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Adhesive properties of polyester treated by cold plasma in oxygen and nitrogen atmospheres

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ABSTRACT

Polyester foil was treated by the surface diffuse barrier discharge (SDBD) plasma at atmospheric pressure in oxygen and/or in nitrogen containing a small amount of oxygen to improve its surface and adhesive properties. Changes in a chemical structure of the polyester were analyzed by electron spin resonance (ESR) spectroscopy, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and by X-ray photoelectron spectroscopy (XPS). The changes in surface morphology were studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). A surface energy as well as an adhesion of polyester modified by the SDBD plasma to polyacrylate significantly increased. The efficiency of the modification by the SDBD plasma depends on the used processing gas as well as on the modification time. The decrease in the surface energy of polyester modified by the SDBD plasma due to hydrophobic recovery was also investigated. A correlation between adhesive properties of polyester modified by the SDBD plasma and its surface has been found.

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1. Introduction

Polyester foils are frequently used in many industrial applications, e.g. in the automotive industry for the car construction, due to its excellent properties. The surface energy of polyester is usually too low for certain important applications, such as bonding, printing, lamination, etc. Several efficient methods have been used to improve the surface and adhesive properties of polymers [1,2]. One of these is based on application of cold plasma for pre-treatment of polymeric surface [3–9], which is a solvent-less, ecological method of modification, aimed mainly to the adjustment of the surface energy and consequently the adhesion to other materials. The most important feature consists in the modification of surface properties of the polymer without changing the intrinsic bulk properties [10–16].

It is well known that the modification of polymers by cold plasma leads to chemical and physical changes in surface parameters and adhesive properties. Depending on the processing gasses used, various functional groups are formed in a very thin surface layer of the polymer [17–19]. Polyester with a substantially higher surface energy than polyolefin usually does not need to be pre-treated by plasma for printing,

because the surface energy in the untreated state is high enough for achieving permanent print [20,21]. However, the surface free energy is insufficient for obtaining strong adhesive joints. The plasma treatment of polyethylene terephthalate (PET) foils by surface diffuse barrier discharge (SDBD) plasma in air introduces oxygen containing groups on the polymeric surface [22–25]. The unpurified nitrogen applied as a processing gas for the surface modification of polymers contains a very small amount of oxygen at around 30 ppm, and can affect the degree of the modification of the plasma treated polymer. The oxygen traces present in nitrogen result in a formation of oxygenic functional groups increasing the polarity of plasma treated PET [25]. The modification of polyester in oxygen and nitrogen by the SDBD plasma was chosen in order to compare the resulting effect on surface and adhesion properties of the plasma treated polymer in these processing gasses. Moreover, the application of nitrogen as the processing gas in terms of the modification of polyester is safer than oxygen also from safety of the process if applied in a large industrial scale. As stated above, for the preparation of strong adhesive joints, the modification of polyester by SDBD plasma is essential. This can be performed as a continuous technological process, which is optimal for plasma treatment of PET foils in an industrial scale. A significant problem with the cold plasma modification of polyester is that the effect of the surface modification is diminishing rather quickly during storage, and surface and adhesive properties of the foil

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are deteriorating. Due to the changes during storage the plasma-treated PET foils should be processed to final stage (printing, adhesion) within 7 days. The modification of PET by the SDBD plasma in oxygen or nitrogen is scalable to a roll-to-roll processing method suitable for industrial production.

In this paper the surface and adhesive properties of polyester modified by the SDBD plasma in either oxygen or unpurified nitrogen have been investigated using contact angle measurements, peel tests, as well as ESR, ATR-FTIR, XPS, SEM and AFM analyses. The process of hydrophobic recovery of modified polyester foil during storage has been investigated and the correlation between adhesive properties of polyester modified by the SDBD plasma and surface energy has been found.

2. Experimental

2.1. Materials

In our experiments polyester/PET foils (Tenolan OAN, Technoplast, Czech Republic) with a thickness of 0.12 mm, (melting enthalpy $\Delta H_m = 64.8$ J/g, degree of crystallinity 47.2%) were used for the modification by discharge plasma. PET foils were immersed in acetone in order to remove additives influencing their surface properties. The solution of poly (2-ethylhexyl acrylate) (PEHA) (Polysciences, USA) in ethyl acetate was used for the preparation of PET-PEHA adhesive joints. A layer with a thickness of 0.12 mm was deposited on supported biaxial oriented polypropylene (BOPP) Tatrafan ON (Chemosvit, Slovakia) with the aid of a coating ruler (Dioptra, Czech Republic). The processing gasses of technical purity – oxygen and unpurified nitrogen containing 30 ppm of oxygen (SIAD, Slovakia) have been used for the preparation of plasma-treated polymer.

2.2. SDBD set-up

The modification of the PET foils by the SDBD plasma was performed on a laboratory plasma equipment at atmospheric pressure in nitrogen or oxygen gasses of technical purity. The nitrogen contained 30 ppm of oxygen. The SDBD plasma generator consists of electrodes separated by an alumina dielectric plate. The discharge electrodes having an area of 80×80 mm, and consisting of 1-mm wide and 80-mm long tungsten strips, are fixed to the upper surface of the alumina. The voltage of the SDBD source was 100 V, current intensity 1 A, and frequency 6 kHz. The power 100 W was used for the modification by SDBD plasma in N_2 or O_2 at atmospheric pressure. The power applied for the whole electric circuit of the SDBD plasma source has been measured using a special device Voltcraft Plus Energy Logger 3500 (Voltcraft, Germany).

2.3. Characterization methods

2.3.1. SEM

The morphology of the PET before and after the SDBD plasma irradiation was investigated by scanning electron microscope JSM-6400 (JEOL, Japan). The foils were sputter-coated (SCD 050, BALTEC) with a Pt layer (4 nm).

2.3.2. 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 (NanoScope™ Dimension IIIa, MultiMode Digital Instr., USA) equipped with a PPP-NCLR tapping-mode probe (Nanosensors™ Switzerland; spring constant $39 \text{ N} \cdot \text{m}^{-1}$, resonance frequency ≈ 160 kHz). The surface properties of all the films were measured in x and y axis sizes between 2 and 25 μm on different positions of the films in order to find characteristic and significant surface features. The AFM analysis provides 2D or 3D information on both the height

and material heterogeneity contrast with high resolution when recording height and phase shifts simultaneously.

2.3.3. ESR

Samples of PET foils were inserted into silica quartz tubes and placed into the resonator of an ESR Bruker-Biospin, ElexSys E-540 spectrometer equipped with a Bruker high-sensitivity cavity ER 4119 HS-W1 operating at 9.75 GHz (X-band) and room temperature. The ESR spectrometer settings were as follows: modulation frequency, 100 kHz; modulation amplitude, 1.0 G; microwave power, 20 mW; receiver gain, 60 dB; time constant, 1.28 ms; conversion time, 5.12 ms; and magnetic field scan, 6 kG (center at 3480 G), number of scans, 30. An Xopr (Bruker) Linux-based package was used for acquisition of data, and the Origin (Origin Lab) software was used for the data analysis and presentation. The ESR measurements of PET were performed at room temperature.

2.3.4. ATR-FTIR

The ATR-FTIR spectroscopy measurements of the PET foils [26,27] were performed with a Nicolet Impact 400 FTIR spectrometer (Nicolet, USA) having a resolution of 4 cm^{-1} , a scan range of $4000\text{--}400 \text{ cm}^{-1}$, and a total of 1024 scans per analysis. The vertical ATR accessory contained a KRS-5 (thallium-bromide-iodide) crystal and the angle of incidence of the infrared beam was 45° .

2.3.5. XPS

The XPS spectra [28–31] were recorded using a VG Scientific ESCALAB 250 system equipped with a micro-focused, monochromatic $\text{Al K}\alpha$ X-ray source (1486.6 eV) and a magnetic lens to increase the sensitivity due to higher electron acceptance angle. An X-ray beam of 650 nm size was used at a power of $20 \text{ mA} \times 15 \text{ kV}$. 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 charge compensation was achieved with an electron flood gun coupled to an argon gun. The energy and emission currents of the electrons were 4 eV and 0.35 mA, respectively. The argon partial pressure in the chamber was set at 2×10^{-6} Pa. Under these conditions, the surface charge was negative but uniform. The Avantage software, version 2.2, was used for digital acquisition and data processing. The 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.

2.3.6. Surface energy determination

The surface energy of PET was determined via measurements of the contact angles (θ) [32,33] of a set of testing liquids (θ): re-distilled water, ethylene glycol, formamide, methylene iodide, and 1-bromo naphthalene with a surface energy evaluation (SEE) system (Advex, Czech Republic). The drops of testing liquid ($V = 3 \mu\text{l}$) were placed on the polymeric 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 [34,35]:

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

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

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

where θ = contact angle (deg), γ_{LV} = surface free energy (SFE) of the testing liquid ($\text{mJ} \cdot \text{m}^{-2}$), γ_{LV}^d , γ_{LV}^p = dispersive component (DC), and polar component (PC) of the SFE of the testing liquid ($\text{mJ} \cdot \text{m}^{-2}$), and

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