

Effect of amylose contents of starches on physical properties and biodegradability of starch/PVA-blended films

Yeon-Hum Yun · Soon-Do Yoon

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Abstract Recently, synthetic plastics are used widely in various fields, and with increased applications, disposal of waste plastics has become a serious problem. Therefore, development of novel plastics that are degradable by microorganisms in soil has recently been attracting much attention. In this study, starch/PVA-blended films were prepared from commercial starches with the different amylose contents, PVA, and additives by using a simple mixing process and casting method. Glycerol (GL), sorbitol (SO), tartaric acid (TA), and citric acid (CA) were used as additives. The physical properties such as tensile strength (TS), elongation at break (%E), degree of swelling (DS), and solubility (S) with amylose contents of starches were investigated. The amylose content of starches was analyzed by the colorimetric method. Thermal analysis of films was measured by using a differential scanning calorimeter (DSC). Finally, biodegradability of the films was evaluated in a 6-month soil burial test. The examination of the physical properties of biodegradable films indicates that with the higher amylose contents of starch used in preparing the film, TS, and DS of films increased, whereas %E and S decreased. The additives containing both carboxyl and hydroxyl groups, i.e. TA and CA, improved the physical properties of films. A thermal analysis of films revealed that the glass transition temperature (T_g) rose because of the increased crystallization of films with the increasing the amylose contents. Also, films degraded rapidly at the beginning and slow degradation took place until the experiment was completed. The films showed 50–80% degradation.

Y.-H. Yun
Department of Geosystem Engineering, Chonnam National University,
300 Yongbong-dong, Buk-gu, 500-757 Gwangju, South Korea

S.-D. Yoon (✉)
Faculty of Applied Chemical Engineering and the Research Institute for Catalysis,
Chonnam National University, 300 Yongbong-dong, Buk-gu, 500-757 Gwangju, South Korea
e-mail: yunsd03@empal.com

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Introduction

Synthetic plastics such as polyvinyl chloride, polycarbonate, polystyrene, polypropylene, and polyethylene are used widely in daily life, food industry, biomedical fields, and agriculture. Use of these synthetic plastics has brought a heavy environmental pollution because they take hundreds of years to degrade. Thus, disposal of waste plastics has become a serious problem [1–3]. In the past two decades, biodegradable materials have been drawing attention as an alternative to the petroleum-derived plastics [4–9].

Natural biopolymers including starch, cellulose, and chitosan were tested, alone or combined with synthetic polymers, to explore the possibility of forming a fully or partially biodegradable film. Of these three materials, starch is the most attractive candidate because of its low cost, easy availability, potential mass production from renewable resources [10], and high molecular weight polymer of anhydroglucose units linked by α -D glycoside bonds. There are two major polymers in starch: amylose and amylopectin (AMp). Amylose is a linear molecule with an extended helical twist. AMp is a branched molecule. Amylose is generally a smaller molecule with a molecular weight of 1–1.5 million. AMp is by comparison large with a molecular weight of 50–500 million [11].

Biodegradable starch-based plastics have recently been investigated for their great potential marketability in agricultural foils, garbage or composting bags, food packaging, fast food industry as well as biomedical fields [12, 13]. However, the low water resistance and high brittleness of starch films have limited their extensive application. Therefore, many attempts have been made to overcome these problems by blending starch with other biodegradable synthetic polymers for numerous applications [14, 15]. Starch/polyvinyl alcohol (PVA)-blended plastics are one of the most popular biodegradable plastics. PVA is a biodegradable synthetic polymer which has the advantages of excellent film forming, adhesive properties, and high thermal stability. In recent years, PVA has been applied more and more in the materials industry. However, the physical properties such as the mechanical properties and water resistance of the starch/PVA-blended plastics are still lower than those of other polymers made from petroleum. In recent studies, these problems were partially solved by irradiation of electron beam and ultraviolet [16], addition of crosslinking agents [17], and use of chemically modified starch [18].

Various starches have been used to the biodegradable starch/PVA-blended plastics: corn starch (CS), wheat starch (WS), potato starch (PS), cassava starch, sweet potato starch (SPS), and tapioca starch. These starches were classified by type, formation, amylose content, etc. Depending on the kind of starch used in the starch/PVA-blended plastics, the physical properties differ. Lawton has reported that films made only of starch from different starch sources have different properties [19]. However, there has been no report on the physical properties of starch/PVA-blended films that used various commercial starches with amylose contents.

In this study, films were prepared with different starches, PVA, and additives by using a casting method. We investigated the physical properties such as tensile strength (TS), elongation at break (%E), degree of swelling (DS), and solubility (S) in terms of the amylose contents of starches and the functional group of additives. The structure of each additive is represented in Fig. 1. The amylose content of starches was analyzed by the colorimetric method [20, 21]. A thermal analysis of films was conducted by using a differential scanning calorimeter (DSC). Finally, biodegradability of the films was evaluated by a soil burial test.

Experimental

Materials

Corn starch (CS) was obtained from Doosan Corn Products Korea, Inc. Wheat starch (WS) was obtained from Sinsong Food Co., Korea. PS and SPS were purchased from Samyang Genex Co., Korea. Amylose, AMP, and high amylose starch (HAM) were purchased from Sigma Chemical Co. (St. Louis, MO). PVA, reagent grade glycerol (GL), sorbitol (SO), tartaric acid (TA), and citric acid (CA) were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI). PVA was 99% hydrolyzed with a molecular weight average of 89,000–98,000. Water used to prepare starch/PVA-blended films was redistilled after deionization.

Determination of amylose contents

Amylose contents in starches were determined according to the colorimetric procedure of Juliano [21] and Chrastil [20]. Twenty milligrams of starch was gelatinized by treatment with 10 mL of 0.5 N KOH and stored for 24 h at room temperature. After adding 100 mL of distilled water, 10 mL of the solution was taken and 5 mL of 0.1 N HCl was added. Then 0.5 mL of 0.2% (w/v) I₂, 2% (w/v)

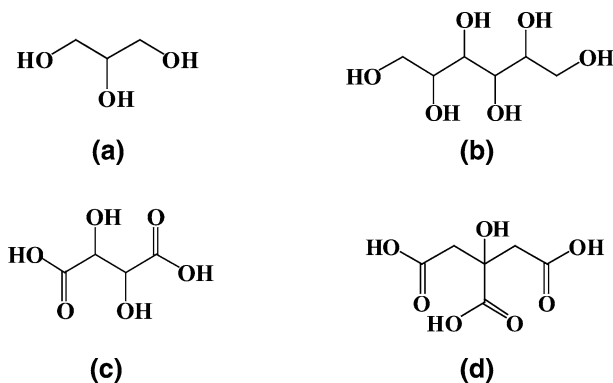


Fig. 1 Chemical structures of the additives used in this study. **a** Glycerol (GL); **b** sorbitol (SO); **c** tartaric acid (TA); **d** citric acid (CA)

KI, and 50 mL of distilled water was added to the solution. The specific wavelength (λ -max) of amylose was measured by using UV–vis spectrophotometer (UV-160A, Shimadzu, Kyoto, Japan). The calibration line of the standard amylase for various concentrations was obtained, and the amylose content of different starches, i.e., HAm, PS, WS, SPS, and CS, was determined.

Preparation of starch/PVA-blended films

Biodegradable starch/PVA-blended films were prepared using a casting method. At first, PVA solution was prepared by dissolving PVA in hot water (95 °C). Each one of the starches (HAm, AMp, CS, WS, PS, and SPS) and additives (GL, SO, TA, and CA) were mixed directly together with water using a Kitchenaid mixer for 15 min. Formulations contained 40% GL, SO, TA, and CA (starch/PVA weight bases). The PVA solution and mixed starch/additives were mixed at 95 °C for 15 min. Then, the mixture was blended to form homogeneously gel-like solution with a mechanical stirrer (500 rpm) at room temperature for 60 min. The mixing composition is shown in Table 1. Bubbles, the by-product of preparation, were removed by using an aspirator. The gel-like solution thus prepared was poured on a pre-warmed (65 °C) Teflon mold (200 × 200 × 1 mm). Water was evaporated from the molds in a ventilated oven at 50 °C for 15 h. Dried films were put in open polyethylene bags and stored at 25 °C and at relative humidity of (RH) 57% for one week before they were measured.

Mechanical properties of films

Tensile strength (TS) and elongation (%E) were evaluated for each film using the Instron 6012 testing machine. Three dumbbell-shaped specimens (ASTM D-412) were cut from each film. Each specimen had a width of 12 mm. The average thickness of the specimen was about 0.12 mm. The thickness of the films was measured on a mechanical scanner (digital thickness gauge ‘Mitutoyo’, Tokyo, Japan) at 12 random positions around the film. The mean standard deviation within the film was about 5% of the average thickness. The gauge length and grip distance were both 50.0 mm. Crosshead speed was 20 mm/min and load cell was 250 kg_f. The tests were carried out at 25 °C and 55% RH in a constant temperature and humidity room.

Thermal analysis

Samples of the biodegradable starch/PVA films were analyzed by using a DSC to determine the glass transition temperatures (T_g). These analyses were performed using a DSC (DSC-50, Shimadzu, Kyoto, Japan). The samples (8 mg) were placed in hermetically sealed aluminum pans and determined from 30 to 150 °C at a heating rate 5 °C/min under helium. An empty pan was used as reference.

Degree of swelling and solubility of films

The DS and S of the films were measured applying the following method. Dried biodegradable starch/PVA-blended films were immersed in distilled water at room

Table 1 Composition of starch/PVA-blended gel-like solutions used to prepared films

Sample name	HAm (%)	AMp (%)	CS (%)	WS (%)	PS (%)	SPS (%)	PVA (%)	GL (wt%)	SO (wt%)	TA (wt%)	CA (wt%)
HAmP	5	–	–	–	–	–	5	–	–	–	–
AMpP	–	5	–	–	–	–	5	–	–	–	–
CSP	–	–	5	–	–	–	5	–	–	–	–
WSP	–	–	–	5	–	–	5	–	–	–	–
PSP	–	–	–	–	5	–	5	–	–	–	–
SPSP	–	–	–	–	–	5	5	–	–	–	–
HAmPGL40	5	–	–	–	–	–	5	40	–	–	–
HAmPSO40	5	–	–	–	–	–	5	–	40	–	–
HAmPTA40	5	–	–	–	–	–	5	–	–	40	–
HAmPCA40	5	–	–	–	–	–	5	–	–	–	40
AMpPGL40	–	5	–	–	–	–	5	40	–	–	–
AMpPSO40	–	5	–	–	–	–	5	–	40	–	–
AMpPTA40	–	5	–	–	–	–	5	–	–	40	–
AMpPCA40	–	5	–	–	–	–	5	–	–	–	40
CSPGL40	–	–	5	–	–	–	5	40	–	–	–
CSPSO40	–	–	5	–	–	–	5	–	40	–	–
CSPTA40	–	–	5	–	–	–	5	–	–	40	–
CSPCA40	–	–	5	–	–	–	5	–	–	–	40
WSPGL40	–	–	–	5	–	–	5	40	–	–	–
WSPSO40	–	–	–	5	–	–	5	–	40	–	–
WSPTA40	–	–	–	5	–	–	5	–	–	40	–
WSPCA40	–	–	–	5	–	–	5	–	–	–	40
PSPGL40	–	–	–	–	5	–	5	40	–	–	–
PSPSO40	–	–	–	–	5	–	5	–	40	–	–
PSPTA40	–	–	–	–	5	–	5	–	–	40	–
PSPCA40	–	–	–	–	5	–	5	–	–	–	40
SPSPGL40	–	–	–	–	–	5	5	40	–	–	–
SPSPSO40	–	–	–	–	–	5	5	–	40	–	–
SPSPTA40	–	–	–	–	–	5	5	–	–	40	–
SPSPCA40	–	–	–	–	–	5	5	–	–	–	40

temperature (25 °C). After the equilibrium (24 h), moisture on the surface of the film was removed, and the weight of the films was measured. DS in biodegradable starch/PVA-blended film was calculated as (1):

$$DS = \frac{(W_e - W_0)}{W_0}, \quad (1)$$

where W_e is the weight of film at the adsorbing equilibrium and W_0 is the first dry weight of film.

The swelled biodegradable starch/PVA-blended films were dried again for 24 h at 60 °C, and its S was calculated with the following equation (2):

$$S = \frac{(W_0 - W_d)}{W_d}, \quad (2)$$

where W_0 is the first dry weight of film and W_d is the dry weight of swelled film.

Soil burial degradation test of films

Soil burial degradation was performed as described by Thakore et al. [4] with a slight modification. The garden pots with an approximate capacity of 10 L were filled with soil taken from a culture field in Naju City (Korea). The film samples were cut into 3×3 cm pieces and buried in the soil at the depth of 10 cm. The pots were placed in an uncovered gazebo. The soil was kept moist by sprinkling water at a regular time interval to maintain 25–50% humidity. The excess water was drained through the hole at the bottom of the pot. The degradation of the specimen was determined at a regular time interval (15 days) by taking the specimen carefully from the soil and washing it gently with distilled water to remove the soil. The specimen was dried in an oven until a constant weight was obtained. Weight loss of the specimen with time was used to indicate the degradation rate in the soil burial test. The degree of degradation of films (Degradation%) was calculated by the following equation (3):

$$\text{Degradation}\% = \frac{(W_1 - W_D)}{W_1} \times 100, \quad (3)$$

where W_D is the dry weight of the specimen after the soil burial test and W_1 is the initial dry weight of the specimen.

The soil burial degradation test started on August 10, 2007 and ended on February 20, 2008.

Results and discussion

Determination of amylose content of starches

Amylose contents in the starches were determined according to the colorimetric procedure of Juliano and Chrastil. The specific wavelength of amylose was measured at 620.0 nm. Therefore, the spectrophotometric measurement for analysis of amylose contents was performed by the absorbance value of each starch at 620.0 nm. The results for amylose contents of starches used in this study are reported in Table 2. This result accords nearly with the result reported by Chrastil except the amylose content of potato starch.

Mechanical properties of biodegradable starch/PVA-blended films

Figure 2 shows the variations of TS and %E of the film using HAM, CS, AMP, and PVA without additives. Amylose contents of HAM, CS, and AMP are 70.30, 20.83, and 0, respectively. Starches and PVA contents are 5% of the total weight of polymer.

Table 2 Amylose contents of starches

Starches	Amylose contents (%)
Amylose	100
High amylose starch	73.30 ± 0.16
Potato starch	34.53 ± 0.20
Sweet potato starch	25.63 ± 0.10
Wheat starch	23.71 ± 0.15
Corn starch	20.83 ± 0.13
Amylopectin	0

TS and %E were equilibrated over 60 min, and their values after equilibrium were 70.6 MPa and 73.30% (HAMp), 56.0 MPa and 20.27% (CSP), and 49.1 MPa and 21.24% (AMpP), respectively. By considering this result, starch/PVA-blended films with additives (GL, SO, TA, and CA) were prepared by the mixing process.

Figure 3a and b shows the results of TS and %E with amylose contents of films to which 40 wt% GL, SO, TA, and CA are added, respectively. With increasing amylose contents, the TS decreased while %E increased. We observed that TS and %E of films have an effect on amylose contents. The mechanical properties of biodegradable films prepared by starch are determined by various factors, i.e., the method of preparing the film, additives, and humidity. Previous studies have been focusing on the effect of additives and humidity [11, 18]. This study investigates the effects of various amylose contents on the properties of the films prepared by using various starches. As above-mentioned, amylose is a linear molecule with an extended helical twist, whereas AMP is a branched molecule.

We were able to confirm that the linear structure of amylose improved the tensile property of films. However, film was not synthesized when only 100% amylose was used because it is not easily dissolvable in water. In addition, amylose has a significant effect on the %E of films. Figure 3b shows that %E of the films prepared with AMP that has a branched structure is lower than others. However, %E values of the films prepared by using CS (containing 20.83% amylose) were significantly increased because amylose played an important role in cross linking, which formed films between AMP and additives.

As has been reported in our previous study [11], the effect of additives is as follows. When GL and SO with hydroxyl group only were added as additives, TS and %E of the SO-added film were higher than the GL-added film. In terms of molecular structure, GL and SO have 3 hydroxyl and 6 hydroxyl groups. Films containing TA with 2 hydroxyl and 2 carboxyl groups have higher TS and %E than either GL-added or SO-added films. Furthermore, TS and %E of the biodegradable starch/PVA-blended film added CA composed of 1 hydroxyl group and 3 carboxyl groups showed the best performance. When the additive containing both hydroxyl and carboxyl groups was simultaneously added, TS and %E were found to be better than GL-added and SO-added film containing only the hydroxyl group.

These films are synthesized by hydrogen bonding between starch, PVA, and additives. We found that TA and CA containing the hydroxyl and carboxyl groups

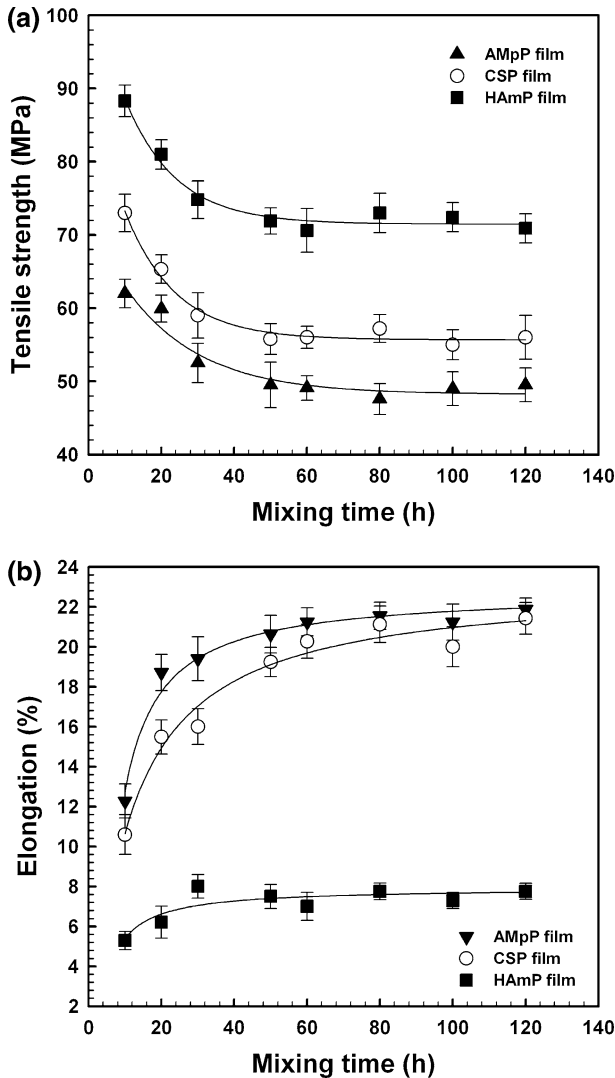


Fig. 2 Tensile strength (TS) and elongation at break (%E) of biodegradable starch/PVA-blended films versus mixing time. **a** TS of biodegradable starch/PVA-blended films without additive; **b** %E of biodegradable starch/PVA-blended films without additive

are stronger than GL or SO containing only the hydroxyl group in hydrogen bonding between starch, PVA, and molecules of additional materials.

Thermal analysis

In many studies, the glass transition temperature (T_g) about films prepared by using different starches has been investigated [1, 4, 22]. Most of the T_g values varied from 40 to 70 °C. In this work, we obtained films of relatively high T_g values.

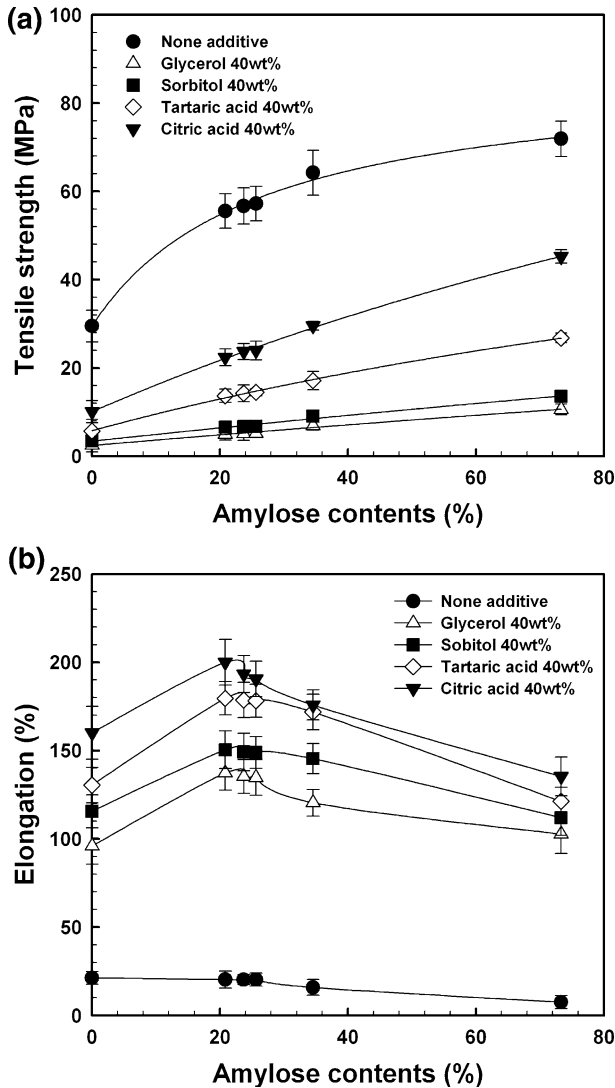


Fig. 3 Tensile strength (TS) and elongation at break (%E) of biodegradable starch/PVA-blended films adding glycerol (GL), sorbitol (SO), tartaric acid (TA), and citric acid (CA) as additives with amylose contents. **a** TS of biodegradable starch/PVA-blended films adding GL, SO, TA, and CA as additives; **b** %E of biodegradable starch/PVA-blended films adding GL, SO, TA, and CA as additives

The DSC curves of biodegradable starch/PVA-blended films are shown in Fig. 4a. In addition, films of T_g were represented. T_g values occurred between 68 and 80 °C for films containing amylose contents (Fig. 4b). With increasing amylose contents, T_g value increased. We observed that amylose improved the degree of crystallinity, and that the higher T_g value, the better tensile property of the film.

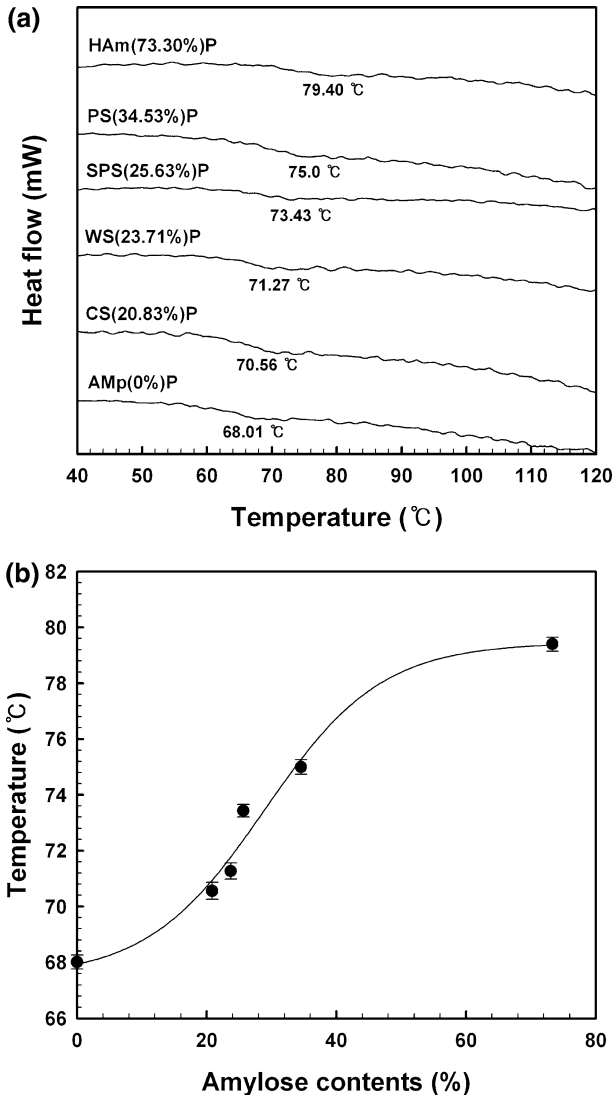


Fig. 4 The results of thermal analysis of biodegradable films. **a** DSC curves of HAmP, PSP, SPSP, WSP, CSP, and AMpP film; **b** films of glass transition temperature (T_g) in terms of the amylose contents

Degree of swelling and solubility of starch/PVA-blended film

The DS and S with the mixing time for preparing films of the biodegradable starch/PVA-blended film containing no additive are shown in Fig. 5. As the mixing time increased, DS was decreased rapidly and equilibrated after 60 min. This phenomenon is attributed to the decrease in the free volume caused by the formation of hydrogen bonding between starches and PVA. Also, the films were not formed until after the mixing time of 20–50 min passed.

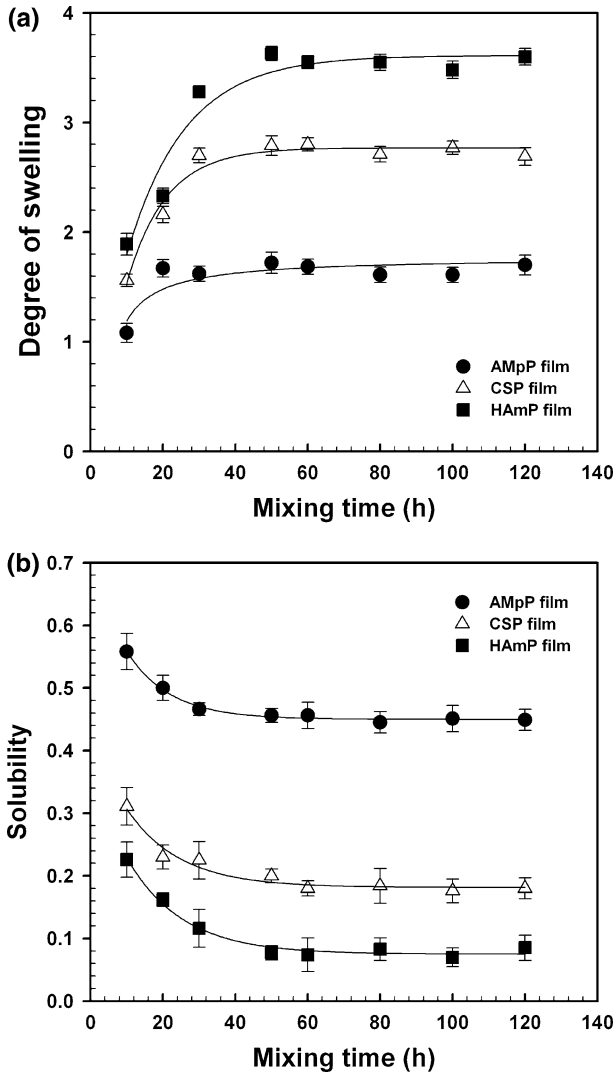


Fig. 5 Degree of swelling (DS) and solubility (S) of biodegradable starch/PVA-blended films versus mixing time for preparing films. **a** DS of biodegradable starch/PVA-blended films with additive; **b** S of biodegradable starch/PVA-blended films without additive

Figure 6a and b represents DS and S of films that used HAm and PVA with/without additives. In conformity with time, DS and S were increased and equilibrated over 18 h. By using this result, DS and S of films which are prepared by using starches contained different amylose contents were measured.

In Fig. 7a, with the increase in the amylose content, DS of the films increased slightly and S decreased (Fig. 7b). This phenomenon could perhaps be explained by the fact that the DS increased the functional group that is combined with water as

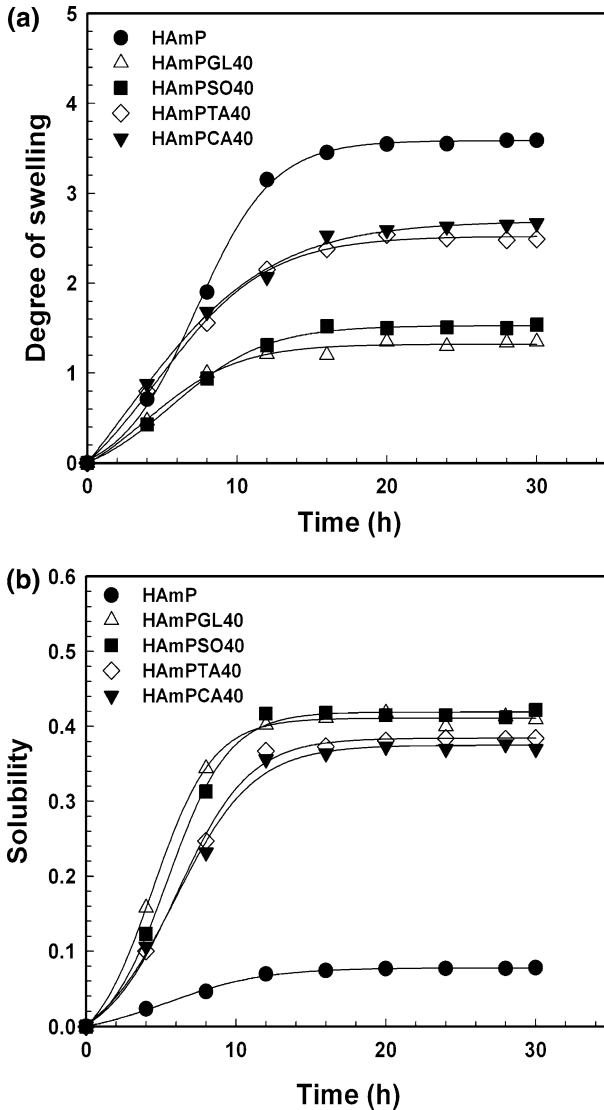


Fig. 6 Degree of swelling (DS) and solubility (S) of high amylose starch (HAM)/PVA-blended films with/without additives versus time. **a** DS of biodegradable HAM/PVA-blended films adding glycerol (GL), sorbitol (SO), tartaric acid (TA), and citric acid (CA) as additives versus time; **b** S of biodegradable HAM/PVA-blended films adding GL, SO, TA, and CA as additives versus time

the amylose contents increased, and S increased because of bonding strength between AMP, PVA, and additives. DS of the films that do not contain additives was superior to the others. Also, S was the lowest. Owing to the effect of additives that are dissolved in water, DS of the films containing the additive had lower values than the films without additives, whereas S of the films containing the additive had higher values than the films without additives. As GL and SO are very strong for

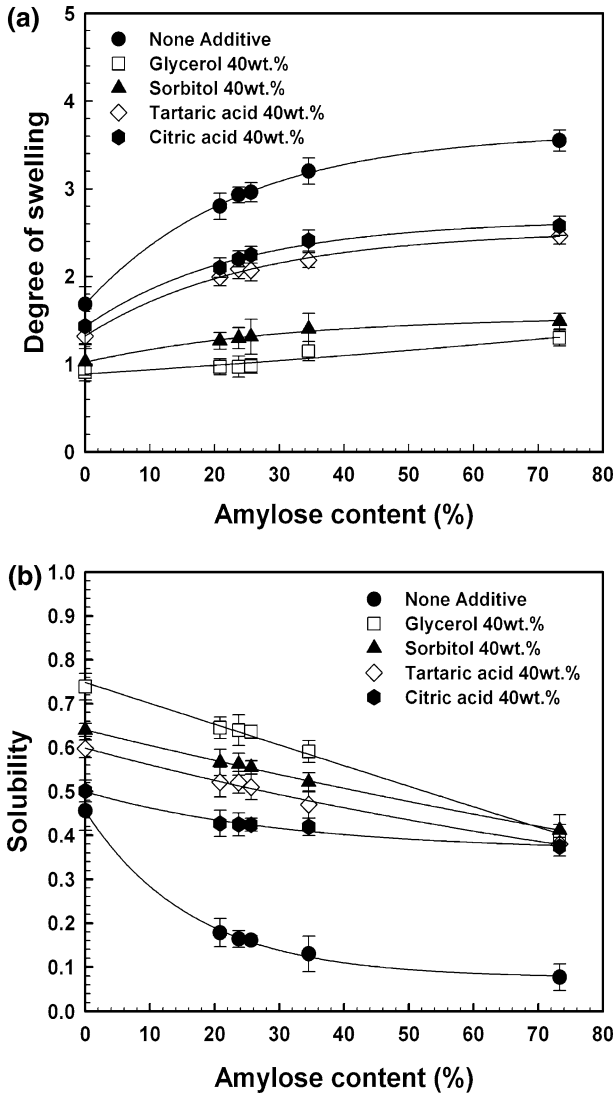
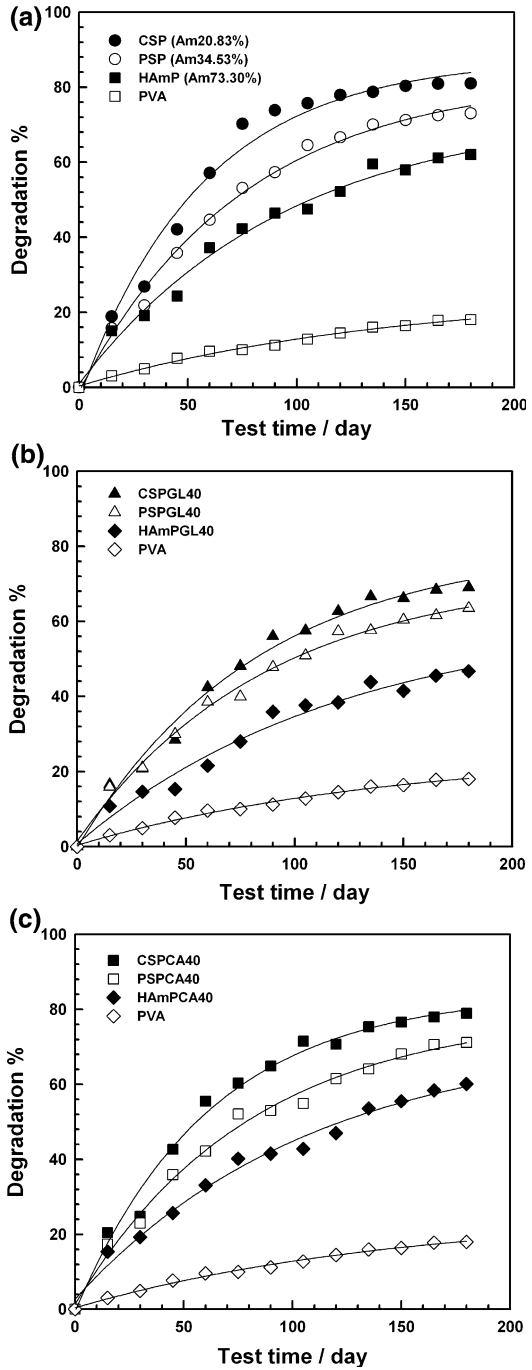


Fig. 7 Degree of swelling (DS) and solubility (S) of biodegradable starch/PVA-blended films adding glycerol (GL), sorbitol (SO), tartaric acid (TA), and citric acid (CA) as additives with amylose contents. **a** DS of biodegradable starch/PVA-blended films adding GL, SO, TA, and CA as additives; **b** S of biodegradable starch/PVA-blended films adding GL, SO, TA, and CA as additives

solubility in water [23], S values were higher than the others. On the other hand, although TA and CA as additives are easily soluble and combine with H₂O molecule, S values of TA- and CA-added films are lower than GL- and SO-added films. As a result, the crosslinkage was well formed by the addition of TA and CA as additives between amylose, AMP, and PVA.

Fig. 8 Degradability of films in the soil burial test. **a** Films using high amylose starch (HAM), potato starch (PS), corn starch (CS), and PVA without additives; **b** films using HAM, PS, CS, and PVA adding glycerol (GL) as additive; **c** films using HAM, PS, CS, and PVA adding citric acid (CA) as additive



Soil burial degradation test of films

The soil burial test provides a realistic environment where soil humidity, temperature, and type and the amount of microorganisms are less controlled and change with seasons. All the tested specimens had the same shape and size to avoid the effects of the shape of the film on its biodegradability. Biodegradability of the samples was studied by evaluating the weight loss of the films over time (Fig. 8a, b, c). The effect of the amylose contents was also evaluated. With the amylose contents, the degree of degradation of biodegradable films without added additives was 81.4% (CSP), 72.9% (PSP), and 62.1% (HAmP), respectively. Compared to GL- and CA-added films, degradation of CA-added films was better than GL-added films because CA was used as the nutritive elements of microorganisms in the soil.

In all the films, rapid degradation of about 50–80% of films occurred in the initial 70 days, followed by a slow degradation until the end of the experiment. In contrast, the PVA film exhibited a higher resistance against soil burial biodegradation (17%).

Conclusions

Starch/PVA-blended films were synthesized by applying a simple mixing process and casting method, and the physical properties, thermal analysis, and biodegradability of the films prepared by using starches with different amylose contents, PVA, and additives were investigated. Our investigation of the physical properties revealed that with increasing amylose contents, the TS and DS increased, whereas %E and S decreased. Thus, amylose plays an important role in the formation of biodegradable films by crosslinkage between AMP, PVA, and additives. In addition, the effect of additives, i.e., GL, SO, TA, and CA, was verified. The physical properties of films added to TA or CA with hydroxyl and carboxyl groups as functional group were better than films added GL or SO with hydroxyl group only. The glass transition temperature (T_g), correlating to TS property, rose with increasing amylose contents of starch because of the increase in crystallization on films. A soil burial test indicates that the extent of film degradation differs according to the amylose contents of starches or additives. However, most of the films degraded about 50–80% after 6 months.

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