

Investigation of poly(ethylene terephthalate) treated by low-temperature plasma

¹IGOR NOVÁK, ¹IVAN CHODÁK, ²JÁN SEDLIAČIK, ¹MARIAN ŠTEVIAR, ¹ANTON POPELKA, ³JÁN KOPNÝ

¹Polymer Institute of the Slovak Academy of Sciences, Bratislava, ²Technical University, Zvolen, ³VIPO, a.s., Partizánske, Slovakia

Abstract: *Investigation of poly(ethylene terephthalate) treated by low-temperature plasma.* Polyethylene terephthalate (PET) surface was pre-treated by surface barrier discharge (DSBD) plasma at atmospheric pressure in various processing gases, and/or by radio-frequency discharge (RFD) plasma to improve its surface and adhesive properties. The changes in chemical structure of the polymer were analyzed by ATR-FTIR spectroscopy. The surface energy, and its polar contribution as well as peel strengths of adhesive joints to polyacrylate of PET modified by DSBD and/or RFD plasma significantly increased. The efficiency of modification depends on the kind of the discharge, used gases, power of plasma source, as well as on time of modification. The correlation between peel strength of adhesive joint of PET modified by DSBD plasma to polyacrylate and its surface energy has been found.

Keywords: ATR-FTIR, barrier discharge plasma, radio-frequency plasma, peel strength, polyethylene terephthalate.

INTRODUCTION

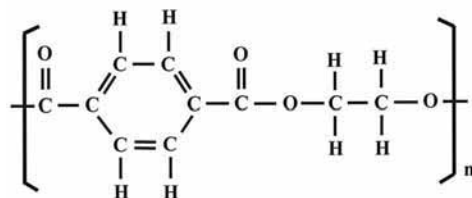
Polyethylene terephthalate (PET) belongs to important polymers, which are frequently used in many industrial applications, e.g. in automotive industry for cars construction or in special applications in furniture industry due to its excellent properties. The surface energy of PET is insufficient in some cases, e.g. bonding, printing, etc. This problem can be solved by using of various surface modification methods. Several efficient methods have been used to improve the surface and adhesive properties of polymers [1, 2]. The application of cold plasmas for pre-treatment of polymeric surface [3-9] belongs to dry, ecological method of modification, which can tailor polymers in order to modify their surface energy and adhesion to other materials. The most important feature of the plasma treatment technique is that the surface properties of polymer can be modified without changing their intrinsic bulk properties [10-19]. PET with substantially higher surface energy than polyolefin usually does not need to be pre-treated by plasma for printing, because the level of its surface energy in the untreated state is higher than the value needed for printing [20, 21].

In this paper the investigation of surface and adhesive properties of PET modified by DSBD and/or by RFD plasma have been studied using contact angle measurement, peel tests, ATR-FTIR, SEM.

EXPERIMENTAL

Polymers used

In PET polymer structure (Scheme 1), the aromatic ring and its associated C-C bonds accommodate rigidity to the macromolecule. The dissociation of chemical bonds in PET macromolecule on the polymeric surface might occur at C-H or C-C when the polymer chains receive energy from activated species during modification by low-temperature plasma.



Scheme 1. The structure of PET polymer

In our experiments oriented PET foils Tenolan OAN (Technoplast, Czech Republic) with thickness 0.12 mm and poly (2-ethylhexyl acrylate) (PEHA) (Polysciences, USA) have been applied. The PET foils were treated in acetone due to elimination of the additives influencing their surface properties. The adhesive joints of modified PET were prepared by using a solution of PEHA in ethyl acetate. The layer with thickness 0.12 mm was deposited on supported biaxially oriented isotactic polypropylene with aid of coating ruler (Dioptra, Czech Republic).

Modification by plasma

The modification of PET foils by DSBD plasma was performed in laboratory source at atmospheric pressure in medium of N_2 or O_2 gases of a technical purity. The DSBD generator consists of electrodes separated by an alumina dielectric plate. The discharge electrodes having the area 80 x 80 mm, and consisting of 1 mm wide and 80 mm long tungsten strips, are fixed on the upper surface of alumina plate. The electrodes are located inside of glass cover allowing passing of the medium gases. The voltage of DSBD source was 100 V, current intensity 1A, and frequency was 6 kHz. The power used for modification by DSBD plasma in N_2 or O_2 was 100 W.

The RFD source working at reduced pressure 40 Pa in air consists of stainless steel locked-up vacuum vessel with two circular brass electrodes having a diameter 240 mm. The voltage of RFD source was 2 kV, current density was 0.6 A, and frequency was 13.56 MHz, and the power applied for modification of the polymer by RFD plasma in air was 200 W.

Measurements methods

ATR-FTIR

The ATR-FTIR spectroscopy measurements of PET foils were performed with Nicolet Impact 400 FTIR spectrometer (Nicolet, USA) having a resolution of 4 cm^{-1} , a scan range was $4000 - 400\text{ cm}^{-1}$, and a total of 1024 scans per analysis. The KRS-5 crystal (thallium-bromide-iodide) has been used for ATR-FTIR measurements.

Surface energy

The surface energy of PET was determined via measurements of contact angles of a set of testing liquids: re-distilled water, ethylene glycol, formamide, methylene iodide, α -bromo naphthalene) with SEE (Surface Energy Evaluation) system (Masaryk University, Czech Republic). The drops of testing liquid ($V = 3\ \mu\text{l}$) were placed with a micropipette (Biohit, Finland) on the PET foil surface, and a dependence $\theta = f(t)$ was extrapolated to $t = 0$. The surface energy of the polymer as well as its polar and dispersive components were evaluated by Owens-Wendt-Rable-Kaelble (OWRK) modified by the least squares method [22]:

$$\frac{(1+\cos\theta)\gamma_{LV}}{2} = (\gamma_{LV}^d \gamma_s^d)^{1/2} + (\gamma_{LV}^p \gamma_s^p)^{1/2} \quad (1)$$

$$\gamma_{LV} = \gamma_{LV}^p + \gamma_{LV}^d \quad (2)$$

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad (3)$$

Where: θ = contact angle (deg),

γ_{LV} = surface free energy (SFE) of the testing liquid (mJ.m^{-2}),

$\gamma_{LV}^d, \gamma_{LV}^p$ = dispersive component (DC), and polar component (PC) of SFE of the testing liquid (mJ.m^{-2}),

γ_s^d, γ_s^p = DC and PC of SFE of the polymer (mJ.m^{-2}).

Where, γ_L is the surface tension, $x_L^p = \gamma_L^p/\gamma_L$ is the polar ratio of the testing liquid.

Peel strength of adhesive joint

The peel strength of adhesive joint (P_{peel}) of PET foil modified by plasma to polyacrylate was found by peeling of adhesive joint (peel tests) at 90° angle using a 5 kN universal testing machine Instron 4301 (Instron, England). The adhesive joints were fixed in aluminium peeling circle. The width of adhesive joints was 20 mm, and its length was 140 mm. The adhesive joints were prepared from modified PET foils and biaxially oriented isotactic polypropylene impregnated with polyacrylate. The speed of peeling of adhesive joint was 1.5 mm.min^{-1} .

RESULTS AND DISCUSSION

ATR-FTIR

The chemical changes in surface layer of plasma-treated polymer are analyzed using ATR-FTIR spectroscopy.

Fig. 1 shows the ATR-FTIR spectra of unmodified PET (Fig. 1 c) as well as the PET modified by DSBBD plasma in N_2 (Fig. 1 b) or O_2 atmosphere (Fig. 1 a). A surface analysis of PET modified by DSBBD plasma in O_2 (10s, Fig. 1 a) and in N_2 (10s, Fig. 1 b) can provide an understanding of the functional chemical groups of the polymer. ATR-FTIR spectra of PET were measured with the same DSBBD plasma treatment times 10s in various processing gases. For unmodified PET foil (Fig. 1c), the characteristic IR bands at $1710, 1505$ and 1173 cm^{-1} were observed for CH, C=O, benzene-ring -C-C- stretching vibrations, and ring C-H in plane bending, respectively. The IR bands at 1358 cm^{-1} of the wagging, benzene-ring in-plane C-H bending, and -C-C- stretching vibration bands appeared near 1173 and 1037 cm^{-1} , respectively. The IR spectrum of DSBBD plasma treated PET in Fig. 1b (N_2 plasma) and Fig. 1a (O_2 plasma) contains some important changes in comparison with IR spectrum of unmodified PET. For DSBBD modified PET the broadening of the C=O stretch at 1710 cm^{-1} have been appeared due to oxygen-containing sites creation. The content of C=O groups is higher for PET modified by O_2 DSBBD plasma (Fig. 1a) comparing to N_2 plasma (Fig. 1b) and consequently the broadening peak at 1710 cm^{-1} for O_2 plasma modified PET was found.

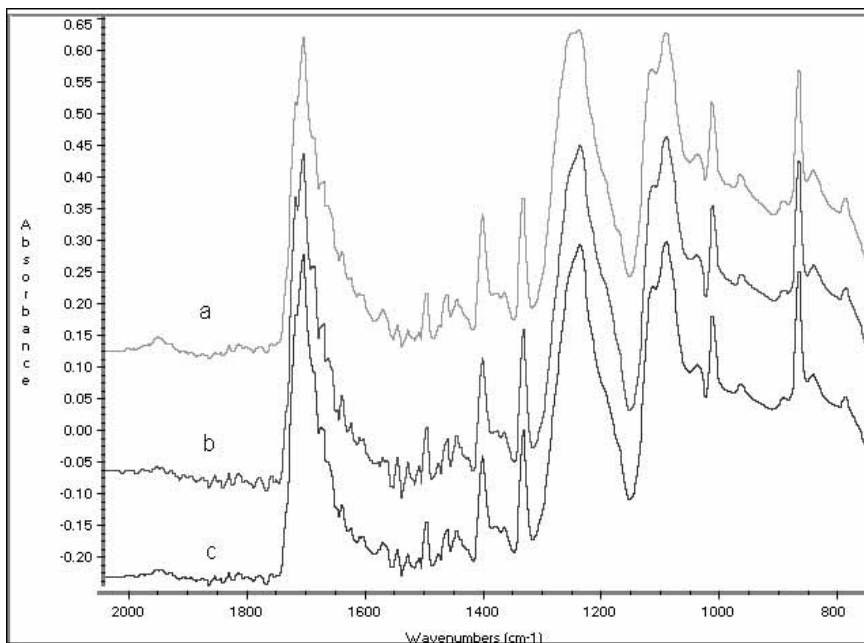


Fig. 1 ATR-FTIR spectra of unmodified PET (1 c), PET modified by DSBD plasma in N₂ (1 b), and in O₂ atmosphere (1 a)

Surface energy and peel strength of adhesive joint

The surface energy of PET foils modified by DSBD in O₂ and N₂ plasma at atmospheric pressure and by RFD plasma in air at reduced pressure vs. activation time is shown in Fig. 2.

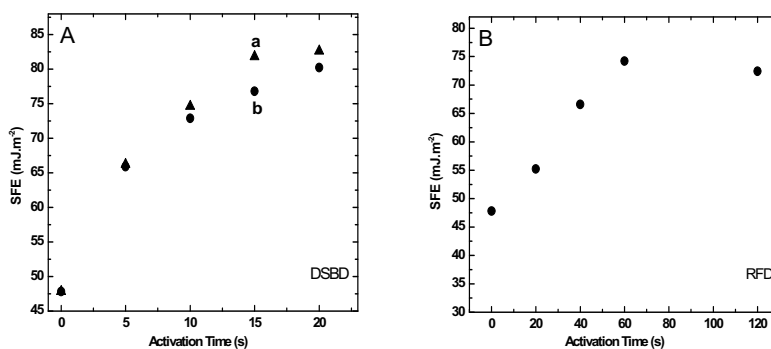


Fig. 2 Surface energy of PET foil modified by DSBD plasma (A): in O₂ (a) and in N₂ (b) or RFD plasma (B) in air vs. activation time

The surface energy of PET during modification by DSBD plasma in O₂ and N₂ significantly increased in comparison with untreated polymer. According to Fig. 2, plot a the surface energy of PET modified by DSBD plasma in O₂ increases from the initial value 47.8

mJ.m^{-2} for untreated PET up to 82.6 J.m^{-2} for 20 s of modification by plasma. Fig. 11A, plot b shows the surface energy of PET modified by DSBD plasma in N_2 . The values of PET surface energy treated in N_2 by DSBD plasma were lower in comparison with surface energy of PET modified by the same method in O_2 . The PET modified by RFD plasma in air (Fig. 11B) reached the same level of pre-treatment for substantially longer time of activation by plasma. The surface energy of PET treated by RFD plasma at reduced pressure in air reached after 60 s of modification 74.2 mJ.m^{-2} . Comparing Fig. 2 A, plot a and Fig. 2 B we can conclude, than the same value of the PET surface energy modified by RFD plasma was achieved for 6 times longer time of modification in comparison with DSBD plasma treatment.

The results of measurements of surface energy of PET modified by RFD plasma, its polar component (PC) and dispersive component (DC) of the surface energy vs. activation time are summarized in Fig. 3. The total surface energy of PET treated by RFD plasma increases with time of activation from 47.8 mJ.m^{-2} (unmodified polymer) up to 72.4 mJ.m^{-2} (modification by RFD plasma, 120 s).

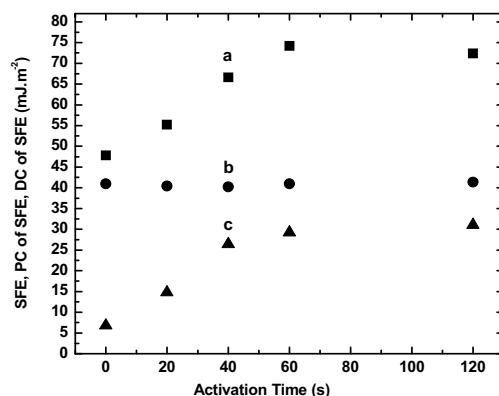


Fig. 3 Surface energy (a), its polar (b) and dispersive (c) component of PET modified by RFD plasma in air vs. activation time

The polar component of the surface energy increased after modification by RFD plasma in argon from 6.8 mJ.m^{-2} (unmodified sample) to 31 mJ.m^{-2} after 120 s of RFD plasma treatment. However, the dispersive component of surface energy of PET modified by RFD plasma with activation time does not change significantly (from 41.0 mJ.m^{-2} , unmodified PET to 41.4 mJ.m^{-2} , RFD, 120 s). Both used processing gases, i.e. oxygen as well as nitrogen reach the same relation between peel strength of adhesive joint and surface energy of PET:

$$P_{\text{peel}} = 309.5 - 1719.8 \cdot \exp(-\text{SFE}/23.9).$$

CONCLUSIONS

- (i) DSBD plasma modified PET shows by ATR-FTIR measurement the broadening of the $\text{C}=\text{O}$ stretch at 1710 cm^{-1} due to oxygen-containing sites creation,
- (ii) surface energy of PET modified by DSBD and RFD plasma significantly increases, this increase was higher for oxygen in comparison with nitrogen,
- (iii) peel strength of PET to polyacrylate modified by DSBD plasma or RFD plasma significantly increased,

- (iv) correlation between peel strength of adhesive joint of PET modified by DSBD plasma in oxygen or nitrogen to polyacrylate have been found:
 $P_{\text{peel}} = 309.5 - 1719.8 \cdot \exp(-\text{SFE}/23.9)$.

Acknowledgements

The authors are grateful to Slovak Grant Agency VEGA (grants No. 2/7103/27 and 1/0517/09) for the financial support of this research.

This paper was processed in the frame of the Project of Slovakian Ministry of Education "Stimuly" Req-00151-0001 as the result of author's research.

REFERENCES

1. CIOFFI, M.O.H., VOORWALD, H.J.C., MOTA R.P., 2003: *Mater. Character.* 50, 209.
2. POLETTI, G., ORSINI, F., RAFFAELE-ADDAMO, A., RICCARDI, C., SELLI, E., 2003: *Appl. Surf. Sci.* 219, 311.
3. SHENTON, M.J., LOWELL-HOARE, M.C., STENENS, G.C., 2001: *J. Phys. D, Appl. Phys.* 34, 2754.
4. ČERNÁKOVÁ, L., KOVÁČIK, D., ZÁHORANOVÁ, A., ČERNÁK, M., MAZÚR, M.: *Plasma Chem. Plasma Process.* 25 (2005) 427.
5. ODRÁŠKOVÁ, M., RÁHEL, J., ZÁHORANOVÁ, A., TIŇO, R., ČERNÁK, M., 2008: *Plasma Chem. Plasma Process.* 28, 203.
6. NOVÁK, I., POLLÁK, V., CHODÁK I., 2006: *Plasma Process. Polym.* 3, 355.
7. OHARE, L.A. SMITH, J.A., LEADLEY, S.R., PARBHOO, B., GOODWIN, A.J., WATTS, J.F., 2002: *Surface Interface Anal.* 33, 617.
8. DESHMUKH, R.J., BHAT, N.V., 2003: *Mater. Res. Innov.* 7, 283.
9. RICCARDI, C., BARNI, R., SELLI, E., MAZZONE, G., MASSAFRA, M.R., MARCANDALLI, B., POLETTI, G., 2003: *Appl. Surf. Sci.* 211, 386.
10. BARNI, R., RICCARDI, C., SELLI, E., MASSAFRA, M.R., MARCANDALLI, B., ORSINI, F., POLETTI, G., MEDA, L., 2005: *Plasma Process. Polym.* 2, 64.
11. ADEMOVIC, Z., WEI, J., JENSEN, B.W., HOU, X., KINGSHOTT, P., 2005: *Plasma Process. Polym.* 2, 53.
12. NOESKE, M., DEGENHARDT, J., STRUDTHOFF, S., LOMMATZSCH, U., 2004: *Intern. J. Adhes. Adhesives* 24, 171.
13. RÁHEL, J., ČERNÁK, M., HUDEC, I., ŠTEFEČKA, M., KANDO, M., CHODÁK, I., 2000: *Plasmas Polymers.* 5, 119.
14. NOVÁK, I., CHODÁK, I., 1998: *Angew. Makromol. Chem.* 260, 47.
15. ŠIMOR, M., RÁHEL, J., ČERNÁK, M., IMAHORI, Y., ŠTEFEČKA, M., KANDO, M., 2003: *Surf. Coat. Technol.* 172, 1.
16. JANČA, J., ŠTAHEL, P., KRČMA, F., LAPČÍK, L., 2000: *Czechoslov. J. Phys.* 50, 449.
17. TSUCHIYA, Y., AKUTU, K., IWATA, A., 1998: *Progress in Org. Coat.* 34, 100.
18. LIU, C., CUI, N., BROWN, N.M.D., MEENAN, B.J., 2004: *Surf. Coat. Technol.* 185, 311.
19. BHAT, N. V., UPADHYAY, D. J., 2003: *Plasma Chem. Plasma Proces.* 23, 389.
20. MANENQ, F., CARLOTTI, S., MAS, A., 1999: *Angew. Makromol. Chem.* 271, 11.
21. CHENG, T. S. LIN, H. T., CHUANG, M. J., 2004: *Mater. Lett.* 58, 650.
22. TOUFIK, M., MAS, A., SHKINEV, V., NECHEV, A., ELHARFI, A., SCHUE, F., 2002: *Eur. Polym. J.* 38, 203.

Streszczenie: *Politeraftalan etylenu traktowany plazmą niskotemperaturową.* Na PET oddziaływano powierzchniowym wyładowaniem plazmy (DSBD) oraz plazmą o częstotliwości radiowej (RFD) w różnych gazach, w celu poprawy własności powierzchniowych i adhezyjnych. Badano zmianę struktur chemicznych polimeru za pomocą spektroskopu ATR-FTIR. Energia powierzchniowa, jej rozkład oraz przylepność PET modyfikowanego plazmą DSBD oraz RFD znacząco wzrosła. Efektywność modyfikacji zależy od typu wyładowania, typu gazu oraz czasu trwania procesu. Wykazano korelację pomiędzy przylepnością połączeń PET modyfikowanych plazmą DSBD a energią powierzchniową.

Corresponding authors:

Ing. Igor Novák, PhD.
Ing. Ivan Chodák, CSc.
Ústav polymérov SAV
Dúbravská cesta 9
845 41 Bratislava
Slovakia
upolnovi@savba.sk

Doc. Ing. Ján Sedliačik, PhD.
Technical University
T.G. Masaryka, 24
960 53 Zvolen
Slovakia
janos@vsld.tuzvo.sk

Ing. Ján Kopný, PhD.
VIPO, a.s. Partizánske
ul. gen. Svobodu 1069/4
958 01 Partizánske
Slovakia
jmatyasovsky@vipo.sk