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Carrageenan-based hydrogels and films: Effect of ZnO and CuO nanoparticles on the physical, mechanical, and antimicrobial properties

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ABSTRACT

Carrageenan-based functional hydrogels and dry films were prepared by blending with metallic nanoparticles such as zinc oxide (ZnO), copper oxide (CuO) NPs, and their combination. Addition of KCl as a cross-linking agent increased the gel strength of carrageenan-based hydrogels. The neat carrageenan hydrogels were transparent, but they became translucent when the metallic nanoparticles were incorporated. Dried hydrogel films were flexible and free-standing. Transmission of UV light of the carrageenan-based films decreased remarkably when metallic NPs were incorporated. The swelling ratio (SR) of carrageenan films with or without cross-linker were 2980% and 2665%, respectively, however, it increased up to 3535% when ZnONPs were incorporated. The carrageenan-based hydrogel films with metallic nanoparticles exhibited strong antibacterial activity against food-bourne pathogenic bacteria, *Escherichia coli*, and *Listeria monocytogenes*. The ZnONPs incorporated hydrogel films exhibited higher mechanical, UV-screening, water holding, thermal stability, and antimicrobial properties than the CuONPs incorporated ones. The nanocomposite hydrogels or films have a high potential for the application in the biomedical, cosmetic, and active food packaging areas.

1. Introduction

Hydrogels are three-dimensional hydrophilic polymer networks that can absorb and retain large quantities of water, saline or physiological solutions (Farris, Schaich, Liu, Piergiovanni, & Yam, 2009). Hydrogels are divided into two groups depending on their source: (1) hydrogels formed from natural polymers such as gelatin, alginate, carrageenan, cellulose, chitosan, and their derivatives and (2) hydrogels formed from synthetic polymers such as poly(vinyl alcohol), poly(amido-amine), poly (*N*-isopropyl acrylamide), polyacrylamide, and poly acrylic acid (Farris et al., 2009; Mateescu, Wang, Dostalek, & Jonas, 2012). Hydrogels have been widely used in agriculture and biomedical areas like tissue engineering, wound dressing, drug delivery, biosensors, and sorbents for removal of dyes and heavy metals, and they have also been used as water or drip adsorption pads in the food packaging industry (Liu, Zhan, Wan, Wang, & Wang, 2015; Mohandas, Kumar, Raja, Lakshmanan, & Jayakumar, 2015; Roy, Saha, Kitano, & Saha, 2012). Recently, hydrogels based on natural biopolymers, especially polysaccharides, have drawn a considerable attention due to their biodegradability, biocompatibility, renewability, and safety, compared with the synthetic polymer-based hydrogels (Bhattarai, Gunn, & Zhang, 2010; Chang & Zhang, 2011; Distantina, Rochmadi, Fahrurrozi, & Wiratni, 2013). Among such polysaccharides, carrageenan has been considered as one of the most attractive candidates for the preparation of bio-hydrogel since it

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has strong gel forming ability with high water holding capacity (Salgueiro, Daniel-da-Silva, Fateixa, & Trindade, 2013).

Carrageenan is a water soluble polysaccharide extracted from various species of *Rhodophyta* (red marine algae) and consists of long linear chains of D-galactose and D-anhydrogalactose with anionic sulfate groups ($-OSO_3^-$) (Liu et al., 2015). The excellent gel forming ability and high swelling property of carrageenan promoted its use for the preparation of hydrogels or hydrogel films using carrageenan alone or combined with other biopolymers such as alginate (Pascalau et al., 2012), agar, konjac glucomannan (Rhim & Wang, 2013), and gelatin (Varghese, Chellappa, & Fathima, 2014). Gelation of carrageenan is known to be induced by the conformational change in the polymer chains from a random coil to a helix form (Rhein-Knudsen, Ale, & Meyer, 2015). Several cations such as K^+ (KCl), Na^+ (NaCl), and Ca^{2+} ($CaCl_2$) have been used as a gelation promoter of carrageenan, among them KCl showed the highest improvement in mechanical and chemical stability of carrageenan gel (Liu et al., 2015; Mangione et al., 2005; Nguyen, Nicolai, Benyahia, & Chassenieux, 2014; Pascalau et al., 2012).

Recently, as the nanotechnology has emerged, various types of nanomaterials have been incorporated into biopolymer-based hydrogels to increase the physicochemical properties of the hydrogels. For example, gold nanoparticles have been incorporated into carrageenan-based hydrogel for optical property modulation and controlled the release of drug (Salgueiro et al., 2013), silver and magnetic nanoparticles (Fe_3O_4) were used to increase the swelling properties and development of drug delivery systems (Daniel-da-Silva et al., 2012; Hezaveh & Muhamad, 2012), sodium montmorillonite (Na-MMT) nano clay was used to enhance the dye adsorption capacity (Mahdavinia, Massoumi, Jalili, & Kiani, 2012), and nanoclay and silver nanoparticles have been incorporated into carrageenan-based films to have UV barrier and antimicrobial properties (Rhim & Wang, 2014).

In addition, zinc oxide nanoparticles (ZnONPs) and copper oxide nanoparticles (CuONPs) are well known for their antimicrobial and UV-light barrier properties (Shankar & Rhim, 2014; Shankar, Teng, Li, & Rhim, 2015). Incorporation of small amounts of ZnONPs or CuONPs in biopolymers has improved the films properties and showed strong antimicrobial and UV barrier properties of biopolymer-based films (Kanmani & Rhim, 2014; Shankar, Teng, & Rhim, 2014; Shankar et al., 2015). For these reasons, ZnONPs and CuONPs have been used in the biomedical and cosmetics industries in the forms of wound dressing, facial mask, sunscreen, and toothpaste (Borkow et al., 2010a; Borkow, Zhou, Page, & Gabbay, 2010b; Serpone, Dondi, & Albini, 2007). Moreover, ZnONPs and CuONPs have been applied for an active food packaging. ZnONPs have been added to LDPE and PVC packaging films to improve the microbial stability and to prolong the shelf life of orange juice, cut apple, and cheese (Beigmohammadi et al., 2016; Emamifar, Kadivar, Shahedi, & Soleimanian-Zad, 2010; Li, Li, Zhang, & Xing, 2011).

In the present study, ZnONPs, CuONPs, and their combinations were used as nanofillers for the preparation of carrageenan-based nano-hydrogel with multifunctional properties. The effects of nanofillers on the morphology, mechanical, thermal, optical, swelling, and antibacterial properties of the hydrogel were tested. The properties of carrageenan-based nano-hydrogels were evaluated with both hydrogel and dried film forms.

2. Materials and methods

2.1. Materials

K-Carrageenan (Hankook Carragen, Whasoon, Jeonnam, Korea), copper chloride ($CuCl_2 \cdot 2H_2O$), and zinc nitrate ($N_2O_6Zn \cdot 6H_2O$) (Duksan Pure Chemical Co., Ltd., Ansan-city, Gyonggido, Korea), sodium hydroxide (NaOH) (Samchun Pure Chemical Co., Ltd., Pyeongtaek, Gyonggido, Korea), potassium chloride (KCl) and glycerol (Daejung Chemicals & Metals Co., Ltd., Siheung, Gyonggido, Korea) were used as received without any further purification. *Escherichia coli* O157: H7 ATCC 43895 and *Listeria monocytogenes* ATCC 15313 were obtained from the Korean Collection for Type Culture (KCTC, Seoul, Korea). The bacterial strains were grown in BHI and TSB agar plates, respectively, and stored at 4 °C before the test.

2.2. Synthesis of zinc oxide and copper oxide nanoparticles

Zinc oxide nanoparticles (ZnONPs) and copper oxide nanoparticles (CuONPs) were prepared by reducing zinc nitrate and copper chloride, respectively, using sodium hydroxide as a reducing agent. For this, 29.75 g (0.1 M) zinc nitrate and 34.96 g (0.2 M) copper chloride, respectively, was dissolved in 1000 mL of distilled water with stirring for 30 min and heated to boil. Then, 40–60 mL of 5 M sodium hydroxide solution was added drop-wise to the solution and heated at 80 °C for 2 h. The white and brown precipitate indicated the formation of ZnONPs and CuONPs, respectively. The precipitate was collected by centrifugation, washed three times with distilled water, and two times with ethanol, and then dried in an oven at 70 °C for 6 h. The ZnONPs and CuONPs powder were kept in air tight bottles until further use.

Zeta potential and particles size distribution of the ZnONPs, CuONPs, and ZnO-CuONPs were determined using a Zetasizer Nano ZS90 (Malvern Instrument, UK) in triplicate. For this, the nanoparticle were dispersed in deionized water using ultrasonication for 30 s, and zeta potential and particles size were measured after dilution with deionized water.

2.3. Preparation of carrageenan-based hydrogels and hydrogel films

Carrageenan-based hydrogels and hydrogel films were prepared by following the solution casting method for the preparation of biopolymer-based nanocomposite films (Oun & Rhim, 2015b). For the preparation of carrageenan hydrogel film solution, 3 g of carrageenan was dissolved into 150 mL of distilled water with 0.9 g of glycerol as a plasticizer. The solution was heated at 90 °C for about 20 min until completely dissolved, then added 2.5 mL of KCl solution (1 M) to promote the gelation of carrageenan (Salgueiro et al., 2013). Also, three different types of carrageenan-based hydrogels were prepared with metallic NPs. For the preparation of carrageenan-based hydrogel solutions, ZnONPs (1 wt% of carrageenan), CuONPs (1 wt% of carrageenan), and their combination (ZnONPs 0.5 wt% and CuONPs 0.5 wt% of carrageenan) were dispersed into 150 mL of distilled water with stirring for 4 h sonicated for 20 min using a bath-type ultrasonic cleaner (FS 140H, Ultrasonic Cleaner, Fisher Scientific, Pittburg, PA, USA). Then, 3 g of carrageenan, 0.9 g of glycerol, and 2.5 mL of KCl were added to the solution following the same procedure as above. Then, two types of hydrogels, i.e., a cylinder type and a facial mask type, were prepared by adding the hydrogel solution into a plastic cylinder (ID × H: 14 mm × 18 mm) and a plastic facial mask mold made of PP, respectively, and gelled at room temperature (22 ± 2 °C) and kept in a refrigerator (4 °C) before test.

For the preparation of hydrogel films, the film solution (150 mL each) was cast onto a leveled Teflon film (Cole-Parmer Instrument Co., Chicago, IL, USA) coated glass plate (24 cm × 30 cm) and dried at room temperature. The films were peeled off from the glass plate and conditioned in a humidity chamber (model FX 1077, Jeio Tech Co. Ltd., Ansan, Korea) controlled at 25 °C and 50% RH for at least 48 h before the further test.