



Antimicrobial agent-free hybrid cationic starch/sodium alginate polyelectrolyte films for food packaging materials



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ABSTRACT

This study aimed to develop polyelectrolyte structured antimicrobial food packaging materials that do not contain any antimicrobial agents. Cationic starch was synthesized and characterized by FT-IR spectroscopy and ¹H NMR spectroscopy. Its nitrogen content was determined by Kjeldahl method. Polyelectrolyte structured antimicrobial food packaging materials were prepared using starch, cationic starch and sodium alginate. Antimicrobial activity of materials was defined by inhibition zone method (disc diffusion method). Thermal stability of samples was evaluated by TGA and DSC. Hydrophobicity of samples was determined by contact angle measurements. Surface morphology of samples was investigated by SEM. Moreover, gel contents of samples were determined. The obtained results prove that produced food packaging materials have good thermal, antimicrobial and surface properties, and they can be used as food packaging material in many industries.

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1. Introduction

There are various forms of antimicrobial packages. First, sachet containing antimicrobial agents are added into packages. This is a good commercial practice of antimicrobial packaging. Second, antimicrobial agents are incorporated directly into polymers. In this process, bioactive agents such as silver and zeolite are preferred as antimicrobial agents (Sung et al., 2013). Third, antimicrobials are coated or adsorbed onto polymer surfaces. For example, surface of the polymer can be coated with quaternary ammonium salts or sorbic acid (Xue, Xiao, & Zhang, 2015; Jipa, Guzun, & Stroescu, 2012). Fourth, antimicrobials are immobilized to polymers by ion or covalent linkages. This type of immobilization requires the presence of functional groups on the antimicrobial. For example, peptides, enzymes, polyamines and organic acids types antimicrobial agents contain functional groups. Lastly, some polymers such as chitosan and poly-L-lysine that are inherently (naturally) possess antimicrobial properties and therefore, can be used for food packaging (Fu, Ji, Fan, & Shen, 2006).

Polyelectrolytes are polymers like polycations and polyanions, whose repeating units bear an electrolyte group. These groups dissociate in aqueous solutions, making the polymers

charged. Some studies show that polyelectrolytes exhibit antimicrobial properties. For example, Gottenbos, van der Mei, Klatter, Nieuwenhuis, Busscher (2002) prepared positively charged product with silanization of silicone rubber. The obtained products showed antimicrobial effects towards Gram-positive and Gram-negative bacteria (Gottenbos et al., 2002). In another study, Cakmak et al. (2004) prepared cationic polyelectrolytes containing quaternary nitrogen atoms within the main chain via condensation polymerization of epichlorohydrin with benzyl amine. Authors reported that the cationic polyelectrolytes showed antifungal, antibacterial and antiyeast properties (Cakmak, Ulukanli, Tuzcu, Karabuga, & Genctav, 2004).

Alginic acid, also called alginate or algin, is an anionic natural polysaccharide. It occurs naturally as the major structural polysaccharide of brown marine algae (*Phaeophyceae*) and as extracellular mucilage secreted by certain species of bacteria. Therefore, it is renewable, biodegradable, non-toxic, water soluble, abundant and biocompatible (Wang, & Wang, 2010). It is a linear copolymer, constituted of repeating 1,4-β-D-mannuronopyranosyl and 1,4-α-L-guluronopyranosyl units known as mannuronic and guluronic acid. It tends to be negatively charged and has a wide range of pH values (Harnsilawat, Pongsawatmanit, & McClements, 2006). It is usually present as sodium salt called sodium alginate. Sodium alginates are commonly used as stabilizers, thickeners and gelling agents in several foods, such as soups, deserts, sauces and beverages (Yang, Xie, & He, 2011).

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Starch is a semicrystalline polymer. It is a tasteless and odorless powder, mostly obtained from potato and cereals such as wheat, rice and corn. It is constituted of repeating 1,4- α -D glucopyranosyl units known as amylose and amylopectin. The amounts of amylose and amylopectin units depend on the source that starch is obtained. The properties of starch based materials are closely related to the ratio of these two units. Corn starch contains almost 70% amylopectin and 30% amylose (Liu, Yu, Xie, & Chen, 2006). Starch based materials are of great interest in food packaging sector because of the advantages such as biodegradability, wide availability and the low cost. On the other hand, unfortunately, they have some drawbacks such as poorer mechanical properties and poorer moisture barrier (strong hydrophilic behaviour) than non-biodegradable polymeric materials used in food packaging industry (Avella et al., 2005). Several starch based materials with antimicrobial properties have been developed (Yoksan, & Chirachanchai, 2010; Corrales, Han, & Tauscher, 2009; Váscónez, Flores, Campos, Alvarado, & Gerschenson, 2009). However, antimicrobial agents are added into these materials. These antimicrobial agents gradually migrate from packaging material to food, which is an unwelcomed situation.

In this study, we aimed to develop polyelectrolyte structured antimicrobial food packaging materials that do not contain any antimicrobial agent. Cationic starch was synthesized to obtain cationic groups. Sodium alginate, which is a natural anionic polysaccharide, was used for anionic groups. Polyelectrolyte structured antimicrobial food packaging materials were prepared using starch, cationic starch and sodium alginate. The antimicrobial activity of materials was defined by inhibition zone method (disc diffusion method). Thermal stability, hydrophobicity and gel content of the samples were determined. Surface morphology of the samples was investigated by SEM.

2. Experimental

2.1. Materials

Corn starch (unmodified regular corn starch containing approximately 73% amylopectin and 27% amylose), glycidyltrimethylammonium chloride (GTAC), sodium alginate, sodium hydroxide (NaOH) were purchased from Sigma Aldrich. The viscosity of sodium alginate is 5.0–40.0 cps. It is extracted from the alga *Macrocystis pyrifera* which has a mannuronate/guluronate ratio of 1.6, obtained from FT-IR spectroscopic analysis (Gómez-Ordóñez & Rupérez, 2011). Ethanol was purchased from Merck. All reagents were used without further purification. *S. aureus* was obtained from microbiology laboratory of Ankara University Dairy Technology Department, and *E. coli* from Ankara University Food Engineering Department. Bacteria stock cultures were transported to the laboratory in cold storage conditions.

2.2. Synthesis of cationic starch

Cationic starch was prepared by attaching positively charged groups onto the H of hydroxyl groups of the starch backbone with NaOH as base catalyst. Firstly, 5 g corn starch, 2.5 g GTAC as cationization reagent, 1.5 mL 1 mol/L NaOH solution and 1.625 mL distilled water were placed in a flask. Then, all the reactants in the flask were well stirred and kept for 5 h at 60 °C in a water bath. The reaction was completed by adding 100 mL of ethanol to the flask and the cationic starch was precipitated. The obtained cationic starch was filtered under vacuum and washed with ethanol twice to remove the unreacted GTAC and NaOH. Product was dried at 50 °C for 6 h in an oven. The obtained white cationic starch was milled to

fine powder. The reaction of preparing cationic starch is shown in Scheme 1a.

The nitrogen content of cationic starch was determined by Kjeldahl method. Degree of substitution of cationic starch was calculated according to the following equation.

$$DS = \frac{162 \times N}{1400 - (151.63 \times N)}$$

where N is nitrogen content determined by Kjeldahl method (%), 162 is the molecular weight of anhydroglucoside unit and 151.63 of GTAC.

The degree of substitution of prepared cationic starch was calculated to be 0.35.

2.3. Preparation of polyelectrolyte films

Polyelectrolyte structured films were prepared using starch, cationic starch and sodium alginate. Cationic starch was used for cationic groups while sodium alginate was used for anionic groups in polyelectrolyte films. Starch was also used to maintain structural stability in polyelectrolyte films. In addition, glycerol as plasticizer and distilled water as solvent were used. Starch and cationic starch were taken in a beaker and dissolved in 70 mL distilled water. Sodium alginate was dissolved in 30 mL distilled water and added dropwise to the starch mixture. Glycerol was added to the starch – sodium alginate mixture and the reaction mixture was stirred at 100 °C for 10 min. The polyelectrolyte homogenous liquid mixture was poured into a petri dish and dried at 50 °C for 4 days in an oven. Polyelectrolyte films were obtained by removing from the petri dishes. The gel contents of the polyelectrolyte films were found to be between 88% and 95%. The reaction of preparing the polyelectrolyte film is shown in Scheme 1b. The recipes and gel contents of the polyelectrolyte films are shown in Table 1.

2.4. Measurements and characterization

Gel contents of the polyelectrolyte films were determined by Soxhlet extraction for 6 h using acetone. Insoluble gel fraction was dried at 40 °C and the gel content was calculated.

Chemical structures of synthesized cationic starch and polyelectrolyte films were examined by Perkin Elmer ATR FT-IR spectrophotometer used in the range of 400–4000 cm^{-1} .

^1H NMR spectrum of cationic starch was measured on Bruker Advance 500 MHz spectrophotometer. Cationic starch was dissolved in dimethyl sulfoxide before analysis.

The antimicrobial activity of produced food packaging materials was defined by inhibition zone method (disc diffusion method). Each bacteria culture was activated by inoculation in Tryptic Soy Broth (TSB), at 37 °C for 24 h. The inoculum (0.1 mL) was spreaded to the surface of Mueller-Hinton (MH) agar petri dishes by spread plate technique, then 6 mm diameter films cut from prepared polyelectrolyte films were placed onto petri dishes. Control samples were prepared under the same conditions. Disc film containing petri dishes and control samples were incubated at 37 °C for 24 h. After incubation, petri dishes were checked for bacterial growth, inhibition zones around the disc films were evaluated qualitatively and quantitatively. Quantitative evaluation was performed according to the inhibition zone diameter. The zones around the disc films were evaluated as an indicator of inhibition of bacterial growth. The polyelectrolyte film that produced a large inhibition zone was considered to show a high antimicrobial activity.

Thermogravimetric analysis spectra were obtained by Perkin Elmer Pyris-1 model TGA instrument in order to determine thermal behaviour of polyelectrolyte films. The measurement was fulfilled under 2 bar N_2 atmosphere and 30–750 °C running range with 10 °C/min heating rate.

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