

Effects of Additives with Different Functional Groups on the Physical Properties of Starch/PVA Blend Film

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ABSTRACT: The effects of additives with different functional groups, that is, hydroxyl and carboxyl groups, on the physical properties of starch/PVA blend films were examined. Starch/PVA blend films were prepared by the mixing process. Glycerol (GL) with 3 hydroxyl groups, succinic acid (SA) with 2 carboxyl groups, malic acid (MA) with 1 hydroxyl and 2 carboxyl groups, and tartaric acid (TA) with 2 hydroxyl and 2 carboxyl groups were used as additives. The results of measured tensile strength and elongation verified that hydroxyl and carboxyl groups as functional groups increased the flexibility and strength of the film. The degree

of swelling (DS) and solubility (S) of the GL/SA-added films were low. However, the DS and S of the films with added MA or TA with both hydroxyl and carboxyl groups were comparatively high. When the film was dried at low temperature, the properties of the films evidently improved, probably because hydrogen bonding was activated at low temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3733–3740, 2006

Keywords: starch/PVA blend film; functional group; physical properties

INTRODUCTION

Plastics made from petroleum have been in widespread use throughout the world. With plastics having an increased number of applications, disposal of waste plastics has become a serious problem. Therefore, the development of novel plastics that could be degraded by microorganisms in soil and seawater has recently been emphasized. Biodegradable plastics that can be easily degraded in the natural environment are arousing public interest.^{1–4} They are designed to be easily destroyed and to finally disappear from a natural environment such as landfill sites. The Biodegradable Plastics Society reported that the results of field degradation tests using 6 plastic materials in soil, sea, and lake differed with each environmental condition (Biodegradable Plastics Society 1992), and the mechanism of the degradation process in a natural environment remains poorly understood and awaits clarification.

It has been known since the 1970s that starch is renewable and biodegradable.⁵ Starch has been incorporated into synthesized polymer matrix, and in the past decades several efforts have been made to convert starch into a thermoplastic material.^{6–12}

The research showed that after starch was filled in or blended with synthesized polymer, the synthetic fraction from the oil source did not have better susceptibility to biodegradation.^{13–15} So the most recent research has focused on pure starch-based materials and starch/degradable polymer blend materials such as starch/cellulose and starch/polyvinyl alcohol (PVA).^{16,17}

The influence of starch sources, starch components, starch molecular mass, and plasticizer, such as water and polyols, has been studied in order to improve the mechanical properties of starch plastics. However, their poor mechanical properties constituted one of the major unresolved problems. Although their tensile strength may be rather high (30–60 MPa), these materials are fragile, with low elongation at break and poor water resistance. After absorbing water, they are very weak and cannot be used.^{18–22}

In the present work, starch/PVA blend film was prepared by the mixing process. Glycerol, succinic acid, malic acid, and tartaric acid were used for additives. The properties of films were compared in terms of the functional group of the additives. The structure of each additive is represented in Figure 1. Succinic acid is a dicarboxylic acid and has received a great deal of attention as a green feedstock for the manufacture of synthetic resins, biodegradable polymers, and chemical intermediates.²³ Malic acid is a naturally occurring substance in many fruits and plants. However, its richest source is apples, which is why it is

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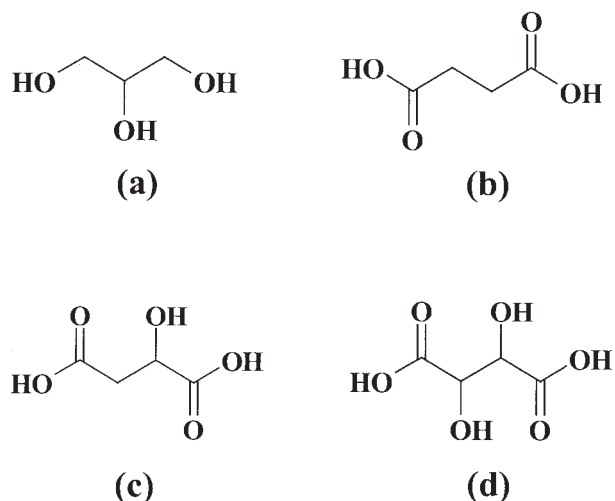


Figure 1 Chemical structures of the additives used in this work: (a) glycerol (GL); (b) succinic acid (SA); (c) malic acid (MA); (d) tartaric acid (TA).

sometimes referred to as apple acid. It is blended with multiple food acids, sugars, high-intensity sweeteners, flavors, and seasonings to create unique tastes in foods, beverages, and confections. Tartaric acid is the strongest and most important acid in grapes and also in wines.²⁴ Its concentration (usually 2–5 g/L) is decisive in the definition of the acidity of wines, thus affecting its characteristics such as odor, color and flavor.

The physical properties tensile strength, elongation, degree of swelling, and solubility of the synthesized starch/PVA blend films using GL, SA, MA, and TA as additives were then measured.

EXPERIMENTAL

Materials

Starch (cornstarch) was obtained from Doosan Corn Products Korea, Inc. (Gangnam, Seoul). Poly(vinyl alcohol) (PVA), reagent-grade glycerol (GL), succinic acid (SA), malic acid (MA), and tartaric acid (TA) were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI). PVA was 99% hydrolyzed, with an average molecular weight of 89,000–98,000. The water used to prepare the starch/PVA blend films was re-distilled after deionization.

Preparation of starch/PVA blend films

Films were obtained by the casting method. First, the PVA solution was prepared by dissolving PVA in hot water (95°C). Starch and additives (GL, SA, MA, and TA) were mixed together with water for 10 min using a Kitchenaid mixer. The formulations contained 10.86, 21.72, 32.57, 43.43, and 54.29 mmol GL, SA, MA, and

TA. SA, MA, and TA were added in the same number of moles as GL. The PVA solution and the mixed starch/additives were kept at 95°C for 5 min. Then the mixture was blended for 50 min with a mechanical stirrer (1200 rpm) at room temperature in order to form a homogeneously gel-like solution. The total amount of polymer was 100 g. Starch and PVA had the same mass ratio, and additive content was expressed as the same number of moles of GL added. Bubbles, the byproduct of the preparation, were removed with an aspirator. The mixing composition is shown in Table I. The gel-like solution thus prepared was poured on a prewarmed (70°C) Teflon mold (200 × 200 × 2 mm). Water was evaporated from the molds in a ventilated oven at 50°C for 12 h and in a cold laboratory chamber at 5°C for 72 h. The dried films were put in open polyethylene bags and stored at 20°C and at 50% RH for 1 week prior to performing the measurements.

Mechanical properties of starch/PVA blend films

Tensile strength (TS) and elongation (%E) were evaluated with an Instron 6012 testing machine. Four 15-mm-wide dumbbell-shaped specimens (ASTM D-421) were cut from each film. The thickness of each piece was measured in 3 places along the test length using a Mitutoyo instrument (Japan). The average thickness of the specimens was found to be about 0.25 mm. Gauge length and grip distance were both 45.0 mm. Cross-head speed was 20 mm/min, and load cell was 25 kg_f. The tests were carried out at 20°C and 50% RH in a room with constant temperature and humidity.

Degree of swelling and solubility of starch/PVA blend films

Dried starch/PVA blend films were immersed in distilled water at room temperature (25°C). Once equilibrium was attained, after about 24 h, the surface moisture of the films was removed, and their weight was measured. The degree of swelling (DS) in the starch/PVA blend films was calculated from the eq. (1):

$$DS = (W_e - W_0)/W_0 \quad (1)$$

where W_e is the weight of the starch/PVA blend film at the adsorbing equilibrium, and W_0 is the weight of the dry starch/PVA blend film before absorbing water.

The swelled starch/PVA blend films were dried again for 24 h at 60°C, and then the solubility (S) was calculated with eq. (2):

$$S = (W_0 - W_d)/W_0 \quad (2)$$

TABLE I
Composition of Starch/PVA Blend Films

Sample name	Starch	PVA	GL	SA	MA	TA
SP	5%	5%	—	—	—	—
SPGL1	5%	5%	10.86 mmol	—	—	—
SPGL2	5%	5%	21.72 mmol	—	—	—
SPGL3	5%	5%	32.57 mmol	—	—	—
SPGL4	5%	5%	43.43 mmol	—	—	—
SPGL5	5%	5%	54.29 mmol	—	—	—
SPSA1	5%	5%	—	10.86 mmol	—	—
SPSA2	5%	5%	—	21.72 mmol	—	—
SPSA3	5%	5%	—	32.57 mmol	—	—
SPSA4	5%	5%	—	43.43 mmol	—	—
SPSA5	5%	5%	—	54.29 mmol	—	—
SPMA1	5%	5%	—	—	10.86 mmol	—
SPAM2	5%	5%	—	—	21.72 mmol	—
SPAM3	5%	5%	—	—	32.57 mmol	—
SPMA4	5%	5%	—	—	43.43 mmol	—
SPMA5	5%	5%	—	—	54.29 mmol	—
SPTA1	5%	5%	—	—	—	10.86 mmol
SPTA2	5%	5%	—	—	—	21.72 mmol
SPTA3	5%	5%	—	—	—	32.57 mmol
SPTA4	5%	5%	—	—	—	43.43 mmol
SPTA5	5%	5%	—	—	—	54.29 mmol
SPGL1SA1	5%	5%	10.86 mmol	10.86 mmol	—	—
SPGL2SA2	5%	5%	21.72 mmol	21.72 mmol	—	—
SPGL3SA3	5%	5%	32.57 mmol	32.57 mmol	—	—
SPGL4SA4	5%	5%	43.43 mmol	43.43 mmol	—	—
SPGL5SA5	5%	5%	54.29 mmol	54.29 mmol	—	—
SPGL5SA1	5%	5%	54.29 mmol	10.86 mmol	—	—
SPGL5SA2	5%	5%	54.29 mmol	21.72 mmol	—	—
SPGL5SA3	5%	5%	54.29 mmol	32.57 mmol	—	—
SPGL5SA4	5%	5%	54.29 mmol	43.43 mmol	—	—
SPGL5SA5	5%	5%	54.29 mmol	54.29 mmol	—	—

where W_d is the dry weight of the swelled starch/PVA blend film.

RESULTS AND DISCUSSION

Mechanical properties of starch/PVA blend films

Figure 2 shows the variation in tensile strength (TS) and elongation (%E) of the films using starch and PVA without additives. Starch and PVA contents were each 5% of total weight of polymer. TS and %E were equilibrated over 40 min; their values after equilibrium were 55.58 MPa and 20.27%. Taking these results into consideration, the starch/PVA blend films with additives (GL, SA, MA, and TA) were prepared by the mixing process.

Figure 3(a,b) shows the TS and %E, respectively, of films to which 10.86, 21.72, 32.57, 43.43, and 54.29 mmol GL, SA, MA, and TA were added. As GL, MA, and TA content increased from 10.86 to 54.29 mmol, TS decreased whereas %E increased. However, in the SA-added film TS increased whereas %E decreased as the content of SA increased.

A comparison of the starch/PVA blend film containing added GL (with hydroxyl groups) with that

containing added SA (with carboxyl groups) showed that the TS of the GL-added film was lower than that of the SA-added film when the same number of moles was added. However, the %E of the GL-added films was higher than that of the SA-added films, which were too brittle to be used in applications.

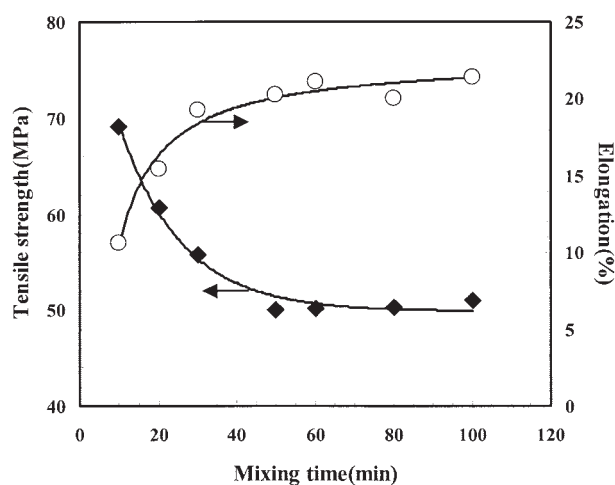


Figure 2 Tensile strength (TS) and elongation (%E) of starch/PVA blend film versus mixing time.

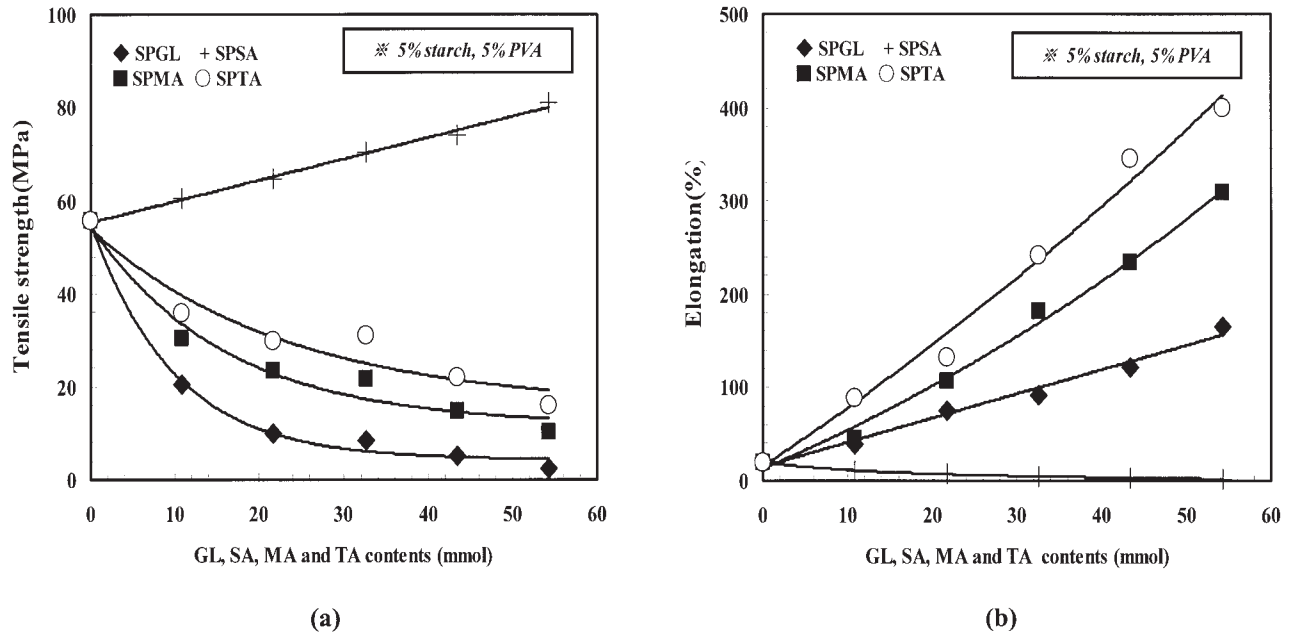


Figure 3 Tensile strength (TS) and elongation (%E) of starch/PVA blend films: (a) TS of starch/PVA blend films adding GL, SA, MA, and TA as additives; (b) %E of starch/PVA blend films adding GL, SA, MA, and TA as additives.

For the film containing MA with 1 hydroxyl and 2 carboxyl groups, which had the same number of carbons as SA, the TS and %E were higher than in the GL-added film. Films containing TA with 2 hydroxyl and 2 carboxyl groups had a higher TS and %E than did the GL- and MA-added films.

When the additive containing both hydroxyl and carboxyl groups was simultaneously added, it was observed that the TS and %E were better than in the GL-added film with hydroxyl groups only.

Figure 4 shows the results of TS and %E of starch/PVA film containing the same number of moles of

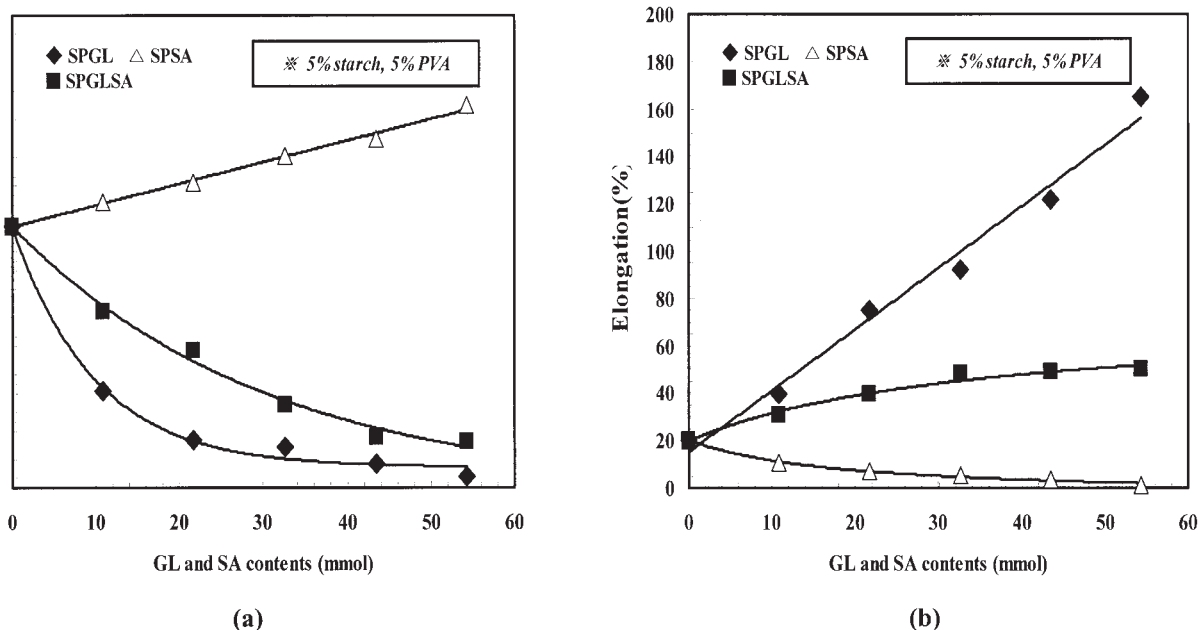


Figure 4 Tensile strength (TS) and elongation (%E) of starch/PVA blend films (SPGL, film with added GL; SPSA, film with added SA; SPGLSA, film with added GL and SA): (a) TS of starch/PVA blend films adding GL, SA, and GL-SA as additives; (b) %E of starch/PVA blend films adding GL, SA, and GL-SA as additives.

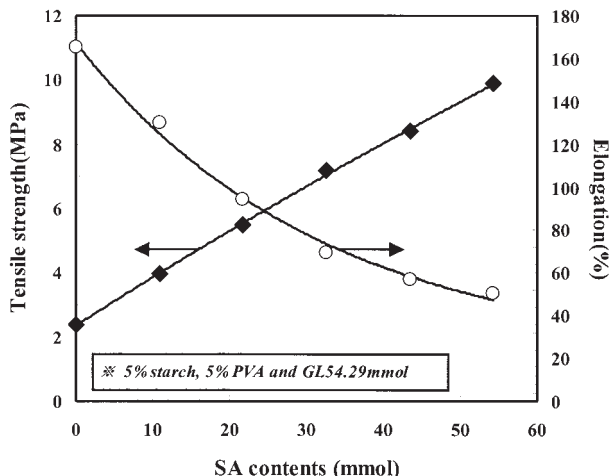


Figure 5 Tensile strength (TS) and elongation (%E) of starch/PVA blend films prepared with increasing SA content in SPGL5.

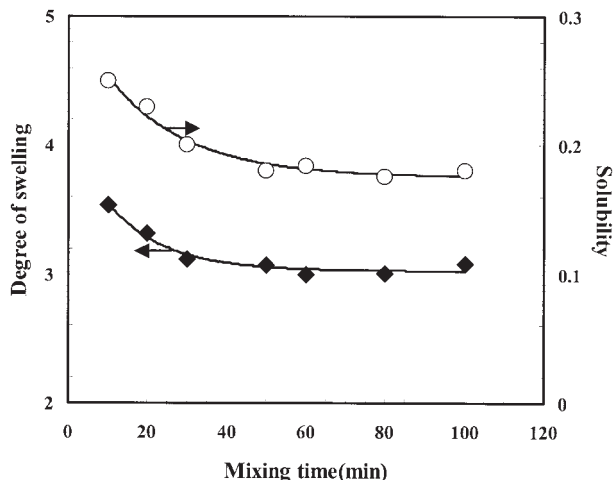


Figure 7 Degree of swelling (DS) and solubility (S) of starch/PVA blend film versus mixing time.

both GL and SA. The %E of the GL/SA-added films increased, whereas that of the SA-added film decreased, as the content of the additive increased. On the other hand, the TS of the GL/SA-added films decreased, whereas that of SA-added film decreased, as the additive content increased.

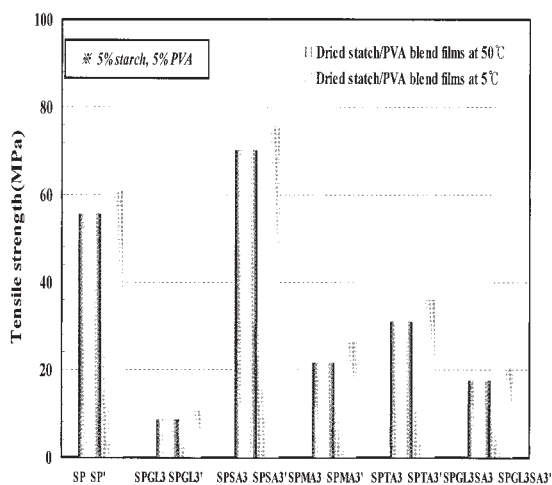
Figure 5 shows the TS and %E of films prepared with an increasing SA content in SPGL5. With SA increasing, the TS increased and the %E decreased. The results of the TS and %E of the GL/SA-added films revealed that the addition of the additives with hydroxyl and carboxyl groups as a functional group increased the flexibility and strength of the films.

Figure 6(a,b) shows the TS and %E results for

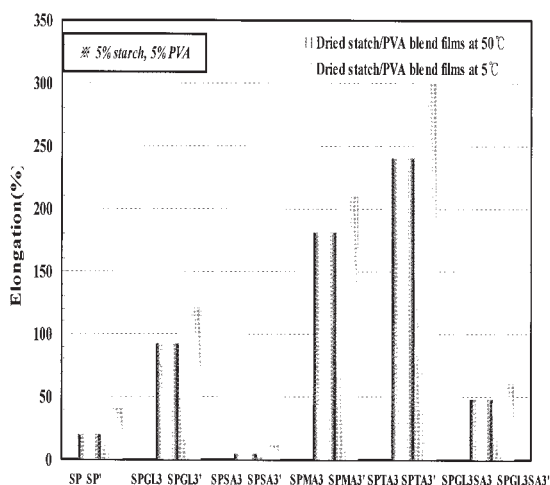
starch/PVA blend films after drying at 50°C and 5°C, respectively. Compared to those of the starch/PVA blend film to which the same number of moles of additives had been added, the TS and %E of the film dried at 5°C were higher than those of the film dried at 50°C. It was believed that this occurred because hydrogen bonding was activated at the lower temperature.

Degree of swelling and solubility of starch/PVA blend films

The degree of swelling (DS) and solubility (S) of the starch/PVA blend films without additives are shown in Figure 7. As the mixing time increased, the DS



(a)



(b)

Figure 6 Tensile strength (TS) and elongation (%E) of drying starch/PVA blend films at 50°C and 5°C where SP', SPGL3', SPSA3', SPMA3', SPTA3', and SPGL3SA3' are films dried at 5°C: (a) TS of drying starch/PVA blend films at 50°C and 5°C; (b) %E of drying starch/PVA blend films at 50°C and 5°C.

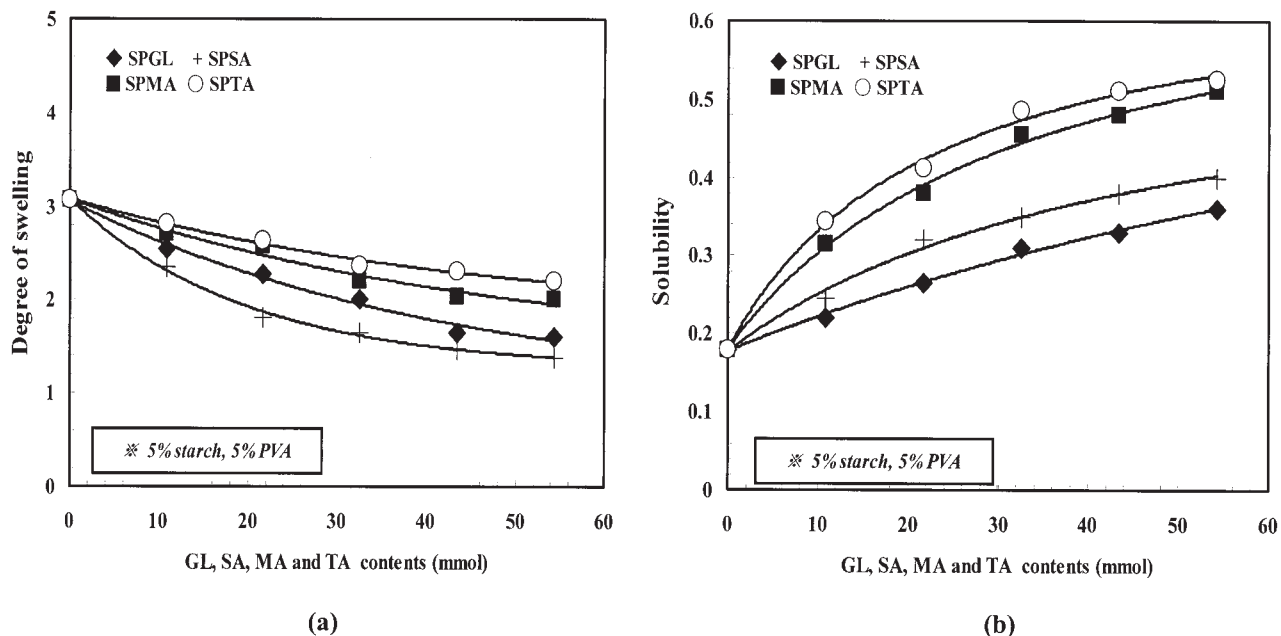


Figure 8 Degree of swelling (DS) and solubility (S) of starch/PVA blend films: (a) DS of starch/PVA blend films with GL, SA, MA, and TA as additives; (b) S of starch/PVA blend films with GL, SA, MA, and TA as additives.

decreased rapidly and equilibrated after 40 min. This phenomenon occurred because the free volume decreased as a result of hydrogen bonding occurring between starch and PVA. Also, on average, film was not formed until 20–40 min of mixing had elapsed. When the film was mixed for more than 40 min, the equilibrium DS and S were 3.07 and 0.18, respectively.

Figure 8(a) shows that the contents of additives GL, SA, MA, and TA increased, the DS of the starch/PVA blend films decreased slightly, and the S increased [Fig. 8(b)]. Starch/PVA blend films containing both added GL (containing hydroxyl groups) and added SA (containing carboxyl groups) showed lower DS and S values.

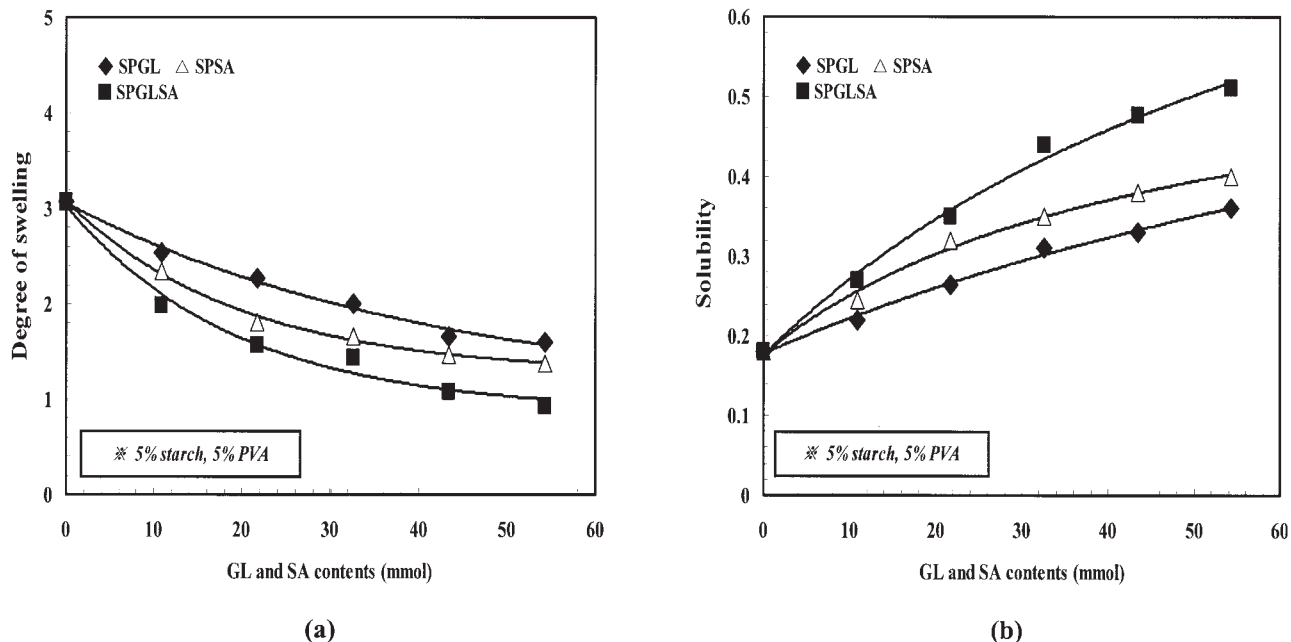


Figure 9 Degree of swelling (DS) and solubility (S) of starch/PVA blend films (SPGL, film with -added GL; SPSA, film with added SA; SPGLSA, film with added GL-SA): (a) DS of starch/PVA blend films with GL, SA, and GL-SA as additives; (b) S of starch/PVA blend films with GL, SA, and GL-SA as additives.

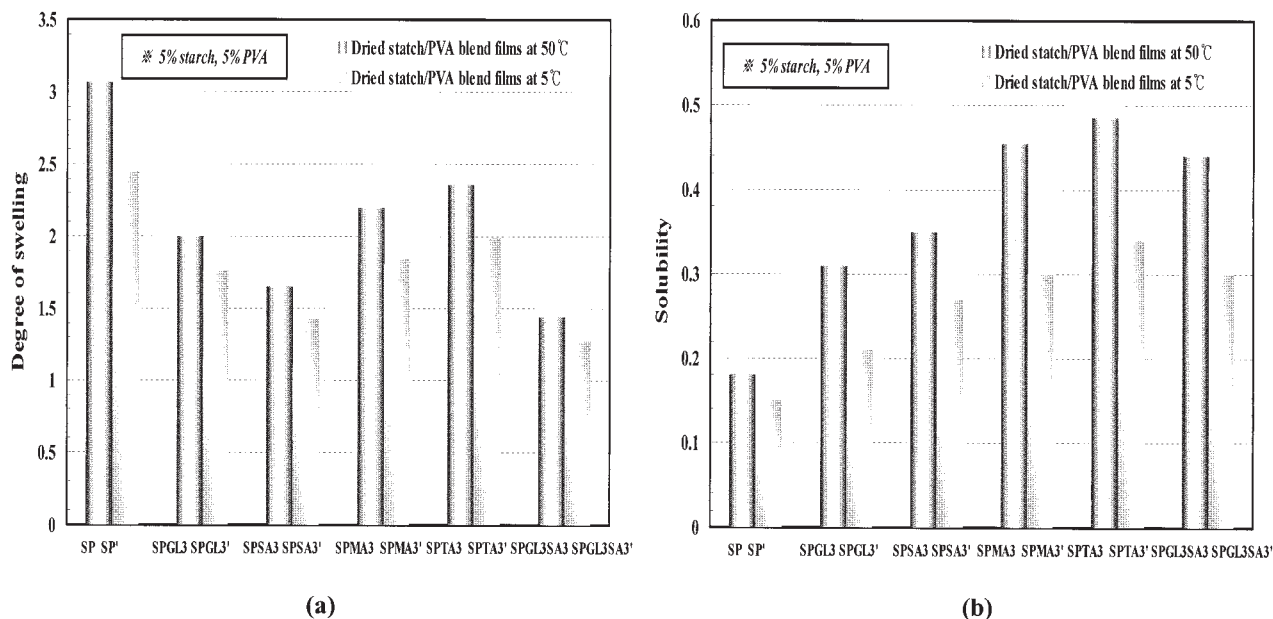


Figure 10 Degree of swelling (DS) and solubility (S) of drying starch/PVA blend films at 50°C and 5°C where SP', SPGL3', SPSA3', SPMA3', SPTA3', and SPGL3SA3' are films dried at 5°C: (a) DS of drying starch/PVA blend films at 50°C and 5°C; (b) S of drying starch/PVA blend films at 50°C and 5°C.

The DS and S values of the films to which MA with 2 carboxyl groups and 1 hydroxyl group and TA with 2 carboxyl and 2 hydroxyl groups were added as the functional group were comparatively higher. As the number of hydroxyl groups of the additive increased, the DS and S values increased. The DS value increased because MA and TA are easily soluble and combine with H₂O molecules. The increased value of S value can be attributed to the hydrophilism of PVA, MA, and TA.

Figure 9(a,b) shows the DS and S values, respectively, of films prepared by adding the same number of moles of GL and SA to the starch/PVA blend films. The DS of the film with both GL and SA added was lower than that of the films with either GL or SA added. However, the S value of GL/SA-added film was higher than that of the GL- and SA-added films. These results showed the same characteristics as those of the MA- and TA-added films.

The DS and S values of the starch/PVA blend films dried at 50°C and 5°C are shown in Figure 10(a,b). When the additives GL, SA, MA, and TA were added in the same number of moles, the films dried at 5°C showed low DS and S values. As discussed earlier, DS and S values were low because hydrogen bonding is activated at low temperatures.

CONCLUSIONS

Materials with hydroxyl and carboxyl groups as functional groups crosslinked between starch and PVA were used as additives of starch/PVA blend films. The

values of TS, %E, DS, and S were investigated. The results verified that hydroxyl and carboxyl groups as functional groups increased the flexibility and strength of the films.

The DS and S values of the MA- and TA-added films were higher than those of the GL- and SA-added films. This is because materials having both hydroxyl and carboxyl groups, that is, MA and TA, are highly hydrophilic.

The TS, %E, DS, and S were superior when the film was dried at 5°C rather than at 50°C. This was believed to be a result of the hydrogen bonding that occurred at the lower temperature.

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