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APPLICATION OF PULSED DISCHARGE FOR DEPOSITION OF ORGANO-SILICON THIN FILMS

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A b s t r a c t. The aim of this work was the investigation of processes, which occurred during plasma treatment of the plastic (PC) surfaces. The plasma was generated from He, O_2 and vapor of tetraethoxysilane (TEOS) or from He, O_2 gas mixture by pulsed dielectric barrier discharge at the atmospheric pressure. Two processes were observed during He/O_2/TEOS plasma treatment: thin film deposition and etching. The surface etching was observed during He/O_2 plasma treatment of PC without TEOS.

K e y w o r d s: barrier discharge, plasma deposition, plasma etching, tetraethoxysilane, polycarbonates.

INTRODUCTION

One of the rapidly emerging plasma technologies is thin film deposition. Typically, the films are deposited from gas phase on various surfaces. Such films can be deposited at the room temperature, which ensures low thermal burden on the substrate. Plasma techniques are ideal for treatment of delicate and heat sensitive materials such as plastics.

In our study we investigated the process of thin films deposition on polycarbonate (PC) taking into account a wide range of its applications. PC have been used in many products, such as windscreens, headlights, lenses and compact discs, because they have very useful properties in the bulk, such as low-density, high elasticity and transparency. However, PC must be coated with organo-silicon thin film, which protects PC substrate against scratching and action of oxygen and solar radiation. Various plasma techniques were investigated for thin film deposition, for example corona discharges, microwave discharges [1,2], dielectric barrier discharges (DBD) [3], atmospheric pressure glow discharges (APG) and pulsed dielectric barrier discharges (PDBD) [4].

In this work, we present the results of PDBD action, being used for treatment of the plastic surface. We investigated two effects, which occurred during plasma treatment, etching and thin film deposition. These effects were observed during deposition of organo-silicon thin films on polycarbonate (PC) substrates in helium-oxygen plasma using PDBD. Vapor of tetraethoxysilane (TEOS) was used as a starting material, being transformed by the discharges into precursors of the organo-silicon films deposited on PC surfaces.

EXPERIMENTAL

The process of thin films deposition was carried out in the apparatus described before [4]. The films were deposited on PC plates, which were characterized by the relative electric permittivity 2.3. In the present work two PC plates were used in each of experiments. The PC plates formed double dielectric barrier on both grounded and high-voltage electrodes. There was a discharge gap, between two PC plates, where discharge was developed and plasma was generated. In the discharge zone chemical reactions were initiated. We observed two processes proceeding at the same time under plasma action: etching of the substrate surface and thin film deposition. Four experimental series were performed:

1. thin film deposition on original PC substrate,
2. original PC plate etching,
3. thin film deposition on PC substrate being etched earlier,
4. etching of PC plate covered with thin film deposited earlier.

The thin films were deposited from mixture of helium, oxygen and vapor of tetraethoxysilane (TEOS) and the process of etching was running without TEOS in the He/O_2 gas mixture. Other experimental parameters are showed in Table 1.

Table 1. Experimental parameters.

Total gas flow rate, L (S.T.P.)/h	100
Pressure, atm.	1
He concentration, % by vol.	95
O_2 concentration, % by vol.	5
Vapor of TEOS concentration, ppm	0-330
Discharge gap, mm	0.2-0.75
Thickness of PC plates, mm	0.75-1.5
Frequency of pulse repetition, Hz	400

TEOS was used as a starting material, which was transformed by PDBD into precursors of the thin films deposited on PC surfaces. PDBD, which was used in our study, was a special form of dielectric barrier discharge. PDBD was characterized by a very high power input of single pulse (to 0.4 MW in peak), which was concentrated at a short time (20 ns). The pulse of discharge was generated by the electric supply system, which was consisted of autotransformer, high-voltage transformer, high-voltage resistor, Blumlein line and spark-gap.

The change of mass of PC plates after plasma treatment was determined gravimetrically using Sartorius BP 221S balance. The roughness of thin films was measured by atomic force microscope (AFM) Nanoscop 1030 Digital Instrument. The electric parameters were recorded using Tektronix TDS 3054 oscilloscope.

RESULTS AND DISCUSSION

It was found that PC plates, used in the experiment, were coated uniformly and remained transparent after deposition of the thin film. The surfaces of deposited films were similar to the surfaces of original PC plates. No wholes were observed on the surfaces after thin film deposition. The surface of films was very smooth and the amplitude of the deflection did not exceed 30 nm.

The deposited films consisted of Si, C, O and H, which were exhibited on EDX spectra and FTIR spectra. FTIR spectra, as showed in our former work [4], exhibited Si-OH, Si-$(CH_3)_x$, Si-O-Si, Si-O-C and other groups. The presence of Si-$(CH_3)_x$ groups indicated that the product of deposition was not pure silica but organo-silica composites.

The changes of mass of PC plates referred to unit of arbitrary defined of PC area (Δm) versus time of plasma treatment (τ) are showed in Figs 1-6. The linear dependence was observed for all experimental series, described by equation $Y=a*X+b$, where $Y=\Delta m$ and $X=\tau$.

In the first series the original PC plates were plasma treated using $He/O_2/TEOS$ gas mixture. The changes of mass of PC plates versus time during this treatment were showed in Figs 1 and 2. The value of a parameter in these equations (Figs 1 and 2) characterizes the deposition rate. The increase of mass of PC plates after plasma treatment was expected in these series, however, as shown in Figs 1 and 2, series (▲), the mass of PC plates decreased during first period of plasma treatment. In other series (■) decrease of mass of PC plates was not observed, but the straight lines, which described these results did not cross the origin of coordinates. This behavior probably was a result of two phenomena occurring on the surface of PC plates during plasma treatment: etching of the substrate surface and thin film deposition. These opposite processes influence the changes of mass of PC plates after $He/O_2/TEOS$ plasma treatment. The etching was faster than film deposition during first minutes and the mass of PC plates was decreasing. After the film was formed on the surface of PC, the etching rate decreased and in this period of time the mass of plates was growing up.

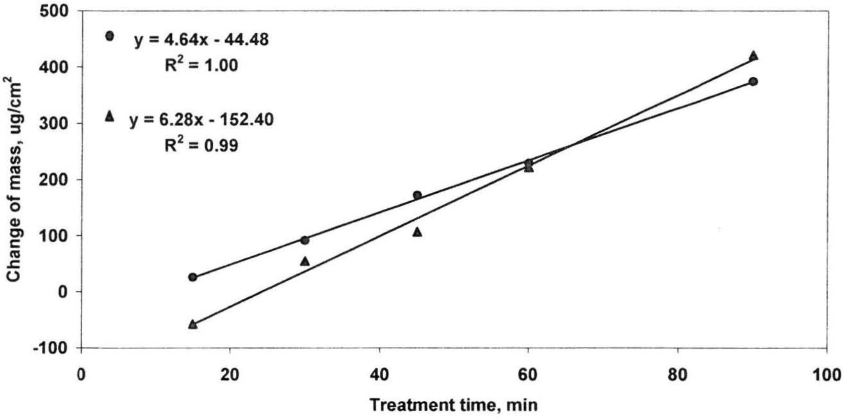

Fig. 1. Variation of the change of mass of PC plates with time of plasma treatment under process conditions of:
PC plates placed at the grounded electrode, discharge gap - 0.2 mm,
discharge power: ● - 0.35MW, ▲ - 0.4MW,
TEOS concentration: ● - 330 ppm, ▲ - 320 ppm,
thickness of PC plates: ● - 0.75 mm, ▲ - 1.5 mm.

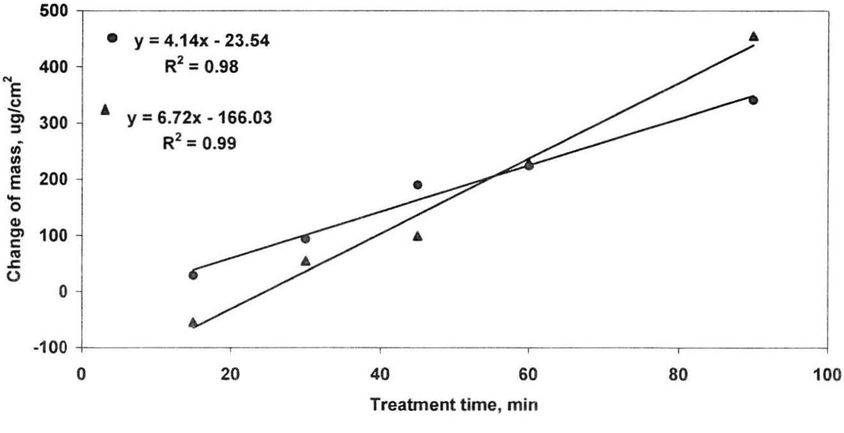

Fig. 2. Variation of the change of mass of PC plates with time of plasma treatment under process conditions of:
PC plates placed at the high-voltage electrode, discharge gap - 0.2 mm,
discharge power: ● - 0.35MW, ▲ - 0.4MW,
TEOS concentration: ● - 330 ppm, ▲ - 320 ppm,
thickness of PC plates: ● - 0.75 mm, ▲ - 1.5 mm.

To verify this hypothesis, the original PC plates and PC plates covered of thin film, was etching in He/O_2 plasma (without TEOS). The results of the change of mass in this process are presented in Figs 3 and 4. The value of *a* parameter in equations characterizes the etching rate. The etching rate of the original PC plates was about two times faster than the etching rate of thin films. The organo-silicon film was more resistant against the discharge action than original PC. The lines, which described process of etching, did not cross the origin of coordinates. This behavior may be also explained - probably at the beginning, some of the pollutants, adsorbed from the ambient atmosphere, were removed from the surface.

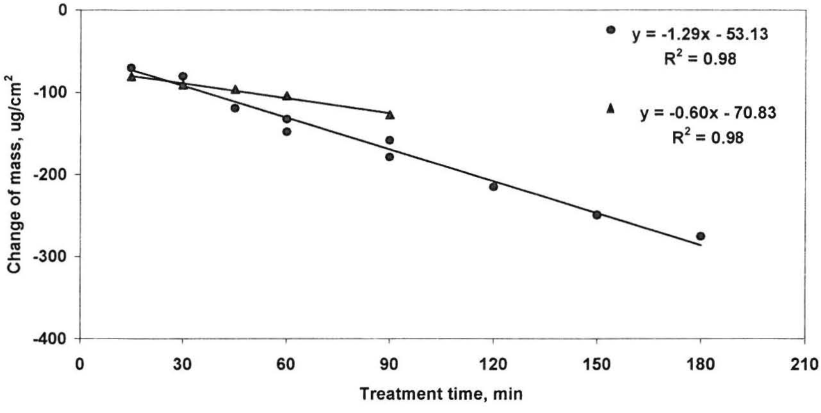

Fig. 3. Variation of change of mass of PC plates with time of plasma etching under process conditions of: PC plates placed at the grounded electrode, discharge gap - 0.75 mm, thickness of PC plates - 0.75 mm, discharge power - 0.25MW, ▲ - PC plates covered of thin film, ● - original PC plates.

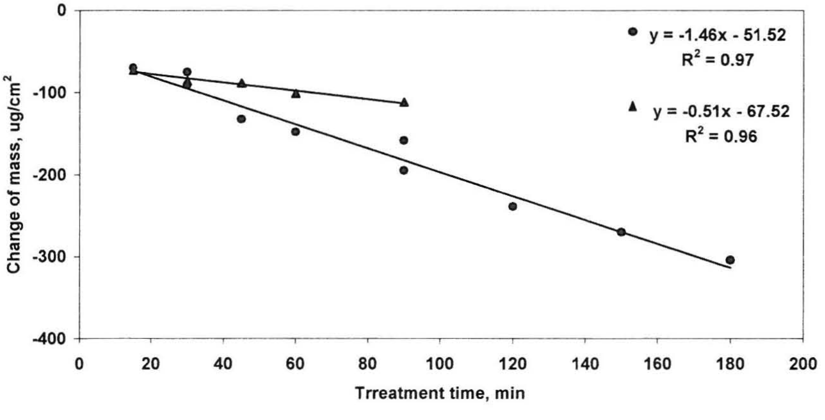

Fig. 4. Variation of change of mass of PC plates with time of plasma etching under process conditions of: PC plates placed at the high-voltage electrode, discharge gap - 0.75 mm, thickness of PC plates - 0.75 mm, discharge power - 0.25MW, ▲ - PC plates covered of thin film, ● - original PC plates.

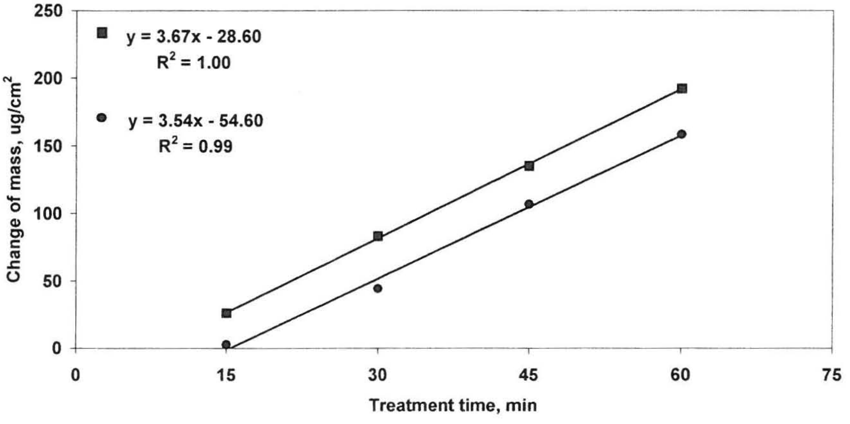

Fig. 5. Variation of the change of mass of PC plates with time of plasma treatment under process conditions of:
PC plates placed at the grounded electrode, discharge gap - 0.75 mm, thickness of PC plates - 0.75 mm, discharge power - 0.25MW, TEOS concentration: ■ - 330 ppm, ● - 270 ppm,
■ - PC plates was activated,
● - original PC plates.

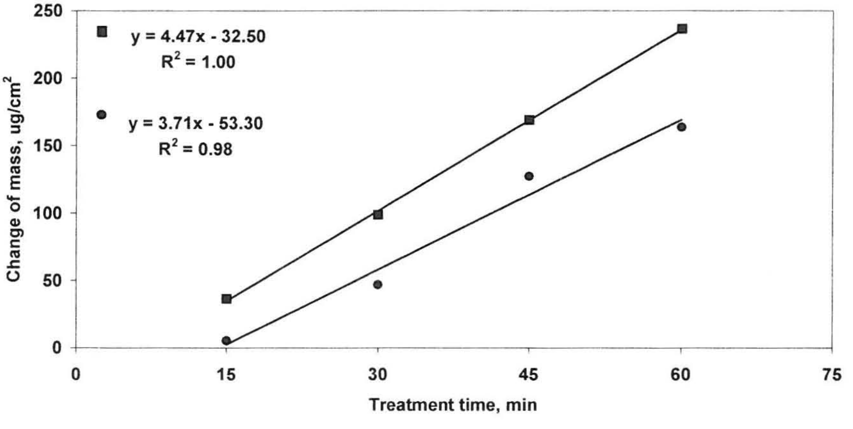

Fig. 6. Variation of the change of mass of PC plates with time of plasma treatment under process conditions of:
PC plates placed at the high-voltage electrode, discharge gap - 0.75 mm, thickness of PC plates - 0.75 mm, discharge power - 0.25MW, TEOS concentration: ■ - 330 ppm, ● - 270 ppm,
■ - PC plates was activated,
● - original PC plates.

To verify this thesis, the original PC plates and plasma activated ones, was treated using He/O_2/TEOS plasma. The changes of mass of PC plates versus time of plasma treatment are shown in Figs 5 and 6. The value of *a* parameter in equations (Figs 5 and 6) characterizes the deposition rate. Unfortunately all the lines did not cross the origin of coordinates, but the value of *b* parameter in equations, which described the process of thin films deposition on the activated surface of PC plates was nearer to zero than the value of *b* in equations, which described this process on the surface of original PC. On other hand, it is clear that the process of PC plasma treatment, during the first period, cannot be described using simple first order equation.

SUMMARY AND CONCLUSIONS

The object of this research was the deposition of organo-silicon thin films on PC plates using pulsed dielectric barrier discharge at the atmospheric pressure. The results of our investigations showed that:

1. Two effects of plasma action was observed during thin film deposition from He/O_2/TEOS gas mixture: etching of the PC substrate and deposition of organo-silicon thin film.
2. The etching of original PC plates was about two times faster than the etching of PC covered with organo-silicon thin film which was more resistant against the action of discharges than original PC.
3. The dependence of mass changes of PC plates on the time of plasma treatment was linear, with the exception of the first period at the beginning of experiment.

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REFERENCES

1. **Hatanaka Y., Sano K., Aoki T., Wróbel A. M.**, Thin Solid Films, 368 (2000) 287-291.
2. **Behnish J., Tyczkowski J., Gazicki M., Pela I., Hollander A., Ledzion R.**, Surf. and Coatings. Technol., 98 (1998) 872-874.
3. **Schmidt-Szałowski K., Rżanek-Boroch Z., Sentek J., Rymuza Z., Kusznierewicz Z., Misiak M.**, Plasmas and Polymers, 5 (2000) 173-190.
4. **Opalińska T., Ulejczyk B., Karpiński L., Schmidt-Szałowski K.**, (2002) 8th Int. Symp. On High Pressure Low. Temperature Plasma Chemistry HAKONE, Pühajärve, pp. 420-424.

ZASTOSOWANIE WYŁADOWANIA IMPULSOWEGO DO OSADZANIA CIENKICH WARSTW KRZEMO-ORGANICZNYCH

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S t r e s z c z e n i e. Celem pracy było badanie procesów, które zachodzą przy plazmowej obróbce powierzchni tworzyw sztucznych. Plazmę generowano z He, O_2 i par tetraetoksysilanu (TEOS) lub z mieszanin He i O_2 w impulsowym wyładowaniu koronowym pod ciśnieniem atmosferycznym. Dwa procesy : osadzanie cienkich warstw i trawienie było obserwowane podczas plazmowej obróbce powierzchni plazmą He/O_2/TEOS. Powierzchniowe trawienie obserwowano przy oddziaływaniu plazmą He/O_2 bez TEOS.

S ł o w a k l u c z o w e: wyładowania barierowe, trawienie plazmowe tetraetoksysilan, poliwęglany.