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# Polymer matrix of polyethylene porous films functionalized by electrical discharge plasma

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ABSTRACT

The polyethylene porous films were treated by dielectric surface barrier discharge (DSBD) plasma at atmospheric pressure in oxygen ($O_2$) or nitrogen ($N_2$), and by radio-frequency discharge (RFD) plasma in air at reduced pressure 46 Pa. The surface energy of films was carried out by direct measurements of contact angles of six testing liquids. The strength of adhesive joints in the system modified polyethylene porous films – polyacrylate was measured by peeling of the joints under the angle of 90°. The significant increase of the surface energy and its polar component of polyethylene porous films modified by all types of plasma were observed. The higher strengths of adhesive joints were found for modification of polyethylene porous films by radio-frequency discharge plasma in comparison with modification of the films by barrier discharge plasma.



## 1. Introduction

The surface energy is a key property for many applications of polymers. The low surface energy of high-density polyethylene (HDPE) causes that their surface and adhesion properties are insufficient for bonding and printing. HDPE exhibits the surface energy of 32–35 mJ $m^{-2}$ due to structure of its macromolecules containing no polar functional groups. The bonding of HDPE and its disability with printing ink represents a permanent problem which cannot be solved without modification of polymer. For instance, the printing on a surface of polymer requires that the wetting substances in liquid state have a lower surface energy value than polymer. For this reason, the securing of good adhesion of printing inks or adhesives to HDPE surface necessitates to raise its surface energy by a convenient modification method. To obtain a higher strength of adhesive joints of HDPE to more polar polymers, it is necessary to increase its surface energy by specific modification methods. The most advanced method of modification of HDPE surface, due to its practical usability, suitability to continuous modification processes, and efficiency the modification, is based on modification by electric discharge plasma [1–8]. If this method of modification is used and convenient parameters of electric discharge are adjusted, the original suitable mechanical properties of polymer remain preserved while the surface energy and polarity of the polymeric surface simultaneously increase.

The polyethylene porous film (PEPF) was modified by surface barrier discharge (DSBD) plasma at atmospheric pressure in oxygen ($O_2$) or nitrogen ($N_2$), and/or by radio-frequency discharge (RFD) plasma in air at reduced pressure 46 Pa.

## 2. Experimental

The experiments were carried out with PEPF samples (Institute of Macromolecular Compounds, Russia) [9].

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Microporous polyethylene films of HDPE have been obtained in the process based on melt extrusion with subsequent annealing and uniaxial extension [10,11]. Commercial grades of HDPE (Stavrolen, Russia) with $M_w = 1.7 \times 10^5$, $M_w/M_n = 4.9$ and $T_m = 132\,^\circ$ were used in this process. The porous films had a thickness 14 μm and an overall porosity 40% and contained through channels 200–500 nm in size.

The adhesive joints modified PEPF – polyacrylate were prepared by using of poly (ethylhexyl acrylate) (Polysciences, USA) solution in ethyl acetate deposited on biaxially oriented polypropylene support foils with a thickness of 0.02 mm.

The modification of PEPF was performed in static conditions by dielectric surface barrier discharge (DSBD) plasma in a laboratory reactor (Fig. 1) in air at atmospheric pressure and in $N_2$ or $O_2$ of a technical purity. The DSBD source consists of electrodes separated by an alumina dielectric plate. The alumina plate contains discharge electrodes fixed on its upper surface. The discharge tungsten electrodes consist of 1 mm wide, and 80 mm long strips, and the distance between strips was 3 mm. The electrodes were located inside of glass cover allowing passing of the medium gases. The maximum power of the DSBD plasma source was 300 W.

The radio-frequency discharge (RFD) reactor working in static conditions at reduced pressure (26 Pa) consists of two 240 mm parallel circular brass electrodes placed in the 40 mm distance, and having a thickness 10 mm. The electrodes of RFD reactor were located in stainless steel locked-up vacuum cylinder, voltage of RFD plasma reactor was 1 or 2 kV, frequency 13.56 MHz, current intensity was maximum 0.6 A, and the power of RF generator was max. 600 W.

The strength of adhesive joints in the system modified PEPF – polyacrylate were measured by peeling of the joints under the angle of 90° on 5 kN universal testing machine Instron 4301 (Instron, England). The measurement was carried out using an aluminum-peeling wheel in which the adhesive joints were fixed. The peeling of adhesive joint proceeded at speed of the dynamometer crosshead speed equal 2.5 mm $min^{-1}$, the length of joint being 100 mm. The peel strength of adhesive joint P (J $m^{-2}$) was calculated from the following equation:

$$P = \frac{F_s}{d}, \tag{1}$$

where $F_s$ are mean force of peeling (N), and $d$ width of the adhesive joint (m).

The deposition of polyacrylate solution in ethyl acetate was performed with coating ruler (Dioptra, Czech Republic) with a thickness of the layer 0.12 mm.

Measurement of the surface energy of polymer was carried out by direct measurements of contact angles of testing liquids set (re-distilled water, ethylene glycol, thiodiglycol, formamide, methylene iodide, and 1-bromonaphthalene) using microscopic Contact Angle Meter (Zeiss, Germany). The dependence of contact angle versus time was then extrapolated to $t = 0$ and the surface energy and its polar component were evaluated by Owens–Wendt equation modified by Fowkes and Kinloch based on method of least squares [4]:

$$\frac{(1+\cos\theta)\gamma_{LV}}{2} = (\gamma_{LV}^{d} \cdot \gamma_{s}^{d})^{1/2} + (\gamma_{LV}^{p} \cdot \gamma_{s}^{p})^{1/2} \tag{2}$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{3}$$

where $\theta$ is the contact angle (deg), $\gamma_{LV}$ is the surface energy of testing liquid (mJ $m^{-2}$), $\gamma_{LV}^d, \gamma_{LV}^p$ is the dispersive, and polar component of surface energy of the testing liquid (mJ $m^{-2}$), $\gamma_s^d + \gamma_s^p$ is the dispersive, and polar component of surface energy of the polymer (mJ $m^{-2}$).

The Attenuated Total Reflection (ATR)–Fourier Transform Infrared (FTIR) spectroscopy measurements of PEPF samples were performed with Nicolet Impact 400 FTIR spectrometer (Nicolet, USA) with ATR vertical extender having a resolution of 4 $cm^{-1}$, a scan range of 4000–400 $cm^{-1}$, and a total of 512 scans per analysis. The KRS-5 crystal (eutectic blend of thallium bromide and thallium iodide) has been used for FTIR–ATR measurements.

Morphology of PEPF before and after plasma irradiation was investigated by scanning electron microscope JSM-35 (Jeol, USA). Chemical changes in the samples were demonstrated by IR spectroscopy (Bucker VERTEX Fourier spectrometer).

The changes in surface morphology were measured by AFM. All measurements were performed under ambient conditions using a commercial atomic force microscope (NanoScope™ Dimension IIIa, MultiMode Digital Instruments, USA) equipped with the PPP-NCLR tapping-mode probe (Nanosensors™ Switzerland; spring constant 39 N $m^{-1}$, resonant frequency ≈ 160 kHz). Surface properties of all films were measured on size of $x$ and $y$ axis from 0.5 μm to 25 μm on different positions of the films in order to find out characteristic and significant surface features. Tapping-mode AFM technique was used for all images.

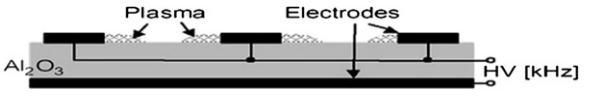


**Fig. 1.** Schematic representation of experimental installation for DSBD plasma treatment.

## 3. Results and discussion

The results of study of surface and adhesive properties of PEPF modified by DSBD, and/or by RFD plasma are shown in Figs. 2–6.

The surface properties of PEPF samples modified by DSBD plasma in $O_2$ and $N_2$ as well as by RFD plasma in air at reduced pressure as a function of modification time are summarized in Figs. 2–4. The surface energy and its polar component of PEPF modified by DSBD (Figs. 2 and 3), and RFD plasma (Fig. 4) increased markedly in comparison with unmodified polymer. The total surface energy of DSBD plasma modified PEPF increased from 33.2 mJ $m^{-2}$ (unmodified sample) up to 51.8 mJ $m^{-2}$ (DSBD, $O_2$, 10 s) and 53.9 mJ $m^{-2}$ (DSBD, $O_2$, 20 s), or 48.9 mJ $m^{-2}$ (DSBD, $N_2$, 10 s) and 51.3 mJ $m^{-2}$ (DSBD, $N_2$, 20 s), respectively (Fig. 2). These results are in good accordance with our pre-