

SURFACE PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE) MODIFIED BY BARRIER PLASMA

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Summary

A polyethylene terephthalate (PET) surface was pre-treated by diffuse surface barrier discharge (DSBD) plasma at atmospheric pressure in various processing gases to improve its surface and adhesive properties. The changes in chemical structure of the polymer were analyzed by attenuated total reflectance. The surface energy, and its polar contribution, as well as the peel strengths of the adhesive joints of PET, modified by DSBD plasma to polyacrylate increased. The efficiency of the modification depends on the kind of discharge, the used gases, the power of the plasma source, as well as on the time of modification. A correlation between the peel strength of the adhesive joint of PET modified by DSBD plasma to polyacrylate, and the surface energy of the PET has been found.

Keywords: adhesion, barrier discharge plasma; peel strength; polyethylene terephthalate; surface free energy.

Introduction

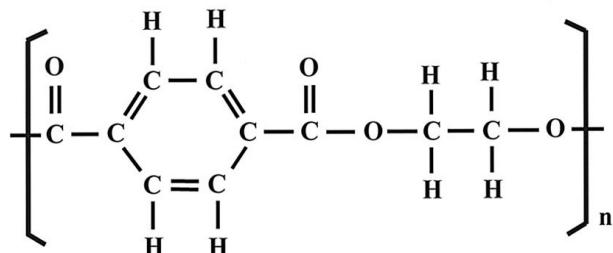
PET is one of the important polymers that are frequently used in many industrial applications, e.g. in the automotive industry for cars construction, due to its excellent properties. The surface energy of PET is insufficient in some applications, e.g. bonding, printing, etc. This problem can be solved by using 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 surfaces [3, 4] is a 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 the polymer can be modified without changing their intrinsic bulk properties [5]. It is well known that the modification of polymers by cold plasma leads to changes in surface and adhesive properties. Depending on the processing gases used, different functional groups are formed in a

very thin surface layer of the polymer [6, 7]. PET, with a substantially higher surface energy than polyethylene (surface energy of PET in the range of $40 - 50 \text{ mJ.m}^{-2}$, and surface energy of polyethylene in the range of $30 - 32 \text{ mJ.m}^{-2}$), usually does not need to be pre-treated by plasma for printing, because the surface energy in the untreated state is higher than the value needed for printing [8]. However, for preparation of strong adhesive joints, modification of PET by diffuse surface barrier discharge (DSBD) plasma is essential.

Experimental

Materials

In the PET polymer structure (Scheme 1) the aromatic ring and its associated C-C bonds give rigidity to the macromolecule. The dissociation of chemical bonds on the surface of the PET macromolecule 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

In our experiments we used oriented PET foils (Tenolan OAN, Technoplast, Czech Republic) with thickness 0.12 mm for modification by discharge plasma, and acrylic based polymer poly(2-ethylhexyl acrylate) (PEHA) (Polysciences, USA) as polar adhesive in PET adhesive joints. The PET foils were treated in acetone in order to eliminate 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 the aid of a coating ruler (Dioptra, Czech Republic).

Plasma modification

The modification of the PET foils by a DSBD plasma was performed in a laboratory plasma source at atmospheric pressure in mediums of N_2 or O_2 gases of technical purity. The DSBD plasma generator consists of electrodes separated by an alumina dielectric plate. The voltage of the DSBD source was 100 V, current intensity 1 A, and frequency 6 kHz. The power used for the modification by DSBD plasma in N_2 or O_2 was 100 W.

Characterization methods

AFM

The surface morphology and local surface heterogeneities of the modified polymer were measured by AFM. All measurements were performed under ambient conditions using a commercial atomic force microscope (NanoScopeTM Dimension

IIIa, MultiMode Digital Instr., USA) equipped with a PPP-NCLR tapping-mode probe (Nanosensors™ Switzerland; spring constant 39 N.m^{-1} , resonance frequency $\approx 160\text{ kHz}$).

ATR-FTIR

The ATR-FTIR spectroscopy measurements of the PET foils [28, 29] were performed with a 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 ATR contained a KRS-5 (thallium-bromide-iodide) crystal.

XPS

The XPS spectra [30-33] were recorded using a VG Scientific ESCALAB 250 system equipped with a micro-focused, monochromatic Al K_{α} X-ray source (1486.6 eV) and a magnetic lens which increases the electron acceptance angle and hence the sensitivity. The spectra were acquired in the constant analyzer energy mode, with pass energies of 150 and 20 eV for the survey and narrow regions, respectively. The Avantage software, version 2.2, was used for digital acquisition and data processing. Spectral calibration was performed by setting the main C1s peak at 285 eV. The O/C atomic ratios were determined by considering the integrated peak areas of C1s and O1s, and their respective Scofield sensitivity factors corrected for the analyzer transmission function.

Surface energy

The surface energy of PET was determined via measurements of the contact angles [34 - 39] of a set of testing liquids: re-distilled water, ethylene glycol, formamide, methylene iodide, and α -bromo naphthalene) with a SEE (Surface Energy Evaluation) system (Advex, Czech Republic). The drops of testing liquid ($V = 3\text{ }\mu\text{l}$) were placed on the PET foil surface with a micropipette (Biohit, Finland), and the 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 the Owens-Wendt-Rable-Kaelble (OWRK) method modified by a least squares method [3].

Strength of the adhesive joint

The peel strength of the adhesive joint (P_{peel}) of the plasma modified PET foil to polyacrylate was determined by peeling of the adhesive joint (peel tests) at a 90° angle using a 5 kN universal testing machine Instron 4301 (Instron, England). The adhesive joints were fixed in the aluminum peeling circle.

Results and discussion

AFM

The changes in the surface topography as well as in the roughness of the plasma modified polymer were investigated by AFM. The AFM results of the PET surface topography and local heterogeneities (phase image) after DSBD and RFD plasma modification are shown in Fig. 1. The surface properties of each PET foil were measured in three different places, but no extensive differences were found between these places. The phase image of the unmodified polymer film (Fig. 1A) shows no significant differences in the phase profiles (local heterogeneities) for untreated PET, except for localized melting marks on the surface. The phase image of unmodified

PET is rather rough, but regular. After plasma treatment very fine heterogeneous regions were formed, and the polymeric surface became more irregular. The local heterogeneities after modification by the DSBD plasma is higher for O₂ (Fig. 1B) than for N₂ (Fig. 1C). The phase image of the PET surface modified by the RFD plasma in air is similar (Fig. 1D). The presence of the heterogeneities in Fig. 1D can be explained by local melting of the polymer during modification by the RFD plasma.

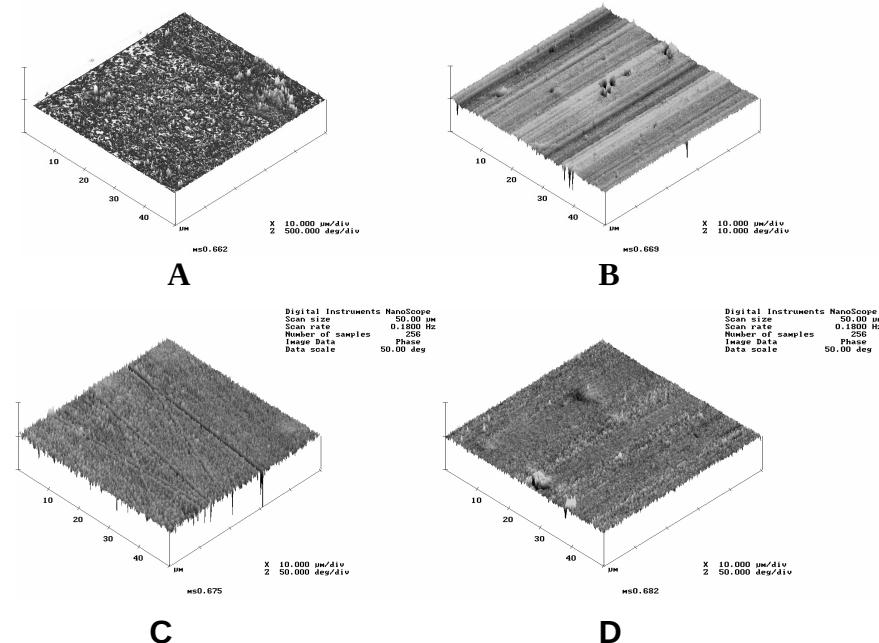


Figure 1 AFM phase images of PET foil: untreated PET (A), PET treated by DSBD plasma in N₂, 10s (B), PET modified by DSBD plasma in O₂, 10s (C), PET treated by DSBD plasma in O₂, 20s (D).

ATR-FTIR

Fig. 2 shows the ATR-FTIR spectra of unmodified PET (Fig. 2 c), as well as the PET modified by a DSBD plasma in N₂ (Fig. 2 b) and O₂ (Fig. 2 a) atmospheres after treatment for 10 s. For pristine PET foil (Fig. 2c), the characteristic IR bands at 1710, 1505 and 1173 cm⁻¹ were observed for the CH, C=O, and benzene-ring -C-C-stretching vibrations, as well as the ring C-H in plane bending. The IR bands at 1358 cm⁻¹ of the wagging, benzene-ring in-plane C-H bending, and the -C-C- stretching vibration bands appeared near 1173 and 1037 cm⁻¹. The spectra of the DSBD plasma treated PET in Fig. 2 b (N₂ plasma) and Fig. 2 a (O₂ plasma) show important differences from that of unmodified PET. The C=O stretch at 1710 cm⁻¹ broadened due to the creation of oxygen-containing sites. The C=O content is higher for the PET modified by the O₂ DSBD plasma (Fig. 2 a) than for the PET modified by the N₂ plasma (Fig. 2 b), and consequently a broadening of the peak at 1710 cm⁻¹ was observed for the O₂ plasma modified PET.

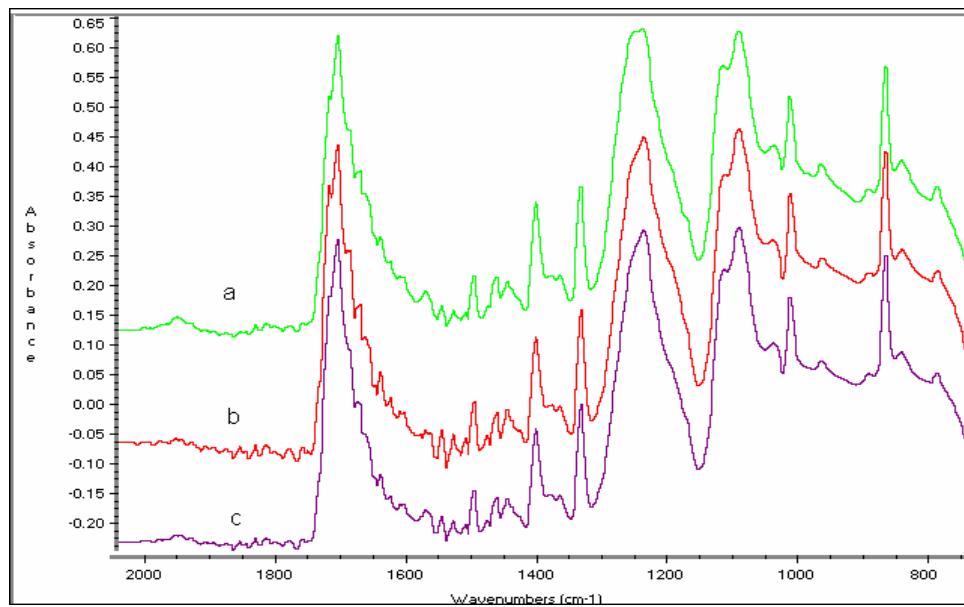


Figure 2 ATR-FTIR spectra of PET foil: (a) treated by DSBD plasma in O₂, (b) treated by DSBD plasma in N₂, and (c) untreated.

XPS

The XPS survey scans and C 1s and O 1s peaks of the untreated PET, as well as the survey scans and C1s, O1s and N1s peaks of the modified PET are shown in Table 1.

Table 1 XPS element amount, O/C, N/C, and (N + O)/C ratio of PET treated by DSBD plasma

| Parameter | PET untreated | DSBD, N ₂ , 5s | DSBD, N ₂ , 10s | DSBD, O ₂ , 5s | DSBD, O ₂ , 10s |
|-----------|------------------|------------------------------|-------------------------------|------------------------------|-------------------------------|
| C1s | 75.59 | 68.23 | 70.06 | 76.51 | 76.67 |
| O1s | 24.41 | 30.12 | 25.95 | 23.49 | 23.33 |
| N1s | 0 | 1.65 | 3.99 | 0 | 0 |
| O/C | 0.323 | 0.35 | 0.370 | 0.416 | 0.441 |
| N/C | 0 | 0.036 | 0.057 | 0 | 0 |
| (N+O)/C | 0.323 | 0.388 | 0.427 | 0.416 | 0.441 |

Surface free energy

The surface free energy of the PET foils modified by DSBD in O₂ and N₂ plasma at atmospheric pressure vs. the activation time is shown in Fig. 3. The surface free energy of PET during modification by DSBD plasma in O₂ and N₂ (Fig. 3, plot a, b)

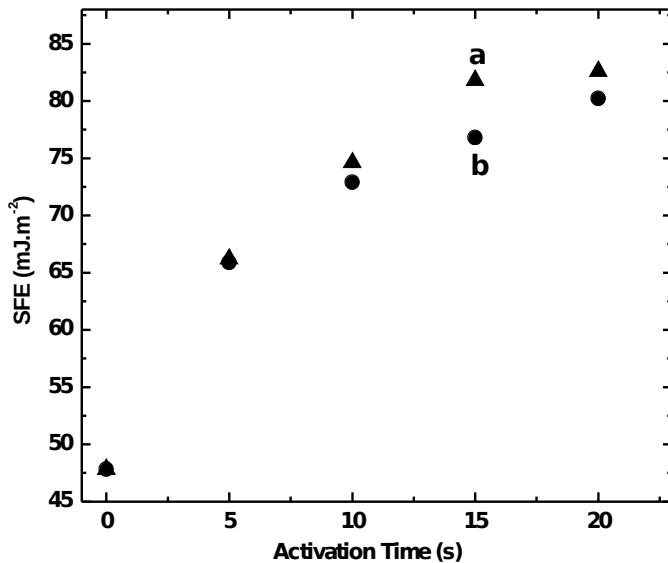


Figure 3 Surface energy of PET foil modified by DSBD plasma: in O₂ (a) and in N₂ (b) vs. activation time.

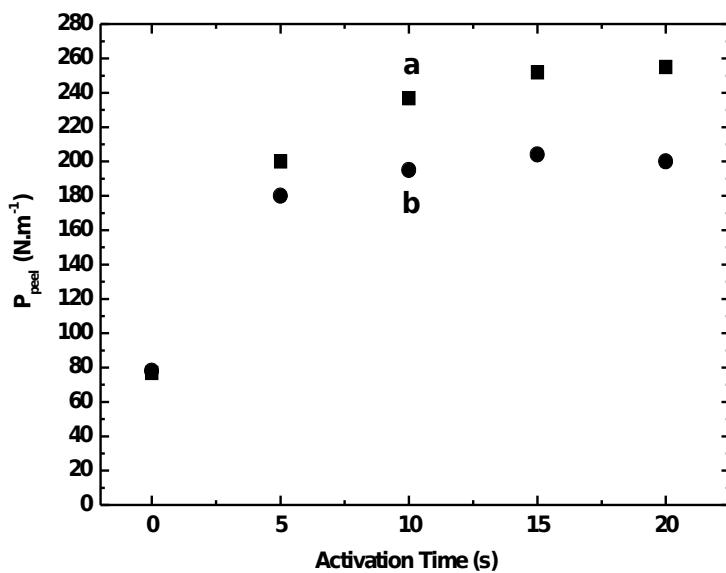


Figure 4 Peel strength of adhesive joint of PET modified by DSBD plasma: a – O₂, b – N₂ to polyacrylate vs. activation time.

significantly increased in comparison with untreated polymer. Fig. 3, plot a shows that the surface energy of PET modified by DSBD plasma in O₂ increases from an initial value of 47.8 mJ.m⁻² for untreated PET to 82.6 J.m⁻² for 20 s of plasma

modification. Fig. 3, plot b shows the surface energy of PET modified by DSBD plasma in N₂. These values are lower than those of PET modified by the same method in O₂.

Strength of adhesive joint

The peel strength of the adhesive joints of PET foils, modified by DSBD plasma (Fig. 4) in nitrogen (4, plot b), in oxygen (Fig. 4, plot b) to polyacrylate vs. time of activation is shown in Fig. 4. The peel strengths of PET to polyacrylate after modification by DSBD plasma significantly increased, and these increases were higher for the samples modified in oxygen. The peel strength of the adhesive joint increased from 77 N.m⁻¹ (unmodified PET) to 180 N.m⁻¹ (DSBD, 10 s, N₂), and 237 N.m⁻¹ (DSBD, 10 s, O₂). These results clearly indicate that plasma irradiation considerably improves the adhesive properties of PET for DSBD plasma.

Relation between adhesion and surface energy

Fig. 5 shows the relation between peel strength of the adhesive joint of PET, modified by DSBD plasma, to polyacrylate and the surface energy of polymer. A 1st order exponential decay was found for modification in O₂. For this processing gas the relation between peel strength of the adhesive joint and surface energy is given by the following relation: $P_{\text{peel}} = 309.5 - 1719.8 \cdot \exp(-\text{SFE}/23.9)$ (SFE = surface free energy).

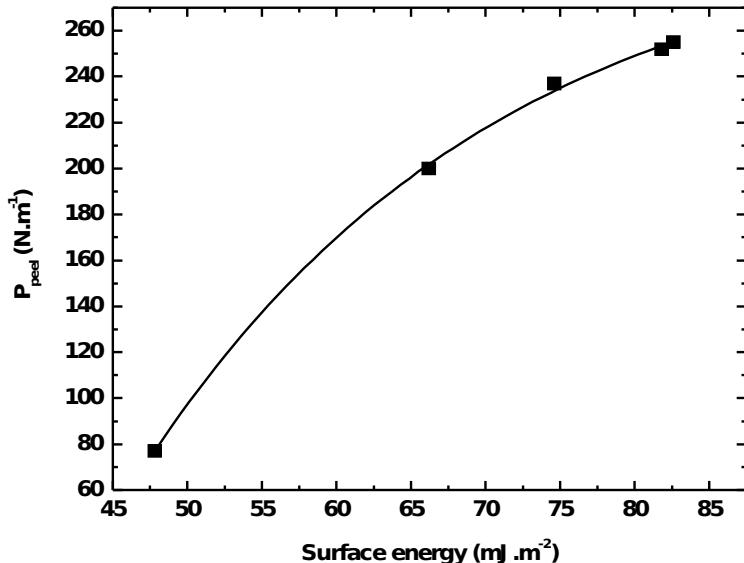


Figure 5 Relation between peel strength of adhesive joint of PET modified by DSBD plasma in O₂ to polyacrylate vs. surface free energy of the polymer

Cocclusions

- (i) The roughness of the PET film modified by DSBD plasma in N₂ and O₂ in air increased;

- (ii) AFM results confirmed the creation of some heterogeneities due to local melting on the surface of PET;
- (iii) DSBD plasma modified PET showed a broadening of the C=O stretch at 1710 cm^{-1} due to the creation of oxygen-containing sites;
- (iv) XPS showed an increase in oxygen and nitrogen content in the PET surface layers after modification by DSBD plasma in N_2 or O_2 , and by RFD plasma in air;
- (v) The surface energy of PET modified by DSBD plasma significantly increased, and this increase was higher for oxygen compared to nitrogen;
- (vi) The peel strength of PET, modified by DSBD plasma or RFD plasma, to polyacrylate significantly increased, and this value was higher in the case of oxygen than in the case of nitrogen.
- (vii) A correlation between the peel strength of the adhesive joint of PET, modified by DSBD plasma in oxygen or nitrogen, to polyacrylate and surface energy of polymer by the following relation: $P_{\text{peel}} = 309.5 - 1719.8 \cdot \exp(-SFE/23.9)$ has been found.

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