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Effect of potassium sorbate on antimicrobial and physical properties of starch–clay nanocomposite films

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ABSTRACT

Using fresh foods which undergo the least processing operations developed widely in recent years. Active packaging is a novel method for preserving these products. Active starch–clay nanocomposite films which contained potassium sorbate (PS) at a level of 0, 5, 7.5 and 10 g PS/100 g starch were produced and their physical, mechanical and antimicrobial properties were evaluated. In order to evaluate antimicrobial properties of films *Aspergillus niger* was used. The results showed that 5% of the PS did not produce antimicrobial property in the film, but by increasing the content of the additive in film formulation, antimicrobial effect increased. PS increased water permeability and elongation at break of the films, but decreased tensile strength. The rate of PS migration into the semi-solid medium in starch–nanocomposites was lower than starch films. This shows that nanocomposite films could retain their antimicrobial property for longer time.

1. Introduction

Active food packaging is an innovative solution to meet the continuous changes in current consumer demands and market trends. Active food packaging extends shelf life and improves the safety of the food by scavenging of oxygen, moisture or ethylene, and by promoting emission of ethanol, flavors, and antimicrobial agents (Appendini & Hotchkiss, 2002; Quintavalla & Vicini, 2002). Antimicrobial packaging is attracting increasing attention from the food and packaging industry, since the use of preservative packaging films offers several advantages compared with the direct addition of preservatives into food products. The incorporation of antimicrobial agents into polymeric films allows industry to combine the preservative functions of antimicrobials with the protective functions of the pre-existing packaging concepts (Persico et al., 2009).

Antimicrobial activity can be achieved by including pads containing volatile antimicrobial agents into packages, incorporating antimicrobial agents into polymers, coating antimicrobials onto polymer surfaces, immobilizing antimicrobials by chemical grafting, using polymers that are antimicrobial by themselves (Appendini & Hotchkiss, 2002).

Starches are polymers that naturally occur in a variety of botanical sources such as wheat, corn, potatoes and tapioca. It is a renewable resource widely available and can be obtained from different left overs of harvesting and raw material industrialization. They are useful for numerous applications in the food industry and their functional properties depend on the source but are also affected by other factors like chemical modifications, system composition, pH and ionic strength of the media (Fama, Rojas, Goyanes, & Gerschenson, 2005).

Sorbic and its potassium salt (sorbates) are considered GRAS additive and are active against yeast, molds, and many bacteria (Flores, Fama, Rojas, Goyanes, & Gerschenson, 2007; Flores, Haedo, Campos, & Gerschenson, 2007). These preservatives are unstable in aqueous solution and can suffer an oxidative degradation or can be metabolized by microorganisms under certain conditions of storage (Gerschenson & Campos, 1995; Sofos, 1989). The addition of sorbates to edible films has been proposed as a way of minimizing surface microbial contamination (Cagri, Ustunol, & Ryser, 2001; Chen, Yeh, & Chiang, 1996). To accomplish this objective, a certain concentration of the preservative must be present at the surface of the product. Reduction of the surface level due to diffuse into the food or due to degradation of the preservative must be taken into account when designing an antimicrobial film (Gliemmo, Campos, & Gerschenson, 2004).

Development of the polymer/clay nanocomposites is one of the latest revolutionary steps of the polymer technology. The nanocomposites obtained by the addition of the low percentage of clay to polymers exhibited an improvement in the properties such as

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barrier, thermal and oxidative when compared with traditional composites (Cyras, Manfredi, Ton-That, & Vazquez, 2008).

Potential effects of nanoclays in human health are not well-known. There has been no conclusive evidence for negative effects of nanoclays in human health. However, a few in vitro studies have been conducted to determine their potential toxicological effects. Maisanaba et al. (2013) investigated the cytotoxic effects of a non-modified clay (Cloisite_Na+) and an organoclay (Cloisite_30B) in the hepatic cell line HepG2. Their result showed that only Cloisite 30B has cytotoxicity.

The objective of this research was to study the mechanical, physical and antimicrobial properties of starch–clay nanocomposite films containing potassium sorbate, and to evaluate the release rate of potassium sorbate from starch starch–clay nanocomposite films into semi solid medium.

2. Materials and methods

2.1. Materials

Potato starch (12.2% moisture) was obtained from Alvand Company (Iran). The amylose and amylopectin contents are 18% and 82%, respectively. Na^+ montmorillonite (MMT) was acquired from Southern Clay Products (USA). Glycerol was purchased from Merck, Germany. Potassium Sorbate was supplied from sdfine- CHMLimi TED (India).

2.2. Preparation of films

On one hand, 4 g starch was added to 100 ml distilled water, which contained 0.3 g glycerol/g starch and gelatinized in 90 °C for 10 min. On the other hand, 0.2 g montmorillonite (0.05 g montmorillonite/g starch), was dispersed in 50 ml distilled water and was stirred under mechanical force in 1200 rpm for 30 min. The obtained mixture was sonicated for 30 min. Finally, the obtained mixture was spread onto Plexiglas plates (20 cm × 30 cm) and dried for 20 h at 50 °C. In order to produce antimicrobial films, 0.05, 0.075 and 0.1 g PS/g starch dissolved in 20 ml distilled water, which contained glycerol, then the rest of the steps was as like as above. For making a starch film without montmorillonite only the first solution was prepared and spread onto Plexiglas for drying. They were removed from casting plates and stored at 25 °C and 50% HR during a week.

2.3. Film thickness

Film thickness was measured with a handheld digital micrometer (Mitutoyo, Japan) having a sensitivity of 0.001 mm. Ten thickness measurements were taken on each testing sample in different points and the mean values were used in water vapor permeability and tensile properties calculations (Alboofetileh, Rezaei, Hosseini, & Abdollahi, 2013).

2.4. X-ray diffraction (XRD)

X-ray diffraction (XRD) studies of the samples were carried outusing aPW3050 Advance X-ray diffractometer (Philips, Netherlands) operating at CuK_α wavelength of 0.1539 nm. The samples were exposed to the X-ray beam with the X-ray generator running at 40 kV and 30 mA. Scattered radiation was detected at ambient temperature in the angular region (2θ) of 1–12° at a rate of 1°/min.

2.5. Water vapor permeability

Water vapor permeability (WVP) tests were conducted using ASTM method (E96, 2000), by using circular glass cups with internal diameter of 3 cm and depth of 3.5 cm. Each film sample was sealed on top of the cups containing 8 ml distilled water to provide RH = 100%. The cups were stored at 25 °C in a silica gel containing desiccator (RH = 0%). The RH inside the cup was always higher than outside, and water vapor transmission rate (WVTR) was determined from the weight loss of the cups. Changes in the weight of the cups were recorded to the nearest 0.0001 g and plotted as a function of time. WVTR ($g/m^2\,s$) and WVP (g/m s Pa) were calculated using the following equations:

$$\mathrm{WVTR} = \frac{\Delta m}{\mathrm{A} \times \Delta t} \tag{1}$$

$$\mathrm{WVP} = \frac{\mathrm{WVTR} \times x}{p_1 - p_2} \tag{2}$$

where Δm: is the weight loss of the cup, A: exposed area ($7.06 \times 10^{-4}\,m^2$), Δt: time of loss, x: the mean film thickness and p_1–p_2: is real vapor partial pressure difference (Pa) across the film.

2.6. Mechanical properties measurement

Mechanical tests including tensile strength (TS) and elongation percentage at break (E) were performed according to ASTM (D882-02, 2002) standard. The films were cut into 6 × 1 cm strips. Texture Analyzer (Zwick, model BZ2.5/TH1S, Germany) was used. Initial grip separation and crosshead speed were 40 mm and 50 mm/min, respectively. TS was calculated by dividing the maximum force by the initial area of the film and E% was calculated by dividing the extension at the moment of specimen rupture by the initial gauge length and multiplying by 100.

2.7. Surface color measurement

Color properties of films were measured using a color meter from Hunter Lab, USA. Measurements are expressed as L^* (lightness), a^* (red/green), and b^* (yellow/blue). The parameters were determined by placing film samples on a standard plate ($L^* = 92.23$, $a^* = -1.29$, and $b^* = 1.19$). Color difference (ΔE) was calculated with respect to standard plate parameters by using following Eq. (3) (Abdollahi, Alboofetileh, Rezaei, & Behrooz, 2013).

$$\Delta E = \sqrt{(\Delta l*)^2 + (\Delta a*)^2 + (\Delta b*)^2} \tag{3}$$

2.8. Antimicrobial activity

2.8.1. Culture preparation

Aspergillus niger Persian Type Culture Collection (PTCC-5012), was obtained from the culture collection at the Iran Institute of Industrial and Scientific Research. The fungal cultures were cultivated on potato dextrose agar (PDA; Merck, Germany) slants for 10 days at 25 °C and the spores harvested with 10 ml of 1 ml/1000 ml tween 80 (Merck) solutions (Sayanjali, Ghanbarzadeh, & Ghiassifar, 2011). The spore suspension was adjusted with the same solution to give a final spore concentration of 10^5–10^6 spore/ml and was used the same day.

2.8.2. Antimicrobial test

The antimicrobial test was carried out according to the method developed by Li Shen, Min Wu, Chen, and Zhao (2010). The inhibitory zone test on semisolid medium was used for determination of the antimicrobial effects of films on *Aspergillus niger*. Films were cut into a disk (diameter = 20 mm) with a punch. During tests, 1 disk placed carefully into each petri dish containing semisolid