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Investigation of plasma-induced thermal, structural and wettability changes on low density polyethylene powder

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ABSTRACT

We demonstrate here the structural, thermal, and wettability characteristics of low density polyethylene powder before and after plasma treatments. The plasma treatment was carried out using different working gas i.e. air, oxygen and a mixture of hydrogen and oxygen at an atmospheric pressure of 100 Pa. The plasma treatment time was kept constant at 2 min for all the specimens. Fourier transform infrared (FTIR), dynamic capillary rising using Washburn method, differential scanning calorimetry (DSC), and thermogravimetric analysis has been carried out for both pristine and plasma treated polyethylene specimens. Our study shows that there is 88% increase in the wettability after plasma treatments. Plasma treatment in air atmosphere gives the maximum wettability. Thermogravimetric analysis (TGA) investigation shows plasma treatment in the $H_2 + O_2$ mixture atmosphere gives maximum thermal stability whereas the DSC results reveal the lowest crystallinity for plasma treatment in air atmosphere. The lowest latent heat of fusion (154 J/g) calculated from the melting curve of DSC is observed for LDPE treated in air atmosphere. The FTIR spectroscopy of the plasma-treated LDPE powder reveals that plasma treatment introduces polar group on the LDPE surface leading to the increased surface free energy and surface active sites. The CH_2 concentration increases after plasma treatments.

1. Introduction

Polyethylene (LDPE) is one of the widespread and most inexpensive commodity thermoplastic polymers used for industrial as well as medical applications due to its excellent material properties like low density, high flexibility and high chemical resistance [1]. The annual production of polyethylene is approximately 80 million metric tons. Apart from other thermoplastic materials used in nanocomposites like PMMA, PS [2–4], LDPE is a very popular thermoplastic. However, despite being a very popular commodity polymer for use worldwide in packaging i.e. plastic bag, plastic films, geomembranes, containers including bottles, etc. LDPE is unsuitable for use because of its low surface free energy, leading to poor wettability and adhesion [5]. Therefore, LDPE surface treatment is necessary to increase the overall surface free energy thereby enabling the surface for bonding and printing inks [6].

Plasma treatment is a convenient and environmentally friendly way to obtain these treatments by introducing new chemical groups such as carboxylic, hydroxyl, amine, and aldehyde groups at the surface without affecting the bulk properties [7,8]. Plasma is commonly used because the treatments take only a few minutes, the chemical treatments are consistent and reproducible and no special chemicals or waste removal procedure is needed since gaseous byproducts are removed under vacuum. Low pressure plasma treatment in fluidized bed has been most frequently used whereas application of mechanical stirring appears to be promising for industrial scale application.

In the surface treatment, good contact of the polymeric surface with plasma has been an important requirement. Although powder find wide application in various branches of industry like paintings, biotechnology, filling for composite materials etc., the plasma treatment of powder surface has not found such application as plasma treatment of flat solid materials which is due to limitations associated with the three dimensional geometry, the necessity of solid mixing (removal of powder aggregation), and the large surface area of powder, which should be treated [9–11].

There are different methods adapted for the plasma treatment of powder such as low pressure plasma reactors, e.g., batch reactors [12] downer reactors [13] drum reactors [14] fluidized-bed reactors [15] and microwave plasma reactors [9] or atmospheric pressure

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dielectric barrier discharge [16]. In our case, a modified mechanical movement in plasma treatment is developed in house which is described in Ref. [17].

Several studies have been focused on improving the wettability (or surface energy) and other surface properties of polymer surfaces [11,18,19]. To the best of our knowledge few works are reported on the thermal properties of polymers after plasma treatments. The aim of the present work is to study the effect of plasma treatments on the thermal and structural properties of low density polyethylene powder. The thermal and structural properties are correlated with the surface chemistry as determined by Fourier transform infrared spectroscopy (FTIR). The wettability properties are also studied and represented.

2. Experimental

2.1. Materials

Low density polyethylene powder of rotational molding grade with specific powder surface of 8.500 m^2/m^3 average particle diameter 300 μm and a bulk density of 0.939 g/cm^3 is obtained from (DOW Chem., Switzerland) was used for the surface treatment. One batch of the LDPE powder treatment consists of 0.25 kg in our case.

2.2. Polyethylene surface treatment

Plasma treatments were performed in a homemade modeled laboratory reactor. The reactor consists of a vacuum chamber made up of stainless steel with inner diameter of 50 cm equipped with a standard ISO K 250 flange on upper and lower side of the reactor. There is a stainless steel blender with a horizontal propeller stirrer for the uniform dispersion of the powder during treatment. The stirrer axis is brought out from the reactor through a vacuum trough placed in the bottom of the reactor. To prevent the penetration of the powder into the bearings a sealing lip was used. An electrical engine was placed outside which drives the propeller via a vacuum and a vertical movable shaft. This construction was made in such a way that it maintains a distance between the blender and the plasma source. An electronic system controls the stirrer speed. One revolution per second was typical for all the experiments. The pressure in the chamber was kept at 100 Pa. A microwave plasma source (2.45 GHz) and a magnet (electron cyclotron resonance) with a power of 1000 W were used. The process gases were air, oxygen and a mixture of hydrogen and oxygen with a flow rate of 100 sccm.

2.3. ATR-FTIR analysis

FTIR spectra of polyethylene and treated polyethylene were acquired in the range of 600–4000 cm^{-1}, using a NICOLET IZ10 (Thermo scientific, USA). The specimens were analyzed directly on an attenuated total reflection (ATR) platform. The spectrometer is equipped with a multireflection variable angle horizontal ATR accessory. The internal reflection element is a Zinc Selenide (ZnSe) crystal and the angle of incidence on the crystal is set to 45 °C. The measuring signal passed the optical way with an aperture diameter of 3 mm, with spectral resolution of 4 cm^{-1}. For optimal signal-to-noise ratio, 8 scans were averaged per specimen spectrum and apodized by applying atmospheric suppression correction functions to avoid interference for the Fourier transform. All the spectra were baseline corrected by automatic software control and were normalized thereafter.

2.4. Differential scanning calorimetry

DSC measurements of pristine and treated LDPE were carried out on a Pyris Diamond S6 DSC (Perkin–Elmer, USA), operating between 25 and 160 °C and then cooling from 160 to 25 °C, with a ramping rate of 10 °C/min, in a nitrogen atmosphere at a flow rate of 20 mL/min. ~13 mg of specimen in a crimped aluminum pans was used. The DSC instrument was calibrated based on the melt onset and heat of fusion of indium at 156.6 °C and 28.4 J/g as the standard materials.

2.5. Thermogravimetric analysis

TGA measurements were carried out on a Mettler Toledo TGA/SDTA851e apparatus working in N_2 atmosphere between 50 and 520 °C, with a heating rate of 10 °C/min and a flow rate of 20 mL/

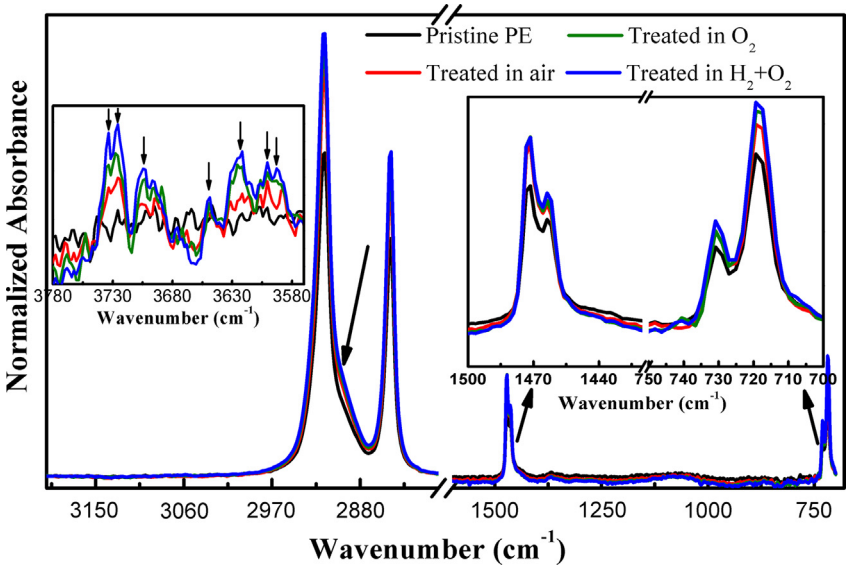

Fig. 1. Normalized ATR-FTIR spectra of pristine and plasma treated polyethylene powder for 2 min at different working gas condition at a pressure of 100 Pa. (Insets: spectral regions from 3580 to 3780 $cm^{-1}$and 700 to 1500 cm^{-1}.)