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Grapefruit seed extract incorporated antimicrobial LDPE and PLA films: Effect of type of polymer matrix

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ABSTRACT

Antimicrobial low-density polyethylene (LDPE) and poly(lactide) (PLA) films were prepared by blending with grapefruit seed extract (GSE) incorporated thermoplasticized starch (TPS) using extrusion blowing and extrusion casting methods, respectively. The effect of polymer matrix was studied by comparing the film properties such as optical, mechanical, water vapor barrier, and antimicrobial properties. Scanning electron micrograph (SEM) result indicated that the TPS was homogeneously dispersed through both polymer matrix. Though transparency, mechanical, and gas barrier properties of the blend films decreased compared with their neat films, the blend films showed UV-light screening function and antimicrobial activity against food-borne pathogenic bacteria, *E. coli* and *Listeria monocytogenes*, which was mainly attributed to the GSE. While PLA/TPS film exhibited strong antibacterial activity against both bacteria, LDPE/TPS film showed lower antibacterial activity. This was presumably because the GSE was entrapped more tightly by the LDPE than the PLA. Packaging application test using minced fish paste also showed that the PLA/TPS film was more effective to prevent bacterial growth than LDPE/TPS film.

1. Introduction

Antimicrobial food packaging films have received great attention because they help to secure food safety and to extend the shelf-life of packaged foods by destroying or inhibiting spoilage and pathogenic microorganisms (Falguera, Quintero, Jiménez, Muñoz, & Ibarz, 2011; Imran et al., 2010). Antimicrobial films are usually prepared by blending or mixing antimicrobial compounds with base polymeric materials. Variety of organic or inorganic materials with antimicrobial functions have been used to develop antimicrobial food packaging films. They include organic acids such as propionic (Ouattara, Simard, Piette, Begin, & Holley, 2000), benzoic (Dobias, Chudackova, Voldrich, & Marek, 2000), and sorbic acids (Cagri, Ustunol, & Ryser. 2001), bacteriocins such as nisin (Jin, Liu, Zhang, & Hicks, 2009) and pediocin (Santiago-Silva et al., 2009), plant extracts such as thymol (Ramos, Jiménez, Peltzer, & Garrigós, 2014b), carvacrol (Ramos, Beltr, á, n, Peltzer, Valente, Garrig, ó, & s, 2014a), and allyl isothiocyanate (Lim & Tung, 1997), natural biopolymers like chitosan (Dutta, Tripathi, Methrotra, & Dutta, 2009), enzymes such as peroxidase (Appendinia & Hotchkiss, 2002) and lysozyme (Nattres, Yost, & Baker, 2001), nanoclays like quaternary ammonium modified montmorillonite (Abreua et al., 2015), and nano-sized metals and metallic oxides such as silver (Yoksan & Chirachanchai, 2010), copper (Shankar, Teng, & Rhim, 2014), gold (Pagno et al., 2015), TiO_2 (Othman, Salam, Zainal, Basha, & Talib, 2014), and ZnO (Shankar, Teng, Li, & Rhim, 2015). Recently, utilization of natural antimicrobial materials such as essential oils, spice extracts, and fruit seed extracts have been increased due to their antimicrobial activity and safety (Ghasemlou et al., 2013; Tan, Lim, Tay, Lee, & Thian, 2015). As one of natural antimicrobial substances, grapefruit seed extract (GSE) has been widely used in a various industries such as food processing and packaging, pharmaceuticals, and cosmetics industries (Reagor, Gusman, McCoy, Carino, & Heggers, 2004; Song, Shin, & Song, 2012). The GSE is extracted from the seed and pulp of grapefruit, and it contains large quantities of polyphenolic compounds, flavonoids (naringin), citric acid, ascorbic acid, tocopherol, limonoid and other trace compounds (Cho, Seo, Choi, & Joo, 1990). To exploit the antimicrobial activity of the GSE, antimicrobial films have been prepared by blending the GSE with various types of biopolymers such as agar (Kanmani & Rhim, 2014a), chitosan (Tan et al., 2015), carrageenan (Kanmani & Rhim, 2014b), and gelatin (Song et al., 2012). Most of the research works on the antimicrobial films using GSE have been focused only

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on the use of natural biopolymers because the GSE can be easily mixed with hydrophilic natural biopolymers. However, their use has been limited due to their relatively poor mechanical and high hydrophilic properties with poor processability (Rhim, Park, & Ha, 2013). Therefore, commodity plastic films were considered as the base polymeric films for the preparation of antimicrobial films by blending with natural antimicrobial agents (Pérez-Pérez, Regalado-González, Rodríguez-Rodríguez, Barbosa-Rodríguez, & Villaseñor-Ortega, 2006). In order to develop the antimicrobial packaging film for the practical use, we chose low-density polyethylene (LDPE) and poly(lactide) (PLA) films as base polymeric films and GSE as an antimicrobial agent. Thermoplastic starch (TPS) has frequently used for blending with petroleum-based plastics or as a carrier for functional materials to prepare functioned plastic films (De Oliveira Pizzoli et al., 2016; Shirai et al., 2015; Suppakul, Sonneveld, Bigger, & Miltz, 2008). Though extensive research works on the blending of TPS with PLA or LDPE films have been performed (Sabetzadeh, Bagheri, Masoomi, 2015; Ayana, Supratim, & Khatua, 2014; Cercle, Sarazin, & Favis, 2013; Taghizadeh, Sarazin, & Favis, 2013), works on the preparation of antimicrobial films incorporated with GSE have not been performed yet.

Therefore, the main objectives of the present study were to prepare antimicrobial plastic films with LDPE and PLA by blending with TPS and GSE, and to test the effect of type of the base plastic polymer on the antimicrobial activity of the blend film.

2. Materials and methods

2.1. Materials

Poly(lactide) (PLA, Biomer® L9000; weight-average molecular weight: 200 kDa) was obtained from Biomer Inc. (Krailling, Germany). Low density polyethylene (LDPE, #2427; density: 0.924 g/cm^3, melt flow index: 4.0 g/10 min, Vicat softening point: 92 °C, melting point: 111 °C) was procured from Hanwha Chemical Co. (Seoul, Korea). Both PLA and LDPE resins were dried under vacuum at 60 °C for 24 h before use. Corn starch was procured from Daejung Chemicals & Metals Co., Ltd. (Siheung, Gyonggi-do, Korea). Grapefruit seed extract (GSE, DF-100) was obtained from Komipharm International Co., Ltd. (Seoul, Korea). Tryptic soy broth (TSB), brain heart infusion (BHI) and agar powder were purchased from Duksan Pure Chemicals Co., Ltd (Ansan, Gyonggi-do, Korea). Frozen minced fish made of hair-tail was donated from OurHome Co., Ltd. (Yongin, Gyonggi-do, Korea).

2.2. Preparation of films

Thermoplasticized starch (TPS) as a carrier of the GSE was prepared by mixing cornstarch with 20 wt% of glycerol and 40 wt% of GSE as plasticizer and antimicrobial filler, respectively, using a mixer at a low speed for 10 min (Ultra Power Series 4.5-Quart Stand Mixer KSM90, KitchenAid, St Joseph, Michigan, USA). The mixture was heated at 120 °C for 30 min using an autoclave, then cooled to room temperature by spreading in the room and powdered using a blender (DA700-G, Daesung Artion Co. Seoul, Korea) to get the GSE incorporated TPS.

Master batches for the blend films were prepared by mixing the TPS and polymer resins (PLA and LDPE) with the weight ratio of 1:10 using a high-speed mixer for 1 h, and the mixture was extruded using a twin-screw extruder (YJC-ST-Ø48/34, Yoojin Eng. Co., Ltd, Siheung, Gyonggi-do, Korea) with a screw diameter of 48 mm, a screw length/diameter (L/D) ratio of 42, and a screw speed of 600 RPM.

LDPE-based blend films were prepared using an extrusion blowing method (Hong & Rhim, 2012). The LDPE/TPS master batch was extruded using a single screw extruder (YJF-Ø50-800L, Yoojin Eng. Co., Ltd, Siheung, Korea) following the method described by Hong and Rhim (2012). PLA-based composite films were prepared using an extrusion casting method. The PLA/TPS master batch was processed using a Lab-scale T-die extruder (Single Screw Extruder L25D19, Bau Eng. Co. Ltd., Seoul, Korea).

2.3. Film thickness and conditioning

Film thickness was measured using a hand-held micrometer (Digimatic Micrometer, QuantuMike IP 65, Mitutoyo, Japan) with an accuracy of 0.001 mm. All the film samples were preconditioned in an environment chamber controlled at 25 °C and 50% RH for at least 3 days before further test.

2.4. Surface color and transmittance of films

The surface color of the film was measured using a Chroma meter (Konica Minolta, CR-400, Tokyo, Japan) with a white standard color plate (L = 98.49, a = −0.49, and b = 1.96) as a background. The total color difference (ΔE) was calculated as follows:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

where ΔL, Δa, and Δb are differences between each color value of standard and the film sample, respectively (Wang & Rhim, 2015).

Transparency and UV-screening effect of films were determined by measuring the percent transmittance of the film at 660 nm and 280 nm, respectively, using a UV–visible spectrophotometer (Model 8451A, Hewlett Packard Co., Santa Alara, CA, USA) (Wang & Rhim, 2015).

2.5. FTIR analysis

Fourier transform infrared (FTIR) spectra of film samples were analyzed using an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrophotometer (TENSOR 37 spectrophotometer with OPUS 6.0 software, Billerica, MA, USA). Samples were placed on the radial exposing stage and the spectra were recorded at wavenumber ranged from 4000 to 500 cm^{-1} with the resolution of 4 cm^{-1}.

2.6. Mechanical properties

Mechanical properties of the films were evaluated by measuring the tensile strength (TS), elongation at break (E), and elastic modulus (EM) following the standard ASTM method D 882–88 using an Instron Universal Testing Machine (Model 5565, Instron Engineering Corporation, Canton, MA, USA) equipped with a 0.5 kN load cell (Wang & Rhim, 2015). Tensile test was performed in both directions, i.e., machine direction (MD) and cross-machine direction (CD), of the films.

2.7. Water vapor permeability (WVP), water contact angle (WCA), and water solubility (WS)

Water vapor permeability (WVP) of film sample was determined gravimetrically following the standard method of ASTM E96-95 with modification (Gennadios, Weller, & Goodings, 1994).

The water contact angle (WCA) of the film was measured using a CA analyzer (Model Phoenix 150, Surface Electro Optics Co., Ltd., Kunpo, Korea) (Wang & Rhim, 2015).

Water solubility (WS) of film samples was determined as the percentage of soluble matter of the film (Rhim, 2012).