

# Properties of Starch-Based Blend Films Using Citric Acid as Additive. II

Soon-Do Yoon,<sup>1</sup> Sung-Hyo Chough,<sup>2</sup> Hye-Ryoung Park<sup>2</sup>

<sup>1</sup>Department of Applied Chemical Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu, Kwangju 500-757, South Korea

<sup>2</sup>Faculty of Applied Chemical Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu, Kwangju 500-757, South Korea

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**ABSTRACT:** Starch/polyvinyl alcohol (PVA) blend films were prepared by using corn starch, polyvinyl alcohol (PVA), glycerol (GL), and citric acid (CA) as additives and glutaraldehyde (GLU) as crosslinking agent for the mixing process. The additives, drying temperature, and the influence of crosslinker of films on the properties of the films were investigated. The mechanical properties, tensile strength (TS), elongation at break (% E), degree of swelling (DS), and solubility (S) of starch/PVA blend film were examined adding GL and CA as additives. At all measurement results, except for DS, the film adding CA was better than GL because hydrogen bonding at the presence of CA with hydroxyl group and carboxyl group increased the inter/

intramolecular interaction between starch, PVA, and additives. CA improves the properties of starch/PVA blend film compared with GL. TS, % E, DS, and S of film adding GLU as crosslinking agent were examined. With increasing GLU contents, TS increases but % E, DS, and S value of GL-added and CA-added films decrease. When the film was dried at low temperature, the physical properties of the films were clearly improved because the hydrogen bonding was activated at low temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2554–2560, 2006

**Key words:** starch-based blend film; physical properties; citric acid

## INTRODUCTION

Plastics made from petroleum have been widely used throughout the world. With increased applications, the disposal of waste plastics has become a serious problem. Therefore, development of novel plastics that could be degraded by microorganisms in soil and seawater has recently been attracting much attention. Starch is renewable and biodegradable;<sup>1</sup> since the 1970s, starch was incorporated into synthesized polymer matrix, and in the past decades, several efforts have been made to convert starch into a thermoplastic material.<sup>2–9</sup>

The research showed that after starch was filled in or blended with synthesized polymer, the synthetic fraction from the oil source has no susceptibility to biodegradation.<sup>10–12</sup>

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).<sup>13,14</sup> Starch-based blends have enormous potential for biomedical and environmental fields because they are biodegradable

and inexpensive and are an almost unfailing source of raw material.<sup>15,16</sup>

Starch is a well-known polymer, naturally produced by plants in the form of granules (mainly from potatoes, corn, and rice). Starch granules vary from plant to plant, but they are in general composed of a linear polymer, amylose (in most cases up to about 20 wt % of the granule), and a branched polymer, amylopectin.<sup>17–19</sup>

The influence of starch sources, starch components, starch molecular mass, and plasticizer, such as water and polyols, has been studied to improve the mechanical properties of starch plastics. However, poor mechanical properties are still 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 in water resistance. After absorbing water, they are too weak to be used.<sup>20–22</sup>

Citric acid (CA) used as additive at this work appears in a natural way in foods like citrus fruits and pineapples where it is the main organic acid. CA is utilized as multi-functional food additive in the processes of producing different foods because it presents antibacterial and acidulant effect, reinforces the antioxidant action of other substances, and improves the flavors of juices, soft drinks, and syrups.

Correspondence to: H.-R. Park (hyrpark@empal.com).

The aim of this study was to make biodegradable films based on corn starch, polyvinyl alcohol (PVA), blends of GL, and CA as additives, and GLU as a crosslinking agent, to determine the mechanical properties, DS, and S of these films.

**EXPERIMENTAL**

**Materials**

Starch (cornstarch) was obtained from Doosan Corn Products Korea, Inc.(Korea). Polyvinyl alcohol (PVA), reagent grade glycerol (GL), and citric acid (CA) were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI). Glutaraldehyde (GLU) was purchased from Yakuri Pure Chemicals Co., Ltd (Kyoto, Japan). PVA was 99% hydrolyzed with an average molecular weight of 89,000–98,000. The water used to prepare starch/PVA blend films was redistilled after deionization.

**Preparation of starch/PVA blend films**

Starch/PVA blend films were prepared using a casting method. At first, PVA solution was prepared by dissolving PVA in hot water (90°C). Starch and additives (GL and CA) were mixed directly together with water using a Kitchenaid mixer for 10 min. Formulations contained 10, 20, 30, 40, and 50% GL and CA (starch/PVA weight bases). GLU was added 0.045, 0.09, 0.19, 0.375, and 0.75% (starch/PVA weight bases). PVA solution and mixed starch/additives were mixed at 90°C for 6 min. Then, the mixture was blended to form homogeneous gel-like solution with a mechanical stirrer (1000 rpm) at room temperature for 50 min. The total polymer amount was 100 g. Starch and PVA had the same mass ratio, and the content of additives was expressed as mass percent ratio of additives to total starch and PVA, respectively. The mixing composition is shown in Table I. Bubbles, the by-product of preparation, were removed by using an aspirator. The gel-like solution thus prepared was poured on a prewarmed (75°C) teflon mold (200 × 200 × 1 mm<sup>3</sup>). Water was evaporated from the molds in a ventilated oven at 50°C for 12 h and in cold lab chamber at 5°C for 72 h. Dried films were put in open polyethylene bags and stored at 25°C and at RH 50% for one week before they were measured.

**Mechanical properties of starch/PVA blend films**

Tensile strength (TS) and elongation (% E) were evaluated for each film using an Instron 6012 testing machine. Three dumbbell-shaped specimens (ASTM D 412) were cut from each film. Specimens had a width of 12 mm. Each piece was measured for thickness in three places along the test length, using a Mitutoyo

**TABLE I**  
**Composition of Starch/PVA Blend Films**

| Sample name | Starch (%) | PVA (%) | GL (wt %) | CA (wt %) | GLU (wt %) |
|-------------|------------|---------|-----------|-----------|------------|
| SP          | 5          | 5       | —         | —         | —          |
| SPGL10      | 5          | 5       | 10        | —         | —          |
| SPGL20      | 5          | 5       | 20        | —         | —          |
| SPGL30      | 5          | 5       | 30        | —         | —          |
| SPGL40      | 5          | 5       | 40        | —         | —          |
| SPGL50      | 5          | 5       | 50        | —         | —          |
| SPCA10      | 5          | 5       | —         | 10        | —          |
| SPCA20      | 5          | 5       | —         | 20        | —          |
| SPCA30      | 5          | 5       | —         | 30        | —          |
| SPCA40      | 5          | 5       | —         | 40        | —          |
| SPCA50      | 5          | 5       | —         | 50        | —          |
| SPGL40GLU1  | 5          | 5       | 40        | —         | 0.045      |
| SPGL40GLU2  | 5          | 5       | 40        | —         | 0.09       |
| SPGL40GLU3  | 5          | 5       | 40        | —         | 0.19       |
| SPGL40GLU4  | 5          | 5       | 40        | —         | 0.375      |
| SPGL40GLU5  | 5          | 5       | 40        | —         | 0.75       |
| SPCA40GLU1  | 5          | 5       | —         | 40        | 0.045      |
| SPCA40GLU2  | 5          | 5       | —         | 40        | 0.09       |
| SPCA40GLU3  | 5          | 5       | —         | 40        | 0.19       |
| SPCA40GLU4  | 5          | 5       | —         | 40        | 0.375      |
| SPCA40GLU5  | 5          | 5       | —         | 40        | 0.75       |

The total polymer amount was 100 g and water is added to 90% of total polymer.

(Japan). The specimens average thickness was about 0.15 mm. The gauge length and grip distance were both 59.0 mm. Crosshead speed was 20 mm/min and load cell was 25 kgf. The tests were carried out at 25°C and 50% RH in a constant temperature and humidity room.

**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). After the equilibrium (24 h), moisture on the surface of the film was removed, and the weight of the films was measured. The degree of swelling (DS) in starch/PVA blend film was calculated as:<sup>1</sup>

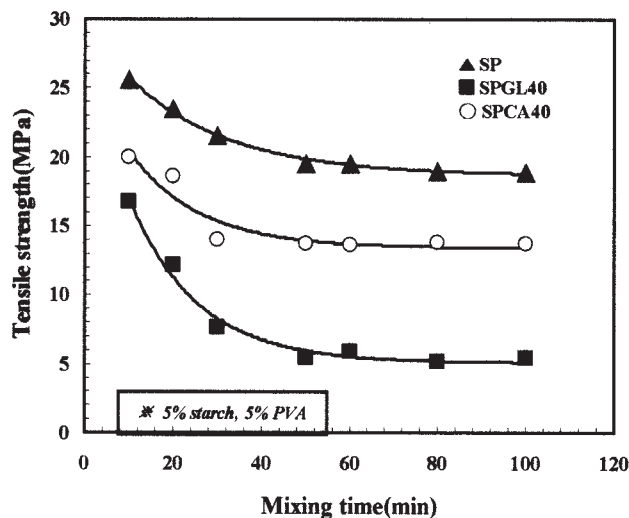
$$DS = (W_e - W_0)/W_0 \tag{1}$$

where  $W_e$  is the weight of starch/PVA blend film at the adsorbing equilibrium, and  $W_0$  is the first dry weight of starch/PVA blend film.

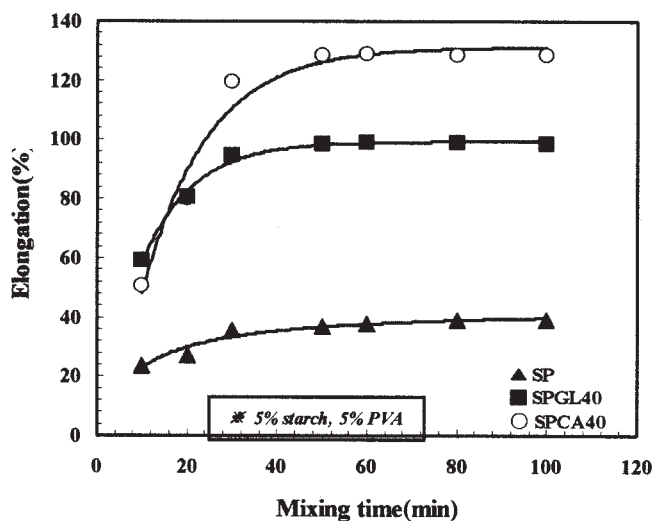
The swelled starch/PVA blend films were dried again for 24 h at 60°C, and its solubility (S) was calculated by the following eq. (2):

$$S = (W_0 - W_d)/W_0 \tag{2}$$

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



(a)



(b)

**Figure 1** Tensile strength (TS) and elongation(% E) of starch/PVA blend film versus mixing time. (a) Tensile strength (TS) of starch/PVA film without additives, GL-added film, and CA-added film and (b) Elongation (% E) of starch/PVA blend film without additives, GL-added film, and CA-added film.

## RESULTS AND DISCUSSION

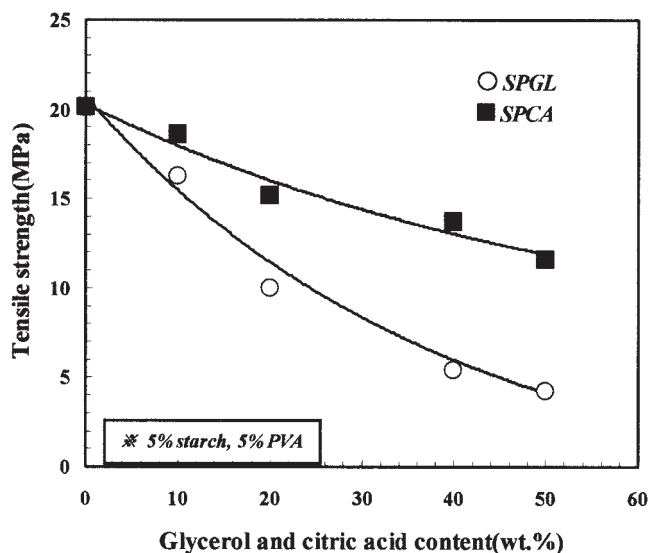
### Mechanical properties of starch/PVA blend films

Figures 1(a) and 1(b) show TS and % E of film using starch and PVA without additives, GL-added, and CA-added film. Starch and PVA contents are the same amount (wt %) containing about 5% total polymer. In SP film, TS and % E were equilibrated over 40 min, and the equilibrium of TS and % E were 20.12 MPa and 36.98%. Also, in SPGL40 and SPCA40 films, TS and % E were equilibrated at 40 min. By this result,

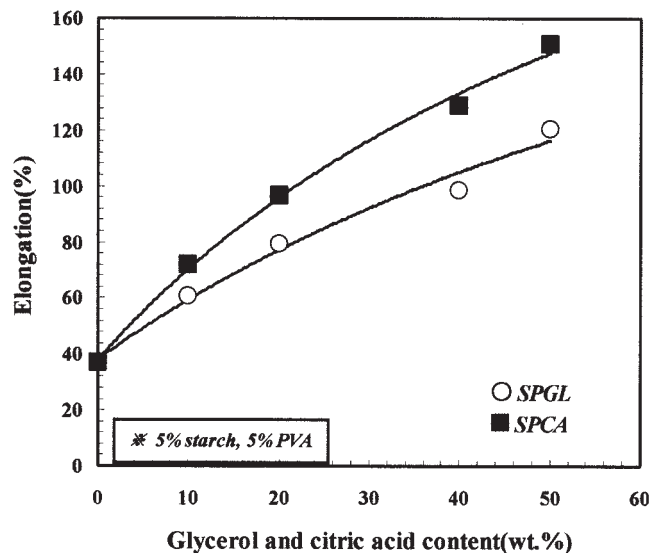
starch/PVA blend films added GL and CA were prepared by mixing process.

Figures 2 and 3 present the result of TS and % E on films, to which GL and CA are added with increasing contents of 10, 20, 30, 40, and 50 wt %. As the wt % of GL and CA increased from 10 to 50 wt %, TS decreased while % E increased. And we observed that TS and % E of films with the addition of CA was higher than the plasticizer using GL.

Structurally, GL has 3 hydroxyl groups and CA has 1 hydroxyl group and 3 carboxyl groups.



**Figure 2** Tensile strength (TS) of starch/PVA blend films adding glycerol (GL) and citric acid (CA) as additives.



**Figure 3** Elongation (% E) of starch/PVA blend films adding glycerol (GL) and citric acid (CA) as additives.

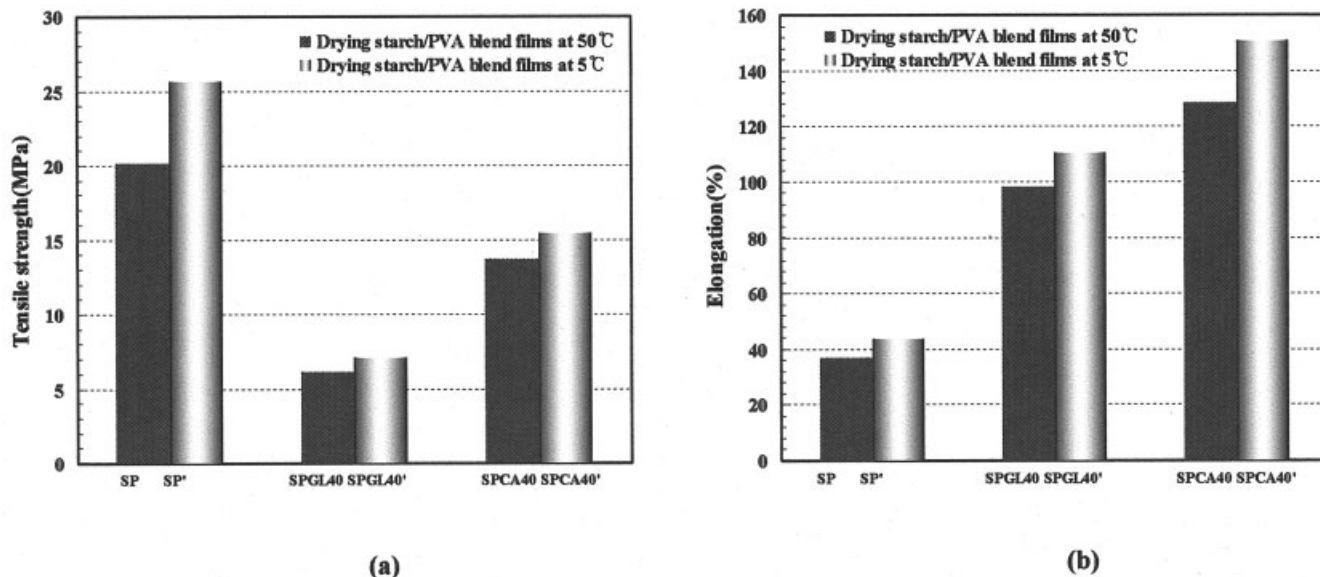


Figure 4 Tensile strength (TS) and elongation (% E) of drying starch/PVA blend films at 50 and 5°C. (a) Tensile strength (TS) of drying starch/PVA blend films at 50 and 5°C and (b) Elongation (%) of drying starch/PVA blend films at 50 and 5°C, where SP', SPGL40', and SPCA40' are films dried at 5°C.

As shown in Figures 2 and 3, we observed that the starch/PVA blend film-added CA composed of 1 hydroxyl group, and 3 carboxyl groups showed the best performance in TS and % E.

These films are synthesized by hydrogen bonding between starch, PVA, and additives. We found that CA with hydroxyl group and carboxyl group is stronger than GL with only hydroxyl group in hydrogen bonding between starch PVA and additive molecules.

Figures 4(a) and 4(b) show the results of TS and % E drying starch/PVA blend film at 50°C and 5°C.

Compared with starch/PVA blend film to which additive of the same amount was added, the results were high TS and % E of drying film at 5°C (Fig. 4). TS and % E of the film dried at 5°C were better than those dried at 50°C because hydrogen bonding was activated at low temperature.

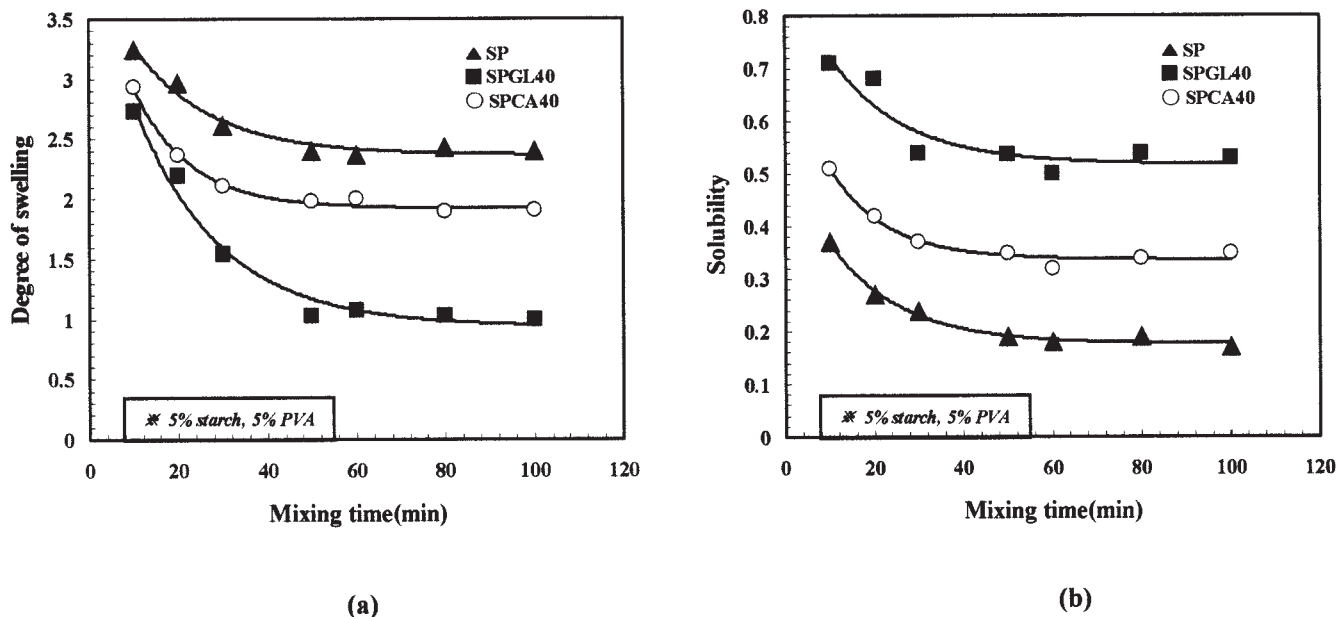


Figure 5 Degree of swelling (DS) and solubility (S) of starch/PVA blend film versus mixing time. (a) Degree of swelling (DS) of starch/PVA blend film adding with/without additive and (b) Solubility (S) of starch/PVA blend film adding with/without additive.

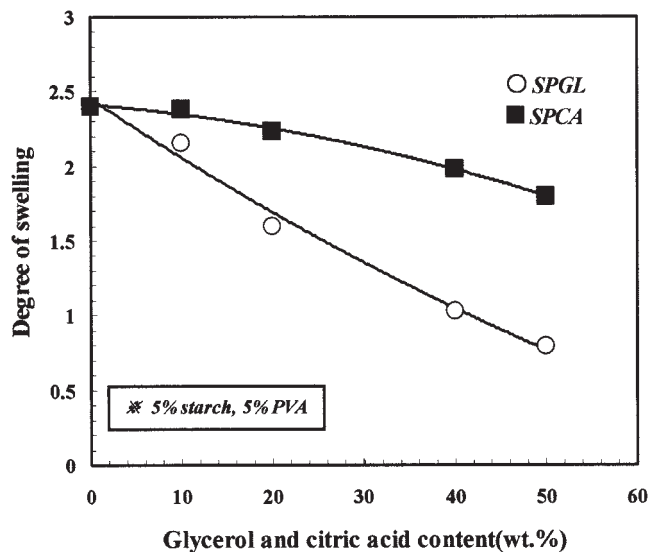


Figure 6 Degree of swelling (DS) of starch/PVA blend films adding glycerol (GL) and citric acid (CA) as additives.

#### Degree of swelling and solubility of starch/PVA blend films

DS and S of the film that used starch and PVA without additives, GL-added, and CA-added films are shown in Figures 6(a) and 6(b).

In conformity with the mixing time, DS was decreased rapidly and equilibrated over 40 min. This phenomenon took place because free volume was decreased in combination with the hydrogen bonding between starch, PVA, and additives.

Also, the mean film was not formed until the mixing time of 20–40 min was reached. When the film is mixed over 40 min, equilibrium DS value of SP, SPGL40, and SPCA40 are 2.4, 1.09, and 1.98, and equilibrium S value of SP, SPGL40, and SPCA40 are 0.19, 0.537, and 0.35, respectively.

In Figure 6, with the increase in the content of GL and CA as additives, DS of starch/PVA blend films decreased slightly and S increased (Fig. 7).

GL-added Starch/PVA blend film showed a low DS value, but it had a high S value because degree of combination related to hydrogen bonding on GL-added film is weaker than CA-added film.

CA-added Starch/PVA blend film showed a higher DS value and a lower S value than the GL-added films. These findings led us to discover that CA was crosslinked by hydrogen bonding between starch and PVA molecule.

DS and S value of drying starch/PVA blend films at 50 and 5°C are shown in Table II. When the same amount of GL and CA as additives was added, drying films at 50°C resulted in higher swelling and solubility in all samples compared with films dried at 5°C.

As in the results mentioned earlier, TS and % E, it was found that DS and S value were low because

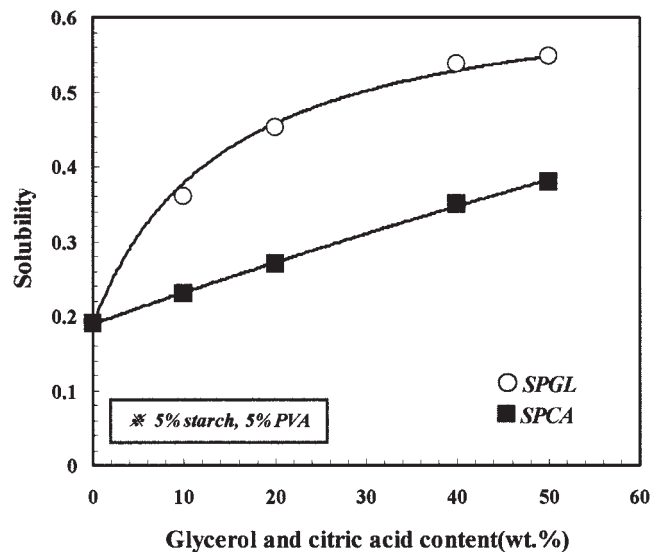


Figure 7 Solubility (S) of starch/PVA blend films adding glycerol (GL) and citric acid (CA) as additives.

hydrogen bonding was activated at low temperature.

#### Effect of glutaraldehyde (GLU) as crosslinking agent

Figures 8(a) and 8(b) show TS and % E of starch/PVA blend film on adding GLU as crosslinking agent. Effect of crosslinking of GLU was reported by Parra et al.<sup>23</sup>

In the report of Parra et al., the mechanical properties and water vapor transmission (WVT) were investigated adding GLU as crosslinking agent on the film. The result reports that with increasing GLU content, TS increased and % E and WVT decreased.

On this work, the mechanical properties, DS, and S adding GLU in SPGL40 and SPCA40 were investigated.

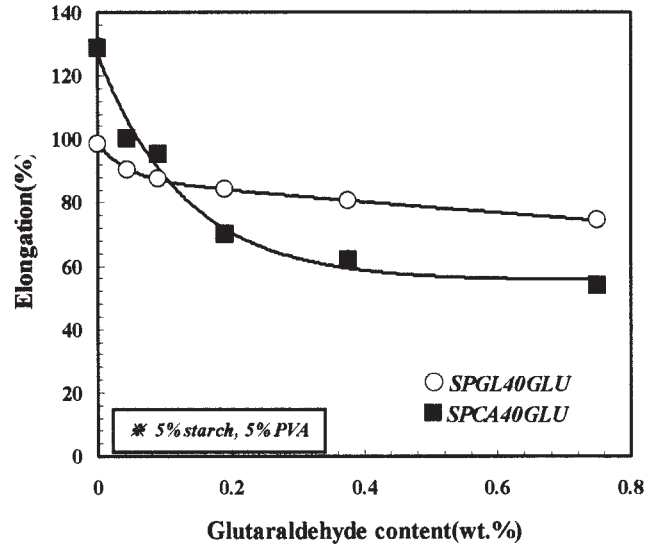
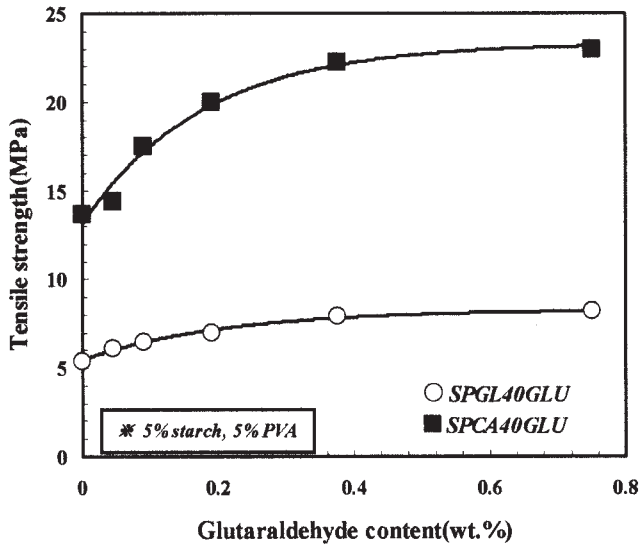
Figures 8(a) and 8(b) show TS and % E of film added with increasing contents of GLU in SPGL40 and SPCA40. As the wt % of GLU increased from 0.045 to 0.75%, TS increases while % E decreases. It was veri-

TABLE II  
Degree of Swelling (DS) and Solubility (S) of Drying Starch/PVA Blend Films at 50 and 5°C

| Sample name | Degree of swelling (DS) | Solubility (s) |
|-------------|-------------------------|----------------|
| SP          | 2.4                     | 0.19           |
| SP'         | 1.97                    | 0.15           |
| SPGL40      | 1.03                    | 0.5            |
| SPGL40'     | 0.96                    | 0.39           |
| SPCA40      | 1.98                    | 0.35           |
| SPCA40'     | 1.41                    | 0.14           |

SP', SPGL40', SPSO40', and SPCA40' are films dried at 5°C.





(a)

(b)

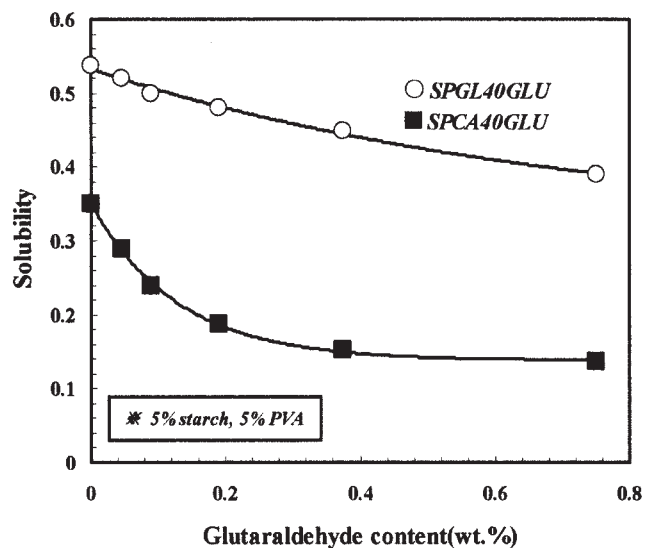
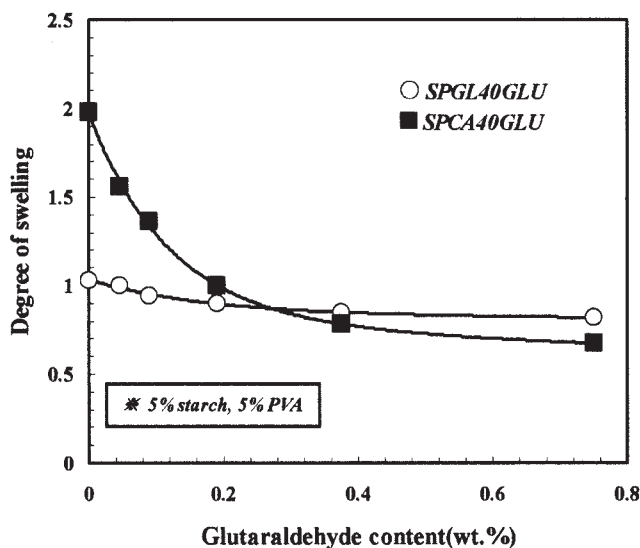
**Figure 8** Tensile strength (TS) and elongation (%) of GL-added film and CA-added film adding glutaraldehyde (GLU) as crosslinker. (a) Tensile strength (TS) of GL-added film and CA-added film adding glutaraldehyde (GLU) as crosslinker and (b) Elongation (%) of GL-added film and CA-added film with glutaraldehyde (GLU) as crosslinker.

fied that sudden change of TS and % E happened in GLU-added SPCA40 film. This phenomenon took place because of superior reactivity of CA and GLU.

Figures 9(a) and 9(b) show DS and S value of film-added GLU. With increasing GLU contents, DS and S value of GL-added and CA-added films decrease.

**CONCLUSIONS**

Starch/PVA blend films were prepared by a mixing process. The results of TS, % E, DS, and S of synthesized films adding GL and CA as additives demonstrated that the film gained superior pro-



(a)

(b)

**Figure 9** Degree of swelling (DS) and solubility (S) of GL-added film and CA-added film adding glutaraldehyde (GLU) as crosslinker. (a) Degree of swelling (DS) of GL-added film and CA-added film adding glutaraldehyde (GLU) as crosslinker and (b) Solubility (S) of GL-added film and CA-added film adding glutaraldehyde (GLU) as crosslinker.

properties with the addition of CA. However, DS value of the CA-added film was higher than GL-added films.

TS, % E, DS, and S values were superior when the film was dried at 5°C than at 50°C because of the hydrogen bonding occurring at low temperature.

The film, added with CA containing both hydroxyl and carboxyl groups, was superior in its properties compared with the GL-added film that had hydroxyl group only.

As GLU contents increase, we were confirmed that DS and S value decrease. The effect of crosslinking is excellent with using small amount because CA was reacted predominantly with GLU. This study demonstrated that CA is useful and harmless to the human body. So, it may be used as plasticizer in place of the widely used GL.

## References

1. Lenz, R. W. *Adv Polym Sci* 1993, 107, 1.
2. Spence, K. E.; Jane, J.; Pometto, A. L. *J Environ Polym Degrad* 1995, 3, 69.
3. Gomes, M. E.; Ribeiro, A. S.; Malafaya, P. B.; Reis, R. L.; Cunha, A. M. *Biomaterials* 2001, 22, 883.
4. Kirby, A. R.; Clark, S. A.; Parker, R.; Smith, A. C. *J Mater Sci* 1993, 28, 5937.
5. Ollett, A. L.; Parker, R.; Smith, A. C. *J Mater Sci* 1991, 26, 1351.
6. Otey, F. H.; Westhoff, R. P.; Doane, W. M. *Ind Eng Chem Prod Res Dev* 1980, 19, 592.
7. Sen, A.; Bhattacharya, M. *Polymer* 2000, 41, 9177.
8. van Soest, J. J. G.; Borger, D. B. *J Appl Polym Sci* 1997, 64, 631.
9. Glenn, G. M.; Hsu, J. *Ind Crop Prod* 1997, 7, 37.
10. Arvanitoyannis, I.; Biliaderis, C. G.; Ogawa, H.; Kawasaki, N. *Carb Polym* 1998, 36, 89.
11. Klemchuk, P. P. *Polym Degrad Stab* 1990, 27, 183.
12. Psomiadou, E.; Arvanitoyannis, I.; Biliaderis, C. G.; Ogawa, H.; Kawasaki, N. *Carb Polym* 1997, 33, 227.
13. Funke, U.; Bergthaller, W.; Lindhauer, M. G. *Polym Degrad Stab* 1998, 59, 293.
14. Ishigaki, T.; Kawagoshi, Y.; Ike, M.; Fujita, M. *World J Microbiol Biotechnol* 1999, 15, 321.
15. Araujo, M. A.; Cunha, A. M.; Mota, M. *Biomaterials* 2004, 25, 2687.
16. Reis, R. L.; Cunha, A. M. *J Mater Sci: Mater Med* 1995, 6, 78.
17. Briassoulis, D. *J Polym Environ* 2004, 12, 65.
18. Chandra, R.; Rustgi, R. *Prog Polym Sci* 1998, 23, 1273.
19. Lawton, J. W. *Carb Polym* 1996, 29, 203.
20. Hulleman, S. H. D.; Janssen, F. H. P.; Feil, H. *Polymer* 1998, 39, 2043.
21. Lourdin, D.; Valle, G. D.; Colonna, P. *Carb Polym* 1995, 27, 261.
22. van Soest, J. J. G.; Benes, K.; de Wit, D. *Polymer* 1996, 37, 3543.
23. Parra, D. F.; Tadini, C. C.; Ponce, P.; Lugão, A. B. *Carb Polym* 2004, 58, 475.