

Film and pharmaceutical hard capsule formation properties of mungbean, waterchestnut, and sweet potato starches

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Abstract

Biodegradable films were developed using mungbean, waterchestnut and sweet potato starches as base raw materials. The physical and mechanical properties of the films were compared with gelatin and HPMC films. The same starches were used to develop hard capsules for utilization in the pharmaceutical industry as a substitute for gelatin or animal based products. Starches with high amylose content had excellent film and hard capsule forming abilities and properties compared to the starches with low amylose content. The starch films also had excellent oxygen barrier properties (0.048 ± 0.008 to 0.070 ± 0.009 fl m/m² s Pa), but water barrier properties (1.1 ± 0.5 to 1.8 ± 0.4 ng m/m² s Pa) were higher than LDPE (0.00064 ng m/m² s Pa) synthetic polymer films. The tensile strength values of starch films (12.1 ± 0.7 to 19.0 ± 2.2 MPa) were not significantly different from gelatin (19.5 ± 1.6 MPa) and HPMC (19.9 ± 1.2 MPa) films. In the case of elongation properties, starch films had lower values (42.2 ± 7.7 to $79.4 \pm 9.2\%$) than gelatin film ($122.0 \pm 14.6\%$), but higher than HPMC film ($13.8 \pm 4.2\%$). Molecular (SEC-MALLS) and physical (viscosity) characterization of vegetable starches, indicated that the starches with high amylose content produced better biopolymer films and capsules compared to the starches with low amylose and high amylopectin content. Biodegradable films and hard capsules for pharmaceutical applications could be developed from vegetable starches with similar physical and mechanical properties as synthetic and gelatin products.

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1. Introduction

Synthetic polymeric food packaging materials, developed in the past 50–60 years, are durable and inert or resistant to microbial degradation (Mali, Grossmann, Garcia, Martino, & Zaritzky, 2002). These synthetic polymeric materials have wide applications in food packaging due to various advantages such as high strength, elongation, gas barrier properties, low cost, lightness and water resistance (Guilbert, 1986). Packaging materials account for approximately 30% by weight of municipal solid waste and two thirds of the volume are trash cans, due to their

bulk. Among the 30% packaging waste, 13% is due to plastic materials which are convenient, safe, strong and economical; but do not biodegrade (Han, 2001). Incineration is a common method of disposing of polyolefins, but this results in high emissions of carbon dioxide (Han, 2001). Since the 1970s, polar biopolymers such as polysaccharides and proteins have been studied as potential alternatives for synthetic polymers in the film and plastic industries, due to environmental concerns (Garcia, Martino, & Zaritzky, 2000). Several studies have been conducted investigating the properties of protein, polysaccharide, and lipid-based films; and these raw materials were successfully formed into films or coatings (Arvanitoyannis, Nakayama, & Aiba, 1998; Chen, 1995; Gennadios, Weller, & Testin, 1993; Gontard, Guilbert, & Cuq, 1993; Gontard, Thibault, Cuq, & Guilbert, 1996; Kim, Ko, & Park, 2002; Lawton, 1996; Lourdin, Valle, & Colonna, 1995; McHugh & Krochta,

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1994; McHugh, Aujard, & Krochta, 1994; Park, Weller, Vergano, & Testin, 1993; Park & Chinnan, 1995). These edible/biodegradable films were reported to have been successfully utilized in a number of commercial applications: (a) gelatin for capsules, supplements, drugs, and flavour encapsulation; (b) corn zein for coatings, confections, supplements, and drug tablets; (c) collagen for wraps and casings for meat products; (d) starch coatings for drug tablets, confections and dried Fruits; (e) HPMC, MC, and HPC coatings for supplements and drug tablets; (f) fatty acid sucrose esters for coatings for fresh produce; (g) wax, oil, and shellac coatings for fresh produce, confections, supplements, and drug tablets (Krochta, 2002).

Starch and starch derivative films have been widely studied due to their great molding and film forming properties, high oxygen barrier and good mechanical strength (Forssell, Lahtinen, Lahelin, & Myllärinen, 2002; Gilleland, Turner, Patton, & Harrison, 2001; Lawton, 1996; Lee & Rhim, 2000; Mali et al., 2002). Even though there have been numerous studies conducted on the properties of starch based films, few studies have related starches from different sources with the resulting film forming characteristics, mechanical and physical properties. In a previous study, films were developed using starches from different plant sources as the base raw materials (rice, sweet rice, potato, sweet potato, mungbean, waterchestnut, amaranth, wheat, and buck wheat starches). The physical and mechanical properties of the starch based films were evaluated (Lawton, 1996; Lee and Rhim, 2000; Forssell et al., 2002; Mali et al., 2002; Muetgeert, Hiemstra, and Hiemstra, 1955). Among the starch films, potato, sweet potato, mungbean and waterchestnut were selected due to their superior film-forming properties when compared with synthetic films. The physical and mechanical properties of the starch films were compared with gelatin and hydroxy propylated methyl cellulose (HPMC) film. The gelatin and hydroxyl propylated methyl cellulose (HPMC) were selected as the control because of the popularity of these films in food and pharmaceutical industries as a result of their good film forming properties, oxygen/water barrier properties, mechanical strength, raw materials availability, and biodegradability. (Jongjareonrak, Benjakul, Visessanguan, Prodpran, & Tanaka, 2006; Li, Kennedy, Jiang, and Xie, 2006; Sakata, Shiraishi, & Otsuka, 2006; Villalobos, Chanona, Hernández, Gutiérrez, & Chiralt, 2005; Yakimets et al., 2005).

Reports indicated that protein-based films had superior mechanical properties than polysaccharide-based films (Jongjareonrak et al., 2006). Polysaccharide-based films were reported to have better oxygen barrier properties than protein-based films. Forssell et al. (2002) reported that starch based polymer films, plasticized with water only had good oxygen barrier properties under ambient humidity as EVOH film. Reports indicated that consumers who are vegetarian and those whose religion prohibits the consumption of animal derived products, may prefer polysac-

charide based biodegradable films and capsules than gelatin based products (Woltjes, Jakob, Roelf, Meima, & Heine, 1999). The occurrence of prion disease (ex. mad cow disease) brought about a concern that consumption of proteinaceous product of animal origin may infect humans (Woltjes et al., 1999). Hard gelatin capsules were developed using selected raw materials by conventional dip-coating process, utilizing water soluble polysaccharides as a base raw material, glycerin as a plasticizer and a gelling agent (Mali et al., 2002).

The objectives of the study were: (1) to develop polysaccharides based biopolymer films and hard capsules with similar physical and mechanical properties as compared to synthetic polymeric films or capsules; (2) to develop hard capsules as a substitute for gelatin or animal protein based products for pharmaceutical industry; (3) to evaluate the physical and mechanical properties of biodegradable films and hard capsules.

2. Materials and methods

2.1. Raw materials

The following raw materials were used to develop films and hard capsules: Hwangso sweet potato starch (Sung Jin Foods, Guang Ju, Kyung Gi, Korea); seoryong sweet potato starch (Biocoats. Co., Ltd, Seoul, Korea); waterchestnut starch (Pan Tang Brand, Guangzhou, China); mungbean starch (Rhee Brothers, Columbia, MD, USA); gelatin (Shinyo Pure Chemicals Co., LTD, Osaka, Japan); HPMC (Shin-Etsu Chemical Co., Ltd., Tokyo, Japan); glycerol (Junsei, Tokyo, Japan); K-carageenan and I-carageenan (MSC Co., LTD, Soju, Ungsang, Yangsan, Kyeongnam, Korea).

2.2. Molecular characterization of starches (amylopectin and amylose)

Molecular characterization of starches (amylopectin and amylose) in 90% DMSO (dimethyl sulfoxide) were performed using a medium pressure system with MALLS (multi angle laser scattering) and RI (refractive Index) detectors (You & Lim, 2000). Five different starches (potato, seoryong sweet potato, hwangso sweet potato, waterchestnut, and mungbean starch) were evaluated. Molecular characterization of starches was performed according to the procedure described by You and Lim (2000). The starches (1 g) were dispersed in 90% DMSO (100 mL) in a boiling water bath for 1 h, and stirred for 24 h at room temperature. The sample was precipitated with ethanol and washed with ethanol and acetone ($\times 3$ volumes). The purified starch was vacuum dried. For solution preparation for SEC-MALLS (size exclusion chromatography-multi angle laser scattering), 2 mg of starch was wetted in 50 μ L ethanol and dissolved in a capped glass vial containing 1 M NaOH (1 mL) by vortexing. The starch solution was diluted with 50 mM NaNO₃ (16 mL) and

neutralized with 1 M HCl following the procedure described by You and Lim (2000). The starch solution was autoclaved at 121 °C for 20 min (Hiclave™ HV-110, Hirayama Manufacturing Corporation, Japan). The SEC-MALLS-RI (size exclusion chromatography-multi angle laser scattering refractive index detector) system consisted of a pump (P2000, Spectra System, San Jose, CA), an injector valve with a 1 mL loop (model 7072, Rheodyne, Cotati, CA), the SEC column, a MALLS detector (632.8 nm, DAWN DSP-F, Wyatt Technology, Santa Barbara, CA), and a RI detector (Optilab DSP, Wyatt Technology, 235 Santa Barbara, CA). The mobile phase used for the SEC was 50 nM NaNO₃ solution that had been filtered through 0.1 µm cellulose acetate filters (Whatman, UK) and degassed. TSK G 5,000 SEC column was used and column temperature and flow rate were 60 °C and 0.4 mL/min, respectively. The starch solution was filtered through 5.0 µm membrane filter before injection into the column. A specific refractive index increment value (dn/dc) of 0.146 mL/g was used.

2.3. Viscosity measurement of starches

The viscosity properties of starches were evaluated with Rapid Visco Analyzer (RVA-4, Newport Scientific, Warriewood, Australia). Viscosity profiles of starches were recorded using starch suspensions in water (6% solids). A programmed heating and cooling cycle was used where the samples were heated from 50 to 95 °C at a heating rate of 6.5 °C/min, held at 95 °C for 4 min, cooled to 50 °C at 7.5 °C/min, and then held at 50 °C for 1 min. Parameters recorded were peak viscosity and final viscosity (viscosity at 50 °C). The data obtained were used for regression analysis to establish correlation between amylose (%) of starches vs. peak viscosities of starches, amylose (%) of starches vs. final viscosities of starches, and starch film tensile strength vs. amylose (%) of starches.

2.4. Solution preparation

Starch-based film solutions were prepared by dissolving 11.25 g of glycerol in 450 mL of 50 °C degassed distilled water and stirring for 30 min at 50 ± 5 °C. The concentration of glycerol was 0.25 g glycerol/g biopolymer. About 0.2 g of K-carageenan and 0.2 g of I-carageenan were added and stirred for 30 minutes at 50 ± 5 °C. A 1:1 combination of K- and I-carageenan was reported to increase film strength by 50% as compared to films formed with 100% K-carageenan. Also, 1:1 combination of K- and I-carageenan was reported to increase the film's elasticity, and reduce the viscosity of film forming solution (Gilleland et al., 2001). Forty five grams of biopolymer was added and stirred for 1 hour with gradual temperature increase up to 90 ± 5 °C. The film solution preparation and development procedure is reported in Fig. 1. The gelatin and HPMC solution was prepared using the same method described above.

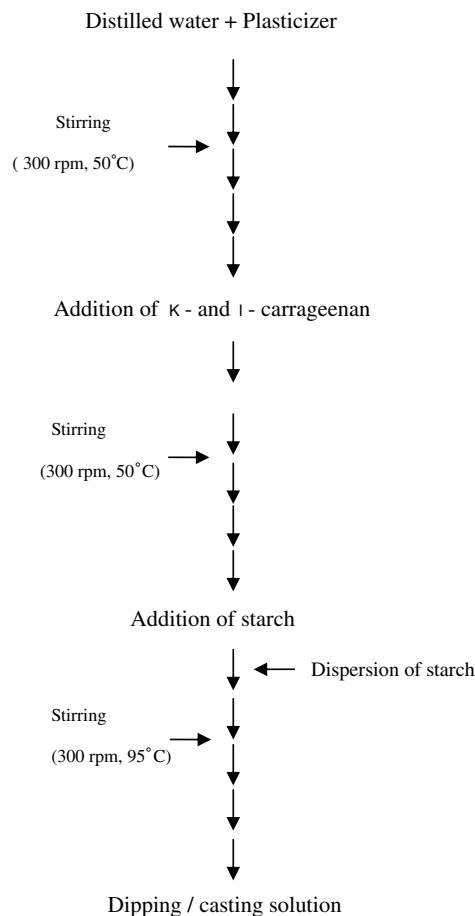


Fig. 1. Flow diagram for preparation of non-animal based capsule dipping/film casting solution.

2.5. Film casting

One hundred millilitres of the film solution was cast onto a BYTAC® (Norton Performance Plastics Corporation, Wayne, NJ, USA) coated 25 cm × 35 cm glass plate which was operated by a film applicator (PI-1210 Filmcoater, Tester Sangyo Co., LTD, Tokyo, Japan). The film applicator used in the experiment, was modified and optimized for casting purposes (Fig. 2). The modification was achieved by attaching specially manufactured solution trough (20 cm × 5 cm) on the film coater. By modification of the casting technique, it became possible to obtain high quality cast films. The gelatin and HPMC films were developed utilizing the traditional pouring method because the viscosity of resulting solution was too low to produce quality films by casting method. Therefore, through trial and error, the following method was finally used to produce gelatin and HPMC films. Three hundred millilitres of the film solution were poured onto a BYTAC® (Norton Performance Plastics Corporation, Wayne, NJ, USA) coated glass plate measuring 30 cm × 30 cm. A common rubber band (1.5 cm × 0.5 cm × 1 cm) was glued around the glass plate in order to trap the poured solution on the plate surface. The films were dried by placing the glass plates in a

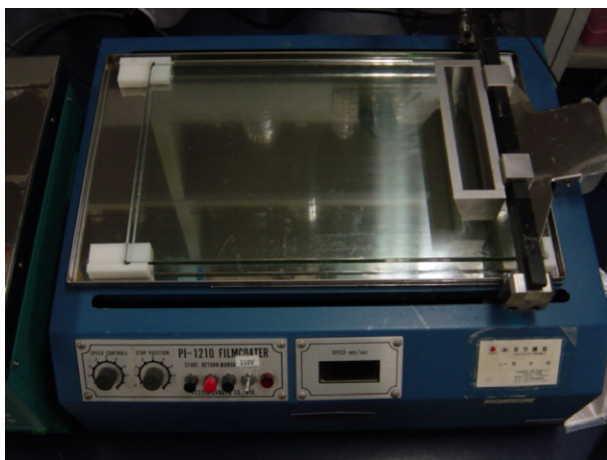


Fig. 2. Film applicator.

constant temperature and humidity chamber (25 °C and 50% RH, Model TR-001-1, Jeio Tech Co., Ltd., Korea) for 24 hours. The dried films were peeled off from the glass plates and cut into test specimens. The cut films were stored in a constant temperature and humidity chamber for 48 h to condition the films before testing.

2.6. Thickness measurement

Film thickness was measured with a digital micrometer (ID-C112, Mitutoyo Corp., Kawasaki, Kanagawa, Japan) at five random positions on each film specimen to an accuracy of $\pm 1 \mu\text{m}$.

2.7. Tensile strength and elongation

The tensile strength (TS) and elongation (E) at break of each film were measured with an Instron Universal Testing Machine (Model 5566, Instron Corp., Canton, MA, USA). Forty specimen samples, 10 cm \times 2.54 cm, were cut from film samples prepared on glass plates (25 cm \times 35 cm). Samples were conditioned for 48 h at 25 °C and 50% relative humidity (RH) in a constant temperature and humidity chamber (Model TR-001-1, Jeio Tech Co., Ltd., Korea) before measuring as reported in 2.5 Film Casting section. Initial grip separation and cross-head speed were set at 5 cm and 500 mm/min, respectively. The TS was calculated by dividing the maximum load by the cross-sectional area of the film, E was calculated and expressed as percentage of change of the original length of a specimen between grips (5 cm) according to the ASTM Standard Method D882-88 (ASTM, 1989). Both TS and E of the test samples were measured as quickly as possible upon removal from the environmental chamber.

2.8. Oxygen permeability

An OX-Tran® 2/60 oxygen transmission tester (Mocon Modern Control, Inc., Minneapolis, MN, USA) was used to measure the oxygen permeability. Film samples were tested according to ASTM Standard Method D 3985-81

(ASTM, 1989b). On one side of the film, 100% oxygen gas was flowing, and on the other side nitrogen gas (98% nitrogen and 2% hydrogen). During testing, samples were exposed to 0% RH at 30 °C. Starch films were cast as thick as possible because thin starch films tended to crack at 0% RH and 30 °C. The thickness of resulting starch films ranged from 199.6 ± 22.6 to $271.4 \pm 581 \mu\text{m}$. Films with thickness within the described range were thick enough for testing.

2.9. Water vapour permeability

Cup method ASTM Standard Method E96-80 (ASTM, 1987), was used to determine water vapour permeability (WVP) in a constant temperature and humidity chamber at 25 °C and 50% RH (Model TR-001-1, Jeio Tech Co., Ltd., Korea). The WVP values were corrected using the WVP Correction Method (McHugh, Avena-Bustillos, & Krochta, 1993). Poly methyl methacrylate cups (Piedmont Plastics, Inc., Greenville, SC, USA) sealed with O-rings were filled with water and film samples (7 cm \times 7 cm) were mounted over the cups. Weight loss was measured as a function of time for 12 h.

2.10. Colour values

Hunter colour L , a , and b values of films were measured by using ColorFlex 45/0 Spectrophotometer with Universal Software version 3.73 (Hunter Associates Laboratory, Inc., Reston, VA, USA). Colour of 0.1 mm thick films (equivalent to conventional pharmaceutical capsule shell thickness) were measured. The machine was calibrated using a white standard plate (Standard No. C6664) and a grey standard plate (Standard No. C6664G). The film specimen was placed on the white standard plate (Standard No. C6664) having colour value of $L = 93.72$, $a = -1.12$ and $b = 0.11$, and mounted at the reflectance port. Colour values were measured at three random positions including the center of the film specimens. Total colour difference (E) was calculated by substituting acquired Hunter L , a and b values into the following equation.

$$\Delta E = [(L \text{ film} - L \text{ standard})^2 + (a \text{ film} - a \text{ standard})^2 + (b \text{ film} - b \text{ standard})^2]^{0.5}$$

2.11. Capsule dipping using starch film solution

The objective of this test was to find out whether starch is a suitable base raw material as a gelatin substitute for pharmaceutical hard capsule production. The conventional dip-coating method was used for hard capsule development. The preheated pins were dipped into the base solution, the starch solution thermally gelled on the surface of the pins. When the pins were withdrawn, a film of gelled starch solution remained on the pins. The coated pins were dried in a controlled temperature and humidity chamber (25 °C and 50% RH, Model TR-001-1, Jeio Tech Co.,

Ltd., Korea) for 24 h. The dried capsule pieces were then stripped, cut into sizes, and fitted together.

2.12. Loss on drying

The loss on drying test of capsules was conducted according to Korea Pharmacopoeia (2002) method. One gram of capsule sample was accurately weighed in a pre-weighing bottle and dried for 30 min under the same controlled temperature and humidity conditions as previously described. The loaded weighing bottle was placed in the chamber, and the capsule was dried at 105 °C for 17 h. After drying, the bottle was cooled in a desiccator containing silica gel as an absorbent. After cooling, the bottle was reweighed accurately and loss on drying percent was calculated according to the following equation.

$$\text{Loss on drying (\%)} = \frac{\text{Undried weight} - \text{dried weight}}{\text{Undried weight}} \times 100$$

2.13. Dissolving test

The objective of the dissolution test was to find out whether capsule samples are soluble in neutral or in slightly acidic solution, within 10 min. The capsules dissolution test was conducted according to Korea Pharmacopoeia (2002) method. The temperature of the test solution was maintained at 37 ± 2 °C. One capsule sample was placed in a 100 mL conical flask with its cap and body part separated. About 50 mL water at 37 ± 2 °C was added, and with constant shaking and temperature maintained at 37 ± 2 °C in 10 min.

2.14. Statistical analysis

The data were analyzed by ANOVA using SAS (version 8.1, SAS Institute Inc., Cary, NC, USA) and differences among mean values were processed by Student–Newman–Keuls multiple-range test. Significance was defined at $P < 0.05$.

3. Results and discussion

3.1. Mechanical properties

Tensile strength (TS) and elongation (E) are used to describe how the mechanical properties of film materials are related to their chemical structure (Ninnemann, 1968). The Mechanical properties of starch, gelatin, and HPMC films are presented in Table 1. Results indicated that TS of mungbean starch film was not significantly different from gelatin and HPMC films (Table 1). Among the starch film samples, mungbean starch film had the highest TS. The TS of gelatin, HPMC and mungbean films were 19.5 ± 1.6, 19.9 ± 1.2, and 19.0 ± 2.2 MPa, respectively, and not significantly different from each other. The TS of hwangso sweet potato, seoryong sweet potato, waterchest-

Table 1
Mechanical properties of starch, gelatin, and HPMC films

Film types	Plasticizer	Concentration (g plasticizer/g starch, gelatin or HPMC)	TS ^A (MPa)	Elongation ^B (%)
NS450	Glycerol	0.25	14.9 ± 1.6 ^b	53.8 ± 10.2 ^d
Hwangso	Glycerol	0.25	12.1 ± 0.7 ^c	79.4 ± 9.2 ^b
Seoryong	Glycerol	0.25	12.5 ± 0.4 ^c	70.1 ± 8.9 ^c
Mungbean	Glycerol	0.25	19.0 ± 2.2 ^a	42.2 ± 7.7 ^e
Water chestnut	Glycerol	0.25	13.1 ± 1.3 ^c	42.8 ± 8.7 ^e
Gelatin	Glycerol	0.25	19.5 ± 1.6 ^a	122.0 ± 14.6 ^a
HPMC	Glycerol	0.25	19.9 ± 1.2 ^a	13.8 ± 4.2 ^f

^A a–c indicate significant differences ($P < 0.05$) within columns TS (MPa).

^B a–f indicate significant differences ($P < 0.05$) within columns elongation (%).

nut and NS450 potato starch films were 12.1 ± 0.7, 12.5 ± 0.4, 13.1 ± 1.3 and 14.9 ± 1.6 MPa, respectively (Table 1). These starch based films were also not significantly different from each other in TS. For elongation properties, gelatin film had the highest value of 122.0 ± 14.6%. The elongation values of starch films were significantly lower than gelatin film. The lowest was mungbean starch film with 42.2 ± 7.7%, and the highest was hwangso starch film with 79.4 ± 9.2%. The elongation of HPMC film (13.8 ± 4.2%) was significantly lower than that of the starch and gelatin films. For comparison with other biopolymer films, Kim et al. (2002) reported that the TS and E of carboxymethylated starch (HCMS) films were 9.7–15.3 MPa and 2.6–7.7%, respectively. Methyl cellulose (MC) film had TS of 55.62–66.33 MPa and E of 11.16–25.60% (Park et al., 1993).

Hydroxypropyl cellulose (HPC) films had TS of 14.79–29.38 MPa and E of 32.76–203.53% (Park et al., 1993). Rhim (2003) reported that the tensile strength and elongation of pullulan, pullulan–carrageenan composite, pullulan–alginate composite, pullulan–agar composite, and pullulan–gellan composite films were within the TS ranges of 29.6–54.1 MPa, and E ranges of 4.7–33.8%.

3.2. Oxygen permeability

Oxygen permeability (OP) of starch films was significantly lower than gelatin and HPMC films (Table 2). Among starch films, seoryong sweet potato starch film had the lowest (0.048 ± 0.008 fl m/m² s Pa) OP, but the OP values were not significantly different between the starch film samples. The results indicated that the OP values of starch films were lower than other edible and biodegradable films. Park and Chinnan (1995) reported that oxygen permeability of corn-zein film was 0.36 ± 0.16 fl m/m² s Pa, and wheat gluten was 0.20 ± 0.09 fl m/m² s Pa. Gennadios et al. (1993) reported oxygen permeability of 0.08 fl m/m² s Pa for wheat gluten film at 25 °C and 0% RH. Park and Chinnan (1995) reported that the oxygen permeabilities of methyl cellulose and hydroxypropyl cellulose films were 2.17 and 3.57 fl m/m² s Pa.

Table 2
Oxygen permeabilities of starch, gelatin, and HPMC films

Film types	Plasticizer	Concentration (g plasticizer/g starch, gelatin or HPMC)	OP ^A (fl m/m ² s Pa)
NS450	Glycerol	0.25	0.053 ± 0.019 ^c
Hwangso	Glycerol	0.25	0.050 ± 0.002 ^c
Seoryong	Glycerol	0.25	0.048 ± 0.008 ^c
Mungbean	Glycerol	0.25	0.070 ± 0.009 ^c
Water chestnut	Glycerol	0.25	0.049 ± 0.021 ^c
Gelatin	Glycerol	0.25	0.117 ± 0.039 ^b
HPMC	Glycerol	0.25	2.098 ± 0.040 ^a

^A a–c indicate significant differences ($P < 0.05$) within columns OP (fl m/m² s Pa).

With regards to synthetic polymers, the oxygen barrier properties of starch films were similar to some synthetic polymer films. The oxygen permeabilities of low density polyethylene, polyethylene, polyvinyl chloride, and polyester were 22.50, 8.30, 0.09–17.99 and 0.13–0.30 fl m/m² s Pa, respectively (Modern Plastic Encyclopedia, 1986).

3.3. Water vapour permeability (WVP)

The water vapour permeabilities of starch samples were lower than gelatin (2.5 ± 0.2 ng m/m² s Pa) and HPMC (2.4 ± 0.5 ng m/m² s Pa) films (Table 3). Among the starch films, NS450 (potato starch) had the lowest (1.1 ± 0.5 ng m/m² s Pa) WVP, and mungbean (1.8 ± 0.4 ng m/m² s Pa) and waterchestnut (1.8 ± 0.1 ng m/m² s Pa) had the highest WVP (Table 3). The WVP of starch films, were however, not significantly different from each other. Park, Bunn, Weller, Vergano, and Testin (1994) reported that the water vapour permeability of wheat gluten film plasticized with glycerol was 1.11 ± 0.04 ng m/m² s Pa. The developed starch films had similar water vapour permeability as that of films made with carboxymethylated starch-based edible films plasticized with glycerol (Kim et al., 2002). With regard to synthetic polymers, WVP of starch films were higher than that of low density polyethylene (LDPE) with 0.0006 ng m/m² s Pa (Modern Plastic Encyclopedia, 1986). When compared with other edible

Table 3
Water vapour permeabilities of starch, gelatin, and HPMC films

Film types	Plasticizer	Concentration (g plasticizer/g starch, gelatin or HPMC)	WVP ^A (ng m/m ² s Pa)
NS450	Glycerol	0.25	1.1 ± 0.5 ^d
Hwangso	Glycerol	0.25	1.6 ± 0.1 ^{cd}
Seoryong	Glycerol	0.25	1.6 ± 0.2 ^{cd}
Mungbean	Glycerol	0.25	1.8 ± 0.4 ^{bc}
Water chestnut	Glycerol	0.25	1.8 ± 0.1 ^{bc}
Gelatin	Glycerol	0.25	2.5 ± 0.2 ^a
HPMC	Glycerol	0.25	2.4 ± 0.5 ^{ab}

^A a–d indicate significant differences ($P < 0.05$) within columns WVP (ng m/m² s Pa).

and biodegradable films such as wheat gluten (0.616 ± 0.013 ng m/m² s Pa) and corn zein (0.116 ± 0.019 ng m/m² s Pa) plasticized with glycerol (Park and Chinnan, 1995), the WVP of the developed starch films were higher.

3.4. Colour

The colour *L*, *a* and *b* values of starch, gelatin and HPMC films are presented in Table 4. The Hunter colour *L* values, which represents brightness of film samples were 83.17–92.25. Hunter colour '*a*' values were –2.65 to –0.51, and '*b*' values were 1.08–13.06. Among the developed starch film samples, waterchestnut film had the highest colour difference (ΔE) value (15.53 ± 1.06), and mungbean film had the lowest value (1.39 ± 0.02), indicating that mungbean formed the most transparent film (Table 4). The ΔE value of hwangso, seoryong, and HPMC films were not significantly different from each other (4.64–5.52). NS450 film had similar ΔE value (1.76 ± 0.22) with mungbean film. The gelatin film ΔE was 13.52 ± 0.28, which was very close to water chestnut film (15.53 ± 1.06). Song and Kim (1999) reported that the ΔE of methyl cellulose edible film was 1.76–3.04. Lee and Rhim (2000) reported ΔE of 2.01–4.19 ΔE for carrageenan films. Whereas, Rhim (2003) reported ΔE of 0.99–1.23 for pullulan-based edible films.

3.5. Molecular and physical characterizations of starches (amylose and amylopectin)

Mungbean starch had the highest amylose content (30%), followed by waterchestnut starch (24%), hwangso sweet potato starch (17%), seoryong sweet potato starch (13%) and NS450 potato starch (11%) as presented in Table 5. The RVA peak and final viscosities of these starches are presented in Fig. 3, and Table 6. The results indicated that starches with lower amylose contents had higher peak and final viscosities. The regression results of starch amylose content vs. peak and final RVA viscosity indicated that there was a correlation between starch amylose content and peak or final viscosity (Figs. 4a and 4b). NS450 potato starch was not included in the regression analysis because it is a physically modified potato starch so as to have high viscosity and improved elasticity when gelatinized. Starches with high amylose content (low peak and final viscosities) produced better biodegradable films and capsules than the starches with low amylose and high amylopectin. Mungbean starch was the easiest polymer to draw film on the casting machine and such properties may be attributed to the high amylose content. The amylose is composed of linear long chain of (1 → 4)-linked α -D-glucopyranosyl units with a few α -D-(1 → 6) branches (perhaps 361 0.3–0.5% of the total linkages), whereas amylopectin is composed of highly branched molecules and is the largest component of starch (You & Lim, 2000). High amylopectin content of starch may be related to higher degree of branching, which is an opposing factor to acquire

Table 4
Colour values of starch, gelatin, and HPMC films

Film types	L^A	a^B	b^C	ΔE^D
NS450	92.25 ± 0.27^a	-1.15 ± 0.02^b	1.08 ± 0.01^c	1.76 ± 0.22^d
Hwangso	89.99 ± 0.73^{bc}	-1.33 ± 0.02^c	2.84 ± 0.06^d	4.64 ± 0.59^c
Seoryong	89.46 ± 0.50^c	-1.37 ± 0.05^{cd}	3.60 ± 0.44^{cd}	5.52 ± 0.62^c
Mungbean	93.17 ± 0.02^a	-1.19 ± 0.01^b	1.39 ± 0.02^c	1.39 ± 0.02^d
Water chestnut	83.17 ± 1.12^d	-0.51 ± 0.09^a	11.48 ± 0.47^b	15.53 ± 1.06^a
Gelatin	90.18 ± 0.27^{bc}	-2.65 ± 0.03^c	13.06 ± 0.25^a	13.52 ± 0.28^b
HPMC	90.82 ± 0.02^b	-1.44 ± 0.11^d	4.06 ± 1.05^c	4.93 ± 0.86^c

^A a–d indicate significant differences ($P < 0.05$) within columns L .

^B a–d indicate significant differences ($P < 0.05$) within columns a .

^C a–d indicate significant differences ($P < 0.05$) within columns b .

^D a–d indicate significant differences ($P < 0.05$) within columns ΔE .

Table 5
Molecular characterizations of amylopectin and amylose

Starch type	M_w ($\times 10^7$ g/mol)		Amylose content (%)
	Amylopectin	Amylose	
NS450	26	18	11
Hwangso	35	13	17
Seoryong	56	26	13
Mungbean	16	3.9	30
Water chestnut	13	3.4	24

Table 6
RVA viscosities of starches at 6% in water

Starch type	P_v (cP)	F_v (cP)
NS450	6953.7 ± 12.0	2198.3 ± 3.2
Hwangso	1330.3 ± 3.2	1450.7 ± 5.0
Seoryong	1212.3 ± 1.5	1466.7 ± 1.5
Mungbean	498.3 ± 0.6	605.7 ± 3.2
Water chestnut	941.3 ± 2.1	875.0 ± 1.7

P_v , peak viscosity; F_v , final viscosity.

smooth surfaced and easy to draw starch film. Mungbean starch with high amylose content also had the highest film tensile strength. The regression results indicated that there was a correlation between biodegradable starch film tensile strength and starch amylose content (Fig. 4c). The oxygen permeability of starch films were reported to be related to the degree of the polymer chain mobility (water content) rather than the differences in the amylose and amylopectin film structures (Forssell et al., 2002). Lawton (1996) reported that the percent elongation of films that had more Amylose, did not vary much during storage for 168 days or ageing. One can predict that mungbean starch may likely form stable capsule during storage or ageing and at different relative humidities. The developed starch, commercial gelatin, and HPMC capsules are presented in Fig. 5. The developed starch capsules were not significantly different from the commercial gelatin and HPMC products in

appearance. The mungbean and waterchestnut starch capsules (Figs. 6 and 7), with high amylose, were developed without the gelling agent, but the two products maintained their structure, texture and appearance because of the amylose linear chains.

3.6. Loss on drying

The loss on drying (LOD) of starch based capsules ranged from 3.88% to 4.92% (Table 7). The LOD results indicated that the developed starch capsules were not significantly different from each other. Reports indicated that conventional gelatin hard capsules are produced with moisture content between 13% and 16% (Bowman and Ofner, 2002). For the HPMC hard capsule, the moisture was about 5%. Forssell et al. (2002) reported that starch films with water content below 15% were good oxygen bar-

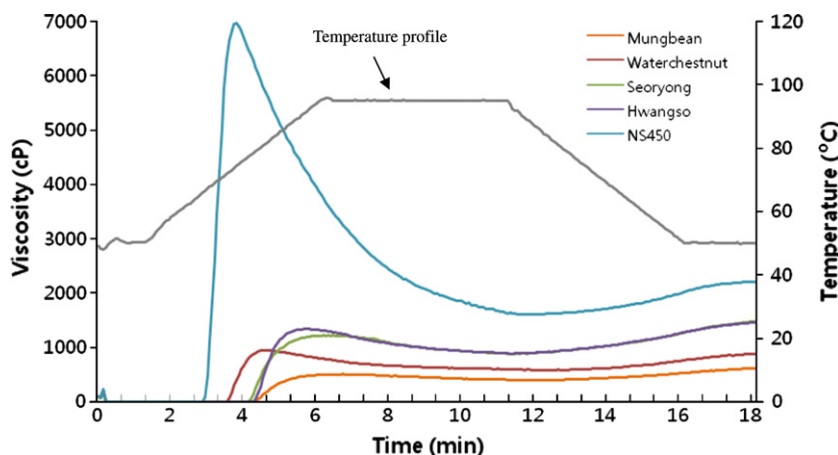


Fig. 3. RVA or Brabender viscosities of starches at 6% in water.

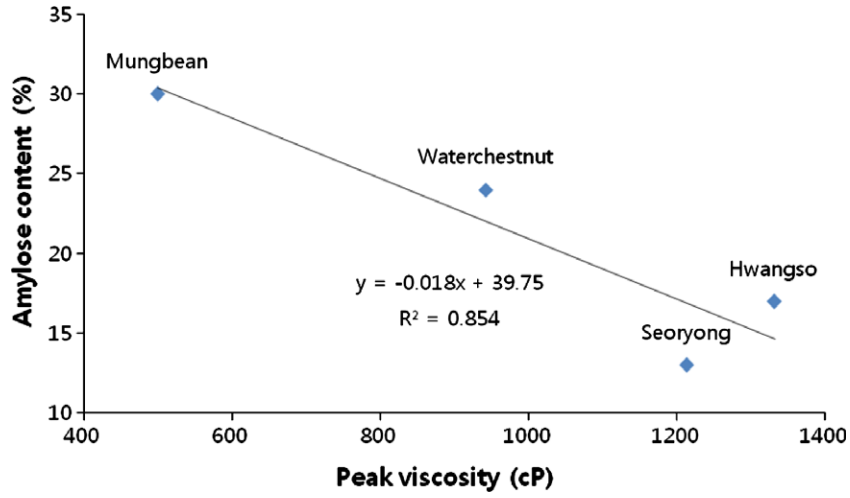


Fig. 4a. Amylose (%) of starches vs. peak or final viscosities (cps) of starches.

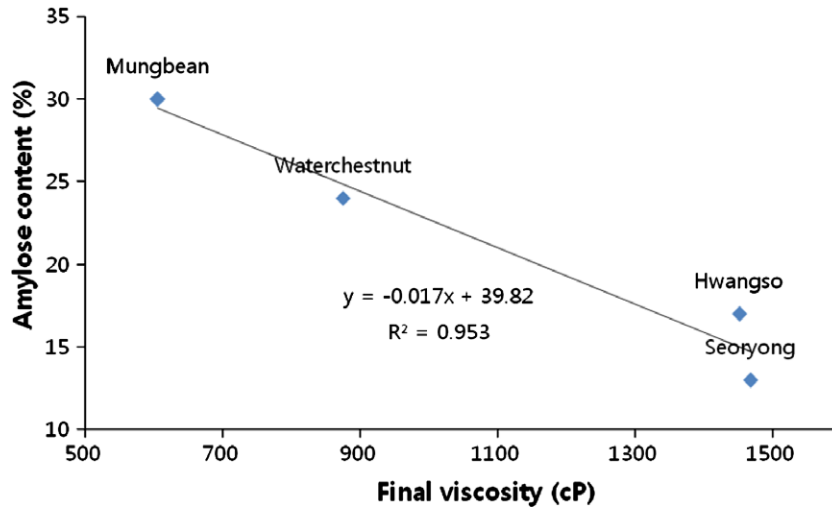


Fig. 4b. Amylose (%) of starches vs. final viscosities (cps) of starches.

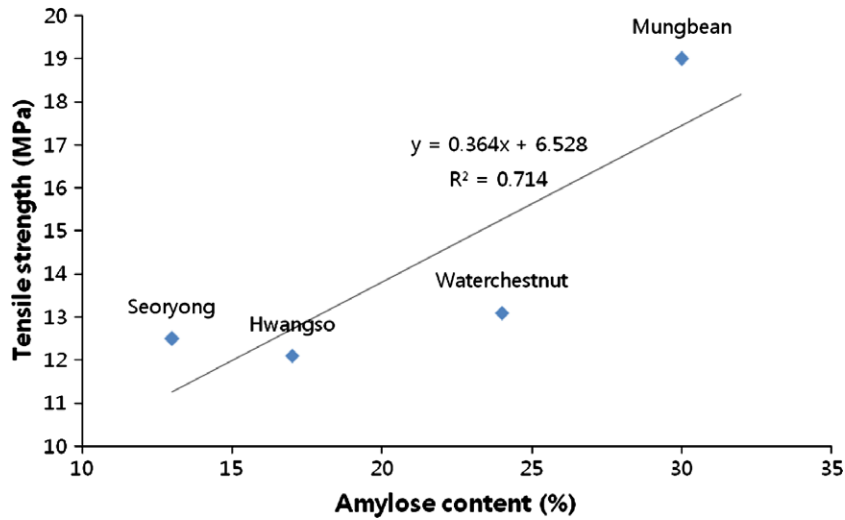


Fig. 4c. Starch films tensile strength (MPa) vs. amylose (%) of starches.



Fig. 5. Developed starch capsules: (a) HPMC capsule, Suheung capsule, Korea; (b) HPMC capsule, Capsugel, France; (c) sweet potato starch capsule; (d) potato starch capsule; (e) mungbean starch capsule; and (f) waterchestnut starch capsule.



Fig. 6. Mungbean starch hard capsule without gelling agent.



Fig. 7. Waterchestnut starch hard capsule without gelling agent.

Table 7
Loss on drying (%) of starch based hard capsule samples

Capsule type	Loss on drying (%)
NS450	4.92
Hwangso	4.50
Seoryong	4.50
Mungbean	4.78
Water chestnut	3.88

Table 8
Dissolving test of starch based hard capsule samples

Capsule type	In water	In HCl solution
NS450	Partly dissolved	Partly dissolved
Hwangso	Partly dissolved	Partly dissolved
Seoryong	Partly dissolved	Partly dissolved
Mungbean	Partly dissolved	Partly dissolved
Water chestnut	Partly dissolved	Partly dissolved

3.7. Dissolving test

The dissolution test results, indicated that the developed starch capsules did not dissolve completely within 10 min in 50 mL water at $37 \pm 2^\circ\text{C}$ or in 50 mL HCl (pH 1.2) solution at $37 \pm 2^\circ\text{C}$. All the developed starch capsules dissolved completely within 10 min of testing time, but small fragments of capsule remained (Table 8). Differences were not observed between water and HCl solution on the developed starch capsules solubility properties.

4. Conclusion

Biodegradable films were developed using starches from various plant sources, and their physical and mechanical properties evaluated. Among the tested samples, potato, sweet potato, mungbean, waterchestnut starches had relatively good mechanical and physical properties as compared with gelatin and HPMC and other LDPE films. Starch films had better O_2 barrier, and improved H_2O barrier properties than gelatin and HPMC films. The potato, sweet potato, mungbean, and waterchestnut starches were also utilized to develop hard capsules for the pharmaceutical industry. The developed capsules had good molding properties and formed quality, hard capsules with conventional dip coating technique. The developed starch capsules were clear, smooth surfaced, and flexible. Starches with high amylose produced better films and capsules than the ones with low amylose and high amylopectin. It was possible to develop hard capsules without the gelling agent with high amylose starches (mungbean and waterchestnut). The developed starch capsules did not completely dissolve and had some fragments in water or HCl solution. Starch based hard capsules have the potentials for utilization in the pharmaceutical industry as a substitute for gelatin or animal protein based products.

riers, and above 20% water, the barrier property was lost. Reports indicated that pregelatinized food products (deep-fried instant noodle and others) with moisture content below 15% were stable against retrogradation (Kim, 2001).

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