

## Pre-treatment of polyester-based veneers

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**Abstract:** *Pre-treatment of polyester-based veneers.* The surface of polyethylene terephthalate (PET) veneers 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 analysed by attenuated total reflectance. The surface energy, and its polar contribution of the adhesive joints of PET, modified by DSBD plasma to polyacrylate increased.

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

### INTRODUCTION

PET is one of the important polymers that are frequently used in many industrial applications, e.g. in the furniture industry, due to its excellent mechanical 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.

### EXPERIMENTAL

#### Materials

In our experiments we used biaxially oriented PET veneers (Technoplast, Czech Republic) for modification by discharge plasma, and acrylic based polymer poly(2-ethylhexyl acrylate) (PEHA) (Polysciences, USA) as polar adhesive in PET veneer 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 veneers 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 veneers by DSBD plasma was performed in a laboratory plasma source at atmospheric pressure in mediums of N<sub>2</sub> or O<sub>2</sub> 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<sub>2</sub> or O<sub>2</sub> was 100 W.

## Characterization methods

### ATR-FTIR

The ATR-FTIR spectroscopy measurements of the PET veneers were performed with a Nicolet Impact 400 FTIR spectrometer (Nicolet, USA) having a resolution of  $4\text{ cm}^{-1}$ , 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 were recorded using a VG Scientific ESCALAB 250 system equipped with a micro-focused, monochromatic Al  $K_{\alpha}$  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 analyser energy mode, with pass energies of 150 and 20 eV for the survey and narrow regions, respectively. The Advantage 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 analyser transmission function.

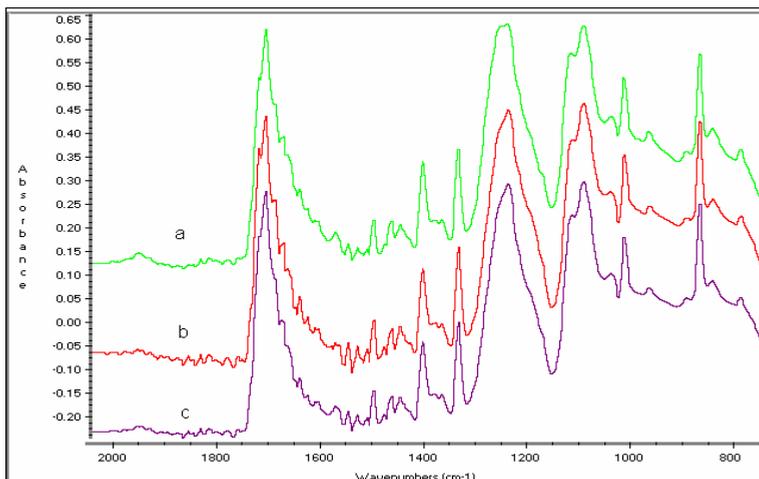
### Surface energy

The surface energy of PET was determined *via* measurements of the contact angles of a set of testing liquids: re-distilled water, ethylene glycol, formamide, methylene iodide, and  $\alpha$ -bromo naphthalene) with a SEE (Surface Energy Evaluation) system (Advex, Czech Republic). The drops of testing liquid ( $V = 3\ \mu\text{l}$ ) were placed on the PET veneer 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].

## RESULTS AND DISCUSSION

### ATR-FTIR

Fig. 1 shows the ATR-FTIR spectra of unmodified PET veneer (Fig. 1 c), as well as the PET veneer modified by a DSBD plasma in  $\text{N}_2$  (Fig. 1 b) and  $\text{O}_2$  (Fig. 1 a) atmospheres after treatment for 10 s. For pristine PET veneer (Fig. 1 c), the characteristic IR bands at  $1710$ ,  $1505$  and  $1173\text{ cm}^{-1}$  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  $1358\text{ cm}^{-1}$  of the wagging, benzene-ring in-plane C-H bending, and the -C-C- stretching vibration bands appeared near  $1173$  and  $1037\text{ cm}^{-1}$ . The spectra of the DSBD plasma treated PET veneer in Fig. 1 b ( $\text{N}_2$  plasma) and Fig. 1 a ( $\text{O}_2$  plasma) show important differences from that of unmodified PET veneer. The C=O stretch at  $1710\text{ cm}^{-1}$  broadened due to the creation of oxygen-containing sites. The C=O content is higher for the PET modified by the  $\text{O}_2$  DSBD plasma (Fig. 1 a) than for the PET veneer modified by the  $\text{N}_2$  plasma (Fig. 1 b), and consequently a broadening of the peak at  $1710\text{ cm}^{-1}$  was observed for the  $\text{O}_2$  plasma modified PET veneer.



**Figure 1.** ATR-FTIR spectra of PET veneer: (a) treated by DSBD plasma in O<sub>2</sub>, (b) treated by DSBD plasma in N<sub>2</sub>, and (c) untreated.

### X-ray photoelectron spectroscopy (XPS)

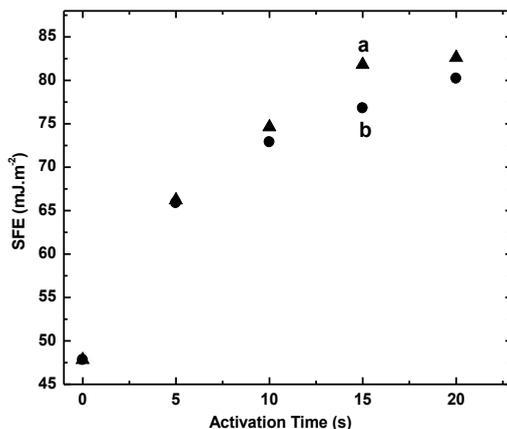
The XPS survey scans and C 1s and O 1s peaks of the untreated PET veneer, as well as the survey scans and C1s, O1s and N1s peaks of the modified PET are shown in Table 1.

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

Parameter	PET untreated	DSBD, N <sub>2</sub> , 5s	DSBD, N <sub>2</sub> , 10s	DSBD, O <sub>2</sub> , 5s	DSBD, O <sub>2</sub> , 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 energy

The surface energy of the PET veneer modified by DSBD plasma in O<sub>2</sub> and N<sub>2</sub> plasma at atmospheric pressure vs. the activation time is shown in Fig. 2. The surface energy of PET veneer during modification by DSBD plasma in O<sub>2</sub> and N<sub>2</sub> (Fig. 2, plot a, b) significantly increased in comparison with untreated polymer.



**Figure 2.** Surface energy of PET foil modified by DSBD plasma: in O<sub>2</sub> (a) and in N<sub>2</sub> (b) vs. activation time

Fig. 2, plot a shows that the surface energy of PET veneer modified by DSBD plasma in O<sub>2</sub> increases from an initial value of 47.8 mJ.m<sup>-2</sup> for untreated PET veneer to 82.6 J.m<sup>-2</sup> for 20 s of plasma modification. Fig. 2, plot b shows the surface energy of PET veneer modified by DSBD plasma in N<sub>2</sub>. These values are lower than those of PET veneer modified by the same method in O<sub>2</sub>.

## CONCLUSIONS

- (i) DSBD plasma modified PET veneer showed a broadening of the C=O stretch at 1710 cm<sup>-1</sup> due to the creation of oxygen-containing sites;
- (ii) XPS showed an increase in oxygen and nitrogen content in the PET veneer surface layers after modification by DSBD plasma in N<sub>2</sub> or O<sub>2</sub>, and by RFD plasma in air;
- (iii) The surface energy of PET veneer modified by DSBD plasma significantly increased, and this increase was higher for oxygen compared to nitrogen.

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**Streszczenie: Obróbka wstępna oklein na bazie poliestru.** Powierzchnia oklein wykonana z politereftalanu etylenu została poddana obróbce wstępnej poprzez wyładowania barierowe plazmy w warunkach ciśnienia atmosferycznego w atmosferze różnych gazów, celem poprawy jej powierzchni i właściwości adhezyjnych. Zmiany w strukturze chemicznej polimeru analizowano metodą osłabionego całkowitego wewnętrznego odbicia. Energia powierzchniowa oraz jej polarna składowa dla politereftalanu etylenu pod wpływem modyfikacji plazmą uległa zwiększeniu.

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