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Development of mono and multilayer antimicrobial food packaging materials for controlled release of potassium sorbate

Metin Uz, Sacide Alsoy Altınkaya*

Department of Chemical Engineering, Faculty of Engineering, Izmir Institute of Technology, 35430 Gülbahçe Köyü, Urla, Izmir, Turkey

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ABSTRACT

In this study, cellulose acetate (CA) based mono and multilayer films including potassium sorbate (Psb) as an antimicrobial agent were prepared using dry phase inversion technique. To achieve appropriate controlled release of Psb, the structure of the films was changed by manipulating the film preparation conditions. In particular, the initial casting composition, wet casting thickness and drying temperature were varied. Results indicate that Psb release rate decreased as the CA content in the casting solution, the wet casting thickness and the drying temperature for both mono and multilayer films were increased. Compared to the results for the monolayer films, a significant decrease of Psb release rate through the multilayer films was recorded. Drying-induced crystallization was observed in the monolayer films. As a consequence of this, a fast initial release of Psb, controlled by Fickian diffusion, was followed by a slower release controlled by dissolution of Psb crystals. In multilayer films, no crystals were detected in the structure and the release rate was regulated only by diffusion of Psb through the film. The results suggest that the films prepared in this study can be used as food packaging materials for achieving controlled and extended release of Psb.

1. Introduction

Recently, the use of antimicrobial packaging has received great attention since it provides foods high quality, safety and long shelf life by reducing, inhibiting or retarding the growth of microorganisms (Appendini & Hotchkiss, 2002; Choi et al., 2005). Traditionally, antimicrobial agents are directly mixed into the initial food formulations. Direct addition, however, may result in a decrease in the concentration of the antimicrobial agent on the food surface due to its diffusion into the interior parts of the food. Therefore, the minimum concentration required for the inhibition of the microbial growth may not be achieved and the antimicrobial compound cannot selectively target the food surface (Min & Krochta, 2005). In addition, the neutralization of the added agent due to its possible complex interactions with the food components may occur (Appendini & Hotchkiss, 2002). Moreover, the direct addition brings about the utilization of excessive amounts of the antimicrobial agent which may change the taste of the food. Antimicrobial packaging offers an alternative way to overcome these limitations.

The most important desired property of the antimicrobial packaging materials is the controlled release of the antimicrobial agent from the film to the food surface. A rapid release causes fast consumption of the agent in a short period of time, after which the minimum concentration required for the inhibition of microbial growth is not maintained on the food surface. On the other hand, spoilage reactions on the food surface may start if the release rate of the antimicrobial agent from the film is too slow. Thus, the controlled release of the active agent for a long period of time is necessary to extend the shelf life of the packed food.

Studies on the development of antimicrobial food packaging films with controlled release properties are increasing. Different controlled release strategies were introduced which are mainly based on changing the structure of the films. Han and Floros (1998) tried to control the release of an active agent by using a three layered film structure. The first layer is the outer barrier layer, whose function is to prevent the migration of the agent to the environment, the second is a matrix layer containing the active agent, and the third controls the release of the active agent to the food. Buonocore, Conte, Corbo, Sinigaglia, and Del Nobile (2005) and Mastromatteo, Barbuzzi, Conte, and Del Nobile (2009) also developed multilayer films consisting of two external control layers and an inner layer containing the active agent. In another work of Buonocore's group, they tried to manipulate the release kinetics of

* Corresponding author. Tel.: +90 232 7506658; fax: +90 232 7506645.
E-mail address: sacidealsoy@iyte.edu.tr (S.A. Altınkaya).

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Nomenclature

List of symbols

A_f	Area of the film (cm^2)
D	Effective diffusion coefficient of active agent in the film (cm^2/sec)
k	Crystal dissolution constant (min^{-1})
K	Partition coefficient (cm^3 solution/cm^3 film),
L	Thickness of the film (cm),
M_{Total}	Total amount of active agent desorbed from the film at any time t (mg),
$M\infty$	Total amount of active agent desorbed from the film at equilibrium (mg),
$M_{Fickian}$	Total amount of active agent desorbed from the film by Fickian diffusion (mg),
$M_{Dissolution}$	Total amount of active agent desorbed from the film by crystal dissolution (mg)
t	Time (min),
V_{sol}	Volume of the solution (cm^3)

active compounds by changing the degree of cross-linking of the polymer matrix (Buonocore et al., 2003; Buonocore, Del Nobile, Panizza, Corbo, & Nicolais, 2003; Buonocore et al., 2004). Ozdemir and Floros (2001) targeted controlling the release by changing the degree of plasticization in the polymer film. Iconomopoulou and Voyiatzis (2005) suggested changing the molecular orientation of the polymer chains as a tool for achieving the controlled release of the active compounds. Guzey and McClements (2006) proposed micro and nano-encapsulation of food ingredients as another alternative method to control the release rate of the active agent. They suggested that the release rate from small capsules directly added into the food can be controlled by changes in pH, temperature or ionic strength of the medium. Han, Castell-Perez, and Moreira (2008) investigated the effect of electron beam irradiation on the release kinetics and they suggested that irradiation may serve as a controlling factor for the release of the active compound. Recently, Gemili, Yemenicioglu, and Altinkaya (2009; 2010) introduced the usage of porous asymmetric films for food packaging applications. They tried to control the release rates by changing the degree of asymmetry and porosity of the films.

Potassium sorbate, which is a potassium salt of the sorbic acid, is well-known for its potential antifungal activity and generally used in the preservation of cheese, dairy products and dough (Valencia-Chamorro, Palou, Del Rio, & Perez-Gago, 2008). Previously, different research groups added Psb in whey protein; k-carregeenan; cellulose triacetate; poly (maleic acid-co-olefine); polystyrene; polyethylene terephthalate; low density polyethylene and copolymer of vinylidene chloride (Choi et al., 2005; Han & Floros, 1997; Fama, Flores, Gerschenson, & Goyanes, 2006; Ozdemir & Floros, 2003; Limjaroen, Ryser, Lockhart, & Harte, 2003; Flores et al., 2007; Vartiainen, Skytta, Enqvist, & Ahvenainen, 2003; Ye, Neetoo, & Chen, 2008). These published results indicate quick desorption of the Psb from the film, inducing a rapid loss of its activity. Thus, it is necessary to control and delay the release of the Psb from the films by investigating new film preparation strategies. In this study, a dry phase inversion technique has been used to prepare cellulose acetate based mono and multilayer food packaging materials including potassium sorbate as an antimicrobial agent. In this technique, the polymer is dissolved in a mixture of a volatile solvent and a less volatile non-solvent. After casting the solution on a glass support, it is exposed to an air stream for drying. During drying, the homogeneous solution phase separates into polymer-lean and polymer-rich phases as a result of the difference in the evaporation rate of the solvent and non-solvent. The polymer-rich phase forms the matrix of the film while the polymer-lean phase rich in solvent and non-solvent fills the pores. Consequently, when the solvent and non-solvent are completely removed from the film, porous structure is obtained. Previously, we have shown that the dry phase inversion technique can be used for controlling the release rate of lysozyme as well as natural antioxidants L-tyrosine and ascorbic acid from cellulose acetate (CA) films by changing the porosity and pore size of the films. The morphological changes in the films have been achieved by changing the CA content in the film forming solutions. In this work, the influences of not only the initial casting composition but also the drying temperature and wet casting thickness on the release rates have been investigated for both mono and multilayer films. The wet casting thickness corresponds to the thickness of the polymer solution immediately after casting on a glass support before drying. To illustrate the advantage of the dry phase inversion technique in delaying the desorption of Psb, the monolayer CA film has also been prepared by traditional solvent evaporation technique commonly used in the literature. The main intent of the current study is to demonstrate that changing the film preparation method or conditions causes differences in the structural features of the films, which leads to obtaining different release profiles and, hence, allows manipulation of the release rate of Psb from these films.

2. Materials

Cellulose acetate with a molecular weight of 50,000 and acetyl content of 39.8% was obtained from Eastman (Kingsport, TN, USA). Acetone (99%) and potassium sorbate were obtained from Merc (Darmstadt, Germany) and AppliChem, respectively.

3. Methods

3.1. Preparation of monolayer and multilayer films by dry phase inversion technique

To prepare the monolayer films, potassium sorbate (Psb) and cellulose acetate (CA) were dissolved in water and acetone, respectively. Then, the Psb/water solution was poured into the CA/acetone solution undergoing stirring. The stirring of the mixture continued until all the Psb solution was added and dissolved into the CA solution. Once the homogeneous mixture was obtained, the solution was left standing for 24h to eliminate bubbles. The solution was then cast on a glass support with the aid of an automatic film applicator (Sheen, Automatic film applicator-1133N, Kingston, England) at a speed of 100 mm/s. The wet thickness of the film was adjusted by a four-sided applicator with the gap size of 300 or 500 micron. Immediately after casting, the film was placed into an environmental chamber (Siemens, Simatic OP7, Massa Martana, Italy) and dried for 1h at 25 °C or 50 °C and 40% relative humidity. Then, the films were peeled off from the glass support and further dried in a vacuum oven at 100 °C for a period of 24h. The Psb concentration in the film forming solutions was kept constant at 2% (w/w) while the CA (10%, 12.5%, 15% by weight), acetone and water concentrations were changed.

In the case of multilayer films, 15% (w/w) CA was dissolved in acetone and cast on a glass support with the aid of an automatic film applicator. Following 2 min of drying at 25 °C or 50 °C and 40% relative humidity, the second layer, prepared in the same way as the monolayer films as described above, was cast on top of the first one. Finally, after 8 min of drying, the third layer, again made of 15% (w/w) CA dissolved in acetone, was cast onto the second layer. The