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Enhanced printability of polyethylene through air plasma treatment

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ABSTRACT

Low-density polyethylene (LDPE) foils were surface-modified by using non-thermal non-equilibrium oxidative air 40 kHz frequency, radiofrequency (RF) and microwave (MW) discharge plasma treatment. The pristine and treated specimens were morphologically and chemically characterised by Scanning Electron Microscopy (SEM) imaging, X-ray Photoelectron Spectroscopy (XPS) and contact angle measurement with surface energy evaluation. In addition, printability and ink adhesion tests were carried out on the samples, and quantitatively appraised by UV–VIS transmission spectroscopy. The overall outcome indicated chemical and physical changes after each treatment, and the improvement of printability. The present approach could serve as a viable and promising method to improve printability of polyethylene.

1. Introduction

Polyethylene (PE) is undoubtedly the foremost polymer employed for food and pharmaceutical packaging. Its applications include food bags, cling wrap, sachets, squeeze bottles and liquid pipes [1]. This material is also used for various other purposes as diverse as car covers, moisture barriers, cable insulation, garment bags, household, toys and sport goods, medical accessories amongst others [2–6]. By virtue of its simple chemical structure, low cost, processability and resilience, PE is deemed as a real asset in today's world, with enormous potential economic impact. In fact, polyethylene represents 40% of the global plastic production (*ca.* 60 tons produced per year) [7]. However, this versatile material has two main drawbacks: the increasing amount of plastic wastes, which implies the development of new plastic biotechnology to help address associated challenges, and also poor adhesion properties on account of its a polarity, which negatively influences printability and/or the attachment of polar agents [8–10]. A common strategy to render a good adhesion is by oxidising the outermost layer of a material. There are several methods for polyethylene surface modification, such as wet-chemical, redox methods [11], flame, UV, ozone treatments, and plasma-based technologies [12].

In this regard, the technique of plasma treatment is an effective tool, which is an easy, quick technology that only requires relatively inexpensive processing devices, is environmentally friendly and has been used by different researchers [13–16]. The primary effect of plasma treatment is to transfer reactivity towards the treated surfaces via plasma species, such as positive and negative ions, neutral species, atoms, metastables, free radicals and UV-radiation; confining the treatment to the top layer without affecting bulk properties. For this reason, plasma surface modification is already a very popular technique, which has been performed on synthetic and biological polymers [17,18], carbon fibres, ceramics [19], and other sort of materials that require enhancement of any surface feature [20]. Oxidative plasmas are known to cause basically three main phenomena: bond destruction leading to molecular rearrangement; ablation or etching, giving rise to volatile products and polarity changes due to the incorporation of oxygen-containing entities; *e.g.,* hydroxyl, carbonyl, carboxyl, ether and peroxide [21–23].

Despite the plethora of publications on polyethylene in general and the relevance of polymer printability on technology, there are few studies about printability of polyethylene [24–26], and detailed information is still lacking in this area. Therefore, the aim of this contribution was to make a comprehensive study of: (i) the effect of air plasma treatment discharge frequency on polyethylene morphology and chemistry by using surface probe techniques (ii) the extent of printability, evaluating how plasma treatment influences ink adhesion to the polymer substrate. The broad demand of this polymer underlies the motivation of choosing this material

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as a target for the current work. Moreover, it is the first time that research on printability of polyethylene is undertaken using air-based plasma treatment.

2. Materials and methods

2.1. Materials

Commercially available LDPE was obtained from Dow Chemical Company, USA. Anhydrous ethylene glycol $C_2H_6O_2$ 99.8% and diiodomethane CH_2I_2 99% were purchased from Sigma–Aldrich, USA. K120 PE printing tape-roll (colour black, size 25 mm × 189 m) supplied by Bohemia Znak, Czech Republic. Scotch magic™ tape from 3M, USA was used in this study. The reagents were used as received without any further purification.

2.2. Plasma treatment of PE

Both sides of 5 × 5 × 0.1 cm PE foils were exposed to non-thermal non-equilibrium air plasma by using the following plasma reactors: Femto (Diener electronic, Germany) with a cylindrical chamber of 100 mm diameter and 270 mm length operated at a frequency of 40 kHz; Femto (Diener electronic, Germany) Ø 150 mm and 320 mm length operated at a frequency of 13.56 MHz; and Pico reactor (Diener electronic, Germany) with a chamber of Ø 150 mm, 320 mm length, operated at a frequency of 2.46 GHz. Pressure, power input and carrier gas feed rate were the same in every experiment *viz.*: 40 Pa, 50 W and 20 sccm respectively. The duration of treatments was 1 and 2 min. Subsequently, the specimens were taken out from the plasma reactor and immediately used for the next experiments.

2.3. Surface chemistry evaluation

X-ray photoelectron spectroscopy (XPS) was conducted on treated and untreated samples in an XPS microprobe instrument PHI Versaprobe (Physical Electronics, USA). The base pressure in the XPS analysis chamber was $\approx 6 \times 10^{-8}$ Pa. The foils were irradiated with X-rays over a 400 μm spot area with a monochromatic Al $K_{\alpha 1,2}$ radiation at 1.48 keV. The emitted photoelectrons were detected by a hemispherical analyser positioned at a take-off angle of 45°. Survey-scan spectra were acquired at a pass energy of 187.85 eV and 0.5 eV step resolution. The spectra were fitted using MultiPak v7.3.1 software from Physical Electronics, USA; which was supplied with the spectrometer.

2.4. Surface morphology evaluation

Scanning electron microscopy (SEM) was performed on both treated and untreated samples in a VEGA II LMU microscope (Tescan s.r.o, Czech Republic) operated in high vacuum/secondary electron imaging mode. The samples were coated with a thin Gold/Palladium alloy layer and tilted 30° to attain better surface topography observation. The images were taken at a magnification of 10,000×.

2.5. Surface wettability assessment

Wettability of the samples was evaluated by contact angle measurement before and immediately after each modification. The sessile drop method was employed for this purpose on a Surface Energy Evaluation (SEE) system equipped with a CCD camera (Advex Instruments, Czech Republic). Deionised water, ethylene glycol and diiodomethane were used as testing liquids at 22 °C and 60% relative humidity. The droplets volume was set to 5 μl for all experiments. Every representative contact angle value was an average of 10 independent measurements. The substrate surface free energy was evaluated by using the acid–basic model.

2.6. Printability test

The untreated and treated specimens were printed by using a Gebr Baier KG (Gebr-Bayer GmbH & Co, Germany) printing machine with a printing tape-roll for LDPE substrates at 105 °C. The ink adhesion test was undertaken with Scotch Magic tape (3M, USA) which was utilised for lifting ink off the printed samples according to a pre-established number of peels (0, 5, 10, 20 and 40) based on the prior experience [27]. The tape was stuck and lifted off with consistent force at an angle of 90° each time. After each set of "ink lift-offs", the UV–VIS spectra were recorded both for treated and untreated samples on a transmission spectrophotometer (Cary 300 conc, Varian, USA) equipped with a thin film sample holder. The spectral range selected was within 350–700 nm.

3. Results and discussion

3.1. Surface chemistry analysis

X-ray Photoelectron Spectroscopy (XPS) is utilised to gain a quantitative insight into the elemental composition of the surface that does not extend beyond 7 nm depth [28]. The surface elemental composition and ratios of untreated and treated polyethylene specimens are listed in Table 1. For convenience, numbers from 1 to 7 have been assigned to the samples, the ascribed notation is below the table, and it shall be used throughout the study. It means, Sample 1 denotes untreated polyethylene, Sample 2 is PE in a 40 kHz for 1 min, Sample 3 is 40 kHz 2 min, Sample 4 signifies a 13.56 MHz radiofrequency (RF) for 1 min, Sample 5 is RF 13.56 MHz 2 min, Sample 6 is 2.46 GHz microwave (MW) for 1 min and Sample 7 is MW 2.46 GHz 2 min.

The XPS records reveal that no traces of any contaminant element were found in the untreated polyethylene. The increase of oxygen and nitrogen contents after air plasma treatment suggests the occurrence of surface oxidation and nitrogenation which may be corroborated by the corresponding ratios of oxygen vs. carbon O/C and nitrogen vs. carbon N/C.

In this regard, two kinds of reactions are involved; the first ones are *in situ*, in the chamber, and the other reactions are initiated once the material is withdrawn from the plasma reactor. This treatment breaks bonds and generates many radicals reacting with oxygen and other reactive species present in the atmosphere leading to surface functionalisation. Conventionally, oxygen-containing plasmas trigger surface oxidation and surface etching [29]. With reference to surface nitrogenation, it was remarkably lower than oxidation. This may be explained, since nitrogen even though is the major component of air, is considered as a low reactive gas, which only reacts spontaneously with few reagents on account of its

Table 1
Surface elemental composition and ratios based on XPS analysis.

Sample	C1s%	O1s%	N1s%	O/C	N/C
1	100				
2	77.2	20.2	2.6	0.26	0.03
3	76.5	20.8	2.7	0.27	0.04
4	82.0	15.7	2.3	0.19	0.03
5	78.5	17.6	3.9	0.22	0.05
6	74.0	20.7	5.3	0.28	0.07
7	77.6	18.0	4.4	0.23	0.06

Sample 1. Untreated PE; 2. 40 kHz 1 min; 3. 40 kHz 2 min 4. RF 13.56 MHz 1 min; 5. RF 13.56 MHz 2 min; 6. MW 2.46 GHz 1 min; 7. MW 2.46 GHz 2 min.