) discharge the heavy particles (gas molecules and ions) are essentially at ambient temperature (~ 0.025 eV), while the electrons have enough kinetic energy (several eV) to break covalent bonds, even to cause further ionization. The chemically reactive species and energetic photons generated by the discharge can participate in homogeneous or heterogeneous reactions with solid surface in contact with the plasma. Since this

type of plasma treatment takes place at near-ambient temperature, it is very appropriate for thermally sensitive materials as polymers [3].

Plasma surface modification of polymers is very efficient method for adhesion enhancement due to combination of plasma induced effects involving surface cleaning, ablation, cross-linking and surface chemical functionalization [3-6]. The effect of plasma treatment depends on a variety of parameters such as the kind of plasma (DC, radio frequency (RF) or microwave (MW)), the discharge power density, the pressure and flow rate of the gas or gas mixture, as well as the treatment time [3, 7- 9].

It has been found that noble gas plasmas (e.g. He or Ar) are effective in creating free radicals, but do not add new chemical functionalities from the gas phase [3]. Typically, a reactive plasma (H_2O or O_2) is used to add a polar functional group (hydroxyl, carboxyl, ether, carbonyl etc.), which can dramatically increase the surface free energy of the polymer [3, 9, 10]. In our previous paper we have shown that the introduction of ethanol in Ar plasma gas leads also to pronounced increase in the polar component of free surface energy of PMMA and PC substrates, but at the same time results in more uniform, defect free and undamaged, polymer surfaces (especially for PMMA) compared to those modified with pure Ar or Ar/water plasma gas [13].

In the present paper we compare the effects of RF plasma treatments of Ar and Ar/C_2H_5OH with those of O_2 and gas mixtures with different ratio of Ar/O_2 on the free surface energy, the morphology and the optical properties of polycarbonate substrates. The influence of plasma treatments on the adhesion of thin SiO_2 films, plasma deposited on the modified PC substrates is also studied.

2. Experimental details

2.1. Plasma treatment

All samples of commercial PC substrates of optical quality, used widely in polymer optics were carefully cleaned before plasma treatment. The cleaning procedure first involved washing with a 1% detergent solution and then with deionised water in an ultrasonic cleaner. The gas plasma was excited by a 13.56 MHz RF generator in a GENUS 8720 plasma enhanced chemical vapour deposition facility at constant power of 1000W and total gas pressure of 150 mTorr. During treatment, the substrates were exposed to plasma gases of pure Ar and O_2, Ar/O_2 gas mixture with ratio of 3:1, 1:1 and 1:3 and Ar/ethanol. Argon was bubbled through ethanol at room temperature, thus saturating the inert gas with alcohol vapours. The plasma treatment time was varied between 1 and 30 min.

SiO_2 films with thickness of about 150 nm were plasma deposited at rate of 0.25 nm s^{-1} by an oxidation of hexamethyldisilazane in the same vacuum cycle immediately after plasma treating.

The transmittance (T) and specular reflectance ® of the samples were measured at normal light incidence in the spectral range λ=350-800 nm by a Cary 5E spectrophotometer with an accuracy of 0.5%.

Scanning electron microscopy (SEM) was applied for characterising the surface morphology of the modified PC substrates.

2.2. Determination of free surface energy

Owens and Wendt [14], and independently Kaelble and Uy [15] proved that the total surface energy of a solid, γ_s, can be expressed as the sum of contributions from dispersion γ_s^d and polar γ_s^p force components. These can be determined from the contact angle (θ) data of polar and non-polar liquids with known dispersion γ_{lv}^d and polar γ_{lv}^p parts of their surface energy, via the equation

$$\gamma_{lv}(1 + \cos\theta) = 2\sqrt{\gamma_s^d \gamma_{lv}^d} + 2\sqrt{\gamma_s^p \gamma_{lv}^p} \tag{1}$$

In our study, the contact angles of bidistilled water and methylene iodide were measured by the sessile drop method proposed by Bickerman [16], described in details in our previous paper [13].

2.3. Adhesion measurement

Adhesion of SiO$_2$ films on PC substrates was evaluated by cutting an "X" mark on the films with angle of 30°. An adhesive tape (3M Scotch Magic Type 810) was carefully adhered to the surface of the film on room temperature. After adhesion for 1 min, the tape was pulled off rapidly back upon itself at about an angle of 180°. The peeling of the film at the X-cut area was then observed by optical microscope. Adhesion scale according to ASTM D3359-97 is following [17]: 5A – no peeling or removal occurs at all; 4A – trace peeling or removal along incisions; 3A - – jagged removal along incisions occurs up to 1.6 mm; 2A – jagged removal along incisions occurs up to 3.2 mm; 1A – most of the area of the X under the tape is removed; 0A - removal of the film beyond the area of X ocurrs.

3. Results and discussion

The higher water contact angle indicates the lower polar part of the free surface energy of the solids. The water contact angle on untreated PC substrates is 88° and the corresponding polar component of surface energy has very low value of 1.2 mJ m^{-2}, which clearly points out the hydrophobic nature of PC substrates. The changes in polar γ_s^p and dispersion γ_s^d parts of the surface energy of PC, determined on the basis of the contact angle data, after Ar, Ar/C$_2$H$_5$OH, O$_2$ and Ar/O$_2$ plasma treatments are shown in Fig. 1. As seen the polar component is altered significantly after all RF plasma treatments. γ_s^p increases rapidly for the first 1 min and then remains almost constant. The exception of this tendency is observed only for plasma gas mixture Ar/O$_2$ = 1:3. For this gas mixture and pure oxygen is obtained the relatively smallest increase in γ_s^p. The increasing of Ar content in the Ar/O$_2$ mixture to the ratio of 3:1 leads to the relatively greatest enhancement of the polar component of the free surface energy which indicates the most hydrophilic and wettable surface. The results obtained show that in contrast to the polar component, the dispersion component decreases slightly after all plasma gases treatments.
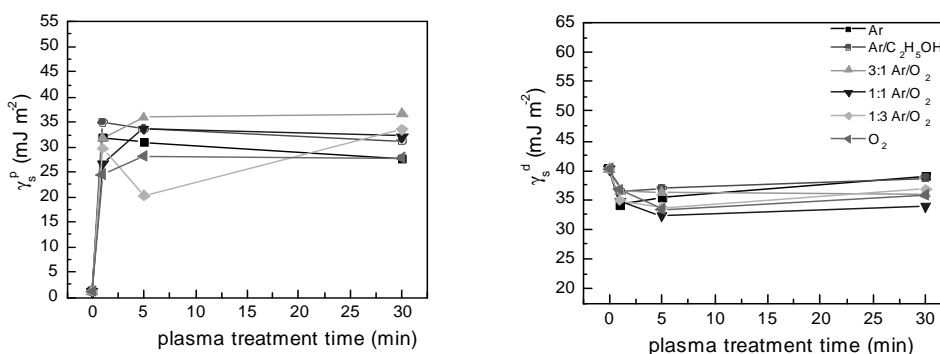

Fig. 1. The polar γ_s^p and dispersion γ_s^d components in free surface energy of PC treated in Ar, Ar/C$_2$H$_5$OH,, O$_2$ and Ar/O$_2$ plasma vs treatment time.

The polar force component arises from the orientation of permanent electric dipoles, which includes dipole-dipole interactions, dipole-induced dipole interactions, hydrogen bonds, π-bonds, charge transfer interactions, etc [14, 15]. From the results, it is apparent that the surface free energy (γ_s) of the modified polymer surfaces increases after all RF plasma treatments due to the increase in the polar character of the surface after modifications. This result indicates that a large incorporation of hydrophilic character capable of hydrogen bonding is added to polycarbonate surface simultaneously with the completely removing the organic contaminants. Dispersion forces, on the other hand, are related to the internal electron motions, independent of the dipole moments [14, 15]. Thus, the incorporation of hydrophilic character capable of hydrogen bonding to a polycarbonate surface should not have much effect on γ_s^d, which is consistent with the results obtained.

It is well known that the wettability of a polymer surface is affected by the surface morphology, especially surface roughness [3]. We performed SEM study to examine the changes in surface morphology induced by the RF plasma treatment. Fig. 2 shows SEM micrographs of PC substrates, plasma treated for 5 min. It is seen some enhancement of surface roughness after treating with pure oxygen and Ar/O$_2$ gas mixture with ratio 1:3, while the other gases used leads to negligible damage in treated surfaces. Therefore, the great drop in water contact angle obtained for all RF treatment is more dependent on polar component in surface free energy rather than surface roughness. It was found, however, that the further increase in plasma treatment time resulted in etched surfaces with signs of patchiness or inhomogeneities. It should be noted that the last effect is the least expressed on surfaces treated with Ar/ethanol plasma.
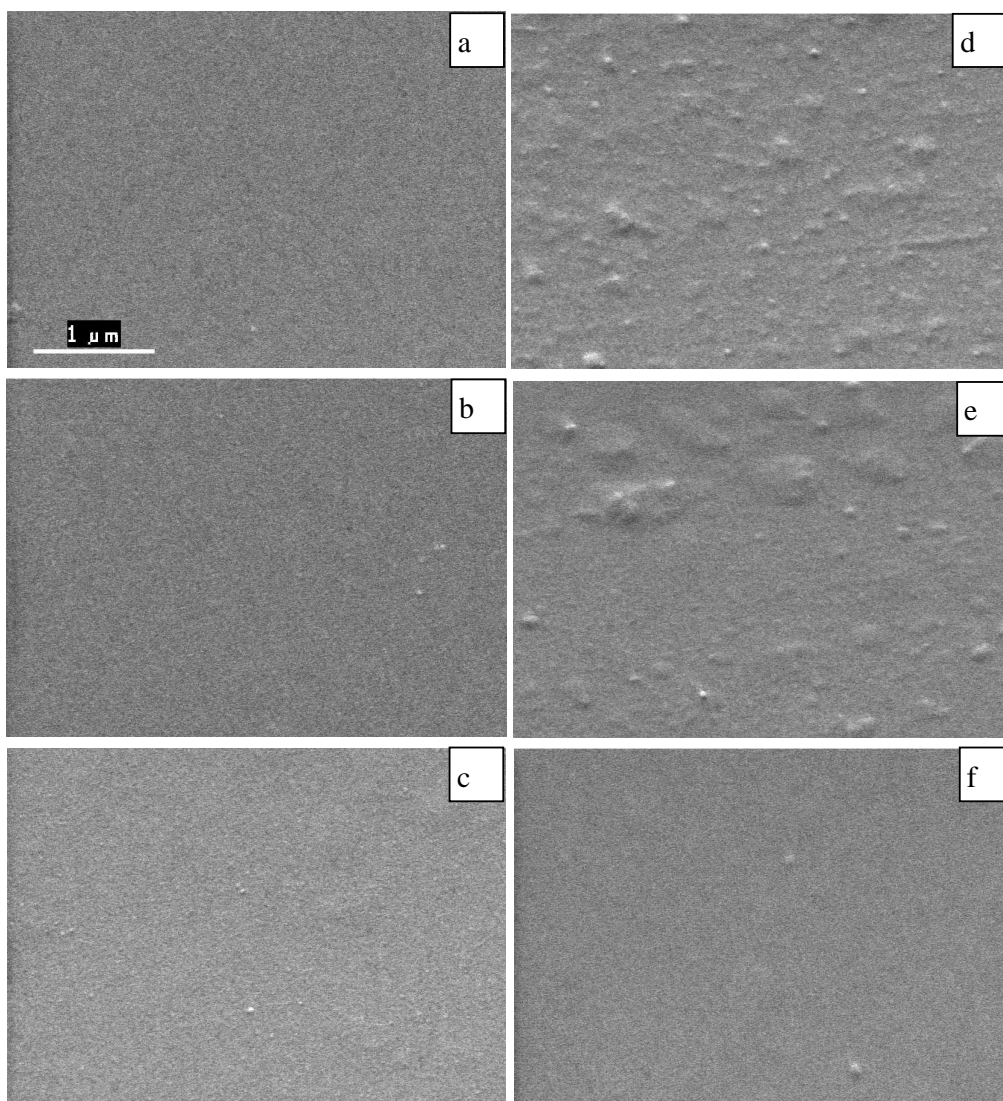
Fig. 2. SEM micrographs of polycarbonate surfaces: untreated (a) and treated for 5 min in plasma of Ar (b); Ar/C$_2$H$_5$OH (c); O$_2$ (d); 1:3 Ar/ O$_2$ mixture (e); 3:1 Ar/ O$_2$ mixture (f).

The spectral transmittance and reflectance of the plasma treated PC substrates are given in Fig. 3. As a rule shortly (up to 5 min.) plasma treated surfaces retain their optical properties.
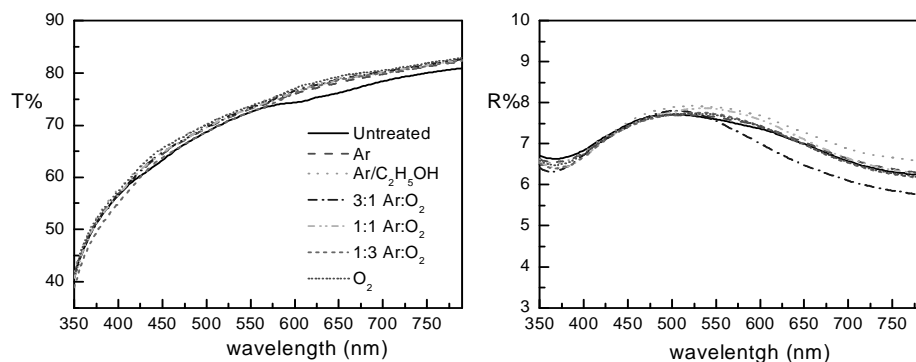
Fig. 3. Spectral transmission (T) and reflectance (R) of PC substrates, plasma treated with indicated gases for 5 min.

The effects of various plasma treatments on the adhesion of thin SiO_2 film were also studied. In order to avoid the deactivation of the cleaned and modified polymer surface by air contaminations, SiO_2 films were plasma deposited in the same vacuum cycle straightaway after plasma treating. The results from the adhesion test are given in Table 1. It is seen that the most effective in improving film adhesion is Ar/O_2 gas mixture with ratio of 3:1, while the pure oxygen plasma has negative effect on the adhesion. With properties similar but not as strong as the 3:1 Ar/O_2 gas mixture, the pure Ar plasma is the second effective one. The introduction of ethanol in Ar plasma gas reduces pronouncedly the adhesion.

Table 1. Adhesion of 150 nm thick SiO_2 films deposited on PC substrates, plasma treated for 5 min with different gases.

Plasma treatment with:	Adhesion
untreated	2A
Ar	3A
Ar/C_2H_2OH	1A
3:1 Ar/O_2	5A
1:1 Ar/O_2	2A
1:3 Ar/O_2	0A
O_2	0A

These results are unexpected and surprising from the point of view of the surface roughness and enhanced surface energy of PC, obtained after all RF plasma treatments. Obviously, the adhesion depends strongly on the type of polar functional groups attached to the plasma modified PC surface. It has been generally observed that plasma deposited films, as SiO_2 films in our case, exhibit adhesion to polymers superior to that of the evaporated or sputtered films [18]. The adhesion improvement was related to the formation of an interfacial region between the underlying polymer and the film. There is strong evidence that upon plasma deposition the interphase contains a cross-linked region followed by a region over which the film is covalently bonded to polymer substrate [3, 18]. Formation of such an interphase may be attributed to the synergistic effects on the polymer surface of charged particles, energetic photons and chemically species generated in the plasma environment during plasma treatment and during initial stage of the film growth. The effects of all these factors depend strongly on the distinct experimental conditions used. Obviously more detailed investigation is necessary to explain the results obtained. Additional insight into the mechanism of

adhesion may be obtained by XPS analysis of the SiO_2/PC interface region, which will be an object of our next study.

4. Conclusion

On the basis of contact angle data it is shown that the surface free energy of the polycarbonate surface increases after all RF plasma treatments. This is attributed to the increase in the polar character of the polymer surface after all modifications. This polar character is mainly due to increased hydrogen bonding ability, which reaches its maximum after short plasma treating with 3:1 Ar/O_2 gas mixture. This treatment also leads to the pronounced improvement of the adhesion to the PC substrates, while treatments with pure oxygen or Ar/ethanol have negative effect on the adhesion. As a rule, all shortly RF plasma treated PC surfaces preserve their optical properties.

References

[1] C. Harper, Handbook of Plastics, Elastomers and Composites, 2nd Ed. McGraw-Hill, New York, 1992.
[2] K. Guenter, Proc. SPIE **896**, 134 (1988).
[3] E. Liston, L. Martinu, M. Wertheimer, J. Adhesion Sci. Technol. **7**, 1091 (1993).
[4] M.Goldman, A.Goldman, R.Sigmund, Pure Appl.Chem. **57**, 1353 (1985).
[5] A. Hollander, M. Wertheimer, J. Vac. Sci. Technol. A **12**, 879 (1994).
[6] D. Clark, A. Dirks, J. Polym. Sci., **15,** 2321 (1997).
[7] S. Dahl, D. Rats, J. von Stebut, L. Martinu, J. Klemberg-Sapiela, Thin Solid Films **355-356**, 290 (1999).
[8] U. Schulz, P. Munzert, N. Kaiser, Surf. Coat. Technol. **142-144**, 507 (2001).
[9] C. Rastpmjee, M. Keil, H. Sotobayashi, A. Bradshaw, C. Lamont, D. Gador, E. Umbach, Appl. Surf. Sci. **136**, 280 (1998).
[10] T. Hook, J. Gardella, L. Salvati, J. Mater. Res., **2**, 11 (1987).
[11] H.Ichijima, T. Okado, Y. Uyama, Y. Ikada, Macromol. Chem. **19**2, 1213 (1991).
[12] Y. Lian, K. Leu, S. Liao, W. Tsai, Surf. Coat. Thechnol. **71**, 142 (1995).
[13] S. Kitova, M. Minchev, G. Danev, J. Optoelectron. Adv. Mater. **7**, 249 (2005).
[14] D. Owens, R. Wendt, J. Appl. Polym. Sci. **13,** 1741 (1969).
[15] D. Kaelble, K. Uy, J. Adhesion **2**, 50 (1970).
[16] R. Johnson and R. Dettre, in Surface and Colloid Science, Ed. E. Matijevic, Vol.2 Ch.2, Wiley-Interscience, 1969.
[17] Standart Methods for Measuring Adhesion by Tape Test, ASTM Designatation D 3359-83 668.
[18] A. Bergeron, J. Klemberg-Sapieha and L. Martinu, J. Vac. Sci. Technol. **A16**, 3227 (1998).