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Characterization of polylactic acid films for food packaging as affected by dielectric barrier discharge atmospheric plasma

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ABSTRACT

Dielectric barrier discharge (DBD) air plasma is a novel technique for in-package decontamination of food, but it has not been yet applied to the packaging material. Characterization of commercial polylactic acid (PLA) films was done after in-package DBD plasma treatment at different voltages and treatment times to evaluate its suitability as food packaging material. DBD plasma increased the roughness of PLA film mainly at the site in contact with high voltage electrode at both the voltage levels of 70 and 80 kV. DBD plasma treatments did not induce any change in the glass transition temperature, but significant increase in the initial degradation temperature and maximum degradation temperature was observed. DBD plasma treatment did not adversely affect the oxygen and water vapor permeability of PLA. A very limited overall migration was observed in different food simulants and was much below the regulatory limits.

Industrial relevance: In-package DBD plasma is a novel and innovative approach for the decontamination of foods with potential industrial application. This paper assesses the suitability of PLA as food packaging material for cold plasma treatment. It characterizes the effect of DBD plasma on the packaging material when used for in-package decontamination of food. The work described in this research offers a promising alternative to classical methods used in fruit and vegetable industries where in-package DBD plasma can serve as an effective decontamination process and avoids any post-process recontamination or hazards from the package itself.

1. Introduction

Petrochemical-based polymers like polyethylene, polypropylene, polystyrene and poly(ethylene terephthalate) are the most extensively used as food packaging materials. Recently, biodegradable polymers have attracted much attention due to the serious environmental problems with accumulation of waste disposal of conventional polymers. PLA is one of the most promising bio-based polymers which is biodegradable, recyclable and biocompatible requiring low manufacturing energy, with good processability, high transparency and water solubility resistance (Gupta, Revagade, & Hilborn, 2007; Rasal, Janorkar, & Hirt, 2010; Siracusa, Rocculi, Romani, & Rosa, 2008). Such properties coupled with a competitive market price have made it one of the first commercially available biopolymers widely used in the packaging of fresh produce. Although PLA offers a substitute for many non-biodegradable polymers, its application is limited due to its brittleness and barrier properties (Chaiwong, Rachtanapun, Wongchaiya, Auras, & Boonyawan, 2010; Rasal et al., 2010).

Nonthermal plasma (NTP) is one of the many techniques which have been used for surface modification of polymers. The term “plasma” refers to a partially or wholly ionized gas composed essentially of photons, ions and free electrons as well as atoms in their fundamental or excited states possessing a net neutral charge (Misra, Tiwari, Raghavarao, & Cullen, 2011). On the basis of relative energy levels of electron and heavy species and the particle distribution function, plasma can be classified into thermal or nonthermal plasma. Unlike thermal plasma, NTP has temperature disequilibrium between electron and heavy species with relatively low electron density ($<10^{19}$ m^{-3}) (Tendero, Tixier, Tristant, Desmaison, & Leprince, 2006). NTP at atmospheric pressures can be generated using various techniques like corona discharges which have a low current density and usually consist of an active electrode of small radius (like a point of wire) and the material to be treated. The type of corona depends on the polarity of the electrode, the voltage for spark breakdown, electrode geometry and surface condition, current and type of gas (Harry, 2010). Corona discharges have low plasma volume and to increase the treatment area small radius electrode can be replaced with a planar electrode but it results in microarcs generation and non-homogenous treatment. To avoid this problem, a dielectric barrier discharge (DBD) was developed (Tendero et al., 2006). DBD is one of such methods which offer versatility in its mode of operation and system configuration. In DBD, plasma is generated between two electrodes, separated by one or more dielectric barriers (Pankaj, Misra, & Cullen, 2013). The dielectric layer plays an important role by limiting the

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discharge current and avoiding the arc transition with randomly distributing streamers on the electrode surface, thereby ensuring a homogeneous treatment.

Recently a novel approach based on DBD plasma has been reported offering potential for decontamination of various food products. The approach involves generation of NTP inside a sealed package which is in contact with a high voltage and a ground electrode. Upon exposure to a sufficiently high voltage, ionization of the gas within the electric field contained by the package occurs, generating significant amounts of reactive species, which in turn will lead to decontamination of the enclosed products (Misra et al., 2011). Based on the product's initial microbial load, gas composition and target micro-organism various processing parameters (treatment time, voltage) can be chosen. The effectiveness of the approach has been reported by Klockow and Keener (2009), Misra, Ziuzina, Cullen, and Keener (2012), Ziuzina, Patil, Cullen, Keener, and Bourke (2013) and Pankaj et al. (2013), but consequences of processing on the packaging materials after DBD treatment have not been reported. Since it is already known that DBD plasma can modify both the surface and bulk properties of polymers (Liu, Cui, Brown, & Meenan, 2004), the aim of this work is to examine the effects of in-package plasma treatment on commercial PLA film and its suitability for the same.

2. Materials and methods

2.1. Materials

Commercial co-extruded plain PLA film (average thickness = 42.8 ± 1.3 μm) from NatureWorks® PLA with a crystallinity degree of 32% was purchased from Amcor Flexibles, UK. It is a tri-layer film with PLA core covered with PLA skin layers on either side without any coating material or prior treatments. The PLA film was used as a pillow pouch packaging material for a polypropylene box of dimensions of 310 mm × 230 mm × 22 mm. The sample in contact with the high-voltage electrode is referred as top-positioned and the sample in contact with ground electrode is referred as bottom-positioned throughout the study.

2.2. Plasma treatment

A schematic of the experimental setup has been presented in Fig. 1. The DBD plasma source consists of two circular aluminium plate electrodes (outer diameter = 158 mm) over perspex dielectric layers (10 mm thickness). When the potential across the gap reaches the breakdown voltage the dielectric barrier acts as a stabilizing material forming of a large number of micro-discharges. The applied voltage to the electrode was obtained from a step-up transformer (Phenix Technologies, Inc., USA) using a variac. The input of 230 V, 50 Hz was given to the primary winding of high voltage step-up transformer from the main supply. The atmospheric air condition at the time of treatment was 45% relative humidity (RH) and 22 °C. The samples were treated at 70 and 80 kV for 0.5, 1.5, 2.5 and 3.5 min and stored at normal room conditions before analysis.

2.3. Material characterization

2.3.1. Atomic force microscopy (AFM)

AFM measurements were carried out to observe the surface topography of the samples before and after DBD plasma treatment. The AFM used was MFP-3D BIO 1126 (Asylum Research, Santa Barbara, CA, USA) operated in intermittent contact (tapping) mode. The images were collected at a fixed scan rate of 0.5 Hz. The sampling rate was 512 lines. The data was processed using MF3D software (version 111111 + 1219). The scanned area was 25 μm^2 and was repeated five times.

2.3.2. Thermogravimetric analysis (TGA)

TGA analysis were performed with a Mettler Toledo thermal analyser, model TGA/SDTA 851e (Schwarzenbach, Switzerland). Approximately 5 g samples were heated at 10 °C min^{-1} from room temperature to 700 °C under nitrogen atmosphere (flow rate 50 ml min^{-1}). Initial degradation temperature (T_5) was determined as the temperature at which 5% of mass was lost and maximum degradation temperature (T_{max}) was determined from the first derivative.

2.3.3. Differential scanning calorimetry (DSC)

DSC analysis was performed with a TA Instruments DSC Q2000 (New Castle, DE, USA) under a dry nitrogen gas flow rate of 50 ml min^{-1}. Approximately 3 mg samples were weighed in aluminium pans (40 μl) and subjected to two heating-cooling cycles from −30 °C to 200 °C at 10 °C min^{-1}. Glass transition temperatures (T_g) and melting endotherm were determined during the first heating cycle in order to evaluate the changes occurred after plasma treatment on the PLA surface.

2.3.4. X-ray diffraction (XRD)

Wide-angle X-ray scattering (WAXS) of PLA films was performed on a Bruker D8-Advance (USA) diffractometer, equipped with a Cu-Kα radiation source (λ = 1.546 Å), operating at 40 kV and 40 mA as the applied voltage and current, respectively. The incidence angle (2θ) was varied between 5°and 90° at a scanning rate of 2°min^{-1}.

2.3.5. Fourier transform infrared spectroscopy (FTIR)

FT-IR was carried out by using a Nicolet Avatar 360 FT-IR E.S.P. (UK) spectrometer from 4000 to 400 cm^{-1} to measure any changes in the spectra intensities. A background spectrum was collected by keeping the resolution as 1 cm^{-1}. After the background scan, treated and untreated film samples were placed in the sample holder and analyzed in triplicates.

2.3.6. Oxygen transmission rate (OTR)

OTR analysis was conducted with an Oxygen Permeation Analyser 8500 from Systech Instruments (Metrotec S.A, Spain). Treated films

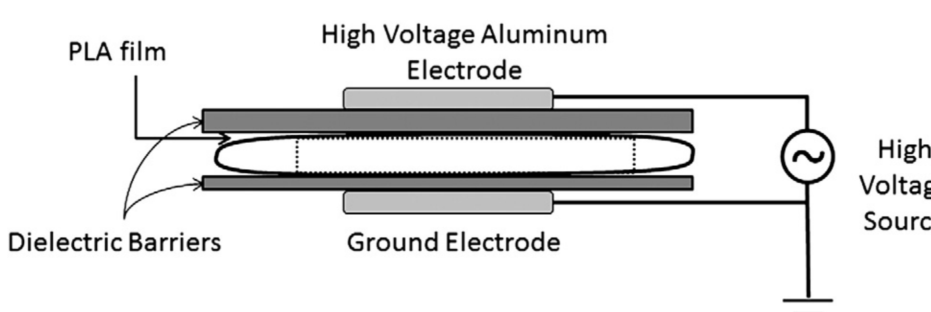

Fig. 1. Schematic of the experimental setup for DBD plasma system.