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# Antimicrobial wrapping paper coated with a ternary blend of carbohydrates (alginate, carboxymethyl cellulose, carrageenan) and grapefruit seed extract

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ABSTRACT

A functional biopolymer-coated paper was prepared by coating a ternary blend of the alginate, carboxymethyl cellulose, and carrageenan with grapefruit seed extract (GSE) for the substitute use of synthetic polymer-coated paper. The microstructure of the surface and cross-section of the coated paper analyzed by field emission scanning electron microscope (FE-SEM) indicated that the biopolymer was compatible with the base paper and filled the pores of the porous fiber to make a smooth-surfaced coating paper. The properties of the biopolymer-coated paper, such as water and oil resistance, water vapor barrier, surface hydrophobicity, and mechanical properties, increased significantly compared with not only the base paper but also commercially used PE-coated paper. The blended biopolymer coating material exhibited strong antibacterial activity against food-borne pathogenic bacteria, *Listeria monocytogenes* and *Escherichia coli*, which were destroyed completely within 3 and 9 h, respectively. The packaging test for a minced fish cake packed with the biopolymer-coated paper showed the complete destruction of surface inoculated bacteria in 6–9 days. The biopolymer-coated paper showed a high potential for disposable food packaging applications to increase the shelf-life of packaged food.

## 1. Introduction

Paper is a biodegradable material that has been widely applied in the packaging sector because of its low cost (Sothornovit, 2009). It is composed of cellulose fibers crosslinks via hydrogen bonding. The formation of hydrogen bonds in cellulose fibers and their derivatives is considered to be one of the most important factors influencing their physical and chemical properties (Kondo, Koschella, Heublein, Klemm, & Heinze, 2008). Cellulose fibers for paper making are microporous with a pore size ranging from 0.1 to 3 Å. However, its porous structure makes it highly permeable to gases and water vapor (Haggkvist, Tie-Qjang, & Odberg, 1998; Despond, Espuche, Cartier, & Domard, 2005). It is still necessary to search for solutions to improve the mechanical properties, moisture and gas barrier properties, grease resistance as well as water absorption capacity because these properties directly influence the integrity and quality of packed products. Water vapor barrier and water resistance properties could be improved by changing the wettability of a paper surface with sizing agents or through hydrophobic coating materials such as paraffin wax, polyethylene, poly (ethylene terephthalate) and poly(butylene terephthalate) (Rhim, Lee, & Hong, 2007). The coating materials based on proteins (whey protein, calcium caseinate, wheat gluten) and polysaccharides (cassava starch, corn starch, chitosan) can potentially act as alternatives, to reduce the need for synthetic polymers, for coating paper (Sothornovit, 2009; Gastaldi, Chalier, Guillemin, & Gontard, 2007).

Also, the incorporation of functional materials such as antimicrobials and antioxidants can make the coating materials more valuable. The remarkable antimicrobial functions obtained in certain nanocomposites can expand the application of nanocomposite materials in various industrial applications such as food packaging and biomedical fields (Duncan, 2011). The nanocomposites with the antibacterial property are active food packaging materials which enable to eliminate the food-borne pathogens and reduce the risks of various food poisoning outbreaks and illness (Llorens, Lloret, Picouet, Trbojevich, & Fernandez, 2012). Antimicrobial composite materials are usually prepared by blending or mixing antimicrobial compounds with polymeric base materials. A variety of organic or inorganic materials with antimicrobial functions have been used to develop antimicrobial food packaging materials (Abreu et al., 2015; Arfat, Ahmed, & Jacob, 2017; Jin, Liu, Zhang, & Hicks, 2009; Ramos, Jimenez, Peltzer, & Garrigos, 2014; Shankar & Rhim, 2017; Shankar, Wang, & Rhim, 2017). Recently, utilization of natural antimicrobial materials such as essential oils and plant extracts has been increased due to their antimicrobial activity and safety (Ghasemlou et al., 2013; Tan, Lim, Tay, Lee, & Thian, 2015). As one of the natural antimicrobial substances, grapefruit seed extract (GSE) has been widely used in various industries such as food

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packaging, biomedical, and cosmetics industries (Reagor, Gusman, McCoy, Carino, & Heggers, 2004; Song, Shin, & Song, 2012). The GSE is extracted from the seed and pulp of grapefruit, which 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 chitosan (Tan et al., 2015), carrageenan (Kanmani & Rhim, 2014), and gelatin (Song et al., 2012). However, there is no report in the literature on the use of GSE in biopolymers for preparing coating material of paper used for food packaging.

Therefore, the main objective of the present study was to prepare effective antimicrobial food packaging paper coated with a ternary blend of alginate, carboxymethyl cellulose, and carrageenan with GSE. The morphology, basis weight, water and oil absorption capacity, water contact angle, water vapor permeability, and mechanical properties of the papers were tested. Also, the antibacterial property of the blended carbohydrate polymers coating solution was tested against two representative food-borne pathogenic bacteria, *E. coli* and *L. monocytogenes*.

## 2. Materials and methods

### 2.1. Materials

Food grade carrageenan (HGE-A, pure κ-carrageenan, viscosity: 60 cps, 1.5% aq. solution at 75 °C) was obtained from MSC Co. Ltd. (Sungnam city, Kyunggi-do, Korea). Sodium carboxymethyl cellulose (CMC) was purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan). Sodium-alginate (MW: 75–150 kDa; guluronate/mannuronate ratio ≥1.5) was purchased from Kanto Chemical Co. (Tokyo, Japan). Glycerol was procured from Daejung Chemicals & Metals Co., Ltd. (Siheung, Gyeonggi-do, Korea). Grapefruit seed extract (GSE, DF-100, 50% glycerol, 0.48% naringin, and other compounds) 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, Gyeonggi-do, Korea). Wrapping food paper (basis weight: 40 g/m$^2$; thickness: 50 μm) for biopolymer coating and PE-coated paper (basis weight: 45 g/m$^2$; thickness: 55 μm) was obtained from Kukil Paper MFG Co., Ltd. (Seoul, Korea). Frozen minced fish made of hair-tail was donated from OurHome Co., Ltd. (Yongin, Gyeonggi-do, Korea). Food-borne pathogenic bacteria, *Escherichia coli* O157: H7 ATCC 43895 and *Listeria monocytogenes* ATCC 15313, were obtained from Korean Collection for Type Cultures (KCTC, Seoul, Korea). The bacterial strains were cultured in tryptic soy broth (TSA) and brain heart infusion broth (BHI) agar media and subsequently stored at 4 °C for further analysis.

### 2.2. Preparation of coating solution and coating papers

For the preparation of coating solutions, 3.6 g of glycerol as a plasticizer was dissolved in 200 mL of distilled water and stirred for 20 min using a magnetic stirrer, followed by the addition of 0.6 g of grape seed extract (GSE) and continued stirring for 10 min. Then, 3 g each of alginate, carrageenan, and CMC were dissolved in the above solution with heating and stirring at 90 °C for 60 min. The blended biopolymer coating solution was cooled to 65–70 °C before use. The biopolymer coating solution was coated on the coarse surface of the paper. For this, the paper was mounted on the glass plate covered with pearlized PS film, and a spoonful of the biopolymer coating solution was loaded on the paper and spread over the paper using a wire bar coater (SA-203 Wire Bar Coaters, Donghak Machine Co., Ltd., Korea). Three different thickness wire bound coating bars (No. 20, 40, and 60) were used to prepare different thickness of biopolymer-coated papers (Rhim, Lee, & Hong, 2006). Then, the coated papers were allowed to dry at room temperature (23 ± 2 °C) for 24 h. Also, uncoated and PE-coated papers were used for comparison. All the test paper samples were conditioned at 25 °C and 50% RH for 48 h in a constant temperature and humidity chamber (model FX 1077, Jeio Tech Co. Ltd., Ansan, Korea) to normalize the moisture content of the paper before the further test.

### 2.3. Morphology of coated paper

Morphology of both the surface and cross-section of the paper samples were observed using a field emission scanning electron microscope (FE-SEM) (FE-SEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan) at an accelerating voltage of 3 kV. For the observation of cross-section, a small piece of paper samples was freeze-fractured in liquid nitrogen to obtain an affected cross-section. The samples were sputtered with platinum to make the sample conductive.

### 2.4. Basis weight and thickness

Basis weight (BW) of uncoated, biopolymer-coated, and PE-coated papers was determined by measuring the weight of the specific size of paper. For this, the papers were cut into the pieces of 5 cm × 5 cm, and the weight of the sample was measured. The weight of 5 samples was measured for the individually prepared paper, and the average value was presented in g/m$^2$ of the paper.

The thickness of papers was measured using a digital hand-held digimatic micrometer (Mitutoyo, Model QuantuMike IP 65, Mitutoyo Corp., Kawasaki, Japan) with a precision of 0.001 mm. Eight random locations around each paper sample were used for the average thickness determination. Coating thickness and coating weight of biopolymer-coated papers were determined by subtracting thickness and basis weight of base paper from those of coated papers, respectively.

### 2.5. Mechanical properties

Mechanical properties of the uncoated, biopolymer-coated, and PE-coated papers were measured using an Instron Universal Testing Machine (Model 5565, Instron Engineering Corporation, Canton, MA, USA) according to the ASTM Method D 882-88. Samples were cut into rectangular strips (2.54 cm × 15 cm) using a precision double blade cutter (Model LB.02/A, Metrotech, S. A., San Sebastian, Spain). Mechanical properties such as tensile strength (TS), elongation at break (EB), and elastic modulus (EM) were measured with an initial grip separation of 50 mm and a crosshead speed of 50 mm/min. The TS (in MP) was calculated by dividing the maximum load by the initial cross-sectional area of the paper. The EB (in%) was calculated by dividing the extension at rupture of the paper by the initial length of the sample (50 mm) and multiplied by 100. The EM (in GPa) was determined from the slope of the linear portion of the stress-strain curve, which corresponds to the stress divided by the strain of the paper. Fifteen replicates were tested for each paper sample, and the average values were used.

### 2.6. Thermal stability

Thermal stability of the coated papers was determined using a thermogravimetric analyzer (TGA; Hi-Res TGA 2950, TA Instrument, New Castle, DE, USA). Each paper sample (about 5 mg) was taken in a standard aluminum cup and scanned at a heating rate of 10 °C/min with temperature ranged from 30 to 600 °C under a nitrogen flow of 50 cm$^3$/min. Empty cup was taken as a reference. The derivative of TGA (DTG) was obtained by differentials of TGA values and calculated using a central finite difference method as follows (Sun, Lui, Ji, Hou, & Dong, 2017):

$$DTG = (W_{t+\Delta t} - W_{t-\Delta t})/2\Delta t$$