

**STUDY OF ARGON PLASMA TREATMENT OF POLYCARBONATE SUBSTRATE
AND ITS EFFECT ON FILM DEPOSITION****L. Zajíčková^{1*}, D. P. Subedi*, V. Buršíková*, K. Veltruská[†]****Department of Physical Electronics, Masaryk University, Kotlářská 2,
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Results of polycarbonate plasma treatment in argon r.f. glow discharges as concern the chemical structure and surface free energy are presented. The oxygen-to-carbon ratio increased after the treatment indicating an increase of oxygen containing functional groups on the polycarbonate surface. Small amount of silicon as a result of previous depositions of organosilicon thin films in the same reactor and small amount of nitrogen coming probably from an exposure of the reactive surface to the atmosphere were found on the surface. The surface free energy increased after the treatment from the original value of 35 mJ/m² to 63–74 mJ/m². Effect of treatment time, gas flow rate, pressure and aging on the surface free energy was studied too. In order to study an improvement of adhesion between the polycarbonate and an additional coatings the organosilicon thin films were deposited on the untreated and plasma treated polycarbonate. The interfacial fracture resistance of such a system was qualitatively tested by “cross-hatch peel test”. The initiation and propagation stage of the fracture were studied by depth sensing indentation method followed by an observation of the samples with an optical microscope.

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1 Introduction

Polycarbonate (PC) belongs to synthetic polymers with very wide field of applications due to its excellent breakage resistance, good transparency, low inflammability and good workability. On the other hand, the low hardness, low scratch resistance and degradation by ultraviolet radiation require to modify the surface properties by an additional coating. In this case, except properties of the coating, the key parameter of the technology is a good adhesion between the coating and the PC. Therefore it is important to study a treatment of the PC with intentions of cleaning, removal of loosely bonded surface layer, creation of new functional groups and cross-linking [1, 2]. As many of other polymers the PC has very low surface energy [3] and therefore the adhesion of any top layer is poor. The most accepted model for adhesion improvement consists in the existence of an “interphase” defined as a region intermediate to two contacting solids that is distinct in structure and properties from either of the phases [4]. According to this model a bulk polymer

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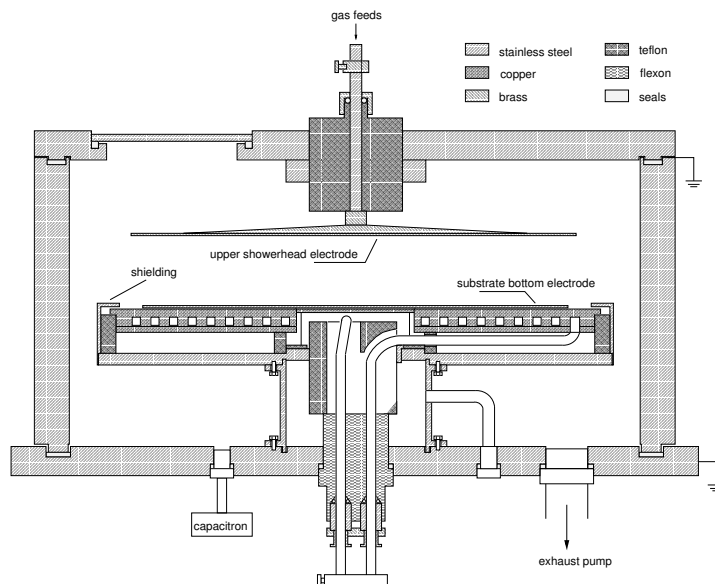


Fig. 1. Detailed drawing of the plasma reactor used in our experiment.

has a crosslinked layer on the surface followed by a region over which the film is covalently bonded to the polymeric substrate [5–7]. Here, we studied an effect of argon plasma treatment on the surface free energy and based on our previous results [8] we compared mechanical properties of the untreated and plasma treated PC coated by two different $\text{SiO}_x\text{C}_y\text{H}_z$ films.

2 Experimental

2.1 Plasma treatment and deposition

The bisphenol A polycarbonate specimens (Lexan and Marlon FS types) were investigated before and after the plasma treatment in argon discharge. Moreover, the system of protective $\text{SiO}_x\text{C}_y\text{H}_z$ films deposited on untreated and plasma treated polycarbonate (PC) was studied as concern its mechanical properties.

The PC samples were cleaned in isopropyl alcohol and dried before inserting into the reactor. Plasma treatment and deposition were carried out in r.f. capacitively coupled glow discharges. The reactor chamber consisted of a stainless steel cylinder, 490 mm in inner diameter and 246 mm in height, closed by two stainless steel flanges. PC samples were placed on the bottom electrode, 20 mm in thickness and 420 mm in diameter, powered by an r.f. generator working at the frequency of 13.56 MHz. Due to an asymmetric capacitive coupling of the bottom electrode and different mobility of electrons and ions there was a superimposed negative dc self-bias U_{bias} on this electrode. The detail drawing of the reactor is in Fig. 1.

Two different upper electrodes were used during the experiments. If not explicitly men-

tioned other way the upper grounded electrode was removed and the upper stainless steel flange served as the grounded electrode in the experiments dealing solely with the plasma treatment. In this case argon was fed into the chamber through a central opening in the upper flange and the distance between the r.f. driven and grounded electrodes was 110 mm. The flow rate of argon Q_{Ar} changed from 9.5 to 86×10^{-3} Pa.m³/s (5.7–52 sccm). The pressure p in the reactor varied from 1.5 to 36.5 Pa independently of the flow rate. The r.f. power P was kept constant at 100 W which corresponded to different dc self-biases -115 and -35 V for the pressure of 1.5 and 36.5 Pa, respectively. Treatment time t varied from 1 to 25 min.

In all cases of the plasma treatment followed by the film deposition, the upper grounded electrode was a showerhead made of brass. SiO_xC_yH_z films were deposited from the hexamethyldisiloxane/oxygen (HMDSO/O₂) feeds 4 hours after the treatment in argon discharge ($Q_{Ar} = 9.5 \times 10^{-3}$ Pa.m³/s = 5.7 sccm, $p = 1.5$ Pa, $P = 100$ W, $U_{bias} = -35$ V, $t = 5$ min). The gases were fed into the reactor through the showerhead electrode to ensure a deposition uniformity. The distance between the electrodes was 55 mm. For deposition 6.7×10^{-3} Pa.m³/s (4 sccm) of HMDSO was diluted in two different O₂ flow rates, namely 75 and 17×10^{-3} Pa.m³/s (45 and 10 sccm). R.f. powers were 100 and 400 W, respectively.

2.2 Contact angle and surface free energy

The wettability has been investigated by measuring the contact angle of the untreated and plasma treated PC with water and glycerine. The experimental arrangement for contact angle measurement is shown in Fig. 2. It consists of a laser fitted coaxially with a holder of samples and a protractor screen. The height of the table holder can be adjusted for the samples of different thicknesses so that the laser beam can pass parallel to the sample surface. Small drops of water and glycerine are made on the sample surface by means of a syringe with a fine needle. Then we can observe on the protractor screen the diffraction of the laser beam falling on the sample-liquid boundary as sketched by dashed lines in the bottom of Fig. 2. The angle between two diffraction lines, which is measured with the protractor, corresponds to the contact angle. The average contact angle was calculated from the measurements on at least 3 drops of liquid placed on different parts of the sample, each drop measured two times at diametrically opposite sides.

The surface free energy of the PC specimens was determined from the contact angles of water and glycerine with the PC surface using Owens-Wendt-Kaelble two-liquid method (OWK) [9–11]:

$$\gamma_i(1 + \cos \theta_i) = 2(\gamma_i^d \gamma^d)^{1/2} + 2(\gamma_i^p \gamma^p)^{1/2} \quad (1)$$

where γ_i^d and γ_i^p are dispersion and polar components of the surface free energy of the probe liquid i , respectively and γ^d , γ^p are dispersion and polar components of the surface free energy of the solid, respectively. The total surface free energy of the liquid i is γ_{li} and the contact angle between the sample and the liquid is θ_i . The polar and dispersion components for water and glycerine were obtained from Ref. [12].

2.3 Depth-sensing indentation test

The Fischerscope H100 depth sensing indentation tester equipped with Vickers indenter was used to study the mechanical properties of the system composed of the SiO_xC_yH_z film on the

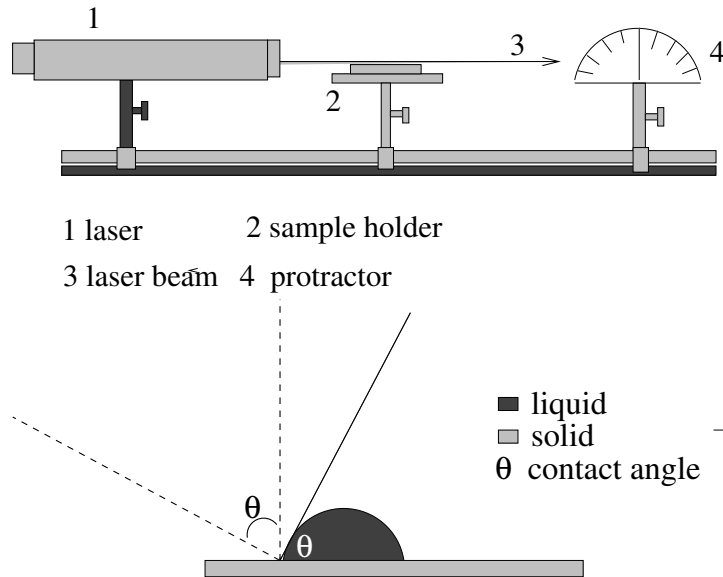


Fig. 2. Experimental arrangement for measurements of the contact angle (top). The contact angle is the angle between the solid line and the sample surface (bottom). In laser beam technique, angle between two diffraction lines (dashed) is measured which corresponds to the contact angle.

PC substrate. The universal hardness HU is defined as

$$HU = \frac{L_{\max}}{A_c} = \frac{L_{\max}}{26.43h_{\max}^2} \quad (2)$$

where A_c is the contact area between the indenter and the studied material at a maximum load L_{\max} . The constant 26.43 contains the Vickers indenter geometry if a maximum indentation depth h_{\max} instead of A_c is used. The universal hardness gives an information about the resistance of the material to both, elastic or plastic deformations. However, one can find in the literature rather plastic hardness that is a measure of the material resistance against plastic deformation only.

Since polymers like the PC exhibit at room temperatures significant creep, i.e., time dependent plastic deformation we studied also the resistance of $\text{SiO}_x\text{C}_y\text{H}_z$ coated PC specimens against the creep deformation keeping for certain time interval $(t-t_0)$ the maximum load constant and recording changes of the indentation depth. Then the indentation creep strain is expressed as follows:

$$Cr = \frac{h(t) - h(t_0)}{h(t_0)} \cdot 100\% \quad (3)$$

where $h(t_0)$ and $h(t)$ are the indentation depths at the beginning and the end of the creep test, respectively.

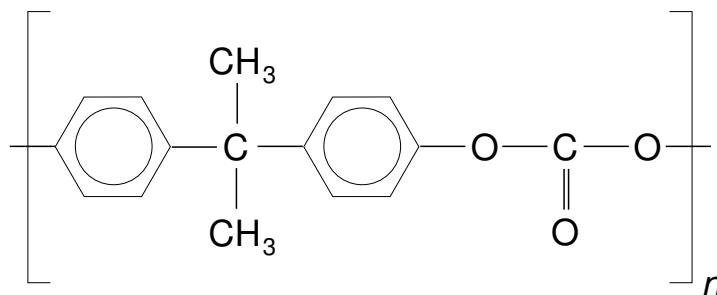


Fig. 3. Chemical structure of polycarbonate (PC).

On the basis of the depth sensing indentation tests it was possible to study also an interfacial strength of the thin film-substrate system [13] using a critical load (critical indentation depth) at which an interfacial crack (decohesion) initiates. The initiation of the interfacial fracture appears as a jump on the loading curve but it may be detected during the creep test too. Moreover, in case of the transparent thin film we can observe also the area of a decohesion around the indentation print after removal of the indenter. Loading above the critical value causes further grow and initiation of the interfacial cracks allowing to study a propagation stage of fracture by a microscope. The fracture resistance of the film-substrate interface was qualitatively studied with a “cross-hatch peel test”. Within this method we cut the deposited film into small squares of size $2.5 \times 2.5 \text{ mm}^2$, sealed an adhesive tape (3M No. 369) to the film and removed it swiftly. Then we counted the number of squares removed from the polycarbonate and determined the ratio of the adhered film area to the total area of the film under the applied tape (percentage of adhesivity).

3 Results and Discussion

3.1 XPS characterisation of PC surfaces

Information about changes induced by argon plasma treatment was obtained by X-ray photoelectron spectroscopy (XPS) that was able to investigate signals from all atoms except hydrogen. The atomic composition of the PC surface before and after the treatment are compared in Table 1. The carbon and oxygen percentages calculated according to the chemical structure of PC (see Fig. 3) without taking into account hydrogen are 84.2 % and 15.8 %, respectively.

This agrees very well with the XPS experimental results. Compared to the original surface composition the treatment caused a decrease in the carbon and increase in the oxygen content on the PC surface. Moreover, a small amount of silicon and nitrogen appeared. The impurity of the silicon was caused by the fact that the same reactor was previously used for deposition of silicon oxides. Although the reactor was cleaned before the PC treatment experiments mechanically as well as in argon and oxygen discharges there was probably still a rest of silica resulting in small impurity of silicon on the PC surface. The nitrogen found on the PC surface after the treatment could be incorporated during the plasma treatment as a result of some nitrogen traces in the feed

Tab. 1. Atomic concentration of carbon, oxygen and nitrogen measured by XPS for untreated and plasma treated polycarbonate. Plasma treatment was performed in argon (flow rate 9.5×10^{-3} Pa.m³/s, i. e., 5.7 sccm) for 5 min at the pressure of 1.5 Pa. R.f. power was 100 W.

gas	C [at. %]	O [at %]	Si [at %]	N [at %]
untreated	84.3	15.7	0	0
Ar	76.4	20.3	0.4	2.2

gas as well as after the exposure of the treated surface to the atmosphere.

Fig. 4 shows C1s and O1s XPS spectra of PC before and after the treatment. The carbon atomic signal C1s was deconvoluted generally into five Gauss-Lorentzian profiles corresponding to different chemical states of carbon. The deconvolution and peak assignment were based on the paper of S. Vallon *et al.* [3]. The largest peak (denoted as C1) was attributed to C-C and/or C-H bonds. These are the most abundant bonds in the PC chemical structure but can be the surface contamination too. This peak, that should occur at 285.0 eV, is often utilized for referencing purposes if the shift of the energy scale occurs due to the charging of the insulating specimens [14]. Therefore C1s and O1s atomic signals measured were shifted after the deconvolution by such an energy that the peak C1 was positioned exactly at 285.0 eV. Other carbon peaks observed for untreated PC were C2 at the binding energy 286.6 eV corresponding to C-O (12.1 %), C4 at 290.9 eV assigned to the carbonate peak O-C(=O)-O (5.4 %) and shake-up satellite C5 at 292.1 eV (4.0 %). After the plasma treatment the shake-up satellite (C5) disappeared due to the surface dearomatization and the carbonate peak C4 that is also a finger-print of the original PC structure decreased to 4.1 %. On the other hand, a new peak C3 that can be attributed to a mixture of ketone [C-C(=O)-C] (binding energy at about 288 eV) and ester [C-C(=O)-O] (289 eV) has been found (5.6 %). This peak results from the surface rearrangement of the radicals after breaking the original PC bonds. The percentage of the peak C2 associated with bonds to oxygen increased after the treatment from 12.1 to 26.7 % and contrary the percentage of C-C and/or C-H bonds (peak C1) decreased from 78.6 to 63.5 %. Therefore we can see in agreement with Table 1 that the PC surface was oxidized in the argon plasma. The source of oxygen atoms was the polycarbonate itself and the atmosphere to which the PC sample was exposed after the treatment. In the deconvolution of O1s signal two peaks denoted as O1 (532.6 eV) and O2 (534.0 eV) can be assigned to O=C and O-C bonds, respectively [15]. According to the fit the number of double bonds increased 1.5× after the treatment.

3.2 Effect of treatment time, flow rate and pressure on surface free energy

In case of argon plasma, direct and radiative energy transfer processes cause a pure physical surface modification, i. e., no new functional groups are incorporated onto a polymer surface. The direct energy transfer is connected with an ion bombardment of the surface which is particularly important in the case of the PC specimens placed on the r.f. driven capacitively coupled electrode. Another important factor is vacuum UV (VUV) radiation emitted by the plasma [16]. The exposure to argon plasma is sufficient to break chemical bonds (e. g. C-C, C-H), leaving free

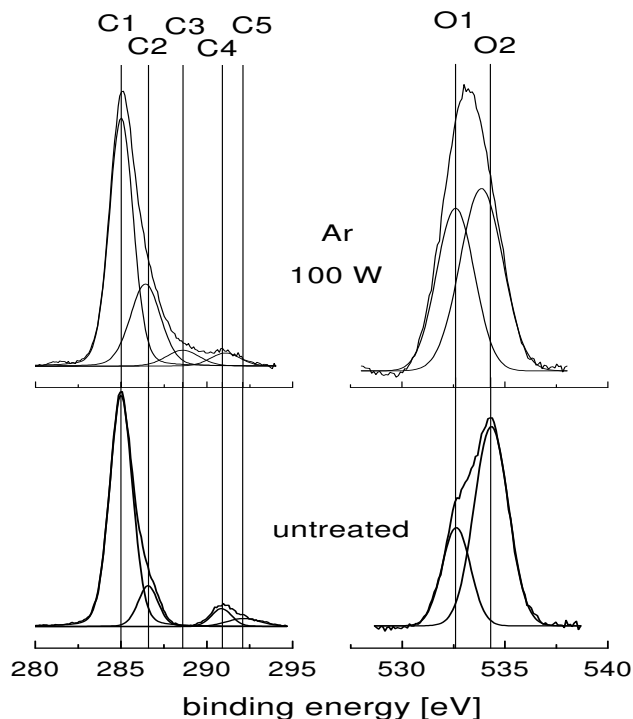


Fig. 4. C1s and O1s XPS spectra of untreated and argon plasma treated. The treatment conditions like r.f. power, flow rate, pressure and treatment time were 100 W, 9.5×10^{-3} Pa.m³/s (5.7 sccm), 1.5 Pa and 5 min, respectively. The measurements were performed 1 day after the treatment.

radicals at or near the surface. These radicals can react only with other surface radicals or by chain-transfer reactions. Therefore they tend to be quite stable [17]. If the polymer chain is flexible, or if the radicals can migrate along it, recombination, unsaturation branching or cross-linking can occur. Moreover, the plasma removes low-molecular-weight materials or converts them to a high-molecular-weight materials by cross-linking reactions. The sputtering of the surface in argon plasma may also increase the surface roughness. Modifications carried out by plasma treatment are confined to the surface of the polymer leaving the bulk properties almost unaffected. The depth of modification is up to tens of nanometers [18]. The cross-linking by activated species of inert gas improves the chemical resistance, barrier property, hardness, optical density, tribological property, cohesive strength of the surface and other surface properties [19, 20].

The PC wettability after the argon plasma treatment at the pressure and r.f. power 1.5 Pa and 100 W, respectively is plotted as a function of the treatment time in Fig. 5. The contact angle decreases rapidly from the original value of 70° to about 30° already after 1 min of the treatment. Fig. 5 shows also the corresponding total surface free energy and its polar and dispersive components. Significant increase in the total surface free energy γ with the treatment time was

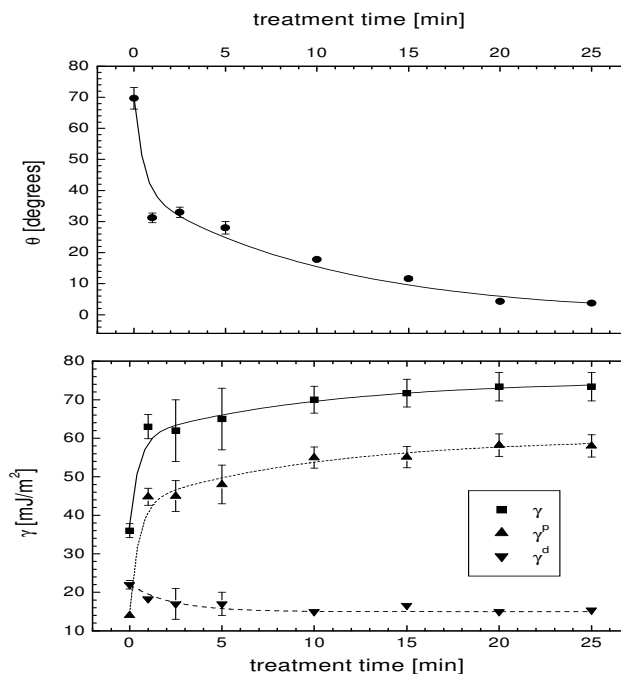


Fig. 5. Dependence of PC wettability on the treatment time in argon plasma: (top) contact angle with water, (bottom) surface free energy. Argon flow rate was 9.5×10^{-3} Pa.m³/s (5.7 sccm), pressure 1.5 Pa and r.f. power 100 W ($U_{\text{bias}} = -85$ V). Measurements were performed 2-5 min after treatment.

observed upto 10 min of the treatment. Since the ion as well as UV radiation doses increase with the treatment time the increase of γ can be caused by a higher level of the surface modification. Moreover, the depth of the modification probably increases. For longer treatment time the surface free energy exhibits a saturation that is a sign of reaching an equilibrium between the surface modification and a removal of the modified surface layer. The sputtering rate as measured by the weighting of PC specimens after 45 min of treatment was 1.6×10^{-8} g cm⁻² s⁻¹, i. e. 80 nm per 10 min. The increase in the total surface free energy corresponds to an increase in its polar component. The dispersive component, on the other hand, is slightly decreasing during the first 5 min and then keeps constant.

An effect of the argon flow rate on the PC wettability for the argon plasma treatment at the constant pressure 36.5 Pa, r.f. power 100 W and treatment time 5 min is shown in Fig. 6. The flow rate is inversely proportional to a residence time of gas in the reactor. As in our experiments the flow rate increased from 9.5 to 86×10^{-3} Pa.m³/s (5.7–52 sccm) the residence time decreased nine times. In case of molecular gases, in which dissociation and subsequent chemical reactions are expected, the residence time can be an important parameter but for argon discharge it is hardly

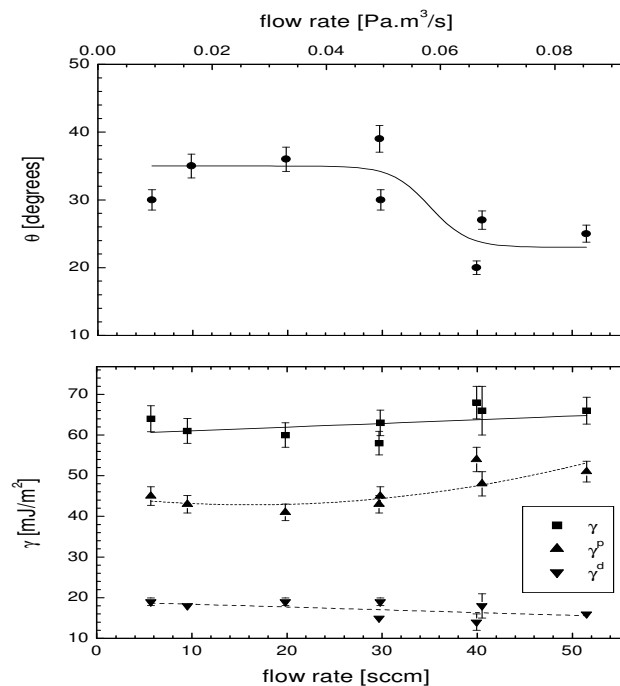


Fig. 6. Effect of argon flow rate on the wettability of polycarbonate: (top) contact angle with water and (bottom) surface free energy. Pressure in reactor was kept constant at 36.5 Pa. Samples were treated for 5 min with r.f. power of 100 W ($U_{\text{bias}} = 25 - 35$ V). Measurements were performed 2-5 min after plasma treatment.

to be of significance. Indeed, we observed only a very weak dependence of the wettability on the flow rate, namely a slight increase of the surface free energy at higher flow rates that is visualised by a linear fit of experimental points. However, this effect is in the range of experimental errors as obvious also from comparison of two extreme flow rates in Table 2.

We measured the surface free energies also after the argon plasma treatment performed with the same argon flow rate of $9.5 \times 10^{-3} \text{ Pa}\cdot\text{m}^3/\text{s}$ (5.7 sccm) but at two different pressures, 1.5 Pa and 36.5 Pa. In this case the residence time at the higher pressure is $24\times$ higher. However, it is not the only parameter that changes with the pressure. The negative dc self-bias U_{bias} that governs the energy of ions bombarding a PC specimen placed on the r.f. driven electrode is influenced by the pressure too [21]. For 36.5 Pa we obtained about 76 V lower self-bias than for 1.5 Pa. Moreover, the collisions in the sheath close to the electrode at 36.5 Pa decrease the energy of bombarding ions in contrast to the pressure of 1.5 Pa at which the sheath is almost collisionless. As the result of both, the higher self-bias and no collisions in the sheath, the energy of ions bombarding the PC specimen is higher at 1.5 Pa than at 36.5 Pa. Although the different

Tab. 2. Comparison of the PC surface free energy γ for different treatment time t , argon flow rate Q_{Ar} and pressure p . R.f. power was 100 W. Measurements were carried out 2–5 min after the treatment. Result with an asterisk was obtained with the upper showerhead electrode.

t [min]	Q_{Ar} [Pa.m ³ /s]	p [Pa]	γ [mJ/m ²]
5	9.5×10^{-3}	1.5	65 ± 8
5	9.5×10^{-3}	36.5	64 ± 3
5	86×10^{-3}	36.5	66 ± 3
10	9.5×10^{-3}	1.5	70 ± 4
10	9.5×10^{-3}	1.5	$71 \pm 1^*$
10	86×10^{-3}	36.5	68 ± 4

pressure changes the residence time as well as the ion energy we did not find a difference of the surface free energy in the range of the experimental errors (see Table 2). From foregoing discussion and Table 2 we can conclude that either the pressure or the flow rate have minor effect on γ and even that there is only slight difference between the treatment time 5 and 10 min.

In the previous experiments all the measurements and values of γ were related to the state of the PC surface just after the plasma treatment, i. e., after 2–5 min. However, the coating processes of the PC surface cannot start immediately after the treatment in some cases and therefore the behavior of the surface free energy with the storage time is important to know. Three different treatment conditions are compared in Fig. 7 from that point of view. The surface free energy γ decreases rapidly during first 2–3 hours of storage at atmosphere indicating a significant decrease in the PC wettability. The absolute values of the slopes are 0.02–0.04 mJ m⁻² min⁻¹ that is by at least one order higher than afterwards. After 6 days of storage (aging time) the surface free energy becomes stabilized at the value 56 ± 6 mJ/m² that is still 1.6× higher than the original value 35 ± 9 mJ/m² for untreated PC. The aging can be attributed, in general, to a mobility of additives or oligomers, mobility of polar species and low molecular weight species and reactivity of residual free radical [22]. Argon plasma treatment increases a cross-linking of the polymer surface and therefore suppresses the mobility of the species on the surface or to the surface. This results in an improved stability of the surface modifications and increased resistance against indentation. Indeed, we observed the increase of the universal hardness of about 11 % for 0.3 μ m depth of indentation.

3.3 Deposition of SiO_xC_yH_z films on plasma-treated PC

In order to study effects of argon plasma treatment on the adhesion of coatings to the PC we prepared SiO_xC_yH_z films which properties have been already determined in Ref. [8]. Such coatings ranged from almost inorganic SiO₂C_{0.2}H_{0.9} films to SiOC_{1.7}H_{6.8} organosilicon polymers by changing the oxygen-to-HMDSO flow rate ratio as well as the r.f. power. Such films can be utilized as coatings protecting the PC against mechanical damages (the hardness of the PC is only 0.2 GPa). According to mechanical testing of large number of different coatings deposited on the PC without any argon plasma pretreatment the deposition conditions could be divided into several regions. If the films are stressed even without an application of the external load they

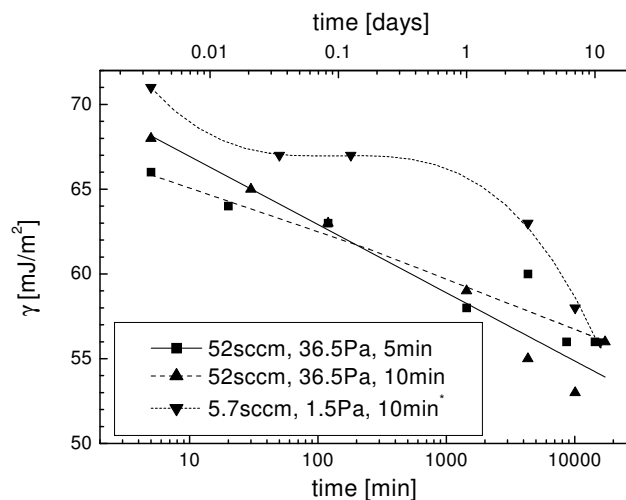


Fig. 7. Aging of PC samples treated in argon discharge at three different conditions. Argon flow rate, pressure and treatment time are given in the figure legend. R.f. power was 100 W. Treatment labeled with asterisk was carried out with showerhead electrode.

exhibit so called internal or residual stress. The internal stresses are sources of many mechanical effects influencing a film quality and applicability as a stable coating. The indentation test introducing into the film locally high stresses added to the existing internal stress can cause a fracture and crack propagation. In case of the tensile internal stress the films have a tendency to crack. The compressive internal stress tends to cause interfacial cracking, especially if the interface has a relatively low toughness. The oxygen-to-HMDSO flow rate ratio influenced significantly the internal stress in the films. For high ratios the internal stress had a tensile character that was converted to a compressive stress when the oxygen flow rate approached zero. With increasing power this tendency was more and more evident. These conclusions are schematically depicted in Fig. 8 for the films thick approximately $1.5 \mu\text{m}$. Films with the hardness 2–4 GPa prepared at powers about 100 W and low flow rate ratios ($Q_{\text{O}_2}/Q_{\text{HMDSO}} < 14$) are suitable for manufacturing of a thick stable film with a good adhesion to PC because their internal stress is almost negligible. Therefore we have chosen this kind of coatings, $0.5 \mu\text{m}$ thick - labeled “Coat1”, to test an improvement of the adhesion after the argon plasma treatment by a peel test. In order to study the adhesion failure in details by the depth sensing indentation method we have chosen other type of coating, $1.2 \mu\text{m}$ thick - labeled “Coat2”, that belongs to highly compressively stressed films. The deposition conditions of both coatings are denoted in Fig. 8 by solid points and given in the experimental section. Both films were deposited 4 hours after the 5 min plasma treatment in argon ($Q_{\text{Ar}} = 9.5 \times 10^{-3} \text{ Pa}\cdot\text{m}^3/\text{s} = 5.7 \text{ sccm}$, $p = 1.5 \text{ Pa}$, $P = 100 \text{ W}$). The summary formula of “Coat1” and “Coat2” films obtained by Rutherford backscattering/elastic recoil analyses were $\text{SiO}_{1.7}\text{C}_{0.5}\text{H}_{2.5}$ and SiO_2CH_4 , respectively [8].

The cross-hatch peel test showed that although the chosen film “Coat1” exhibited a very low internal stress the adhesion could be further improved by the plasma treatment. The percentage

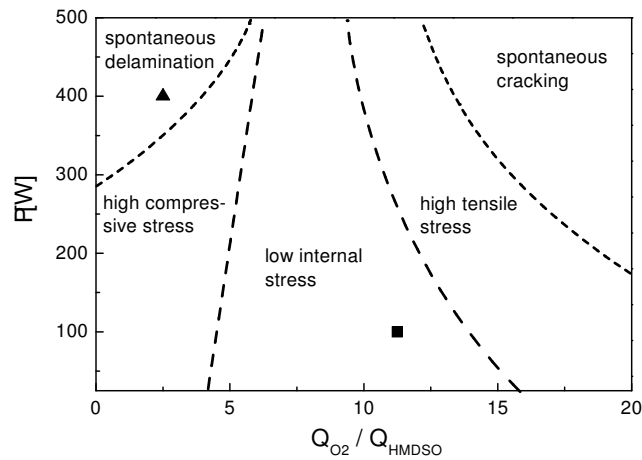


Fig. 8. Schematic representation of the internal stress in the approx $1.5 \mu\text{m}$ thick $\text{SiO}_x\text{C}_y\text{H}_z$ films for different r.f. powers P and oxygen-to-HMDSO flow rate ratios $Q_{\text{O}_2}/Q_{\text{HMDSO}}$. A full square and triangle represent the deposition conditions for “Coat1” and “Coat2”, respectively.

of adhesivity increased from 10 to 90 % after the treatment. In case of film “Coat2” the peel test could not be performed because this coating on the untreated PC peeled off from the substrate spontaneously after the deposition. An optical micrograph of the delaminated film in Fig. 9 demonstrates an effect of the compressive internal stress causing a buckling and debonding of whole large film areas from the substrate. On the other hand the film “Coat2” on the plasma treated PC was quite stable. We observed that the reproducible load-penetration curves without any steps or jumps caused by the crack initiations could be measured upto 6 mN. As an example we depicted several load-penetration curves obtained with the maximum load of 4 mN on the system Coat2-treated PC in Fig. 10. On the load-penetration curves we have studied a creep effect at the maximum load. The interesting creep area is zoomed in the same Fig. 10. Even here we could not observed any cracking of the film. From other indentation test at different maximum load we found statistically that the critical depth for indentation induced crack initiation was $0.82 \pm 0.02 \mu\text{m}$. This result is demonstrated in Fig. 11 by eight load-penetration curves measured upto 7 mN load. It is worth to notice that the critical depth is in 68 % of the total film thickness which shows good protection quality of the coating. Although the film has rather polymeric character it acted as an efficient protection of the PC against the mechanical damages. This is demonstrated by Fig. 12 where the universal hardness of the film-substrate system is compared with that of the uncoated PC. We have to emphasize that the values obtained on the coated PC seem low due to a significant influence of the elasto-plastic deformation of the PC itself. The estimated plastic hardness of the film is approx 6 GPa.

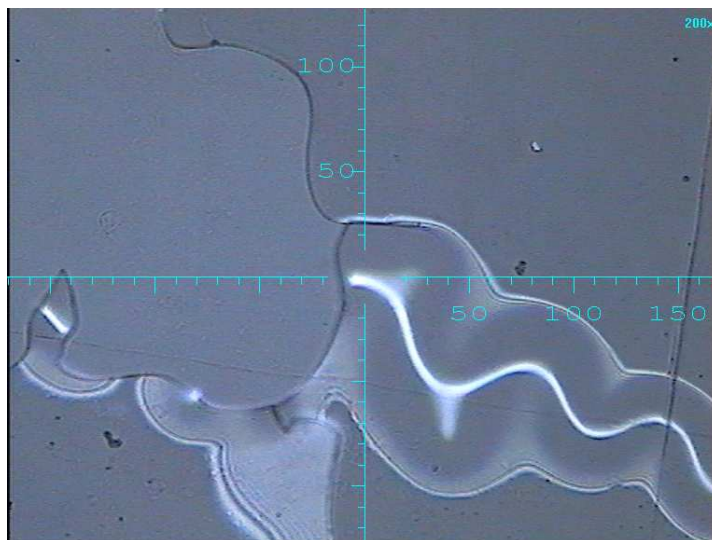


Fig. 9. Effect of high compressive residual stress in the film "Coat2" deposited on the untreated PC.

4 Conclusion

After the argon plasma treatment the XPS signals from the finger-prints of the PC chemical structure, aromatic benzene cores and the carbonate groups, disappeared and decreased, respectively. This means that 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 oxygen-to-carbon ratio increased after the treatment, i. e., an oxidation of the PC surface was induced. The source of oxygen atoms was the polycarbonate itself and the atmosphere to which the PC sample was exposed after the treatment. Small amount of silicon as a result of previous depositions of organosilicon thin films in the same reactor and small amount of nitrogen coming probably from an exposure of the reactive surface to the atmosphere were found on the surface too.

The surface free energy increased after the treatment from the original value of 35 mJ/m^2 to $63\text{--}74 \text{ mJ/m}^2$ depending on the treatment time. A steep increase was observed for the treatment time upto 10 min. For longer treatment duration the changes were almost saturated due to reaching an equilibrium between the surface modification and a removal of the modified surface layer. The residence time and the dc bias did not have a significant influence on the surface free energy. The storage (aging) time was, on the other hand, an important parameter. The surface free energy decreases rapidly during first 2–3 hours of storage at atmosphere indicating a significant decrease in the PC wettability. After 6 days of storage it becomes stabilized at the value $56 \pm 6 \text{ mJ/m}^2$ that is still $1.6\times$ higher than the original value of untreated PC. Argon plasma treatment increased a cross-linking of the polymer surface and therefore suppresses a recovery of the surface to the original state. Indeed, an improved resistance against indentation that is also

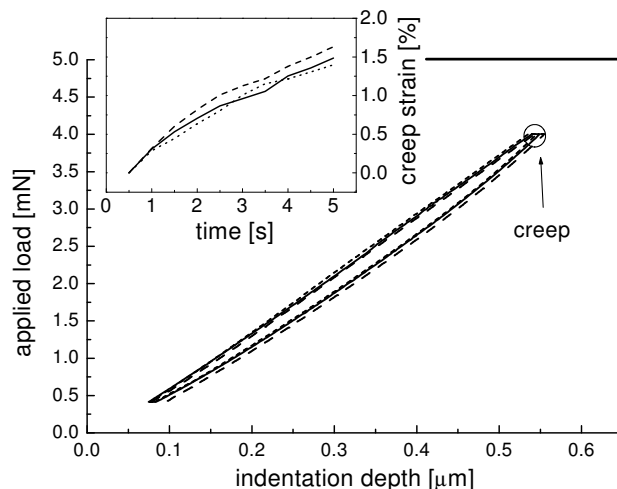


Fig. 10. Load-penetration and creep curves obtained on the system of $\text{SiO}_x\text{C}_y\text{H}_z$ film (Coat2) on argon plasma treated PC with the maximum load of 4 mN. Treatment conditions were $Q_{\text{Ar}} = 9.5 \times 10^{-3} \text{ Pa}\cdot\text{m}^3/\text{s} = 5.7 \text{ sccm}$, $p = 1.5 \text{ Pa}$, $P = 100 \text{ W}$, $t = 5 \text{ min}$. Film deposition ($Q_{\text{HMDSO}} = 6.7 \times 10^{-3} \text{ Pa}\cdot\text{m}^3/\text{s} = 4 \text{ sccm}$, $Q_{\text{O}_2} = 17 \times 10^{-3} \text{ Pa}\cdot\text{m}^3/\text{s} = 10 \text{ sccm}$, $P = 400 \text{ W}$, film thickness $1.2 \mu\text{m}$) was carried out 4 hours after the treatment.

a result of the cross-linking was observed.

Results of the cross-hatch peel test applied to the system of $\text{SiO}_{1.7}\text{C}_{0.5}\text{H}_{2.5}$ on the PC showed that although the chosen film exhibited a very low internal stress the adhesion could be further improved by the plasma treatment. In contrary, the second testing coating, SiO_2CH_4 , was compressively stressed and peeled off spontaneously from the untreated PC just after the deposition. However, when the fracture toughness of the film-polycarbonate interface was improved by the PC treatment the film acted as an efficient protection of the PC against the mechanical damages. The critical depth for indentation induced crack initiation was in this case 68 % of the total film thickness.

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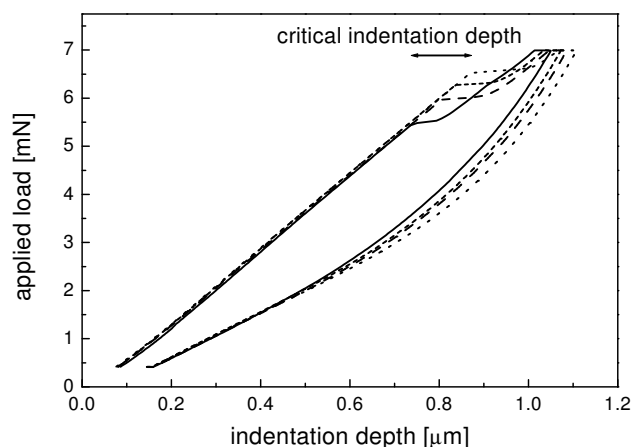


Fig. 11. Load-penetration curves obtained on the same specimen as in Fig. 10 with the maximum load of 7 mN.

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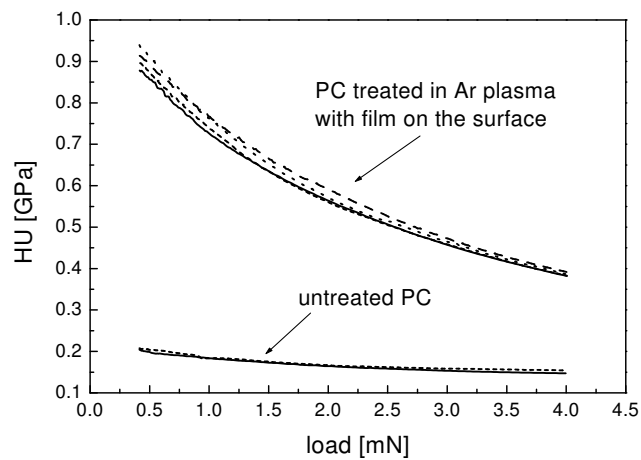


Fig. 12. Comparison of the universal hardness HU of untreated PC and argon plasma treated PC with the $\text{SiO}_x\text{C}_y\text{H}_z$ film (Coat2) on the surface. For conditions of the specimen preparation see caption of Fig. 10.

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