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Antimicrobial plastic film: Physico-chemical characterization and nisin desorption modeling

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ABSTRACT

Antimicrobial active films represent an innovative concept in food packaging, developed to answer to consumer's expectation for better microbiological safety. In this study, the growth of pathogenic micro-organisms on the surface of food is proposed to be controlled by coating, on the surface of polyethylene/polyamide/polyethylene film (PE/PA/PE), a film-forming solution containing Nisaplin, a commercial form of bacteriocin produced by *Lactococcus lactis* subsp. *lactis*: nisin. The bioactivity of these multi-layer films coated with Nisaplin loaded HydroxyPropylMethylCellulose film is based on the release of this antimicrobial molecule towards a food simulant. Nisin mass transfer was studied and modeled, for different operating conditions, generally encountered in food products. pH didn't seem to interfere with nisin release kinetics, while the variation of NaCl concentration between 0.8% and 3.2% decreased the desorption coefficient (k_d) by 18% and the temperature increase from 10 °C to 28 °C resulted in an increase of k_d from 1.78×10^{-2} m s^{-1} to 2.10×10^{-2} m s^{-1}. Coating of PE/PA/PE film with this antimicrobial layer induced little mechanical properties modifications without compromising industrial applications. Water barrier capacity was not altered.

Industrial relevance: This paper concerns active packaging, considered as a new approach to preserve food shelf life. Active packaging is a real gain for plastic and Food industrials. Coating was used to obtain antimicrobial packaging. The impact of coating on film characteristics is investigated.
Also, antimicrobial agent desorption is determined during storage conditions.

1. Introduction

To prevent microbial contamination of food products, antimicrobial agents can be either incorporated in foods during their preparation, or applied on their surface (Kim et al., 2002). Both of these operations present a limited efficiency as they result in a rapid loss of antimicrobial activity. Antimicrobial active packaging — consisting in the incorporation of the active molecules in the packaging films — present an innovative option. In fact, they allow a better efficiency in food protection as they offer a better stability of the antimicrobial agent, and ensure the control of its release towards food. The commonly used antimicrobial molecules in food are organic acids (Cagri et al., 2001), enzymes (Padgett et al., 1998), essential oils (Tunc et al., 2007) or bacteriocins (Jacquet et al., 1998). Among the latter, only nisin (amphiphilic cationic peptide produced by *Lactococcus lactis* subsp. *lactis*) is allowed for use as food additive in the European Union (E 234). When used as antimicrobial agent in food packaging, the efficiency of nisin depends on several parameters: pH, temperature, salt and fat concentrations (Jung et al., 1992; Dean & Zottola, 1996). These parameters play a major role on nisin solubility, bioactivity, stability, desorption rate from films and diffusion into food matrices. Some previous studies investigated nisin diffusion into food matrices (Sebti et al., 2004; Ripoche et al., 2006), but very few were interested in the desorption phenomenon of the antimicrobial agent from biopolymer films (Buonocore et al., 2003). The purpose of this study was to investigate the desorption phenomenon of nisin from a polyethylene/polyamide/polyethylene PE/PA/PE film coated with HydroxyPropylMethylCellulose (HPMC) film-forming solution containing Nisaplin. Nisaplin is a commercial form of nisin at 2.5% of purity. At the same time, this study proposed to verify the impact of Nisaplin incorporation in films on the mechanical and water barrier properties of films.

2. Materials and methods

2.1. Nisaplin solutions preparation

Nisaplin powder was from DANISCO (Denmark; 2.5% purity, 77.5% NaCl, 20% non-fat dry milk compounds). Nisaplin solutions

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Nomenclature

A	Area of mass exchange
a_w	activity of water
c	constant related to the heat of sorption
C_a	water concentration in the air in contact with gel
C_{1a}	water concentration at the surface of agar gel
C_{2a}	water concentration at the film surface
C_b	water concentration in the air
C^*_{sol}	equilibrium concentration of nisin between the solution and the HPMC film
$C_{to,sol}$	initial nisin concentration in the solution at t=0
$\%EB$	percentage elongation at break
g	time gravity
k	constant related to the heat of sorption.
K_c	Effective water transfer coefficient
k_d	desorption coefficient
K_{EQ}' and K_{EQ}	equilibrium partition constant
RH	relative humidity
rpm	rotation per minute
S	film surface area
$TWDR$	Total Water Desorption Rate
V_{sol}: volume of the desorption solution	
x	water content (g water/100 g dry film)
x_m	weight of water (g) in a complete monolayer per 100 g of polymer
Y	Young modulus (Pa)

were obtained by suspending Nisaplin powder in HCl 0.01 N (pH 2) at a concentration of 48 mg ml^{-1} (corresponding to a calculated nisin concentration of 800 µg mL^{-1}) for desorption experiments and 10 mg ml^{-1} (corresponding to a calculated nisin concentration of 166.7 µg mL^{-1}) for the characterization of Nisaplin-loaded films. Nisaplin suspensions had to be centrifuged at 4000 g (8500 rpm, rotor radius equal to 5 cm) for 15 min at 4 °C and the supernatant recovered. Centrifugation was necessary to take off insoluble fractions in acid solution. Nisaplin solutions were stored at 4 °C until their use.

2.2. Preparation of antimicrobial active films

The film forming solution was 6% and 3% (w/w) of HydroxyPropylMethylCellulose (HPMC) for desorption experiments and film characterization respectively. HPMC (culminal 50, Aqualon France, le Pecq) is prepared in 1/3 (w/w) ethanol (96%; Chimie-Plus Laboratoires, Denice, France) and 2/3 (w/w) HCl 0.01 M with a requested final nisin concentration of 800 µg mL^{-1} for desorption experiments and 166,7 µg mL^{-1} for film characterization respectively. After 1–2 h of homogenization at room temperature, the film forming solution was used to coat the polyethylene/polyamide/polyethylene (PE/PA/PE) on one side of the film using an automatic K control coater (Erichsen®, Rueil-Malmaison, France) equipped with a spiral film applicator (120 µm-wet thickness). Eight layers are deposited successively with a drying step at 60 °C during 10 min after each deposit. The final thickness was measured with a Käfer micrometer (Erichsen, Rueil-Malmaison, France). It was of 10±1 µm for standard PE/PA/PE films and 60±1 µm and 110±8 µm for multilayer PE/PA/PE films coated with Nisaplin loaded HPMC film used for characterization and for film desorption experiments respectively. Before each experiment, the antimicrobial activity of films was verified using microbial agar diffusion method on *Kocuria rhizophila* ATCC 9341 (formerly *Micrococcus luteus*). All multilayer PE/PA/PE films coated with Nisaplin loaded HPMC film showed clear zones of inhibition of about 10 mm surrounding the diameter of the circular film.

2.3. Evaluation of physico-chemical properties of plastic films

2.3.1. Sorption isotherms

Sorption isotherms were established for PE/PA/PE films, multilayer PE/PA/PE films coated with nisin-loaded HPMC film and multilayer PE/PA/PE films coated with Nisaplin-loaded HPMC film. Films were cut into 0.5×0.8 cm pieces. 0.12 g of each cut sample were put into aluminum dishes and stored in sealed glass jars containing saturated salt solutions corresponding to constant water activity values (a_w) at 23 °C. a_w values used were: 0.10, 0.22, 0.33, 0.44, 0.55, 0.68, 0.76 and 0.85. Equilibrium moisture content of samples was reached after a maximum of two months storage (Coupland et al., 2000; Sebti et al., 2007). It was then determined by drying cut samples at 103 °C during 2 h. The experimental sorption isotherms were then plot and fitted by the Guggenheim–Anderson–DeBoer (GAB) model (Eq. (1)), commonly used to describe water sorption in food products.

$$x = \frac{x_m \times c \times k \times a_w}{(1-k \times a_w) \times (1-k \times a_w + c \times k \times a_w)} \quad (1)$$

Where x is the weight (g) of sorbed water per 100 g of polymer, a_w is the water activity, x_m is the weight of water (g) in a complete monolayer per 100 g of polymer, c and k are constants related to the heat of sorption.

2.3.2. Total Water Desorption Rate

(TWDR) measurements were determined using a modified method developed by Desobry and Hardy (1993) as described in the Fig. 1. Open agar (3% w/w) and agar coated with films were put in an environment with controlled humidity and temperature (50±5% RH and 23±1 °C) during 3 days. The slope of the linear part of the desorption curve (mass loss versus time) corresponds to TWDR, expressed as $kg_{water}\ m^{-2}\ s^{-1}$. The effective water transfer coefficient K_c was then determined using the following equation:

$$TWDR_{agar} = K_c(C_{1a} - C_b) \quad (2)$$

The water concentration of the air in contact with the agar gel (C_{1a}) was calculated with *Mollier* diagram from air characteristics of open agar surface (100% RH and 23 °C) and C_b by surrounded air characteristics (50% RH and 23 °C). The water concentration of the air in contact with the film surface (C_{2a}) was then determined using the following equation:

$$TWDR_{film} = K_c(C_{2a} - C_b) \quad (3)$$

2.3.3. Mechanical properties

A TA.XT2 Texture Analyzer (Texture Technology Corp.) was used to measure Young's modulus (Y (Pa)) and elongation at break (EB (%)) on 20 mm×45 mm samples previously stored for 7 days at 23 °C and 50% RH. Films were uniaxially stretched at a constant velocity of 0.1 mm s^{-1}. The computer-recorded force–deformation curves were then used to determine Y and EB. Y reflects the film stiffness and is calculated from the slope of the initial linear region of the force–deformation curve, as follows:

$$Y = \frac{Curve\ slope}{Film\ section} \quad (4)$$

The film section was: width * thickness.