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Preparations and characterization of alginate/silver composite films: Effect of types of silver particles

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ABSTRACT

Alginate-based films reinforced with different types of silver particles such as metallic silver (AgM), silver zeolite (AgZ), citrate reduced silver nanoparticles ($AgNP^{C}$), laser ablated silver nanoparticles ($AgNP^{LA}$), and silver nitrate ($AgNO_3$) were prepared using a solvent casting method and the effect of silver particles on the optical, mechanical, water vapor barrier, and antimicrobial properties the composite films was evaluated. Size and shape of the silver particles were varied depending on the types of silver source and the preparation method. The alginate films incorporated with $AgNP^{C}$, $AgNP^{LA}$, and $AgNO_3$ showed a characteristic surface plasmon resonance absorption peaks of AgNPs around 420 nm. Film properties such as mechanical, optical, and water vapor barrier properties were greatly influenced by the types of AgNPs used. Alginate/AgNPs composite films except AgM and $AgNP^{LA}$ incorporated ones exhibited strong antimicrobial activity against two food-borne pathogenic bacteria, *Escherichia coli* and *Listeria monocytogenes*. The developed films have a high potential for the application as antimicrobial food packaging films.

1. Introduction

There is a growing interest in the development of innovative food packaging materials using biopolymers due to the environmental problems and depletion of natural resources caused by non-biodegradable petroleum-based plastic packaging materials, as well as consumer's demand for the safe and high quality foods (Duncan, 2011; Rhim, Park, & Ha, 2013; Tang, Kumar, Alavi, & Sandeep, 2012). Biopolymers from various natural resources have been considered as attractive alternatives for the non-biodegradable plastic packaging materials since they are abundant, renewable, environmentally friendly, biodegradable, and biocompatible (Duncan, 2011; Rhim, Park et al., 2013). In addition, biopolymer-based packaging materials have some beneficial properties such as improving food quality, securing food safety, and extending shelf-life of food (Rhim, Wang, & Hong, 2013; Yu et al., 2013). Since food quality and safety are major concerns in the food industry, biopolymer-based antimicrobial packaging has been considered as an emerging technology that has a significant impact on maintaining food quality and extending shelf-life of packaged foods. Among various types of biopolymers, carbohydrate based polymers have been widely used to prepare innovative food packaging materials because of their good film forming properties (Rhim, Park et al., 2013). As one of such carbohydrate biopolymers, alginate is a good candidate for being explored in the food packaging applications.

Alginate is a naturally occurring poly-anionic polysaccharide derived from brown marine algae (*Phaeophyceae*), and it is commercially extracted from brown seaweed including giant kelp (*Macrocystis pyrifera*, *Ascophyllum nodosum*) and various types of *Laminaria* species such as *Laminaria hyperborea*, *Laminaria digitata*, and *Laminaria japonica* (Lee & Mooney, 2012). Alginate is made up of a linear block co-polymer of 1, 4-linked β-D-mannuronic and α-L-guluronic residues in varying proportions. As a low-cost, abundantly available, biocompatible and environmentally friendly biopolymer, it has been used in numerous applications in the food and biotechnology industries such as a non-toxic food additive, thickening and gelling agent, and colloidal stabilizer (Carneiro-da-Cunha et al., 2010).

Recently, application of nanotechnology has been emerging in the food packaging industry to develop bio-nanocomposite packaging materials by homogeneous blending biopolymers with various types of nano-sized filler materials to improve the properties such as mechanical and gas barrier properties with extra functional properties like ultraviolet light screening and antimicrobial properties (Duncan, 2011; Rhim, Park et al., 2013). As one of such nanofiller

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materials, silver nanoparticles (AgNPs) have been widely used in various industries including electrical, medical, pharmaceutical, food, and food packaging industries because of their unique physicochemical, optical, catalytic, and antimicrobial properties, as well as their large surface to volume ratio and thermal stability (Duncan, 2011; Shankar, Jaiswal et al., 2015). A variety of methods have been used to synthesize AgNPs (Rhim, Wang, Lee, & Hong, 2014; Shankar, Chorachoo, Jaiswal, & Voravuthikunchai, 2014, Shankar, Jaiswal, Aparna, & Prasad, 2014; Shankar & Rhim, 2015). One of the most important properties of AgNPs for the application in the food packaging, biomedical, and pharmaceutical industries is their antimicrobial activity. Generally, antimicrobial activity of AgNPs is known to depend not only on the type of silver, size, and shape, but also on the synthesis methods, although their mode of action has not been fully understood yet (Duncan, 2011; Shankar, Chorachoo, et al., 2014; Shankar, Prasad, Selvakannan, Jaiswal, & Laxman, 2015; Wani, Ganguly, Ahmed, & Ahmad, 2011). The AgNPs are known to possess more toxicological effects against microbial invaders than the silver nitrate, which is mainly due to the large surface area of AgNPs to act as a reservoir for Ag ions (Duncan, 2011). However, the effect of various sources and types of silver on the properties of biopolymer films has not been explored.

Therefore, the present study has been performed to prepare alginate-based composite films with silver particles from different sources such as metallic AgNPs (AgM), silver zeolite (AgZ), citrate reduced AgNPs ($AgNP^{C}$), laser ablated AgNPs ($AgNP^{LA}$), and ionic silver ($AgNO_3$) and to test their effect on the film properties. The effect of various sources and types of silver on the mechanical, water vapor barrier, UV-light barrier, color, and optical properties of alginate-based films were studied. In addition, the antimicrobial properties of the films were performed against two representative food-borne pathogenic bacteria, *Listeria monocytogenes* and *Escherichia coli*.

2. Materials and methods

2.1. Materials and microbial strains

Sodium-alginate (MW: 75–150 kDa; guluronate/mannuronate ratio ≥1.5) was purchased from Kanto Chemical Co. (Tokyo, Japan). Metallic silver (99.2% silver) and silver zeolite (silver ~2 wt%) were purchased from Nano Bio Co., Ltd. (Seoul, Korea) and AgION Technologies, Inc. (Wakefield, MA, USA), respectively. Silver nitrate ($AgNO_3$), brain heart infusion broth (BHI), and tryptic soy broth (TSB) were obtained from Duksan Pure Chemicals Co., Ltd. (Gyeonggi-do, Korea). *E. coli* O157:H7 ATCC 43895 and *L. monocytogenes* ATCC 15313 were procured from the Korean Collection for Type Cultures (KCTC, Seoul, Korea).

2.2. Preparation of silver and silver nanoparticles suspensions

Suspensions of metallic silver or silver zeolite were prepared by dispersing metallic silver (50 mg) or silver zeolite (2.5 g, equivalent to 50 mg of silver) in 500 mL of distilled water with vigorous stirring at room temperature for 12 h and subsequently mixed thoroughly using a high speed homogenizer at 20,000 rpm (T25 basic, IKa Labotechnik, Janke & Kunkel Gmbh & Co., KG Staufen, Germany) followed by sonication for 1 min using a high intensity ultrasonic processor (VCX 750, Sonics & Materials Inc., Newtown, CT, USA). Citrate-reduced AgNPs ($AgNP^{C}$) were prepared following the method of Rhim, Wang et al. (2013). First, 500 mL of 1 mM solution of $AgNO_3$ was heated to boiling. Then, 3 mL of 1% trisodium citrate (TSC) solution was added to the silver salt solution and boiled until the color of the solution changed to bright yellow. Laser ablated AgNPs ($AgNP^{LA}$) were prepared by the method of Rhim et al. (2014). For this, Q-switched Nd:YAG laser (Brilliant b, Quantel, Les Ulis, France) with a pulse duration of 8 nano sec and 10 Hz repetition rate at the fundamental wavelength of 1064 nm was employed for ablation of silver. A silver plate (2.54 × 2.54 cm) was located in a cubic glass cell containing 500 mL of 0.5% polyvinyl pyrrolidone (PVP) solution. The PVP solution was used as a stabilizing agent for the ablated AgNPs. The laser output power was 100 mJ/pulse. The laser beam was focused on the silver target by a plano-convex lens (f = 7 cm). The ablation was carried out for predetermined duration and the ablated amount of AgNPs was determined by weight difference of the silver plate before and after laser ablation. The concentration of the silver was controlled to maintain at 1 mM for all the samples prepared above.

2.3. Characterization of silver suspensions and silver nanoparticles

The formation of AgNPs was monitored by the color change of the solution, and the absorption of light was measured in the range of 200–600 nm using a UV–vis spectrophotometer (Mecasys Optizen POP Series UV/Vis, Seoul, Korea). Shape and size of silver particles were determined using a scanning transmission electron microscopy (STEM) in FE-SEM instrument in transmission mode (FE-SEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan). For X-ray diffraction (XRD) pattern, the samples were analyzed using an X-ray diffractometer (PANalytical X′pert pro MRD diffractometer, Amsterdam, Netherlands). The spectra were recorded using Cu Kα radiation (wavelength of 1.54056 Å) and a nickel monochromator filtering wave at 40 kV and 30 mA with a scanning rate of 0.4°/min at room temperature.

2.4. Preparation of alginate/silver composite films

Alginate/silver composite films were prepared with a solution casting method following the method of Rhim, Wang et al. (2013) 150 mL (1 mM) suspension of four different types of silver particles (metallic silver, silver zeolite, citrate reduced AgNPs, and laser ablated AgNPs) and $AgNO_3$ were taken into 500 mL beaker and stirred constantly for 30 min followed by the addition of glycerol (1.2 g) as a plasticizer and kept stirring for another 20 min. Then, 4 g of alginate powder was added slowly in the solution with stirring and heating at 90 °C until they dissolved completely. The film forming solutions were cast evenly onto a leveled Teflon film (Cole-Parmer Instrument Co., Chicago, IL, USA) coated glass plate (24 × 30 cm), and allowed to dry at room temperature (23 ± 3 °C) for 2 days. The dried films were peeled off from the glass plate and conditioned at 25 °C and 50% relative humidity (RH) for at least 48 h. For the comparison, the control alginate film was prepared by the same procedure without adding silver particles. The films were designated as alginate/AgM, alginate/AgZ, alginate/$AgNO_3$, alginate/$AgNP^{C}$, and alginate/$AgNP^{LA}$ for the composite films reinforced with metallic silver, silver zeolite, silver nitrate, citrate reduced AgNPs, and laser ablated AgNPs, respectively.

2.5. Characterization of alginate/silver composite films

2.5.1. Morphology and optical properties

The scanning electron microscopy (SEM) analysis was used to observe surface microstructure of alginate and alginate/silver composite films. The film sample was cut into small pieces and directly placed on a specimen holder and observed using a Field Emission Scanning Electron Microscopy (FE-SEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan) with an accelerating voltage of 5.0 kV.

The surface color of the films was measured using a Chroma meter (Konica Minolta, CR-400, Tokyo, Japan) with a white color plate (L = 97.75, a = −0.49, and b = 1.96) as a standard background.