ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 9, No. 4. 2003

Polyethylene Terephthalate Film Surface Relaxation after Plasma Treatment

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Received 26 September 2003; accepted 29 October 2003

This article describes relaxation processes of the Polyethylene terephthalate (PET) film surface after two different plasma treatment methods. It has been found that after direct plasma treatment the PET film wetting angle returns into its initial value. The change of the wetting angle is related to the structural or chemical changes of the surface under atmospheric conditions. The surface was investigated by XPS (X-ray Photoelectron Spectroscopy) method. During the investigation there has been established that alternating current plasma treatment method induces significant chemical properties changes of PET film surface. These changes can be a reason of residual wetting angle value and slower wetting angle relaxation evolution.

Keywords: polyethyleneterephthalate (PET), XPS, wetting angle, plasma processing.

1. INTRODUCTION

Polyethylene terephthalate (PET) film has been widely used as a substrate material with particular physical properties [1] (e.g. for packing, electrical insulation, photography, magnetic tapes and other fields of visual aids). Thus the PET film adhesion properties have a very great practical importance. Modification of the film surface by plasma treatment gives an opportunity to increase wetting angle and at the same time adhesion properties [2]. PET film adhesion properties, stability and nature of the wetting angle relaxation evolution have an extreme practical importance.

In the current work we have examined PET film surface properties relaxation after two different plasma treatment methods.

2. EXPERIMENTAL

Commercial specimens of PET films of 25 μm thick made by Vladimir Chemical Group of Enterprises was treated by two plasma treatment methods:

(a) direct current plasma (“A”), with total discharge power of about 1.5 kW; pressure of vacuum chamber of about 1.33×10 Pa; operating gas – residual gas of atmospheric pressure; equipment – YBH71P-3; treatment time varied in the range between 1 – 30 seconds.

(b) alternating current plasma (“B”) (13.56 MHz), with gaseous phase O_2 (9 %) + N_2 (10 %); plasma power density – 0.3 W/cm^2; chamber pressure – 1.33 Pa; instrument - “Plasma 600 T”; treatment duration – 1 – 30 seconds.

After plasma treatment the films were kept under usual atmosphere regularly monitoring the changing of the wetting angle. The film wetting angle was determined with deionised water in the equipment with the accuracy of ±5°; drop volume and temperature were being adjusted.

The XPS spectra were recorded using the KRATOS Analytical XSAM spectrometer. The X-ray source with AlK$_\alpha$ ($h\nu = 1486.6$ eV) and MgK$_\alpha$ ($h\nu = 1253.6$ eV) anodes were used. The resolution of the spectrometer was determined according to Au4f 7/2 peaks, the analyzer being in the constant pass energy mode. The C1s and O1s peaks were determined at the pass energy of the analyzer 20 eV. Charge compensation was calculated from C1s spectra for C–C peak at 284.9 eV. Standard fitting procedure made with original XSAM DS800 software.

3. RESULTS AND DISCUSSIONS

The relaxation of the wetting angle after plasma treatment according to the “A” method (direct current plasma) is shown in Fig. 1. Duration of the treatment was 5 and 30 seconds, accordingly. It can be seen from the given curves that after approximately 20 hours the wetting angle increases up to about 35° and remains stable for about 30 hours, and then after 50 – 70 hours the wetting angle returns into its initial value (55 degree).

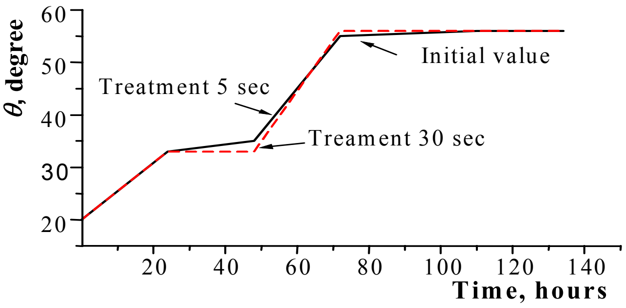

Fig. 1. Change of wetting angles after the “A” plasma treatment

An analysis of the relaxation processes after the treatment according to the “B” method (alternating current plasma) in Fig. 2 shows different relaxation nature. The wetting angle remains stable up to 70 hours, being treated by plasma for 1 second, and then transfer takes place. In case of 5 seconds treatment the relaxation nature changes –

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the wetting angle begins to increase already after 40 hours; however, it has an intermediate value and only after 100 hours reaches initial value. Treating for 30 seconds, the relaxation nature corresponds to the 5 seconds case, except that initial value (55 degree) is not reached.

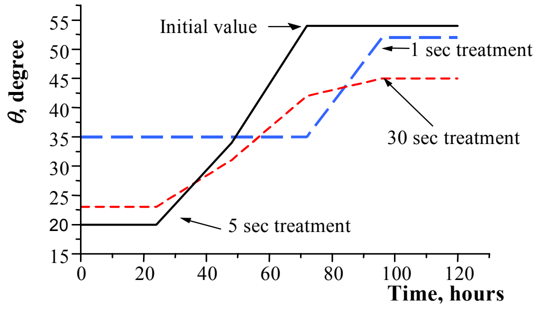

Fig. 2. Change of wetting angle after the "B" plasma treatment

The surface energy after plasma treatment depends on chemical and molecular structure of the surface. Fig. 3 and Fig. 4 illustrate variations of PET film surface chemical structure. Fig. 3a shows XPS C1s spectra of the untreated PET film. The spectrum is composed of six peaks the energy and relative concentration of which partly coincide with those that are given in [1]. The additional C–X peak may be associated with the PET film nature and its contaminants. C1s spectra immediately after treatment according to "A" plasma (wetting angle 20°) are presented in Fig. 3b and in Fig. 3c (after wetting angle relaxation to the initial value). An increase of C=O, C–X and C–O peaks at the expense of the C–C bounds (shown as C1s) and C–H bounds is followed with slight relaxation in Fig. 3c. Significant increase of C=O, C–O and especially O–C=O peaks can be seen in Fig. 3d, immediately after plasma "B" treatment. Almost no relaxation of C–O peak is seen in Fig. 3e. After plasma "B" treatment absence of the C–X peak even after relaxation can be notified.

In Fig. 4a an XPS O1s spectrum of the untreated PET film is represented. It also differs with O–X bond at 535.2 eV energy that not appeared in [1]. After plasma "A" treatment the increase of O–C and C–O–C peaks is shown in Fig. 4b and slight relaxation – in Fig. 4c is represented. Plasma "A" treatments change the proportions of the O–C and C–O–C peaks more significantly. Only after plasma "B" treatment the O–X peak disappears. The results of the XPS spectra are summarized in the Table 1.

Analyzing the results after two plasma types treatment, there may be noticed a significant increase in carbonyl group concentration that corresponds to the results in [2, 3], also an increase of the O–C=O group concentration that is similar to [4, 5]. The "A" plasma treatment concentration is similar to [4, 5]. The "A" plasma treatment does not practically affect the surface chemical properties with the exception of the given above proposition of the existence of the C=O, O–C=O groups. The concentration of C–X, O–X bounds after plasma "A" treatment increases and relaxation even slightly amplifiers these peaks. The "B" type plasma treatment obviously stimulates significant changes of the surface chemical bonds, and therefore the relaxation processes are taking place slower than in the first case. Both C–X and O–X peaks disappear from the spectra simultaneously, suggesting the same origin of these peaks. Two effects appear after plasma "B" treatment – wetting angle does not reach initial value and C–X and O–X peaks do not appear after prolong time of relaxation. That suggests that a change in these particular bounds is directly responsible for the wetting angle changes. The assertion

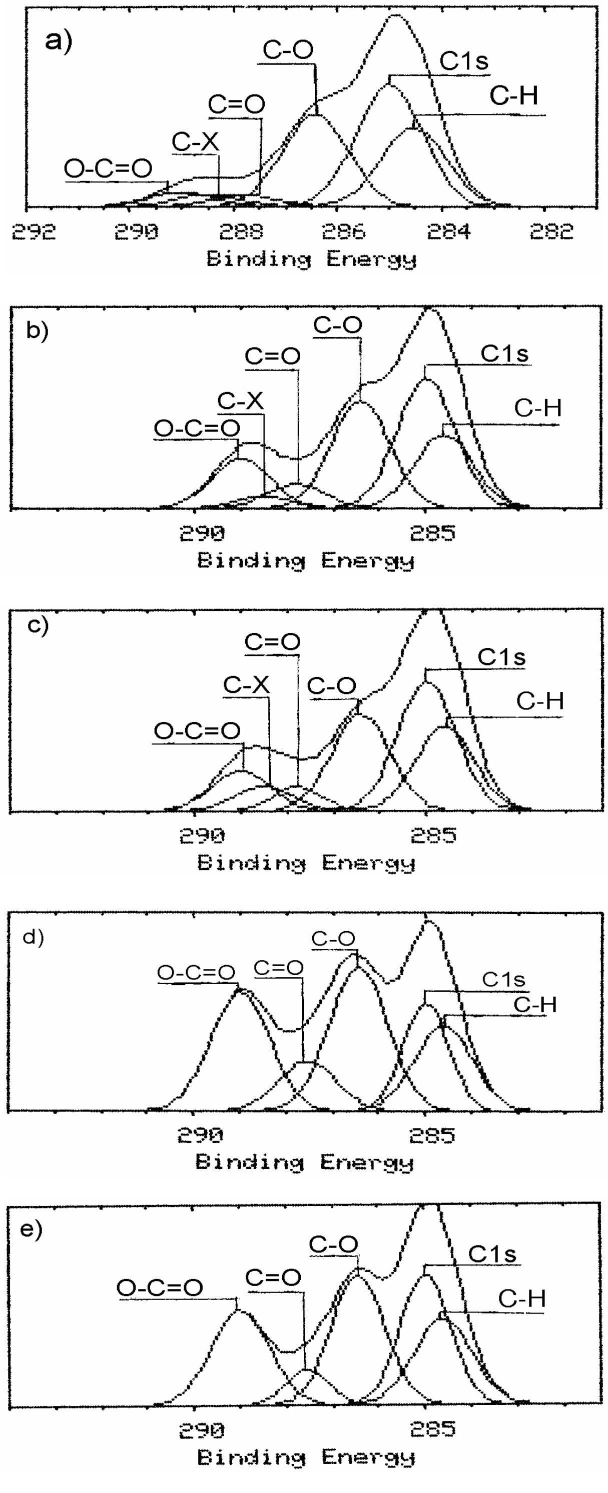

Fig. 3. XPS C1s spectra: a –untreated PET film; b – after plasma "A" treatment; c – relaxation after plasma "A" treatment; d – after plasma "B" treatment; e – relaxation after plasma "B" treatment

Table 1. The summarized results of the XPS spectra

PET	C elemental composition (%)						O elemental composition (%)			
	C–C	C–O	C=O	O–C =O	C–H	C–X	O1s	O– C	C–O–C	O–X
Theoretical	60	20	20	–	–		50	50		
Untreated	34.4	25.9	3.34	3.91	21.9	3.35	21.1	36.3	28.9	2.39
Plasma “A”	31.4	26.0	5.86	12.2	17.9	2.92	25.5	28.7	36.3	8.0
Relaxation “A”	31.8	23.9	4.95	9.92	20.6	5.94	30.1	23.2	34.6	9.35
Plasma “B”	16.7	28.5	9.87	23.6	18.8	–	29.1	35.5	33.1	–
Relaxation “B”	25.0	26.8	5.91	21.5	19.2	–	30.7	2.9	38.4	–

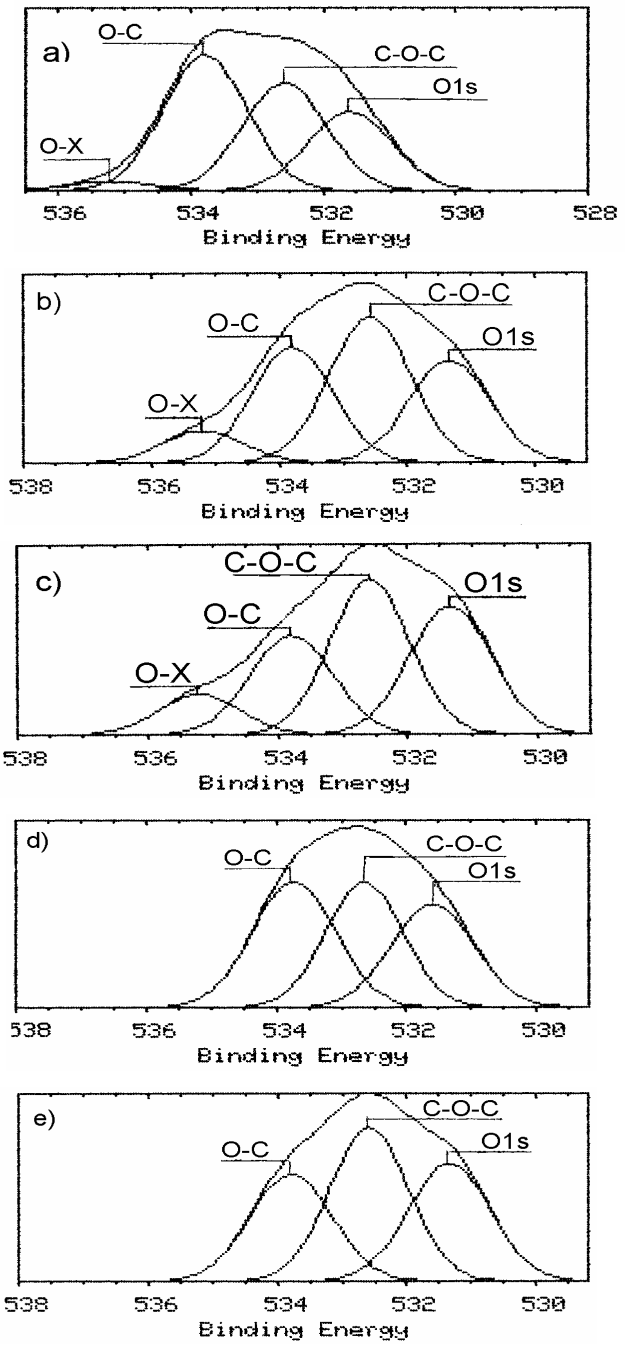

Fig. 4. XPS O1s spectra: a – untreated PET film; b – after plasma “A” treatment; c – relaxation after plasma “A” treatment; d – after plasma “B” treatment; e – relaxation after plasma “B” treatment

that in the case of treating by direct current plasma the surface over molecular structure varies and in the case of treating by alternating current plasma together with the surface over molecular also changes its chemical bonds structure may be deemed as general.

4. CONCLUSIONS

1. After two different (DC and AC) plasma treatment methods, there has been obtained a different PET film surface properties change.

2. Alternating current plasma treatment method induces significant chemical properties changes of PET film surface.

3. The chemical properties changes can be related to the “residual” wetting angle value and slower wetting angle relaxation evolution.

Acknowledgments

The Lithuanian Science and Study Foundation has supported this work.

REFERENCES

1. **Cueff, R., Band, G., Benmalek, M., Besse, J. P., Butruille, J. R., Jacquet, M.** X-Ray Photoelectron Spectroscopy Studies of Plasma Modified PET Surface and Alumina-PET Interface *Applied Surface Science* 115 1997: p. 292.
2. **Le, Q. T., Pireaux, J. J., Verbist, J. J.** Surface Modification of PET Films with RF Plasma and Adhesion of In Situ Evaporated Al on PET *Surf. Interf. Anal.* 22 1994: p. 224.
3. **Gerenser, L.J.** XPS Studies of In Situ Plasma-Modified Polymer Surfaces *J. Adhes. Sci. Technol.* 7 1993: p. 1019.
4. **Weiss, J.** Parameters That Influence the Barrier Properties of Metallized Polyester and Polypropylene Films *Thin Solid Films* 204 1991: p. 203.
5. **Gerenser, L. J., Elman, J. F., Mason, M. G., Pochan, J. M.** E.S.C.A. Studies of Corona-Discharge-Treated Polyethylene Surfaces by Use of Gas-Phase Derivatization *Polymer* 26 1985: pp. 1162 – 1166.