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Comparative study of surface free energy and surface resistivity of polypropylene and polystyrene thin films after DC plasma treatment

Summary — The surfaces of polypropylene (PP) and polystyrene (PS) thin films were subjected to oxygen plasma treatment, produced by glow discharge (direct current, vacuum chamber, temp. 27—30 °C, pressure 200 Pa). The effects of time (up to 110 s) and power (1 W or 5 W) of the treatment on the values of free energy (γ_s) of PS and PP samples and γ_S components — dispersive (γ_S^D) and polar (γ_S^P) ones — were determined. With prolonged time of interaction the values of γ_S and γ_S^P increased, especially in the region of first 35—50 s, while γ_S^D values kept the similar level during the whole time of exposure. The dependence of PP and PS surface resistance on the same parameters as above (time and power of interaction) has been also found. For both polymers this resistance decrease with prolonged time and growing power of exposure.

Key words: oxygen plasma, polymer films, interaction, polypropylene, polystyrene, free surface energy, surface resistance.

PORÓWNAWCZE BADANIA SWOBODNEJ ENERGII POWIERZCHNIOWEJ I OPORNOŚCI POWIERZCHNIOWEJ CIENKICH FOLII POLIPROPYLENOWYCH I POLISTYRENOWYCH PO PODDANIU ICH DZIAŁANIU PLAZMY STAŁOPRĄDOWEJ

Streszczenie — Powierzchnie cienkich folii polipropylenowych (PP) i polistyrenowych (PS) poddawano działaniu plazmy tlenowej uzyskiwanej pod wpływem wyładowań jarzeniowych (prąd stały, komora próżniowa, temp. 27—30 °C, ciśnienie 200 Pa). Określono wpływ czasu (do 110 s), a także mocy (1 W lub 5 W) takiego oddziaływania na wartość swobodnej energii powierzchniowej (γ_S) próbek PP i PS oraz składowych γ_S — dyspersyjnej (γ_S^D) i polarnej (γ_S^P) (rys. 1—4). Z przedłużaniem czasu oddziaływania wartości γ_S i γ_S^P zwiększały się, zwłaszcza wyraźnie w przedziale pierwszych 35—50 s, natomiast wartości γ_S^D utrzymywały się na zbliżonym poziomie w ciągu całego okresu ekspozycji. Określono także zależność oporności powierzchniowej PP i PS od tych samych parametrów (czasu oraz mocy oddziaływania — rys. 5 i 6). W przypadku obydwu typów polimerów oporność ta maleje wraz z przedłużaniem czasu i zwiększeniem mocy ekspozycji.

Słowa kluczowe: plazma tlenowa, folie polimerowe, oddziaływanie, polistyren, polipropylen, swobodna energia powierzchniowa, oporność powierzchniowa.

Polymers have many desirable properties such as high strength to weight ratio, resistance to corrosion, relatively low cost [1] *etc*. Polymer thin films have numerous applications such as low dielectric electronic packaging, photo resists or metal coatings [2]. There are fundamental differences between polymers and engineering solids which have created technical challenges. An important example is characteristic low surface free energy and high surface resistivity. Because of low surface free energy of polymers they show poor adhesion. Adhesion can be estimated by tangent of contact angle between the sessile drop and the surface of solid substrate hosting the drop [3, 4]. Conducting polymers can be used as driving electrodes for polymer dispersed liquid crystal display devices [5].

Contact angle measurement is one of the best methods for estimation of the chemical changes which occur at the surface of polymers modified by plasma [6]. This method gives important information regarding different intermolecular interactions such as Van-der Walls's or electrostatic ones [7—13].

Polymer surfaces have been modified using different methods ranging from wet chemical, through atmosphere pressure plasma, laser treatment to dry glow discharge treatment [14—24]. Among these methods glow discharge plasma, because of uniformity of treatment, has been of great importance. Glow discharge plasma comprises neutral species, electrons and ions. These particles do not only introduce functional groups at the surface but induce crosslinking, degrade the polymer surface by chain scission and change the crystallinity [25] of the surface.

In this work we used DC glow discharge [26] to modify surface free energy (SFE) and surface resistivity of thin films of polypropylene (PP) and polystyrene (PS). Contact angle (Θ) measurements of deionized water and formamide were employed to monitor the effect of glow discharge plasma, at two different discharge powers, on the surface of thin films of polypropylene and polystyrene.

EXPERIMENTAL

Materials and method of treatment

Thin films of area 10 × 10 mm and thickness 100 and 150 μm of PP and PS were used in this study. Acetone was used in order to remove the dust contaminations from the surfaces of the samples. The test liquids used to evaluate the polar and dispersive components of surface free energy of PP and PS, through measurement of their contact angle, were deionized water and formamide with known polar and dispersion components of surface tensions. The samples of PP and PS, after their cleaning by acetone, were treated under direct current (DC) glow discharge in a vacuum chamber. The set up contained of 450 mm height and 300 mm diameter closed glass chamber. Through an inlet, oxygen was introduced into the glass chamber. The anode, which was kept fixed and the spacing between the two electrodes, could be controlled by adjustable cathode. The spacing between the electrodes was kept equal 20 mm. Cleaned PP and PS samples were kept on the cathode. A pressure of 200 Pa (measured by a Pirani gauge) and temperature 27—30 °C was maintained inside the glass chamber. At this low pressure DC voltage 250 V was applied between the electrodes to generate glow discharge. The treatment of polymer films was carried out at two different power levels (1.0 or 5.0 Watt) and for different exposure times (5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 90 or 110 seconds in both cases).

Surface free energy and its components measurement

Droplets of size 5—8 μl of the test liquids — deionized water or formamide — were placed on the surfaces of the samples by syringes, and the contact angle was measured by stereo zoom microscopy. Estimation of SFE and its polar and dispersive components for both PP and PS was done using the following equations according to [21]:

$$(1 + \cos\theta)\gamma_{LV} = 2(\gamma_S{}^D\gamma_{LV}{}^D)^{1/2} + 2(\gamma_S{}^P\gamma_{LV}{}^P)^{1/2} \tag{1}$$

and

$$\gamma_S = \gamma_S{}^P + \gamma_S{}^D \tag{2}$$

where: γ_S, $\gamma_S{}^P$, $\gamma_S{}^D$ — *surface energy and its polar and dispersive components, respectively;* $\gamma_{LV}{}^P$ *and* $\gamma_{LV}{}^D$ *— appropiate values for test liquids, known from [1] (see table 1).*

Table 1. Surface free energy (γ_{LV}) and it's dispersive ($\gamma_{LV}{}^D$) and polar ($\gamma_{LV}{}^P$) components for test liquids

Test liquid	$\gamma_{LV}{}^P$, mJ/m^2	$\gamma_{LV}{}^D$, mJ/m^2	γ_{LV}, mJ/m^2
Water	51.0	21.8	72.8
Formamide	19.0	39.0	58.0

Resistivity measurement

The untreated and treated samples of PP and PS films were first coated by silver from one side in a vacuum chamber. The pressure during coating of samples was kept on the level 10^{-6} Pa, and the temperature was 27—30 °C. These silver coated films were held on a plane surface of polycarbonate sheet. This whole set up was kept in a test holder. The pressure contacts were connected with the electrode of a high resistance measuring electrometer. The electrometer could measure the resistance up to 10^{16} Ω. To see the effect of DC glow discharge treatment on the resistivity of treated and untreated samples of PP and PS the resistivity measurements were carried out by electrometer directly.

RESULTS AND DISCUSSION

The changes in the surface free energy and its components, with the significant change in the surface resistivity for both kinds of the samples (PP and PS) have been observed. For the treatment power of 1 Watt the SFE values of PP and PS samples, for treatment time up to 110 s, are presented in Fig. 1 and 2, respectively. With the increase in the power level to 5 Watt the surface free energy of PP film reached 60 mJ/m^2 for treatment time of 35 seconds (for untreated film this value was equal 23 mJ/m^2) (Fig. 3). For PS it was 68 mJ/m^2 for 35 seconds of treatment time (Fig. 4) (in comparison with 38 mJ/m^2 for untreated samples). The polar component, for both the sample films of PP and PS, changes almost

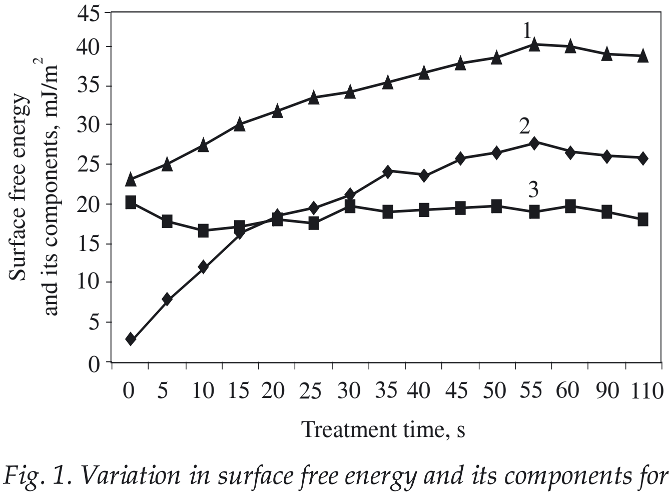

Fig. 1. Variation in surface free energy and its components for polypropylene, power = 1 Watt: 1 — surface free energy, 2 — polar component, 3 — dispersive component

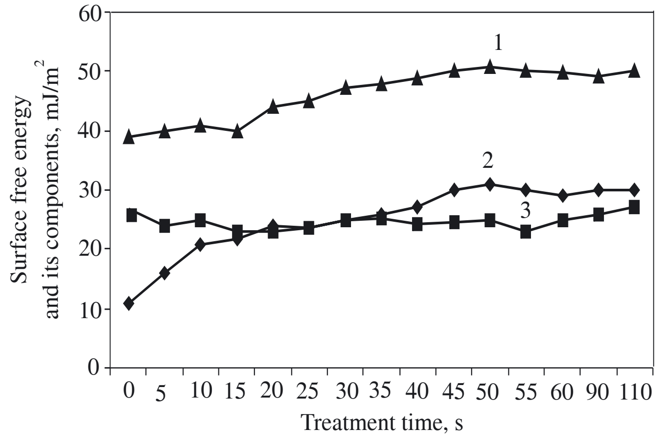

Fig. 2. Variation in surface free energy and its components for polystyrene, power = 1 Watt (curves denotations — see Fig. 1)

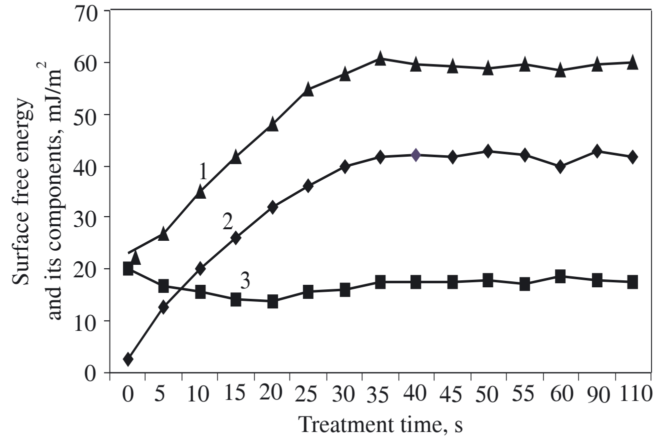

Fig. 3. Variation in surface free energy and its components for polypropylene, power = 5 Watt (curves denotations — see Fig. 1)

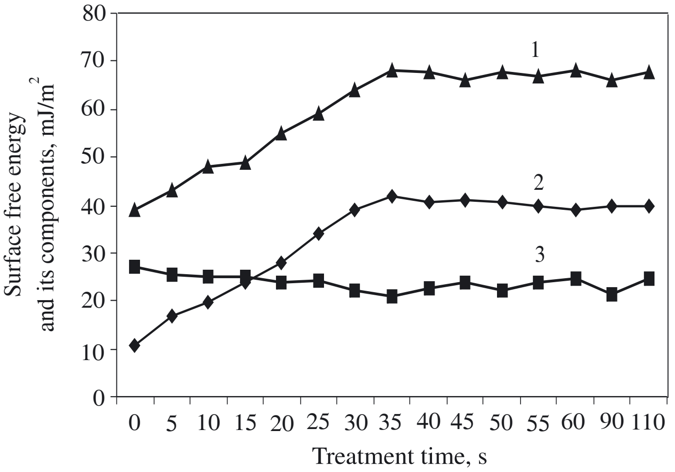

Fig. 4. Variation in surface energy and its components for polystyrene, power = 5 Watt (curves denotations — see Fig. 1)

in the same way as the surface free energy changes, while the dispersive component changes in a different way.

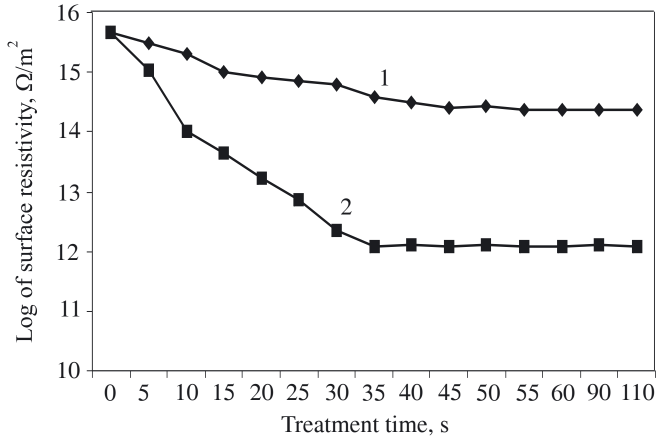

Fig. 5. Variation in the surface resistivity of polypropylene at different power levels: 1 — power 1 Watt, 2 — power 5 Watt

The reason of the observed phenomenon of γ_S and $\gamma_S{}^P$ increase with increasing both time and power of treatment is probably the presence of the charged species in plasma of oxygen abundance. Charged species get accelerated between electrodes when DC voltage is applied between them and transfer their energies to the atoms of the polymer chain what results in chain breaking. The chain gets oxidized at the points of chain scission in the oxygen abundance environment. So the increase in the treatment time and treatment power leads to enhancement of polar groups at the polymers' surfaces.

Fig. 5 and 6 shows the change in the surface resistivity of thin films of PP and PS. It has been observed that surface resistivity for both types of samples decreased with an increase in treatment time. Resistivity values for PS and PP decrease also with treatment power increase from 1 to 5 W. The change is more significant for the power equal 5 W. For PP film at power level of 1 W the surface resistivity decreases from 4.58×10^{15} Ω/cm^2 to 2.36×10^{14} Ω/cm^2, at the treatment time of 55 seconds;

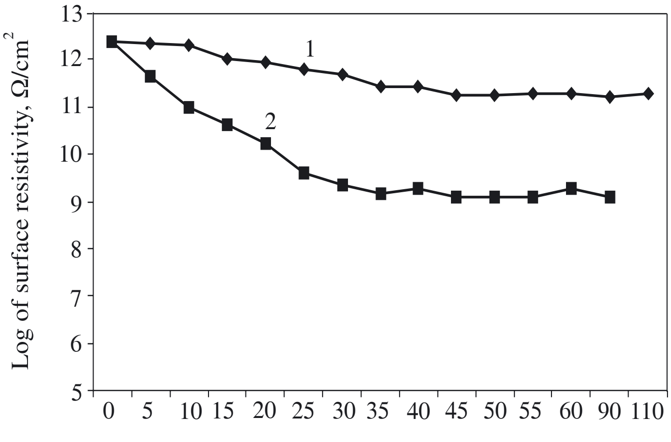

Fig. 6. Variation in the surface resistivity of polystyrene at different power levels (curves denotations — see Fig. 5)

for prolonged time it remains almost constant (Fig. 5, curve 1). At the same power level the surface resistivity of polystyrene decreases from 2.32×10^{12} Ω/cm^2 to 1.69 $\times 10^{11}$ Ω/cm^2 for the treatment time of 50 seconds (Fig. 6, curve 1). For the power level of 5 Watt surface resistivity of PP decreases to 1.24×10^{12} Ω/cm^2 and for PS it decreased to 1.43×10^9 Ω/cm^2 for the treatment time of 35 seconds for both the sample films (curves 2, Fig. 5 and 6).

Although no characterization has been done in this study, but it is clear from the results that the decrease in the surface resistivity mainly depends upon polar component of surface energy increasing.

REFERENCES

1. Švab I., Musil V., Leskovac M.: *Acta. Chim. Slov.* 2005, **52**, 264.
2. Ade H., Winesett D. A.: *Appl. Phys. Lett.* 1998, **25**, 73.
3. Żenkiewicz M.: *Polimery* 2005, **50**, 365.
4. Żenkiewicz M.: *Polimery* 2005, **51**, 584.
5. Roussel F., Buisine J. M.: *Eur. Phys. J. E 11* 2003, 293.
6. Mahlberga R., Niemib H. E.-M., Denesc F., Rowe R. M.: *Intern. J. Adhes.* 1998, **18**, 283.
7. Morra M., Occhiello E., Garbassi F.: *Adv. Coll. Interf. Sci.* 1990, **32**, 79.
8. Van Oss C. J.: "Interfacial Forces in Aqueous Media", Dekker, New York 1994.
9. Yamada K., Kimura T., Tsutaya H., Hirata M.: *J. Appl. Polym. Sci.* 1992, **44**, 993.
10. Yamada K., Tsutaya H., Tatekawa S., Hirata M.: *J. Appl. Polym. Sci.* 1992, **46**, 1065.
11. Brzoska J. B., Ben Azouz I., Rondelez F.: *Langmuir* 1994, **10**, 4367.
12. Fadeev A. Y., McCarthy T. J.: *Langmuir* 1999, **15**, 3759.
13. Schreiber H. P.: *J. Adhes.* 1992, **37**, 51.
14. Żenkiewicz M.: *Polimery* 2005, **50**, 4.
15. Chou N. J., Change C. A., Tong H. M., Saraf R. F., Kowalczyk S. P.: "Characterization of Polymers", Butterworth-Heinemann, Stoneham 1994.
16. Millard M., Hollahan J. R., Bell A. T.: "Techniques and Applications of Plasma Chemistry", Wiley, New York 1974.
17. Niino H., Yabe A.: *Appl. Surf. Sci.* 1993, **69**, 1.
18. Strobel M., Lyons C. S., Mittal K. L.: "Plasma Surface Modification of Polymers", VSP, Zeist 1994.
19. Wertheimer M. R., Martinu L., Liston E. M., Glocker D. A., Shah S. I.: "Handbook of Thin Film Process Technology", IOP, Bristol 1996.
20. Nie H. Y., Walzak M. J., Berno B., McIntyre N. S.: *Appl. Surf. Sci.* 1999, **144/145**, 627.
21. Liston E. M., Martinu L., Wertheimer M. R.: *J. Adhes. Sci. Technol.* 1993, **7**, 1091.
22. Kinloch A. J.: *J. Mater. Sci.* 1980, **15**, 2141.
23. Liston E. M., Martinu L., Wertheimer M. R.: *J. Adhes. Sci. Technol.* 1993, **7**, 1077.
24. Zisman W. A.: "Relation of Chemical Constitution to the Wetting and Spreading of Liquids on Solids", U. S. Govt. Printing Office: Washington D. C., 1957.
25. Wertheimer M. R., Klemberg-Sapieha J. E., Martinu L.: *J. Pure Appl. Chem.* 1996, **68**, 1047.
26. Strobel M., Jones V., Lyons C. S., Ulsh M., Kushner M. J., Dorai R., Branch M. C.: *Plasmas Polym.* 2003, **8**, 61.