



Effect of PLA lamination on performance characteristics of agar/ κ -carrageenan/clay bio-nanocomposite film

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ABSTRACT

Multilayer films composed of PLA and agar/ κ -carrageenan/clay (Cloisite® Na⁺) nanocomposite films were prepared, and the effect of lamination of PLA layers on the performance properties such as optical, mechanical, gas barrier, water resistance, and thermal stability properties was determined. The tensile strength (TS) of the agar/ κ -carrageenan/clay nanocomposite films (67.8 ± 2.1 MPa) was greater than that of PLA films (43.3 ± 3.6 MPa), and the water vapor permeability (WVP), water uptake ratio (WUR), and water solubility (WS) of the nanocomposite films were higher than those of PLA films. The film properties of the multilayer films exhibited better properties of the component film layers. Especially, the WVP and water resistance of the bionanocomposite film were improved significantly, while the OTR of the PLA film decreased profoundly after lamination with PLA layers. Thermal stability of the bionanocomposite also increased after lamination with PLA layers.

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1. Introduction

The main function of food packaging is to maintain the quality and safety of food products during storage and distribution, and to extend the shelf-life of food products by controlling the mass transfer of water vapor, gases (O₂, CO₂, flavors, and taints), and transmission of light that may occur between the internal and external environment of the package (Brown & Williams, 2003; Marsh & Bugusu, 2007; Mckinlay, 2004; Singh & Singh, 2005). To fulfill the packaging functions, a variety of packaging materials such as paper and paperboard, plastic, glass, metal, and a combination of the materials of various chemical nature and physical structures have been used (Marsh & Bugusu, 2007). Among the four basic packaging materials, plastic-based materials have been widely used since they are cheap and convenient to use with good processability, good aesthetic quality, and excellent physico-chemical properties such as mechanical, barrier, optical, and surface properties. Annually, plastics are produced about 260 million tons worldwide, of which one-third is used in packaging in the form of films, sheets, bottles, cups, tubs, trays, etc. (Plackett, 2011; Robertson, 2008).

Recent advance of new food packaging technologies, such as active and intelligent packaging developed as a response to consumer trends towards minimally processed, fresh, tasty and conveniently packaged food products (Danielli, Gontard, Spyropoulos, Beuken, & Tobback, 2008; Imran et al., 2010), and public concerns on the environmental problems

have raised interest in using biodegradable packaging materials produced from renewable resources (biopolymers). Biopolymers produced from various natural resources through direct extraction, chemical synthesis, or fermentation by microorganisms, such as starch, cellulose, proteins, polylactide (PLA), and polyhydroxyalkanoates (PHAs), have been considered as attractive alternatives for non-biodegradable petroleum-based plastics since they are abundant, renewable, inexpensive, environmentally friendly, and biodegradable (Clarival & Halleux, 2005; Luckachan & Pillai, 2011; Siracusa, Rocculi, Romani, & Rossa, 2008; Weber, Haugaard, Festersen, & Bertelsen, 2002; Zhao, Torley, & Halley, 2008).

However, there are some limitations to the commercial use of biopolymer films due to their poor mechanical and barrier properties and high sensitivity to moisture (Cabedo, Feijoo, Villanueva, Lagarón, & Giménez, 2006; Luckachan & Pillai, 2011; Yoo & Krochta, 2011). Various efforts have been made to overcome these problems and to improve the property of biopolymer-based films through not only physical, chemical, or enzymatic treatments, but also blending with hydrophobic additives, or making multilayer films with different film properties (Cabedo et al., 2006; Luckachan & Pillai, 2011; Rhim, Mohanty, Singh, & Ng, 2006a,b). Recently, nanocomposite technology, compositing biopolymer with layered silicate clay materials such as montmorillonite (MMT), has been tested to improve biopolymer film properties (Bordes, Pollet, & Avérous, 2009; Pandey et al., 2005; Ray & Bousmina, 2005; Rhim & Ng, 2007; Sorrentino, Gorrasi, & Vittoria, 2007; Yang, Wang, & Wang, 2007). Though significant improvements in film properties of biopolymer films have been reported through using each of the methods, they are still not comparable to those of the commodity plastic films. This indicates more efficient methods or a combination of the methods are needed to

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improve the film properties sufficient to substitute for the non-biodegradable plastic films for packaging use.

To date, PLA is the most widely used biopolymer-based packaging material with the highest potential for a commercial major scale production synthesized from lactic acid which is derived from renewable resources, such as corn or sugar beets (Garlotta, 2001; Gupta & Kumar, 2007; Lim, Auras, & Rubino, 2008). Structurally, PLA is a linear aliphatic polyester, which is a thermoplastic with high-strength, high-modulus, good processability, being completely biodegradable, compostable, and biocompatible, and therefore perfectly safe for the environment and for the food packaging application. PLA presents a medium water and oxygen permeability level comparable to polystyrene (Auras, Harte, & Selke, 2004). In addition, PLA is safe and “Generally Recognized As Safe” (GRAS) for use in food packages (Conn et al., 1995). However, its high polarity, brittleness, stiffness, noise, and low deformation at break limit its use. Considerable efforts have been made to improve the properties of PLA so as to compete with low-cost and flexible commodity polymers. These attempts were carried out either by modifying PLA with biocompatible plasticizers or by blending PLA with other polymers (Luckachan & Pillai, 2011).

Previously, we prepared blend film with agar and κ -carrageenan by exploring good compatibility between the carbohydrate polymers caused by their similarity in chemical structure, and we also prepared a nanocomposite film by compositing the blend film with layered silicate nanoclay (Rhim, 2012). Though the film properties have been improved significantly through the blending, and the water vapor barrier and water resistance properties have been further improved after formation of nanocomposite with nanoclay, they were not still enough to compare with those of commodity plastic films. One way to overcome such weakness of the biopolymer-based packaging materials is to associate them with a moisture resistant polymer with good mechanical properties, while maintaining the overall biodegradability of the product. For such purposes, multilayer films formed through coating or lamination methods have been widely used to combine the properties of two or more polymers into one single multilayered structure (Martin, Schwach, Avérous, & Couturier, 2001; Martucci & Ruseckaite, 2010; Park et al., 2012; Rhim et al., 2006b; Rhim, Lee, & Ng, 2007; Thellen, Schirmer, Ratto, Finnigan, & Schmidt, 2009).

Various types of food packaging application of multilayer structures exhibiting with substantially improved gas barrier and mechanical strength have been explored in the food packaging industry. One of the traditionally used multilayers is in the form of barrier layer in the middle and outside structural layers. This is used as a passive barrier in which the middle layer is composed of high barrier films. Other use is an active barrier composed of gas (O_2 or CO_2) scavenger incorporated film layer. The other use of the multilayer film is the combination of passive and active barrier. The multilayer films or sheets with improved barrier or mechanical properties can be formulated into several different types of packaging shapes such as bags, pouches, plates, cups, trays, and clamshells. They are expected to be used for the packaging of various types of food materials including retail packaging for meats, cheese, confectionery, as well as fresh fruits and vegetables.

Therefore, the main objective of this study was to prepare multilayer films with a blended carbohydrate nanocomposite films (agar/ κ -carrageenan/clay) and PLA to modify the mechanical and barrier properties of the film for the food packaging application by exploiting the advantages of each component film.

2. Materials and methods

2.1. Materials

Food grade agar and κ -carrageenan were obtained from Fine Agar Agar Co., Ltd. (Damyang, Jeonnam, Korea) and Hankook Carrageen (Whasoon, Jeonnam, Korea), respectively. Poly-L-lactide (PLLA, Biomer®

L9000), which had a weight-average molecular weight of 200 kDa and was polymerized mainly (>98%) from L-lactic acid, was obtained from Biomer Inc. (Krailing, Germany). A natural MMT (Cloisite® Na⁺: cation exchange capacity, CEC = 92.6 mequiv./100 g) was purchased from Southern Clay Products (Gonzales, TX, USA). Analytical grade chloroform and glycerol were purchased from J.T. Baker (Mallinckrodt Baker, Inc., Phillipsburg, NJ, USA).

2.2. Preparation of films

For the preparation of agar/ κ -carrageenan blend films, film solutions were prepared by dissolving 2 g each of agar and κ -carrageenan in 150 mL of distilled water with mixing vigorously for 30 min at 95 °C using a magnetic stirrer, and then added 1 g of glycerol as a plasticizer. For the preparation of the nanocomposite film solution, clay and biopolymer solutions were prepared separately as described by Rhim, Lee, and Hong (2011). First, clay solution was prepared by dispersing precisely weighed nanoclay (Cloisite® Na⁺, 5 wt.% of agar/ κ -carrageenan) into distilled water and swelling for 24 h while stirring using a magnetic stirrer then homogenized using a high shear mixing homogenizer (T25 basic, Ika Labortechnik, Janke & Kunkel GmbH & Co., KG Staufen, Germany) at 20,500 rpm for 10 min, and followed by sonication for 10 min using a high-intensity ultrasonic processor (Model VCX 750, Sonics & Materials Inc., Newtown, CT., U.S.A.). Two grams each of agar and κ -carrageenan were dissolved into the nanoclay solution with heating and stirring at 95 °C for 30 min then added 1 g of glycerol. PLA films were prepared using the solvent casting method (Rhim et al., 2006a). Four grams of PLA was dissolved in 100 mL of chloroform while mixing vigorously at room temperature.

All the film preparation solutions were poured onto a leveled Teflon film (Cole-Parmer Instrument Co., Chicago, IL, USA) coated glass plate (24 × 30 cm) and then allowed to dry for about 24 h at room temperature (22 ± 2 °C). The resultant film was peeled off the casting surface.

Double layer (a PLA layer and a nanocomposite layer) and triple layer (PLA outer layer, a nanocomposite middle layer, and another PLA outer layer) films were prepared following the method of Rhim et al. (2006b) with basically the same method as above using the same amount of solid content as control carbohydrate composite or PLA films to control the film thickness. For the preparation of double layer film, first PLA layer was prepared by casting PLA solution (2 g PLA in 80 mL chloroform) and drying, then a nanocomposite film solution (1 g each of agar and κ -carrageenan with 5 wt.% of clay) was cast over it. Triple layer film was prepared with the same method except reducing the PLA content of each outer layer to the half of that of the double layer film. To remove the remaining solvent which is known to work as a plasticizer in the solvent cast PLA film (Rhim et al., 2006a), all the PLA films prepared were vacuum dried at 60 °C.

2.3. Film thickness and conditioning

Film thickness was measured using a micrometer (Dial Thickness gauge 7301, Mitutoyo, Japan) at an accuracy of 0.01-mm. All film samples were preconditioned in a constant temperature humidity chamber set at 25 °C and 50% RH for at least 48 h before further test.

2.4. Color and transparency

Surface color of the films was measured using a Chroma meter (Minolta, CR-200, Tokyo, Japan). A white standard color plate ($L = 97.75$, $a = -0.49$ and $b = 1.96$) was used as a background for color measurements. Hunter color values were averaged from five readings of each sample. The total color difference (ΔE) was calculated as follows:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

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