



# Mechanical and water barrier properties of agar/ $\kappa$ -carrageenan/konjac glucomannan ternary blend biohydrogel films

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## ABSTRACT

Multicomponent hydrogel films composed of agar,  $\kappa$ -carrageenan, konjac glucomannan powder, and nanoclay (Cloisite® 30B) were prepared and their mechanical and water barrier properties such as water vapor permeability (WVP), water contact angle (CA), water solubility (WS), water uptake ratio (WUR), water vapor uptake ratio (WVUR) were determined. Mechanical, water vapor barrier, and water resistance properties of the ternary blend film exhibited middle range of individual component films, however, they increased significantly after formation of nanocomposite with the clay. Especially, the water holding capacity of the ternary blend biopolymer films increased tremendously, from 800% to 1681% of WUR for agar and  $\kappa$ -carrageenan films up to 5118% and 5488% of WUR for the ternary blend and ternary blend nanocomposite films, respectively. Water vapor adsorption behavior of films was also tested by water vapor adsorption kinetics and water vapor adsorption isotherms test. Preliminary test result for fresh spinach packaging revealed that the ternary blend biohydrogel films had a high potential for the use as an antifogging film for packaging highly respiring agricultural produce. In addition, the ternary blend nanocomposite film showed an antimicrobial activity against Gram-positive bacteria, *Listeria monocytogenes*.

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## 1. Introduction

Hydrogels are highly hydrophilic polymer gels with macromolecular three dimensional networks that swell by absorbing and retaining large amounts of water without dissolving or losing their integrity in water (Farris, Schaich, Liu, Piergiovanni, & Yam, 2009; Kopeček & Yang, 2007). Structurally, they are polymers crosslinked via chemical interactions such as covalent bonds, ionic interactions, and hydrogen bonds, physical interactions such as coordinative, electrostatic, hydrophobic, and dipole–dipole interactions, or chain entanglements between the network segments (Mateescu, Wang, Dostalek, & Jonas, 2012). Generally, they are classified as natural and synthetic hydrogels based on their source; physical hydrogels, chemical hydrogels, and interpenetrating polymer networks based on their polymer interaction mechanism; degradable and non-degradable hydrogels based on their biodegradability (Farris et al., 2009; Kopeček & Yang, 2007; Mateescu et al., 2012). Hydrogels have wide range of applications such as membranes (Xu, Bartley, & Johnson, 2003), superabsorbent pads (Fernández, Picouet, & Lloret, 2010; Wu, Deng, & Lin, 2013; Yadav & Rhee, 2012), biosensors

(Fernández, López, López-Cabarcos, & Mijangos, 2005; Mateescu et al., 2012; Zhang, Guan, & Zhang, 2012), encapsulation of bioactive compounds (Jen, Wake, & Mikos, 1996; Öztóp, Hepokur, & Saraydin, 2009), largely in the biomedical field (contact lens, wound dressing, tissue engineering, drug delivery, etc.) (Berger et al., 2005; Liu & Chan-Park, 2009; Ma and Tu, 2010; Pourjavadi & Barzegar, 2009; Wang et al., 2012; Yu, Xu, Chen, Hao, & Jing, 2006), and for food packaging as well (Farris et al., 2009; Roy, Saha, Kitano, & Saha, 2012). Hydrogels can be prepared from a wide variety of materials, of natural origin, obtained from microorganisms, plants, and animals, as well as from materials prepared by modification or blending of aforementioned natural structures and from synthetic polymeric materials with various crosslinkers (Farris et al., 2009; Gibas & Janik, 2010; Hennink, & van Nostrum, 2002; Mateescu et al., 2012). Among the synthetic polymeric hydrogels, acrylate derivatives such as poly([meth]/acrylic acid) and poly([meth]/acrylamide) have been frequently used due to their high water holding capacity with good optical, mechanical, and gas barrier properties (Kundakci, Üzümlü, & Karadağ, 2008; Mateescu et al., 2012; Okay, Sarişik, & Zor, 1998; Öztóp et al., 2009; Zhang, & Zhuo, 2002). However, most of the plastic materials are practically neither biodegradable nor biocompatible. In addition, polyacrylamide and acrylamide residues in the polyacrylamide-based hydrogels might cause probable health hazards (Andersen, 2005;

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Yener & Kalipci, 2009). As an alternative for the non-biodegradable synthetic plastic materials, biopolymers produced from various natural resources, such as starch, cellulose, and proteins, have been considered since they are abundant, renewable, inexpensive, environmentally friendly, and biocompatible (Luckachan & Pillai, 2011; Siracusa, Rocculi, Romani, & Rossa, 2008). However, there are some limitations to the commercial use of biopolymer films due to their poor mechanical properties and high sensitivity to moisture (Cabedo, Feijoo, Villanueva, Lagarón, & Giménez, 2006; De Azeredo, 2009; Luckachan & Pillai, 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 other biopolymers (Cabedo et al., 2006; Luckachan & Pillai, 2011; Rhim, 2012). Recently, nanocomposite technology, compositing biopolymer with layered silicate clay materials such as montmorillonite, has been tested to improve the biopolymeric film properties (Bordes, Pollet, & Avérus, 2009; De Azeredo, 2009; Rhim, & Ng, 2007). Generally, hydrogels with improved properties can be obtained by blending with more than two polymers, in which polymer–polymer interactions can be strengthened by combining biopolymers with different structures introducing predominantly charge interactions rather than hydrogen bonding (Farris et al., 2009).

The bio-hydrogels with improved physicochemical properties can offer new opportunities for the design of efficient biopolymer-based biodegradable and/or biocompatible polymeric materials with desirable properties. Though the earliest and most widely used applications of hydrogels are in medicine and pharmaceuticals (Kopeček & Yang, 2007), much less attention has been paid to the use of bio-hydrogel films for the food packaging application.

The main objectives of this study were to prepare highly water absorbing hydrogel films by blending with biopolymers, such as agar,  $\kappa$ -carrageenan, and konjac glucomannan powder, and nanoclay (Cloisite® 30B) through the solvent casting method to improve mechanical and water resistant properties of the blended hydrogel film and to test their applicability as a food packaging material.

## 2. Materials and methods

### 2.1. Materials

Food grade agar and  $\kappa$ -carrageenan, and konjac powder were obtained from Fine Agar Agar Co., Ltd. (Damyang, Jeonnam, Korea), Hankook Carragen (Whasoon, Jeonnam, Korea), and Milyang Agar Co., Ltd. (Milyang, Kyungnam, Korea), respectively. Organically modified nanoclay (Cloisite® 30B) was procured from Southern Clay (Gonzales, TX, USA) and glycerol was purchased from Daejung Chemicals & Metals Co., Ltd. (Siheung, Gyonggido, Korea). Nine analytical reagent grade salts (LiCl, CH<sub>3</sub>COOK, MgCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, KI, NaCl, KCl, and KNO<sub>3</sub>) were used for the preparation of saturated salt solutions.

### 2.2. Preparation of films

Three different polysaccharide-based films, agar,  $\kappa$ -carrageenan, and konjac, and their ternary blend films with and without nanoclay (Cloisite® 30B) were prepared using a solvent casting method (Rhim, Lee, & Hong, 2011). For the preparation of single component film solution, three grams of each of agar,  $\kappa$ -carrageenan, and konjac powder were dissolved in a constantly stirred mixture of distilled water (150 mL) and glycerol (30 wt% of solid, 0.9 g) with heating above 90 °C for 30 min. The ternary blend film solution was prepared by dissolving 1 gram of

each polysaccharide powder with 30 wt% of glycerol and followed the same procedure. And the ternary blend/clay nanocomposite film solution was prepared according to the method described by Rhim et al. (2011). In short, precisely weighed nanoclay (5 wt% of biopolymers) was first dispersed into distilled water (150 mL) and swelled by stirring using a magnetic stirrer for 24 h, 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, USA). Then one gram each of agar and  $\kappa$ -carrageenan, and konjac powder were dissolved into the nanoclay solution then heating the mixture at 95 °C for 30 min with constant stirring and added 0.9 g of glycerol. The film solutions were cast onto a glass plate (24 × 30 cm) coated with Teflon layer (Cole-Parmer Instrument Co., Chicago, IL, USA). The cast films were dried for about 24 h at room temperature (2261 ± 2 °C), and then peeled off from the casting surface. The ternary blend films prepared with and without nanoclays were marked as A/C/K and A/C/K/Clo30B films, respectively.

### 2.3. Film thickness and conditioning

Film thickness was measured using a micrometer (Dial Thickness gauge 7301, Mitutoyo, Japan) with 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 (Konica Minolta, CR-400, 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 ( $L$ ,  $a$  and  $b$ ) values were averaged from five readings from each sample. The total color difference ( $\Delta E$ ) was calculated as follows:

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

where  $\Delta L$ ,  $\Delta a$ , and  $\Delta b$  are difference between each color values of standard color plate and film specimen, respectively.

The percent transmittance at wavelength of 660 nm ( $T_{660}$ ) was determined using a UV/vis spectrophotometer (Model 8451A, Hewlett-Packard Co., Santa Alara, CA, USA) (Rhim, Hong, Park, & Ng, 2006).

### 2.5. Mechanical properties

The mechanical properties of the films including the tensile strength (TS), elongation at break (EB), and elasticity of modulus (E) were determined according to 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. Rectangular strips (2.54 × 10 cm) were cut from individually prepared film using a precision double blade cutter (model LB.02/A, Metrotec, S.A., San Sebastian, Spain). Initial grip separation was set at 50 mm and cross-head speed at 50 mm/min. The TS (MPa) was determined by dividing the maximum load (N) by the initial cross-sectional area (m<sup>2</sup>) of the film sample, the EB (%) was determined by dividing the extension at rupture of the film ( $L$ ) by the initial length of the film ( $L_0$ ; 50 mm) multiplied by 100, and the  $E$  ( $\sigma/\epsilon$ , GPa) was determined from the slope of linear portion of the stress–strain curve, which corresponds to the stress ( $\sigma = F/A$ ) divided by the strain ( $\epsilon = L/L_0$ ) of the film samples.

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