Materials Science and Engineering C 33 (2013) 1583–1591

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Potassium sorbate controlled release from corn starch films

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ARTICLE INFO

Article history:
Received 1 October 2012
Received in revised form 20 November 2012
Accepted 17 December 2012
Available online 23 December 2012

Keywords:
Active corn starch films
Potassium sorbate
Controlled release
Mathematical modeled
Antimicrobial capacity

ABSTRACT

Active starch films with glycerol and potassium sorbate were obtained by casting. Native and acetylated corn starches, as well as the mixture of them in equal proportions were used and filmogenic suspensions with pH 4.5 were also prepared. Sorbate concentration decreased during film storage due to its oxidative degradation. Active films resulted more yellow and less transparent than films without sorbate. The minimum inhibitory concentration of sorbate resulted 0.3%, regardless of the starch type and the formulation pH. The use of antimicrobial package was more effective to prevent microbial growth on food surfaces than the use of conventional methods. Additive kinetic release was neither affected by the starch type nor by the formulation pH. Sorbate diffusion process was mathematically modeled satisfactorily. Active films were able to inhibit *Candida spp.*, *Penicillium spp.*, *S. aureus* and *Salmonella spp.* growth. Active films extended 21% the shelf life of refrigerated cheese, regardless of the formulation pH.

1. Introduction

Food industry is focusing their efforts towards offering to the consumers safer, more nutritious and high quality products. Microbial contamination of food products causes serious diseases and consequent economic losses [1]. Thus, the addition of bactericidal agents or growth inhibitors into food formulation by spraying or immersion methods had been employed to overcome food contamination. However, direct application of the antimicrobial agents has some limitations since they could be neutralized, evaporated or diffused rapidly and inadequately into the food bulk, reducing their effective concentration on the surface [2,3]. In this context, current trend with good perspectives consists in the incorporation of the additives to the food packages, improving their functionality [4,5]. The active agents are added to the film matrix and slowly released to food surface, where they remain at high concentration for a long time [6].

Although synthetic polymers could be employed to develop these active packages, the actual tendency is targeted to the use of natural and biodegradable polymers due to environmental concerns. Within natural polymers, starch is one of the most promising candidates due its abundance, availability, low cost and biodegradability [7,8]. In previous works corn starch based films had been developed and characterized, resulting homogeneous and transparent [8–10]. The addition of glycerol as plasticizer at 1.5% p/p improved the material flexibility and decreased significantly their water vapor permeability. Besides, the use of acetylated corn starch into formulations led to develop films more resistant and less permeable to the water vapor [8,9]. Moreover, films based on native and acetylated corn starch presented a good heat sealing capacity making them appropriate materials to develop food packages [10].

Sorbic acid and its mineral salts are among the safest food preservatives; they are efficient and versatile due to their highly effective inhibition of most common microorganisms (fungi, molds and yeasts) which can attack foods causing their deterioration [11].

The use of potassium sorbate as antimicrobial agent in film formulation was studied by several authors and its antimicrobial capacity was also demonstrated. Flores and coworkers [12] studied the performance of tapioca starch based films as carriers of sorbate and established that films were effective in controlling the growth of *Z. bacilli* population, acting as a preservative release agent or as a barrier for external yeast contamination. On the other hand, Türe and coworkers [1] developed films based on wheat gluten containing potassium sorbate and they demonstrated the antifungal properties of these active materials. It was also reported the antifungal effectiveness of sorbate potassium incorporated in guar gum and pea starch coatings [13]. Pranoto and coworkers [2] informed that chitosan films with potassium sorbate presented antimicrobial activity against *S. aureus*, *L. monocytogenes*, and *B. cereus*. It was also demonstrated that the use of an antimicrobial coating based on CMC with potassium sorbate controlled the molds growth on pistachios, inhibiting substantially the development of some mycotoxigenic *Aspergillus* species [14].

Despite many works present in the literature concerning active films with potassium sorbate, it is still relevant to study the diffusion kinetic of the additive from the polymeric matrixes to the packaged product and its migration profile inside the food bulk. Besides, a mathematical

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http://dx.doi.org/10.1016/j.msec.2012.12.064

model of this phenomenon could allow to determine active agent diffusion coefficients in both, the film and the product, hence it would be feasible to estimate concentration profiles and to predict the time period in which the antimicrobial concentration will be maintained above the critical inhibitory concentration in the packaged food.

The aim of this work was to demonstrate the effectiveness of the addition of potassium sorbate to corn plasticized starch films to prevent microbial growth on a food product surface extending its shelf life. For this purpose, the sorbate controlled release from the polymeric matrix to a semisolid medium was evaluated and a mathematical model of the diffusion process was proposed.

2. Material and methods

2.1. Starch samples

Native and acetylated corn starches were provided by Arcor (Tucumán, Argentina); modified starch presented an acetylation degree of 2.2% [9].

2.2. Filmogenic suspensions

Aqueous suspensions (5% w/w) of native and acetylated corn starch, as well as a mixture of them in equal proportions were prepared. These suspensions were gelatinized at 90 °C during 20 min. Then, glycerol as plasticizer (1.5% w/w) and potassium sorbate (PS) as antimicrobial agent (0.1–0.5% w/w) were added. Filmogenic suspensions with pH adjusted at 4.5 were also prepared by adding 5 M citric acid (Parafarm, Argentina) in order to increase preservative effect of PS, since the undissociated form is the effective one. For further analysis and discussions, plasticized films without active agent were used as control ones.

2.3. Active starch films

Films were obtained by casting method, employing a relation of 2 g of filmogenic suspension per cm^2 of casting area. They were dried at 50 °C during 2 h and 7 days at 20 °C. They were removed from casting plates and stored at 20 °C and 65% HR during a week.

2.4. PS dosage

Official method AOAC [15] to determine sorbic acid with some modifications was employed. Film disks of 1 cm diameter were weighed and dissolved in 50 mL of distilled water, heating softly to facilitate their dissolution. From this solution 5 mL was taken and transferred to a volumetric flask, and 625 μL of 0.1 N HCl was added and diluted to 100 mL with distilled water. Absorbance solution was measured at 260 nm using distilled water as reference and quartz cells. Reported values corresponded at least to five determinations.

2.4.1. Calibration curve

PS standard solution at 1 mg/mL was prepared; 0, 10, 20, 30 and 40 mL of this standard solution were pipetted into separate 100 mL volumetric flasks and diluted with distilled water. 2.5 mL of each solution was pipetted into 250 mL volumetric flasks, and 625 μL of 0.1 N HCl was added and diluted with distilled water. Absorbance was read at 260 nm using distilled water as blank solution. Calibration curve corresponded to the solution absorbance as a function of PS concentration (mg/mL) and experimental data were linearly regressed.

2.5. PS minimum inhibitory concentration

The method proposed by Fajardo and coworkers [16] was employed. Commercial cheese with high humidity content (55%), elaborated with full cream milk acidified with lactic acid bacteria, was used. Approximately 25 g of cheese was deposited onto starch films containing different PS concentrations (0.1–0.5% w/w). Samples were stored at 20 °C during 6 days; visual observation and photographic record were done daily. Lowest additive concentration which did not allow visual observation of fungi growth on cheese surface was regarded as PS minimum inhibitory concentration (MIC). A cheese sample deposited on starch films without PS stored under the same described conditions was used as control.

2.6. Surface color evaluation

Measurements were performed employing a colorimeter Minolta (CR 400, Osaka, Japan). The Hunter parameters: L^*, a^* and b^* were recorded according to CIE scale, in at least 10 randomly selected positions for each film sample. Color parameters range from $L = 0$ (black) to $L = 100$ (white), –a (greenness) to +a (redness) and –b (blueness) to +b (yellowness). From these values, ΔL, Δa and Δb were calculated, taking into account the standard values of the white background. Besides, the color difference parameter ($\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$) was also determined.

2.7. PS diffusion

Polymeric matrix effectiveness to retain PS was evaluated. Diffusion assays of this active agent from starch films to a semisolid medium (agar gel), simulating a food product, were carried out. Besides, experiments analyzing PS diffusion from a potassium sorbate solution to the same semisolid medium were also performed. All diffusion tests were performed at least in duplicate.

These two assays were performed in order to compare the use of an active package based on starch and PS with the traditional application techniques (immersion or spray) of this antimicrobial agent to food products.

2.7.1. Agar gels

An aqueous agar (Parafarm, Argentina) solution at 2% w/w was prepared and heated softly to facilitate its dissolution. The warm solution was molded in cylinders of 2 cm height and 2.5 cm diameter (volume $= 9.80 \times 10^{-6}$ m^3) and solidified by cooling.

2.7.2. PS solution

An aqueous PS solution at 1.31% w/v (87.2 mol/m^3) was prepared; this concentration was used in order to maintain the same preservative amount in both the aqueous solution and in the active film.

2.7.3. Samples preparation

Three different experiments were carried out:

a) Gels in contact with active films: film disks of 2.5 cm diameter containing PS were weighted and deposited onto the top surface of the agar gel cylinders. This sample contained 3.27×10^{-3} g (2.18×10^{-5} mol) of PS.
b) Gels in contact with PS solution: 250 μL of the PS solution (1.31% w/v) was placed on the agar gel cylinders. This solution volume contained the same preservative content than that of the active film disks (3.27×10^{-3} g or 2.18×10^{-5} mol).
c) Control gels: agar gel cylinders without film or solution were used as controls (blanks) for the sorbate spectrophotometric determination. They were submitted under the same treatment than samples to consider matrix agar gel absorption.

Gels were stored at 4 °C and at different times, samples were taken to evaluate sorbate release. Tested times were 0.17, 0.33, 0.5, 0.83, 1, 1.16, 1.5, 2, 2.42, 4.32, 6, 12, 24, 36, 48 and 60 h.

2.7.4. Released PS determination

To determine PS concentration in agar gels, official method for sorbic acid [15] with some modifications was used. In the case of assays in