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Preparation of chitosan/polyvinyl alcohol blended films containing sulfosuccinic acid as the crosslinking agent using UV curing process

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ABSTRACT

This paper reports on a method of preparing chitosan-based films to which sulfosuccinic acid (SSA) is added for crosslinking agent with/without UV curing treatment and applications of a coating materials for foods. The physical, thermal, and optical properties of the UV cured chitosan-based films are investigated including their tensile strength (TS), elongation at break (%E), degree of swelling (DS), solubility (S), and water vapor absorption as well as their biodegradability in soil and applicability of the coating on a fruit. We also evaluated the physical properties of the prepared films to which glycerol (GL), xylitol (XL), and sorbitol (SO) are added to be used as plasticizers. The surface and topography of the prepared films are investigated by scanning electronic microscopy (SEM) and atomic force microscopy analysis (AFM). The results indicate that the films UV cured for 20 min possess optimal physical and thermal properties compared to that of non-cured films. The mechanical, thermal, and water barrier properties of SO-added film are also found to be superior to other films with added GL and XL. The degree of biodegradability revealed that the films are degraded by about 40–65% after 220 days.

1. Introduction

Recently, widespread concerns regarding the quality and safety of food has led to the development of packaging materials, such as specific packaging for the preservation of the food, apart from providing a barrier property. Active compounds and ingredients like antioxidant, antimicrobial agents, and/or nutrients can be incorporated into the packaging materials to impart several functions to the active packing systems, which do not exist in conventional packaging systems. Furthermore, many researchers have used natural preservatives in biodegradable materials for active packaging to avoid health-related and environmental problems (Cazóon, Velazquez, Ramírez, & Vázquez, 2017; Shahbazi, 2017; Siripatrawan & Harte, 2010). Thus, increase in the biodegradability of biodegradable materials is an important topic for their food, industrial, and agriculture applications. As an active packaging material, edible films have attracted much attention for food or pharmaceutical packaging because they can replace traditional plastic films, most of which are not biodegradable in soil, activated sludge, or compost. Edible films can improve food quality and safety by acting as a barrier to moisture, gas, aroma, and atmospheric bacteria and by providing protection to a food product even after the packing material is opened or used (Cao, Fu, & He, 2007; Elsabee & Abdou, 2013).

Edible films are usually synthesized by biodegradable polysaccharides, proteins and lipids having nontoxic and gas-barrier properties. They can be used as protective coating materials to retain food quality and to reduce packaging wastes (Dutta, Tripathi, Mehrotra, & Dutta, 2009; Farhan & Hani, 2017). Among substances used for the preparation of edible films, chitosan is an interesting material because it is nontoxic, biodegradable, biofunctional, biocompatible, is an intrinsic antioxidant, and possesses antimicrobial properties. The film-forming property of chitosan has found several packing applications in tissue engineering and drug delivery, due to its physical properties and slow biodegradability. Chitosan, a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine and *N*-acetyl-D-glucosamine, is a deacetylation product of chitin, which is the second most abundant natural polysaccharide after cellulose and is considered an eco-friendly biomaterial (Altiok, Altiok, & Tihminlioglu, 2010; Raju & Haris, 2016; Yuan, Chena, & Li, 2016).

Many studies have reported the application of chitosan-based active coating or edible films in various fields such as food and pharmaceutical processes and medical and agricultural drugs. Several studies have been

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dedicated to enhancement of the low mechanical, thermal, gas barrier, and water resistance properties of these films. Zhai, Zhao, Yoshii, and Kume (2004) and Suzuki et al. (2005) have prepared chitosan-starch blend films and have investigated their physical and antimicrobial activity properties. In addition, many natural and synthetic polymers such as alginate (Sweeneya, Miraftaba, & Collyerb, 2014), gelatin (Nagahama et al., 2009), poly(ethylene glycol) (Kiuchi, Kai, & Inoue, 2008), and poly(vinyl alcohol) (Sakai, Khanmohammadi, Khoshfetrat, & Taya, 2014; Yang, Liu, Chen, Yu, & Zhu, 2008; Dutta et al., 2009) are commonly blended with chitosan to improve the performance of chitosan-based biomaterials. However, in case of chitosan-based films using polysaccharides and synthetic polymers, their mechanical properties, elongation at break, and water resistance are lower than those of other synthetic materials made from petroleum. Other methods for the enhancement of various properties and the expansion of applications of chitosan-based films, that is, separation and purification technology and electrochemical properties, involve the preparation of chitosan nanocomposite films using TiO_2, Ag, Au, Fe_3O_4, clay, whisker, and graphene nanoparticles (Armentano, Dottori, Fortunati, Mattioli, & Kenny, 2010; Jia, Jiang, Jin, Wang, & Huang, 2015; Shahbazi, Rajabzadeha, & Ahmadi, 2017; Zhou et al., 2016).

Generally, chitosan based biomaterials are crosslinked by various methods like using crosslinking agents, heat curing process, and electron-beam or ultraviolet irradiation. Most researchers have reported that chemically crosslinked chitosan-based biomaterials are prepared using glutaraldehyde (Chen et al., 2016; Kadam & Lee, 2015; Kumari, Basha, & Sudha, 2012; Miles, Ball, & Matthew, 2016), formaldehyde (Garavand, Rouhi, Razavi, Cacciotti, & Mohammadi, 2017), or 1,5-pentane-dial (De Souza Costa-Junior, Pereira, & Mansur, 2009) as the crosslinking agents and have investigated their physical properties and degree of crosslink. However, the use of harmful crosslinking agents or metallic nanoparticles in active packing or edible films can affect human health as well as the environment. Muzzarelli, Mehtedi, Bottegoni, and Gigante (2016) have prepared crosslinked chitosan-based biomaterials using genipin as a non-toxic crosslinking agent and have analyzed their various physical properties such as morphology, roughness, porosity, hydrophilicity, ζ-potential, surface area and surface energy. They reported the effects of non-cytotoxic concentrations of genipin and applicability for chitosan-based biomaterials. However, although genipin is a natural and non-toxic cross-linking agent, it is relatively expensive and, moreover, the extraction process is complicated. Rivero, García, and Pinotti (2012) reported that physical properties such as thermal stability, color, barrier properties, and water resistance of crosslinked chitosan-based films were improved by heat curing and addition of tannic acid. In our previous study (Yoon, 2014) physical properties of biodegradable films were improved by the heat curing process, and their possible application in various fields were gauged by investigating of the degree of their decomposition in soil. However, the physical properties of biodegradable films treated by the heat curing process were still relatively lower than other commercial petroleum films. Therefore, it is essential to add crosslinking agents. In this work, we prepared crosslinked chitosan based films using sulfosuccinic acid (SSA) as the crosslinking agent (Jegal & Lee, 1999). SSA makes a good crosslinking agent with strong hydrophilic property effective for biodegradable materials. It has a relatively bulky chemical structure: two carboxylic acid groups and one sulfuric acid as crosslinkable sites.

The main objective of this study is to prepare eco-friendly biodegradable films based on chitosan, and polyvinyl alcohol (PVA) using SSA as the crosslinking agent, and glycerol (GL), xylitol (XL), and sorbitol (SO) as plasticizers, by applying a casting method and UV curing process. We evaluated the effect of the time of UV curing, SSA contents, and plasticizer contents on the optical and physical properties, thermal properties, and biodegradability in soil of the prepared chitosan/PVA blend films.

2. Experimental

2.1. Materials

The medium molecular weight chitosan (MCh) (Mw: 190,00–310,000 and the degree of deacetylation (DD): 75–85%), polyvinyl alcohol (PVA) (Mw: 89,000–98,000 and the degree of hydrolysis (DH): 99%), reagent grade glycerol (GL), xylitol (XL), sorbitol (SO), and sulfosuccinic acid (SSA) were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA). Lactic acid (LA) was obtained from Duksan (Pharmaceutical Co., Ltd., Korea). Distilled deionized water (DW) was used in all experiments.

2.2. Preparation of crosslinked MCh/PVA blend films

MCh/PVA blended films were obtained by a casting method. First, MCh (2.0 g) solution was prepared by dissolving MCh in a 1.0 wt% aqueous solution of LA at room temperature. PVA (2.0 g) solution was prepared by dissolving PVA in hot DW (95 °C). Then, the plasticizers (GL, XL, or SO) and the crosslinking agent (SSA) were mixed with water using a kitchen-aid mixer (Anymix, Hyun-woo Star, Seoul, Korea) in PVA solution for 30 min. The total amount of D.W. used in the preparation of MCh/PVA blended films was 140 g. The PVA/plasticizers/SSA solution and the MCh solution were mixed at 95 °C for 30 min, and the resultant mixture was blended to form a homogeneous gel-like solution using a mechanical stirrer (500 rpm) at room temperature for 60 min. MCh and PVA had the same mass ratio, and the plasticizer and SSA contents were expressed as a mass percent ratio to the total MCh and PVA weight. The mixing composition is shown in Table 1. The bubbles formed as the by-product of the process were removed using an aspirator. Thus, 23.0 g of the prepared gel-like solution was poured onto Petri dishes (10 cm diameter). Water was evaporated from the Petri dishes in a ventilated oven at 50 °C for 24 h, and the as-dried films were put in open polyethylene bags and stored at 25 °C and 50% relative humidity (RH) for 1 week. The prepared films were then irradiated for 5, 10, 15, 25, and 30 min by using a UV lamp (OSRAM ULTRA-VITALUX, 300 W) at atmospheric pressure. After being UV cured, the films were conditioned again at 50% RH and 25 °C for

Table 1
Compositions for preparations of crosslinked MCh/PVA blend films.

Samples	Chitosan (MCh) (g)	PVA (g)	GL (wt%)	XL (wt%)	SO (wt%)	SSA (wt%)	D.W. (g)
MChP	2.0	2.0	–	–	–	–	140
MChPS5	2.0	2.0	–	–	–	5	140
MChPS10	2.0	2.0	–	–	–	10	140
MChPS15	2.0	2.0	–	–	–	15	140
MChPS20	2.0	2.0	–	–	–	20	140
MChPS30	2.0	2.0	–	–	–	30	140
MChPGLS15	2.0	2.0	0–60	–	–	15	140
MChPXLS15	2.0	2.0	–	0–60	–	15	140
MChPSOS15	2.0	2.0	–	–	0–60	15	140