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Short Communication

Mechanical properties of gellan and gelatin composite films

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Abstract

The effect of gellan to gelatin ratio and NaCl concentration on the mechanical properties of gellan/gelatin composite films were studied using a Texture Analyzer. Tensile strength (TS) of the composite films linearly decreased as the gelatin ratio increased, whereas the tensile elongation (TE) increased with increasing gelatin proportion. TS and TE were also significantly affected by the NaCl concentration. TS decreased with increasing NaCl concentration for gellan film, whereas TS showed the maximum values at NaCl concentration of 50 mM for the other composite films. Water solubility and swelling ratio decreased with increasing gelatin proportion up to 40%. These results suggest that modifying the ratio of gellan and gelatin improves the mechanical properties of the composite film. These films appears to have potential as packing and/or coating materials, replacing synthetic polymer films.
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Keywords: Gellan; Gelatin; Composite film; Tensile strength; Water solubility

1. Introduction

Biodegradable films are generally made from biopolymers such as polysaccharides, proteins and lipids. Since biodegradable films have many potential benefits, such as food protection and preservation during storage, enhancement of food appearance and alleviation of environmental pollution. They have been widely considered as prospective replacers of synthetic polymers. Hydrophilic polymers such as starch and gelatin have been investigated for film and other material properties (e.g. Lourdin, Della Valle, & Colonna, 1995; Stepto & Tomka, 1987). The main disadvantages of biopolymer films are their poor mechanical properties. Thus, there have been many studies to improve the mechanical properties of polysaccharide-based films by incorporation of hydrophobic materials and plasticizers (Gontard, Guilbert, & Cuq, 1993; Hagenmaier & Shaw, 1990; Koelsch & Labuza, 1992; Park, Weller, Vergano, & Testin, 1993; Yang & Paulson, 2000). It has been reported that incorporation of gellan into gelatin gels resulted in a synergistic increase of gel network strength (Shim, 1985) and an improvement of gel firmness (Wolf, Beach, La Velle, & Clark, 1989). Thus, the composite films made from blending two different biopolymers can be expected to have better mechanical properties. Gellan is an extracellular polysaccharide produced by fermentation of *Pseudomonas elodea* (lately referred to as *Sphingomonas paucimobilis*), and consists of a tetrasaccharide repeat units of β-D-glucose, β-D-glucuronic acid and α-L-rhamnose in molar ratios of 2:1:1 (Sanderson, 1990). After heating and then cooling to the gelling temperature, gellan forms three-dimensional gel networks with monovalent or divalent cations (Chandrasekaran & Radha, 1995; Sanderson & Clark, 1983). Gelatin is a derived protein produced from the protein 'collagen' by partially hydrolysis and also forms a gel on cooling. The strength and texture of gellan gels are dependent on the ionic strength and pH and concentration, while those of gelatin gels depend primarily on the concentration of gelatin (Hsu & Jamieson, 1993). Gellan forms hard and brittle gels, while gelatin forms a soft, flexible, and elastic gel (Nussinovitch, 1997). In addition, these two materials showed synergism at particular ratios and salt concentrations (Lau, Tang, & Paulson, 2000). Thus, new composite film could be produced from mixture of gellan/gelatin. Studies on the mechanical properties of composite films made from polysaccharides and protein have been limited. The objective of this study is to

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determine the effect of gellan/gelatin ratio and NaCl concentration on the mechanical properties of these films.

2. Experimental

2.1. Materials

Gellan gum was purchased from Wack Pure Chemical (Osaka, Japan) and gelatin (type A: from Porcine Skin Approx. 300 Bloom) was purchased from Sigma Chemical (St. Louis, USA).

2.2. Preparation of composite films

Composite films were prepared by adapting the method described by Yang and Paulson (2000). First, mixed solutions of 2% total solid (TS) with different ratios of gellan to gelatin (100:0 (I), 80:20 (II), 60:40 (III), 40:60 (IV), and 20:80 (V)) were prepared by dissolving 3 g of gellan/gelatin mixture in 150 ml distilled water, followed by heating to 90–95 °C. Three different levels of sodium chloride (0, 50, 150 mM) and 1.5 g of glycerol were added to the solution during heating. After complete dissolution, the hot solution was poured onto the Teflon film coated glass plates (24 × 24 cm^2), and spread evenly. The plates were then placed in a dry oven at 40 °C for 24 h. The dried films were peeled out from the glass plates and then cut into 2 × 2 cm strips for water solubility tests and 10 × 2.5 cm strips for tensile strength (TS) and elongation tests. All samples were conditioned in a constant humidity controlled chamber (50% RH) at 25 °C for 2 days prior to testing.

2.3. Tensile strength and elongation tests

TS and tensile elongation (TE) at break of the films were determined using a Texture Analyzer (Instron 4465, USA) according to the ASTM standard method (ASTM D882-88, 1989). In these tests, pre-conditioned films cut into 2.54 cm (W) × 10 cm (L) strips and mounted between the grips of the machine with initial grip gap of 50 mm. Sample was uniaxially pulled until break at a cross-head speed of 500 mm/min. The results of tensile and elongation tests were expressed by MPa and percentage (%), respectively. Each test trial consisted of nine replicate measurements.

2.4. Water solubility (WS) tests

Water solubility of sample was determined as described by Gontard, Guilbert, and Cuq (1992). Three film samples, 2 × 2 cm strips, were dried at 105 °C for 24 h in a dry oven and then the initial solids content was measured. Three film samples were put in a 50 ml beaker with 30 ml distilled water and sealed by parafilm, and then placed in a thermostat at 25 °C for 24 h. After drying for 24 h, films were dried for 24 h in a dry oven and then the solid contents were measured. Water solubility (%) of film was defined as ratio of the water soluble solids to the initial solids content.

2.5. Swelling ratio (SR) tests

The SR of a sample was determined according to the method on Rhim, Park, Jung, and Park (1997). A sample strip (2 × 2 cm) was plused in distilled water at 25 °C for 6 h and the surface water removed by gentle contact with a filter paper (Whatman No 1) for 1 min. The SR was determined as the weight gain of the swollen sample divided by the initial dry solid content. Each test consisted of three replicate measurements and expressed as is the mean value.

2.6. Statistical analysis

A one-way ANOVA was used to determine the differences between samples using Statistical Package for Social Science (SPSS). When there were any significant differences between samples, Duncan's multiple range tests were used to determine the significance of the average.

3. Results and discussion

3.1. Mechanical properties

TS is the most important mechanical property for many applications (Park, Rhim, Jung, & Kang, 1995). Fig. 1 shows the effect of gellan/gelatin ratio on the TS and the TE. The TS of the composite films decreased linearly as the gelatin ratio increased, whereas the TE increased with increasing gelatin ratio. For example, TS of the gellan film (I) decreased by 21% and the elongation increased by 38% as gellan was replaced by 80% of gelatin (film V). Here, gelatin seems to act as a plasticizer, which enhance film flexibility and decrease brittleness. The relatively low molecular weight of gelatin could allow it to be more readily inserted into gellan networks, resulting in a more flexible and less hard composite films. In the gel state,

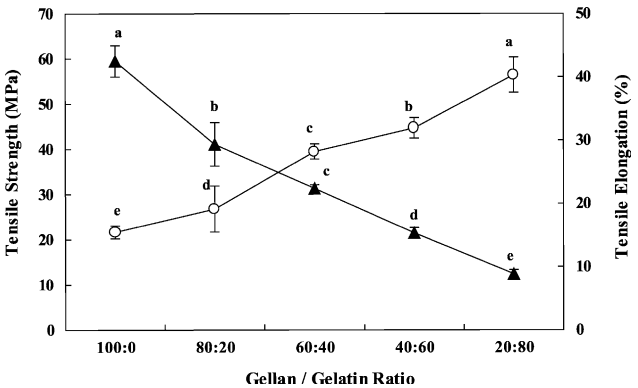

Fig. 1. Tensile strength (▲) and tensile elongation (○) of gellan/gelatin composite films in the absence of NaCl as a function of the gellan/gelatin ratio.

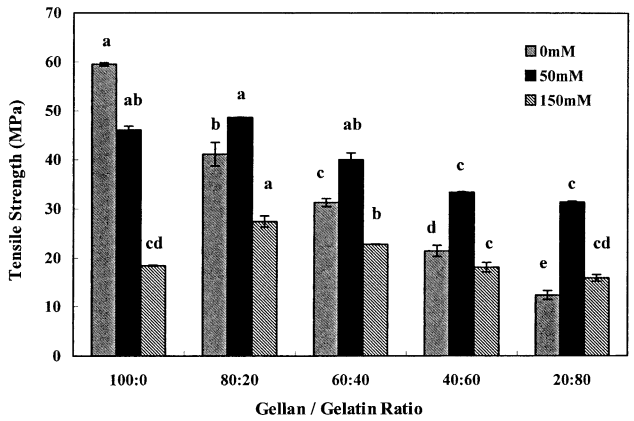

Fig. 2. Effect of NaCl concentration on the tensile strength of gellan/gelatin composite films.

gellan and gelatin also form hard/brittle gel and soft/flexible gel, respectively (Nussinovitch, 1997). Similar to the gel state, replacing gellan by gelatin forms soft and flexible films. Thus, it was apparent that the strength and flexibility of the composite films could be modified by changing the ratio of gellan to gelatin. The TS of gellan/gelatin composite films ranged from 12.4 to 59 MPa which compared with values, such as 56 MPa for methlycellulose film (Park et al., 1993) and 13.9 MPa for whey protein film (McHuge & Krochta, 1994). The effect of gellan to gelatin ratio and NaCl concentration on the TS and TE are shown in Figs. 2 and 3. TS and TE were significantly ($P < 0.05$) affected by both the NaCl concentration and gellan to gelatin ratio. TS decreased with increasing NaCl concentration for gellan film (I), whereas TS showed the maximum values at NaCl concentration of 50 mM for others (II, III, IV, and V). Incorporation of moderate amounts of sodium ion into gellan/gelatin composite film probably enhanced the interaction between gellan and gelatin, resulting in high values of TS. TE linearly increased with increasing gelatin proportion and significantly ($P < 0.05$) decreased with the adding of NaCl for all composite films. The overall mechanical properties of gellan/gelatin composite films depend on the ratio of gellan to gelatin, NaCl concentration.

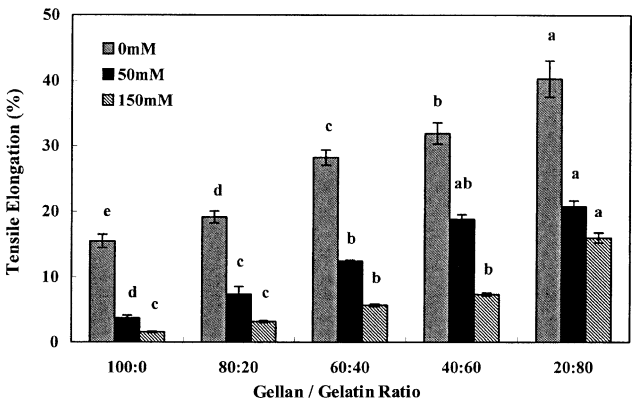

Fig. 3. Effect of NaCl concentration on tensile elongation (%) of gellan/gelatin composite films.

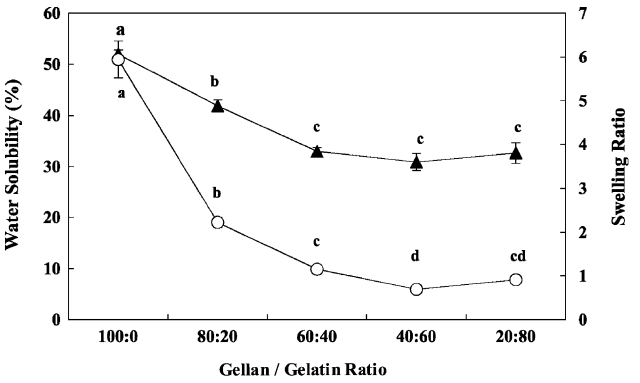

Fig. 4. Water solubility (▲) and swelling ratio (○) of gellan/gelatin composite films.

3.2. Water solubility and swelling ratio

Water solubility and SR of gellan/gelatin composite films are shown in Fig. 4. The water solubility defines the tolerance to water and is determined by their chemical structure unlike the water permeability (Rhim et al., 1997). Water solubility ranged from 30 to 52% and decreased with increasing gelatin ratio up to 40% (film III). These solubility values were relatively lower than other biopolymer films, such as cellulose (55–84%) or carrageenan (41%). Edible films can be used as coating materials to inhibit exudation from frozen foods. Their stability will be poor if they have a high water solubility, but on the other hand, they have the advantage that food being coated with edible films temporarily can be easily eaten after washing. SR defines the amount of water absorbed by films and is an important property of carbohydrate and protein films. Biopolymer films made by carbohydrates or proteins initially swell when they absorb water and then result in the changes of their structure. Thus, examination of SR is necessary for the efficient application of biopolymer films. The SR of composite films is significantly ($P < 0.05$) decreased as gelatin proportion is increased to 40% (film III) (Fig. 4). Gellan/gelatin composite films had lower values of SR than carrageenan films, indicating a higher tolerance for water.

4. Conclusions

Mechanical properties of gellan/gelatin composite films significantly depend on the ratio of gellan to gelatin and NaCl concentration. As the proportion of gelatin increases, TS decreases and TE increases. Changing the ratio of two polymers can modify the strength and extensibility of the composite films. Salt concentration also affects the mechanical properties of films, which is dependent upon the ratio of gellan/gelatin ratio. Water solubility and SRs decrease with increasing gelatin proportion. From these results, it could be suggested that gellan and gelatin films of different ratios appears to have potential as packaging and coating materials. Because of their biodegradability they

have advantages over synthetic polymer films for certain applications.

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