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Full Length Article

Influence of ethanol vapor addition on the surface modification of polyethylene in a dielectric barrier discharge

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ABSTRACT

In this paper, ethanol vapor up to 50% is added to an argon, air or nitrogen dielectric barrier discharge at medium pressure to profoundly investigate the effect of ethanol addition on the surface modification of low density polyethylene (LDPE). Water contact angle (WCA) and X-ray photoelectron spectroscopy (XPS) measurements show that the ethanol vapor addition effect on the LDPE surface depends on the used carrier gas. Adding ethanol to an argon plasma has no significant effect on the wettability nor on the chemical composition of LDPE compared to a pure argon plasma treatment. Ethanol addition does however slightly increase the LDPE surface roughness. Addition of small amounts of ethanol vapor to an air plasma makes it possible to incorporate additional nitrogen and oxygen groups on the LDPE surface, resulting in an extra decrease of 11% in WCA value. Moreover, the LDPE surface roughness is slightly increased due to the ethanol vapor addition. The most significant effect of ethanol addition is however observed when nitrogen is used as carrier gas. After an N_2/2% ethanol plasma treatment, an 85% reduction in WCA value to 8.5° is found compared to a pure N_2 plasma treatment. This very hydrophilic LDPE surface is obtained due to a significantly high incorporation of oxygen and nitrogen groups on the surface with an O/C and N/C ratio reaching 32% and 53% respectively. FTIR measurements also reveal that the observed extremely high wettability of LDPE is not the result of plasma activation but is due to plasma polymerization effects occurring on the surface resulting into the deposition of a plasma polymer containing ketones, amides as well as C=N groups. In addition, ageing studies have also been conducted and these studies reveal that for all carrier gases, ethanol addition to the discharge gas significantly suppresses the ageing effect. All the above mentioned conclusions therefore indicate that ethanol vapor based plasmas can be an excellent tool to increase the surface energy of polymers.

1. Introduction

Low density polyethylene (LDPE) is widely used for industrial and medical applications due to its excellent material properties (low density, high flexibility and high chemical resistance). [1] However, despite these excellent characteristics, LDPE is often unsuitable for use due to its low surface free energy, making it non-receptive to bonding, printing inks, coatings and adhesives. [2] An increase in surface free energy can be obtained using wet chemical processes; however, ecological requirements force the industry to search for alternative environmentally friendly methods. [3] One of these benign techniques to substantially increase the surface free energy of different substrates is plasma treatment, which is quite often performed using dielectric-barrier-discharges (DBDs). [4] The effects obtained upon plasma treatment are very desirable because these treatments can significantly increase the surface free energy or the surface wettability of a material without modifying its bulk properties. In this way, plasma treatments are able to enhance adhesion, printability and dye uptake of several substrates. During the plasma surface activation process, radicals created in the plasma disrupt chemical bonds in the surface layer causing the formation of new species with different properties [5] resulting in a modification of the near-surface region without interfering with the desirable bulk properties of the material. [6] Plasma treatment is also an environmentally benign surface modification technique since it does not require the use of water, solvents and chemicals. [4] The method has already shown its effectiveness and different types of non-thermal plasmas operating at low, medium or atmospheric pressure have already been used for polymer surface

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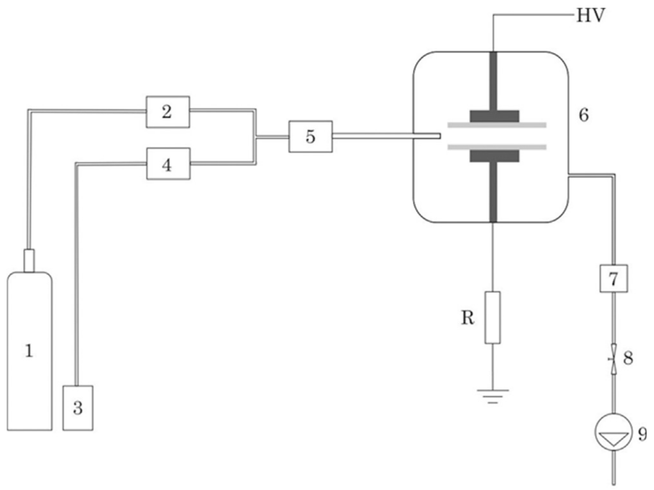

Fig. 1. Schematic diagram of the plasma reactor (1. Carrier gas cylinder, 2. Mass flow controller for the carrier gas, 3. Ethanol container, 4. Liquid flow controller for ethanol, 5. CEM® system, 6. Plasma reactor, 7. Pressure gauge, 8. Valve, 9. Pump).

modification. [3,7–11] In the case of LDPE, plasma modifications are mostly performed in a single discharge gas, such as oxygen, argon, air, nitrogen [1,2,8,11,12] or a discharge mixture like He/O_2 and Ar/O_2. [13] The beneficial effect of adding water vapor to the discharge gas on LDPE surface modification has already been shown in previous studies. [13–15] The effect of adding ethanol vapor to the discharge gas is however not been studied yet. Plasma treatment using a gas/ethanol vapor mixture might result in a substantial enhancement of the LDPE wettability due to the available oxygen atoms in the ethanol molecule. Therefore, the influence of ethanol vapor addition on the surface modification of LDPE in a DBD is investigated profoundly using different carrier gases in this work.

The plasma used is a DBD operating at medium pressure (5.0 kPa). A DBD or 'silent discharge' can be obtained between two electrodes, at least one of which should be covered with a dielectric, when an AC high voltage is applied between the electrodes. [16] The DBD in this study is created at medium pressure instead of atmospheric pressure since medium pressure plasmas have some important advantages. [17,18] First, it is easier to create a large plasma volume which can result in an overall higher production efficiency. Furthermore, the pumping equipment is relatively inexpensive and medium pressure plasmas work in a closed system enabling plasma modifications in a controlled atmosphere. In this paper, it is investigated whether it is possible to increase the LDPE modification efficiency by adding an amount of ethanol vapor (up to 50% ethanol content) to different carrier gases, resulting in a gas/ethanol vapor mixture as discharge gas. The influence of the plasma treatment on the surface properties of LDPE using different gas mixtures will be explored in detail using water contact angle (WCA) measurements for the wettability determinations, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) for chemical composition determinations and atomic force microscopy (AFM) for surface morphology determinations. Finally, the ageing effect of the plasma treated LDPE films will also be investigated in detail using WCA and XPS analyses.

2. Material and methods

2.1. DBD set-up and characterization

The medium pressure DBD reactor was built in the lab and is schematically presented in Fig. 1. The discharge occurs between two copper electrodes (diameter = 4 cm), placed within a cylindrical enclosure. Both electrodes are covered with a ceramic plate (Al_2O_3) (5 cm × 5 cm – thickness = 0.7 mm) and the inter-electrode distance is set to 4 mm. The upper electrode is connected to a high frequency AC power source, while the lower electrode is connected to earth. The frequency of the applied high voltage is kept constant at 50 kHz.

Before starting the experiment, an LDPE film with a thickness of 0.1 mm is placed on the lower ceramic plate. This commercially available LDPE foil was purchased from Goodfellow Cambridge Ltd. and has not been subjected to any pretreatment step prior to plasma modification. After introducing the sample into the reactor, the discharge chamber is pumped down to 0.5 kPa and then filled with the carrier gas to atmospheric pressure. As carrier gas, three different gases are used in this work: argon, air and nitrogen (Air Liquide – Alphagaz 1). After reaching atmospheric pressure, the plasma reactor is flushed with the selected carrier gas at a flow rate of 3.0 slm (standard liters per minute) for 3 min. After this purging step, the pressure in the plasma reactor is lowered to 5.0 kPa. At this pressure, different concentrations of ethanol vapor are added to the selected carrier gas while maintaining a total gas flow rate of 0.5 slm. The ethanol vapor content in the discharge mixture is varied from 0 to 50% using an innovative liquid delivery system (CEM® – Controlled Evaporation and Mixing) purchased from Bronkhorst. This system consists of a liquid flow controller, a mass flow controller for the carrier gas and an evaporation and mixing device. With the use of the flow controllers, a predefined amount of ethanol and carrier gas is distributed to the evaporation device where the temperature of the gas mixture is brought to 30 °C to ensure complete evaporation of the supplied ethanol. Compared to a bubble system, the selection of the gas/liquid ratio is more flexible. In addition, the CEM® system ensures a very stable vapor flow and can accurately control the gas/vapor mixture. In this study, the liquid ethanol flow is varied between 0 and 30 g/h. Using the ideal gas law and taking into account the ethanol vapor pressure, it is possible to calculate the necessary carrier gas flow to maintain a total discharge gas flow rate of 0.5 slm. After the introduction of ethanol vapor to the discharge gas, the AC power source is turned on to modify the LDPE surface while the pressure in the discharge chamber is maintained at 5.0 kPa by slightly pumping during plasma treatment.

The most common electrical diagnostic of a DBD consists of the measurement of the voltage applied to the electrodes and the resultant discharge current. [19] The voltage V(t) applied to the high-voltage electrode is measured using a 1000:1 high voltage probe (Tektronix P6015A), whereas the discharge current I(t) is monitored by measuring the voltage over a 50 Ω resistor, which is connected in series with the lower electrode and the ground. The voltage-current waveforms are then recorded using a Tektronix TDS 1002 digital oscilloscope. Using these voltage-current waveforms, the average power P of the discharge is calculated according to the following equation (T = period of the discharge): [20]

$$P = \frac{1}{T}\int_{t}^{t+T} I(t)V(t)\,dt \tag{1}$$

To identify the reactive species generated in the discharge, optical emission spectra are recorded by means of an Ocean Optic S2000 spectrometer in the range 200–900 nm with a low resolution of 0.7 nm.

2.2. Surface characterization

The wettability of the untreated and plasma treated LDPE films is evaluated using static water contact angle (WCA) measurements. The static WCA of the foils are obtained at room temperature using a Krüss Easy Drop system. Within a few minutes after plasma treatment, a 2 μl drop of distilled water is deposited on each sample.