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Optimization of cold nitrogen plasma surface modification process for setting up antimicrobial low density polyethylene films

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ABSTRACT

In order to prevent microbial contamination and food-borne illnesses, antimicrobial active packaging represents an innovative option. The aim of this paper was to optimize the experimental parameters of the plasma treatment. Such pre-treatment can be used to develop an active packaging film by adsorbing a natural antimicrobial peptide "Nisin" on the surface of a commonly used polymer in the agro-food sector "low density polyethylene (LDPE)". Cold nitrogen (N_2) plasma treatment was used to functionalize LDPE and generate a hydrophilic polymer suitable for the adsorption of the peptide. The experimental design technique allowed determining the optimal conditions of the plasma treatment. The lowest contact angle and highest hydrophilic character were obtained for a gas flow rate of 500 cm^3/min, a generator power of 300 W and an exposure time of 300 s. The surface characterization techniques X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), contact angle and surface free energy measurements were used to confirm the surface modification after cold plasma treatment. The antimicrobial tests permitted to validate the efficiency of the active packaging films. The plasma treated films showed higher antimicrobial activity after nisin adsorption as compared to the native ones.

1. Introduction

Recent and continuous foodborne microbial outbreaks are driving a search for innovative ways to inhibit microbial growth in the foods while maintaining quality, freshness, and safety. One option is to adsorb antimicrobial peptides on the packaging polymers to impart functional active properties and an increased margin of safety and quality. Polymer materials are inexpensive, easy to process, and exhibit excellent bulk and mechanical properties. However, their chemical inertness and their low surface energy represent generally a great barrier for their food packaging applications [1]. Plasma treatments have been used to expand the applications and transform these materials into highly valuable finished products. They can increase the wettability, polar groups, surface energy and improve the printability, adhesion, mechanical and barrier properties of polymer films [1–5]. From one side, these particular advantages of plasma treated films are highly desirable in food packaging applications to minimize leakage, reduce the risk of microbial contamination, and improve package integrity. From another side, the increase in hydrophilicity can improve the adsorption of peptides on surfaces as reported in previous studies [6–14]. Popelka *et al.* and Bílek *et al.* investigated antibacterial treatments on cold plasma pretreated low density polyethylene (LDPE) foils using benzalkonium chloride [15] and allylamine [16], respectively. Nisin is a well-known antimicrobial peptide, produced by *Lactococcus lactis* subsp. *Lactis* and widely used in the food industry as a safe and natural preservative [17]. It has an antimicrobial activity against a broad spectrum of Gram-positive bacteria and food pathogens such as *Listeria innocua*, *Listeria monocytogenes*, *Staphylococcus aureus* and *Clostridium botulinum* [18,19].

Therefore, the aim of this study was to assess the possibility of elaborating an antimicrobial polymer by adsorbing nisin on nitrogen (N_2) plasma treated low density polyethylene (LDPE) film. This entailed the determination of the optimum conditions for using nitrogen plasma treatment, the use of physico-chemical methods to confirm the surface modification after the plasma treatment, the adsorption of nisin on both treated and native films, and finally the determination of the antimicrobial activity and/or the ability of nisin to retain its activity on the N_2 plasma treated films.

2. Materials and methods

2.1. Film preparation

Low density polyethylene (LDPE) was obtained from Polimeri Europa, France SAS (Density of 0.922 g/cm^3 and thickness of

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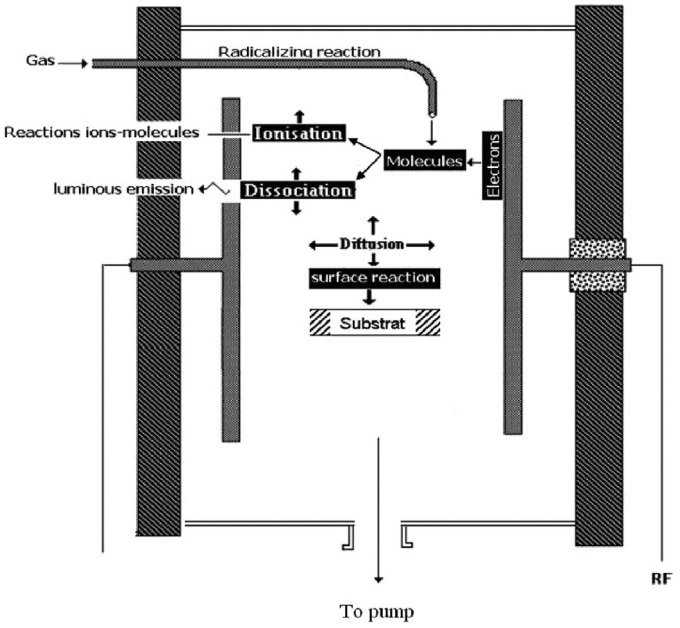

Fig. 1. Schematic representation of the experimental set-up.

70 μm). LDPE films were cut into square shape (2 cm × 2 cm) and washed with ethanol in an ultrasonic bath to remove possible dusts or any oily compounds adsorbed on the film surface. They were then dried in an oven at 55 °C for 3 h. Those films were either used directly or treated for nisin adsorption.

2.2. Plasma treated films

2.2.1. Design of experiments

Plasma treatments were performed in LDPE samples were plasma treated in a EUROPLASMA CD 1200 set-up reactor using cold radiofrequency plasma (13.56 MHz) fitted with a capacitively coupled, parallel-electrode system with an automatic matching device. A schematic representation of the experimental set-up is shown in Fig. 1. A pure nitrogen glow discharge was generated in an aluminium reactor chamber with a continuous out power ranging from 0 to 600 W. The chamber was pumped down to 10.7 Pa using a pump Edwards (80 m^3/h), and the N_2 gas was introduced into the chamber. When the pressure became constant, the generator was switched on and adjusted to a certain power value, which gave rise to a continuous glow discharge. The sample holder was placed in the center between the electrodes without any bias. The distance between the electrodes is equal to 10 cm. Optimization of the plasma treatment was carried out using response surface methodology (RSM). The influence of three main process parameters was studied namely the nitrogen flow, the time of treatment and the power during the plasma treatment. A central composite design (CCD), consisting of 17 experimental runs, was used including:

- a 2^k fractional factorial design, k being the number of studied variables,
- 6 axial points at a distance of $\alpha = 1.68$ from the design center,
- 3 replicates of the center point.

Experiments were carried out randomly to provide protection against the extraneous factors, which could affect the measured response.

For statistical calculations, the variables U_i were coded as X_i according to the following transformation (Eq. (1)):

$$X_i = \frac{(U_i - U_0)}{\Delta U} \quad (1)$$

where X_i is the dimensionless coded value of the variable U_i, U_0 represents the value of U_i at the center point and ΔU is the step change.

The experimental values associated to the coded levels of the different variables are given in Table 1.

The quadratic model for predicting the optimal conditions was expressed according to Eq. (2):

$$Y_{pred} = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i<j}^{n} \beta_{ij} X_i X_j + \sum_{i=1}^{n} \beta_{ii} X_i^2 \quad (2)$$

where Y is the predicted response, β_0 is the value of the fitted response at the center point, β_i, β_{ii} and β_{ij} correspond to the linear, quadratic and interaction terms respectively.

2.2.2. Surface characterization

Contact angle and surface free energy measurements: Static contact angle measurements of the samples were carried out at room temperature on a Digidrop goniometer (GBX, France) using pure water for the optimization step. A 5 μL drop of water was applied onto the sample surface and the contact angle formed with the surface was instantaneously measured. Triplicate tests were performed for the films, immediately after the plasma treatment, and at least six different measurements were made on each sample surface. The average values for contact angles and the standard deviation were then calculated. The contact angles were also determined using two other test liquids (formamide and diiodomethane) in order to calculate the surface free energy values with the Owens–Wendt model [20–22]. This method takes into account dispersive and polar components of the surface energy and using different test liquids, it is possible to determine the solid surface free energy (γ) as the sum of polar (γ^p) and dispersive (γ^d) contributions [21,23–25].

X-ray photoelectron spectroscopy (XPS): X-ray photoelectron spectroscopy (XPS) experiments were carried out using a Kratos Analytical AXIS Ultra^{DLD} spectrometer. A monochromatized aluminium source (Al Kα = 1486.6 eV) was used for excitation. The X-ray beam diameter was around 1 mm. The analyser was operated at constant pass energy of 160 eV for survey spectra using an analysis area of approximately 700 μm × 300 μm. The electron take off angle was 90°. Charge compensation was applied to compensate for the charging effect occurring during the analysis. The C 1s hydrocarbon (285.0 eV) binding energy (BE) was used as internal reference. The spectrometer BE scale was initially calibrated

Table 1
Coded and real values of experimental parameters used for the CCD.

Coded variables	Parameter	Levels				
		$-\alpha$	−1	0	+1	$+\alpha$
X_1	U_1, nitrogen flow (cm^3/min)	100	180	300	420	500
X_2	U_2, time of treatment (s)	30	85	165	245	300
X_3	U_3, power (W)	100	180	300	420	500