International Journal of Biological Macromolecules 104 (2017) 303–310

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Development of chitosan based extended-release antioxidant films by control of fabrication variables

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ARTICLE INFO

Article history:
Received 7 January 2017
Received in revised form 1 June 2017
Accepted 9 June 2017
Available online 10 June 2017

Keywords:
Chitosan
Controlled release
Biodegradable film
α-tocopherol
Ethanol

ABSTRACT

In this study, mechanical, optical and permeability to water vapor of chitosan containing α-tocopherol film as the function of preparation conditions including concentration of emulsifier and speed of homogenization have investigated. In addition, the effect of above mentioned variables and presence of ethanol as co-surfactant on the release rate of α-tocopherol from chitosan film to fatty food simulant (ethanol 95%) were investigated. Fourier transform infrared spectroscopy and differential scanning calorimetry were employed to analyze the structural and thermal properties of the films. Results showed that the incorporation of α-tocopherol and preparation conditions affected the physical and mechanical properties of the chitosan films. Obtained results indicated that increasing the concentration of Tween 80 increased the release rate of α-tocopherol in the most studied films. Increasing the stirring speed of homogenization and the presence of ethanol considerably decreased the release rate of α-tocopherol at the most film samples. The lowest amount of released antioxidant was 8.6–10% of total incorporated α-tocopherol at the first stages and is obtained when ethanol used during preparation of film forming solution. Our results indicated that the release rate of α-tocopherol could be controlled by changing the stirring speed of homogenization and especially ethanol presence, considerably.

1. Introduction

Nowadays, there is an increasing interest for using biopolymers in packaging industry due to concerns about the use of synthetic polymers. Biopolymers are such polymers that are bio-based, biodegradable or both [1]. Biodegradable polymers, depending on synthesis and sources, can be classified into four categories: 1) polymers from biomass, including polysaccharide, protein and lipids; 2) Microbially produced polymers, e.g., polyhydroxyalkanoates; 3) chemically synthesized polymers which their monomers are from agro-resources, e.g., polylactic acid; 4) chemically synthesized polymers which both of their monomer and polymeric segments are from fossil resources, e.g., polycaprolactones [2].

Chitosan, second most abundant polysaccharide, belongs to the first group. It is one of the common biodegradable materials that is frequently used to produce bio based films [3]. It is the deacetylated form of chitin to various degrees and consists of (1 → 4) linked residues of N-acetyl β-D-glucosamine (acetylated segment) and (1 → 4) β-D-glucosamine (deacetylated segment)[4].

Oxidation is one of the most important deteriorative processes that affects the nutritional and sensorial properties of the foods containing oils and fats. [5]. Therefore, the oxidation process in packed foods must be prevented [6]. Biodegradable active packaging containing active compounds such as antioxidant compounds has been considered recently [7].

Due to the safety concerns of synthesized antioxidants as food additives, natural antioxidants such as tocopherols, plant extracts, and essential oils from herbs and spices have been studied extensively [8]. Within tocopherols, which are methylated phenols, the α-tocopherol is the most biologically active compound [9]. Due to its antioxidant activity, the α-tocopherol has been incorporated into several pachaging materials, such as low-density polyethylene films [10], chitosan based films [11], polyester based films [12], carboxymethyl cellulose films [13], poly(L-lactic acid)/starch blends films [14], polylactic acid (PLA) film [15], etc. However, the controlled release packaging, as an interesting food protection method, is taken into consideration, the release of the α-tocopherol from the biopolymer packaging matterials, has been less investigated.

Controlled delivery of bioactive compounds is the most important issue, since the release rate and its pattern has a major effect on the efficiency of drugs and biocompounds. The desired result cannot be achieved, If the effective compound is released too fast

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http://dx.doi.org/10.1016/j.ijbiomac.2017.06.055
0141-8130/

or slow [16]. Therefore, it is important that compounds releases at controlled manner depended on intensity of bacterial infection, food oxidation and other deteriorative reactions. Until now, design of the antioxidant carrying system with the controlled and prolonged release time is a big challenge. Incorporation of drugs and biocompounds within a substrate with specific mechanical, chemical and biological properties is an approach to achieve foregoing objective [17]. Natural biopolymers have low manufacturing and disposal costs. Their biodegradability and biocompatibility make them an encouraging candidate for aforementioned delivery applications [18]. Due to its plentiful functionalities, non- toxicity and antibacterial characteristics, chitosan has frequently applied for planning drug and biocompound delivery systems [19].

Due to the lipophilic nature of the α-tocopherol, its incorporation into chitosan film, as a packaging material used in this study, is performed by emulsification method. Due to the thermodynamically instability of the emulsion systems, the preparation conditions and the concentration of ingredients are important factors affecting the stability of the emulsions. The use of emulsifying agents and appropriate homogenization techniques, can improve the stability of emulsion systems [20]. In addition, these factors affect the physicochemical properties of the emulsified films and consequently the release rate of incorporated components. The positive and diverse effect of homogenization speed on mechanical properties and permeability to water vapor have reported elsewhere [21], but there are no sufficient studies were observed about the influence of such fabrication conditions on the release of incorporated components from chitosan films for packaging purposes. Therefore, the aim of this study was to evaluate the influence of the concentration of Tween 80, as emulsifying agent, the stirring speed of homogenization and the presence of ethanol, as the solvent of α-tocopherol, on the physicochemical properties of the α-tocopherol incorporated chitosan film and the release of α-tocopherol into ethanol 95%, as the fatty food simulant.

2. Material and methods

2.1. Materials

Chitosan powder with medium molecular weight and 75–85% deacetylation degree and α-tocopherol with an assay ≥96% were obtained from Sigma-Aldrich (Germany). Tween 80 was used as an emulsifier agent (Merck, Germany). Also, glacial acetic acid (Mojallali, Iran), extra pure (about 87%) glycerol (Merck, Germany) and ethanol (Ghadir Industries, Iran) were used.

2.2. Preparation of the films

The film forming solutions were prepared according to Siripatrawan and Harte [22] with some modifications. In brief, a certain amount of chitosan powder was added into 1% (v/v) glacial acetic acid solution under constant stirring at 700 rpm using a magnetic stirrer (RH basic 2, IKA, Germany) at 40 °C for 12 h to obtain the final concentration of 2% (w/v). Then the prepared solution was filtered through filter paper to remove probable undissolved impurities. After filtration, glycerol was added to the solution at a concentration of 30% (w/w) of chitosan present in the solution, and it was let to stirring for 1 h at 40 °C. Tween 80, as an emulsifier, was added to the solution at two different concentrations of 50 and 100% (w/w) relative to the weight of the α-tocopherol. After that, to complete emulsifier dissolution, the solutions agitated for 1 h at 40 °C. Subsequently, α-tocopherol was added to each group of solutions at a concentration of 0.1% (w/v) using two different procedures: 1) α-tocopherol was added directly to half of the prepared film-forming solutions, and 2) α-tocopherol was first dissolved in 95% (v/v) ethanol solution at a concentration of 1% (w/v) and then this solution was added to the other half of prepared film-forming solutions at a final concentration of 10% (v/v). Afterward, the solutions were homogenized using a homogenizer (T25 Digital Ultra-Turrax, IKA, Staufen, Germany) at two speeds of 10,000 and 15,000 rpm for 4 min. Finally, 20 ml of the each solution was cast on Petri dishes with 67.89 cm^2 surface areas and dried in the oven at 30 °C for 48 h. Also, control films were prepared at the same chitosan concentration with 30% (w/w) glycerol with nothing addition else. All other preparation conditions were same. The dried films then were removed from the Petri dishes and placed in a desiccator containing the saturated salt of $Mg(NO_3)_2$ at 20 °C (RH = 54%) for 48 h. The abbreviations presented in Table 1 were used in the text for convenience.

Table 1
The film preparation conditions and used abbreviations in the text.

Condition	Tween 80 (% w/w)	Homogenization speed(rpm)	Films code
Without Ethanol	50	10,000	CT_1H_1
	50	15,000	CT_1H_2
	100	10,000	CT_2H_1
	100	15,000	CT_2H_2
With Ethanol	50	10,000	CET_1H_1
	50	15,000	CET_1H_2
	100	10,000	CET_2H_1
	100	15,000	CET_2H_2
Control	–	–	Control

2.3. Thickness

The thickness of the films was measured using a micrometer (Mitutoyo, ID C112PM, Kawasaki-shi, Japan). For each related experiment, at least three measurements were determined at random positions and then the mean of measured thicknesses was used as film thickness.

2.4. Moisture content

The moisture content of the films was measured according to Dehnad, Emam-Djomeh, Mirzaei, Jafari and Dadashi [23] with some modifications. The film's sample was dried at 110 °C in the oven until reaching to constant weights. The moisture content of the films was calculated according to the following equation:

$$MC_{Wb}(\%) = \left(\frac{\text{Wet sample weight - Dry sample weight}}{\text{Wet sample weight}}\right) \times 100$$

2.5. Opacity

The opacity of the films was measured according to the method of Siripatrawan and Harte [22] with some modifications. For this, the film samples put directly into a cell of UV spectrophotometer (SP-UV 500DB spectrophotometer, Spectrum instruments, Canada). An empty cell was used as the blank cell. Then, the opacity of the films was determined at 600 nm, and calculated using the following equation:

$$\text{Opacity} = \frac{\text{Absorbance at 600 nm}}{\text{Thickness of the film}}$$

2.6. Solubility in water

The solubility of the films in water was measured according to the method of Ojagh, Rezaei, Razavi and Hosseini [24] with some modifications. In brief, the film samples were cut into 3×2 cm^2 and weighed by a lab balance (W_1). Afterward, the film samples