Preparation of Resistant Starch/Poly(vinyl alcohol) Blend Films with Added Plasticizer and Crosslinking Agents

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ABSTRACT: We report on the physical properties of films synthesized with native corn starch (NCS) and resistant starch (RS4) prepared with NCS. NCS and RS4/poly(vinyl alcohol) (PVA) blend films were synthesized with a mixing process and casting method. Glycerol (GL) and citric acid (CA) were used as additives. Glutaraldehyde (GLU) was used as a crosslinking agent of the films. RS4 was synthesized with sodium trimetaphosphate and sodium tripolyphosphate as a crosslinker. Then, the RS4 thus synthesized was confirmed by the pancreatin–gravimetry method, swelling power, differential scanning calorimetry, and X-ray diffraction. The tensile strength, elongation, swelling behavior, and solubility of the films were measured. The results of the measurements indicated that the RS4-added film was better than the NCS-added film. In particular, the RS4/PVA blend film with CA as an additive showed physical properties superior to those of the other films. Also, the physical properties with GLU added as a crosslinking agent to the films were investigated. With increasing GLU contents, the tensile strength increased but the elongation, swelling behavior, and solubility values of the GL-added and CA-added films decreased. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2485–2493, 2007

Key words: films; mechanical properties; resistant starch; crosslinking

INTRODUCTION

Recently, with increasing concern about the environmental pollution resulting from nondegradable plastic materials, much research to develop environmentally friendly biodegradable plastic materials as replacements for synthetic polymeric materials has been carried out. The development of environmentally friendly polymeric materials can be divided into two categories on the basis of their raw materials: degradable synthetic polymers and renewable natural polymers. Among these, starch, a biodegradable natural polymer that exists abundantly in nature, is very cheap and is mainly composed of two homopolymers of D-glucose, amylose and amylopectin. Amylose is almost a linear polymer with α-D-(1/4) glycosidic linkages, whereas amylopectin is a highly branched polymer that also contains α-D-(1/6) glycosidic linkages at the branching points in addition to α-D-(1/4) glycosidic linkages.[1,2] The molecular weights of amylose and amylopectin have been estimated to be $\sim 10^5$ and $\sim 10^7$, respectively.[3]

Biodegradable starch-based plastics such as starch/cellulose and starch/poly(vinyl alcohol) (PVA) have recently been investigated for their great potential marketability in agricultural foils, garbage and composting bags, and food packaging, in the fast food industry, and in biomedical fields.[4–7]

PVA is a versatile polymer with many industrial applications, and it may be the only synthesized polymer whose backbone is mainly composed of C—C bonds that is absolutely biodegradable.[8] PVA is the most readily biodegradable of vinyl polymers. It is readily degraded in wastewater-activated sludge. The microbial degradation of PVA has been studied, as well as its enzymatic degradation by secondary alcohol peroxidases isolated from soil bacteria of the *Pseudomonas* strain.[9–11] The initial biodegradation step involves the enzymatic oxidation of the secondary alcohol groups in PVA to ketone groups. Hydrolysis of the ketone groups results in chain cleavage. Other bacterial strains, such as *Flavobacterium* and *Acinetiobacter*,[12] are also effective in degrading PVA.

In most studies, films have been synthesized from corn starch,[13,14] wheat starch,[15,16] rice starch,[17] potato starch,[18] and cassava starch[19,20] and the investigations of their mechanical properties have revealed that the amylose content of starch affects the properties of the films. Starch-based films have an effect on the physical properties because of the linear structure of amylose and the branch structure of amylopectin of starch. In particular, these films are soluble in water

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because of the branch structure of amylopectin. Thus, many studies are being conducted on starch-based films based on chemically modified starch.[21]

In this work, films were synthesized with resistant starch (RS4) and native corn starch (NCS), and their physical properties were investigated. The films were prepared by a casting method.

Starch/PVA blend films synthesized with glycerol (GL) and citric acid (CA) as additives and glutaraldehyde (GLU) as a crosslinking agent were investigated for their mechanical properties (tensile strength and elongation) along with the relative humidity, swelling behavior, and solubility.

EXPERIMENTAL

Materials

Starch (NCS) was obtained from Doosan Corn Products Korea, Inc. (Gangnam, Seoul, Korea). PVA, reagent-grade GL, CA, sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), and sodium sulfate were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI). GLU was purchased from Yakuri Pure Chemicals Co., Ltd. (Kyoto, Japan). PVA was 99% hydrolyzed with a weight-average molecular weight of 89,000–98,000. The water used to prepare the starch/PVA blend films was redistilled after deionization.

Preparation and determination of RS4

Crosslinked RS4 was prepared with the methods of Seib and coworkers.[22,23] NCS (50 g, dry basis), distilled water (70 mL), and sodium sulfate (5.0 g, 10%, starch basis) were placed in a beaker and stirred for 30 min, and then STMP (5.99 g, 11.98%, starch basis) and STPP (0.01 g, 0.02%, starch basis) were added with stirring for 30 min. The mixture was adjusted to pH 11.5 by the addition of a 1.0*M* sodium hydroxide solution. The slurry was stirred continuously, warmed to 45°C, and reacted at 45°C over 3 h. After the reaction period, the slurry was adjusted to pH 6.5 by the addition of 1.0*M* hydrochloric acid, and the starch was collected by centrifugation, washed with water (five times), dried at 40°C (oven), and passed through a 100-mesh sieve.

Synthesized RS4 was measured by the pancreatin–gravimetry method, swelling power, differential scanning calorimetry (DSC; DSC-50, Shimazu, Kyoto, Japan), and X-ray diffraction (XRD; D/MAX Uitima III, Rigaku, Tokyo, Japan).[23]

Starch/PVA blend film preparation

Films were obtained with the casting method.[24] First, a PVA solution was prepared through the dissolution of PVA in hot water (98°C). NCS, RS4, and additives (GL and CA) were mixed together with water with a Kitchen Aid mixer (Anymix, Hyunwoostar, Seoul, Korea) for 10 min. The formulations contained 10, 20, 30, 40, or 50 wt % GL and CA (starch and PVA weight bases). GLU as a crosslinking agent was added in concentrations of 0.045, 0.09, 0.19, 0.375, and 0.75 wt % (starch and PVA weight bases). The PVA solution and mixed NCS or RS4/additives were kept at 98°C for 10 min. Then, the mixture was blended to form a homogeneous gel-like solution with a mechanical stirrer (1500 rpm) at room temperature for 50 min. The total polymer amount was 100 g. NCS, RS4, and PVA had the same mass ratio, and the content of the additives was expressed as the mass percentage ratio of additives to the total NCS, RS4, and PVA weight. 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 into a prewarmed (75°C) Teflon mold ($200 \times 200 \times 2$ mm^3). Water evaporated from the molds in a ventilated oven at 50°C for 12 h. The dried films were put in open polyethylene bags and stored at 25°C and at 52% relative humidity for 1 week before the measurements were performed.

Mechanical properties of the films

The tensile strength and elongation were evaluated for each film with an Instron 6012 testing machine. Five dumbbell shaped specimens (ASTM D 412) were cut from each film. Each specimen had a width of 12 mm. The average specimen thickness was about 0.2 mm. The thickness of the films was measured with a mechanical scanner (digital thickness gauge, Mitutoyo, Tokyo, Japan) at 15 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. The crosshead speed was 20 mm/min, and the load cell was 250 kgf.

The tensile strength and elongation of each film were evaluated after storage at different relative humidities for 7 days. Constant relative humidities were obtained with saturated salt solutions of Na_2SO_4 (~ 93% relative humidity), $Ca(NO_3)_2 \cdot 4H_2O$ (~ 51% relative humidity), $CaCl_2$ (~ 33% relative humidity), and LiCl (~ 15% relative humidity). The films were stored in desiccator chambers over the salt solutions at 25°C. The tests were carried out at 25°C and 54% relative humidity in a constant-temperature and -humidity room.

Swelling behavior and solubility of the films

Dried starch/PVA blend films were immersed in distilled water at room temperature (25°C). After the equilibrium was reached (24 h), moisture on the surface of the films was removed, and the weight of the

TABLE I
Compositions of the NCS and RS4/PVA Blend Films

Sample	NCS (%)	RS4 (%)	PVA (%)	GL (wt %)	CA (wt %)	GLU (wt %)
NCSP	5	—	5	—	—	—
RS4P	—	5	5	—	—	—
NCSPGL10	5	—	5	10	—	—
NCSPGL20	5	—	5	20	—	—
NCSPGL30	5	—	5	30	—	—
NCSPGL40	5	—	5	40	—	—
NCSPGL50	5	—	5	50	—	—
RS4PGL10	—	5	5	10	—	—
RS4PGL20	—	5	5	20	—	—
RS4PGL30	—	5	5	30	—	—
RS4PGL40	—	5	5	40	—	—
RS4PGL50	—	5	5	50	—	—
NCSPCA10	5	—	5	—	10	—
NCSPCA20	5	—	5	—	20	—
NCSPCA30	5	—	5	—	30	—
NCSPCA40	5	—	5	—	40	—
NCSPCA50	5	—	5	—	50	—
RS4PCA10	—	5	5	—	10	—
RS4PCA20	—	5	5	—	20	—
RS4PCA30	—	5	5	—	30	—
RS4PCA40	—	5	5	—	40	—
RS4PCA50	—	5	5	—	50	—
NCSPGL40G	5	—	5	40	—	0.045–0.75
RS4PGL40G	—	5	5	40	—	0.045–0.75
NCSPCA40G	5	—	5	—	40	0.045–0.75
RS4PCA40G	—	5	5	—	40	0.045–0.75

The total amount of the polymer was 100 g, and water was added to a concentration of 90% with respect to the total polymer.

films was measured. The swelling behavior in the starch/PVA blend films was calculated as follows:

$$\text{Swelling behavior} = (W_e - W_0)/W_0 \tag{1}$$

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

The swollen starch/PVA blend films were dried again for 24 h at 60°C. Their solubility was calculated with the following equation:

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

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

RESULTS AND DISCUSSION

Determination of RS4

RS4 was synthesized, and the characterization of the resistant starch (RS) level was verified with the pancreatin–gravimetry method, swelling power, DSC, and XRD, as reported by Mun and Shin.[23]

The RS level of chemically modified corn starch was about 12% when measured by the pancreatin–gravimetry method.

The crosslinkage was molded by covalent bonds between starch molecules. The structure of RS4 includes structures of modified starches obtained by chemical treatments such as distarch phosphate ester (Fig. 1).[25]

Figure 2 shows the results of the XRD analysis of NCS and RS4. NCS and RS4 exhibited peaks at 2θ

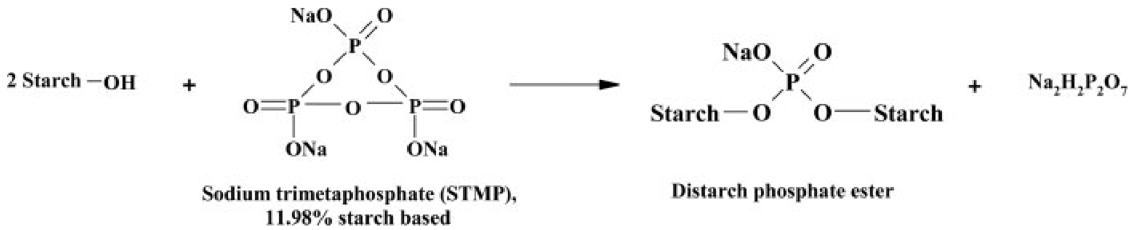


Figure 1 Synthesis of crossbonded starch (RS4).

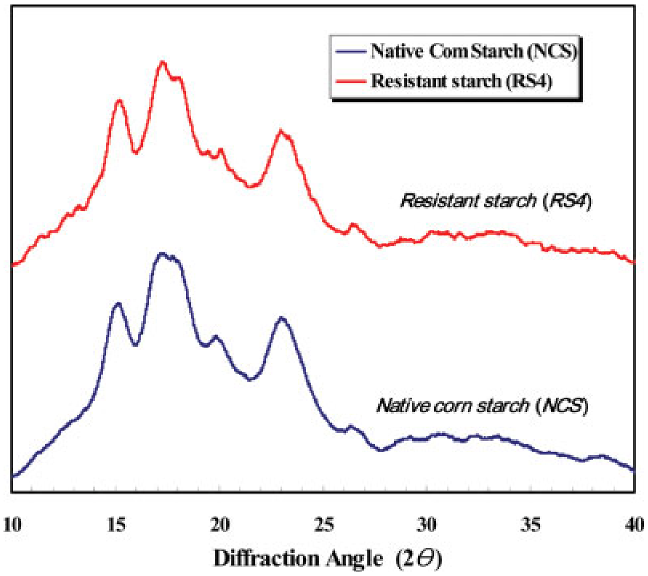


Figure 2 X-ray diffractograms of NCS and RS4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

values of 15, 17, 20, and 23° because only crosslinkage occurred without a change in the starch structure.[26]

Figure 3 presents the results for the swelling power of NCS and RS4. As the temperature increased from 25 to 95°C, the swelling power of NCS increased faster than that of RS4 and NCS.

The gelatinization properties of NCS and RS4 were analyzed with the method of Donovan.[27] Figure 4 shows the DSC curves of NCS and RS4. From the results, we determined the onset gelatinization temperature, peak temperature, and conclusion temperature. All samples had one endothermic curve. The onset temperature, peak temperature, and conclusion temperature of NCS were 49.6, 63.8, and 76.4°C, respectively. Also, those of RS4 were 96.9, 114.2, and 127.3°C, respectively. The gelatinization temperature of RS4 was about twice as high as that of NCS. This result agreed with previous results reported by Mun and Shin.[23]

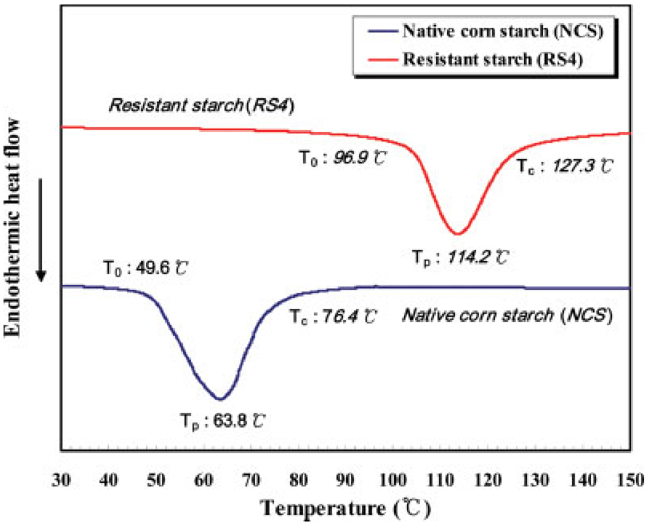


Figure 3 DSC thermograms of glutinous NCS and RS4. T_0, T_p, and T_c are the onset, peak, and conclusion gelatinization temperatures, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

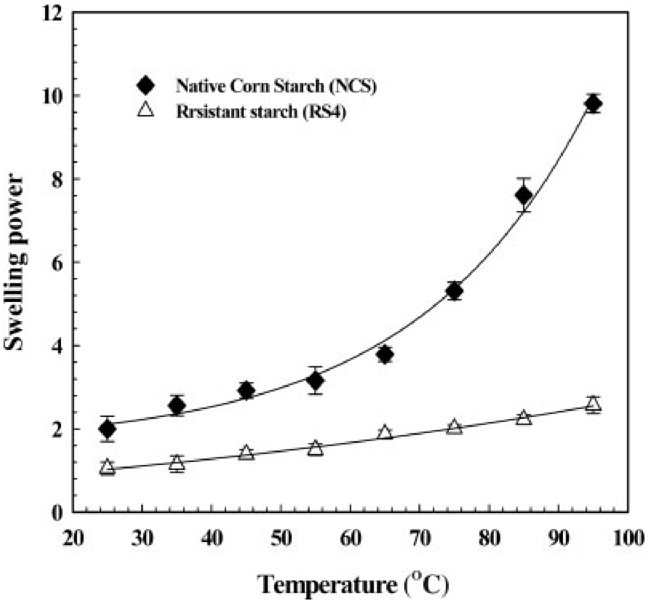


Figure 4 Swelling power of NCS and RS4.

Mechanical properties of the films

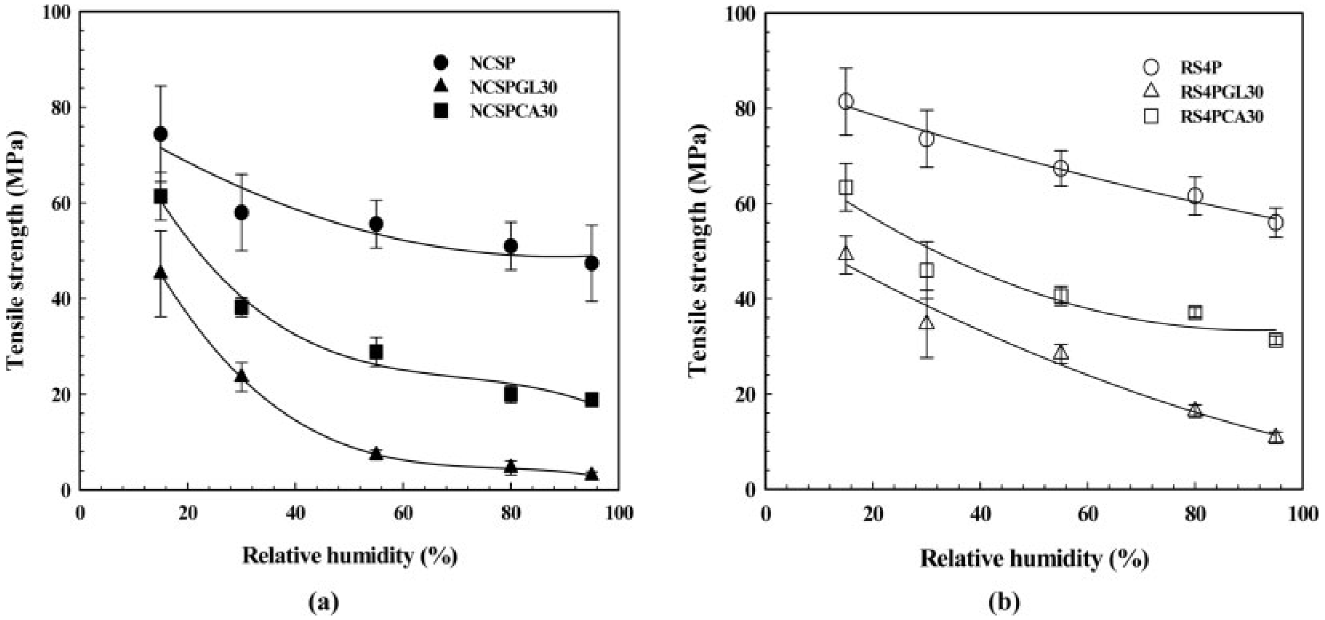
Films were prepared with the method developed in our previous work.[24]

Figures 5 and 6 show the effects of the tensile strength and elongation with the relative humidity on films containing NCS or RS4 in which GL and CA were used as additives.

The tensile strength of the films decreased because the relative humidity increased when a plasticizer was added to the polymers.

Figure 5(a,b) shows that there was a large decrease in the tensile strength in all the films tested as the storage relative humidity increased from 15 to 33%. In particular, for films with additives, the tensile strength was exponentially changed. There was a large decrease in the tensile strength between 15 and 33% relative humidity, probably because water was absorbed by GL and CA as additives through solubility. The tensile strength change was smaller in films with NCS rather than RS4.

Figure 6(a,b) shows the change in the elongation with the relative humidity. The elongation of the films increased as the relative humidity increased in



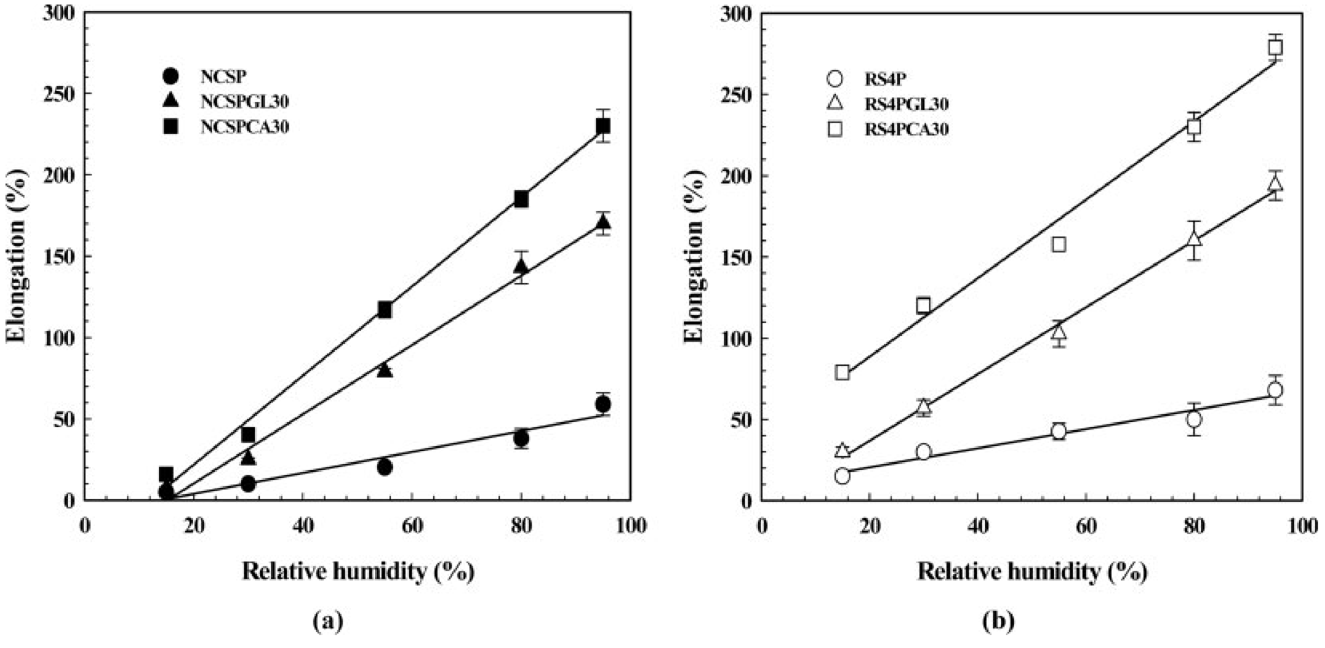
(a)

(b)

Figure 5 Tensile strength of starch/PVA blend films stored for 7 days at different relative humidities: (a) NCS/PVA blend films with or without additives and (b) RS4/PVA blend films with or without additives.

the tested films. Starch is hygroscopic and will gain or lose water to achieve an equilibrium with the ambient air. Water is also a plasticizer for starches. When starch-based films are placed in different relative humidities, the films will either lose or gain water to be in equilibrium with the air in the humidity chamber. Because water is a plasticizer, changing the water content in the film will change the properties of the film. Increasing the plasticizer levels in the synthetic plastic has been shown to increase elongation. This is consistent with other work done with starch-based films and is consistent with systems in which the plasticizer is increasing.

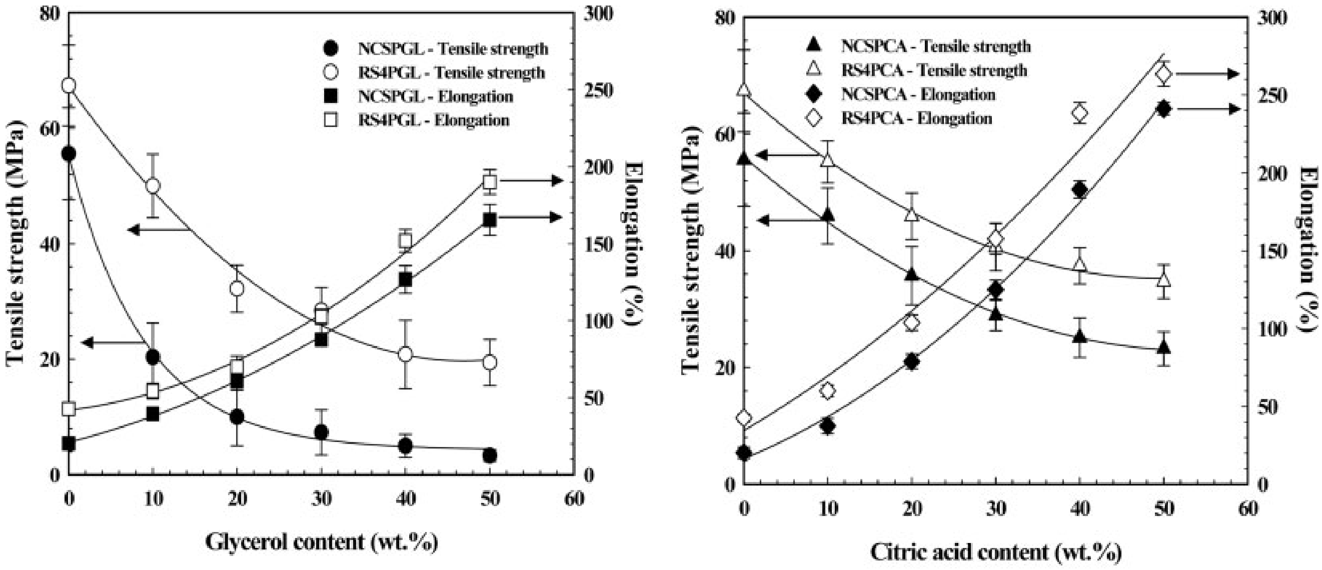
The slopes of the regression lines for films using RS4 seemed parallel to one another and different from those of the other films tested. The slopes for RS4P, RS4PGL30, and RS4PCA30 were 0.5887, 2.0528, and 2.4157, respectively, whereas the slopes



(a)

(b)

Figure 6 Elongation of starch/PVA blend films stored for 7 days at different relative humidities: (a) NCS/PVA blend films with or without additives and (b) RS4/PVA blend films with or without additives.

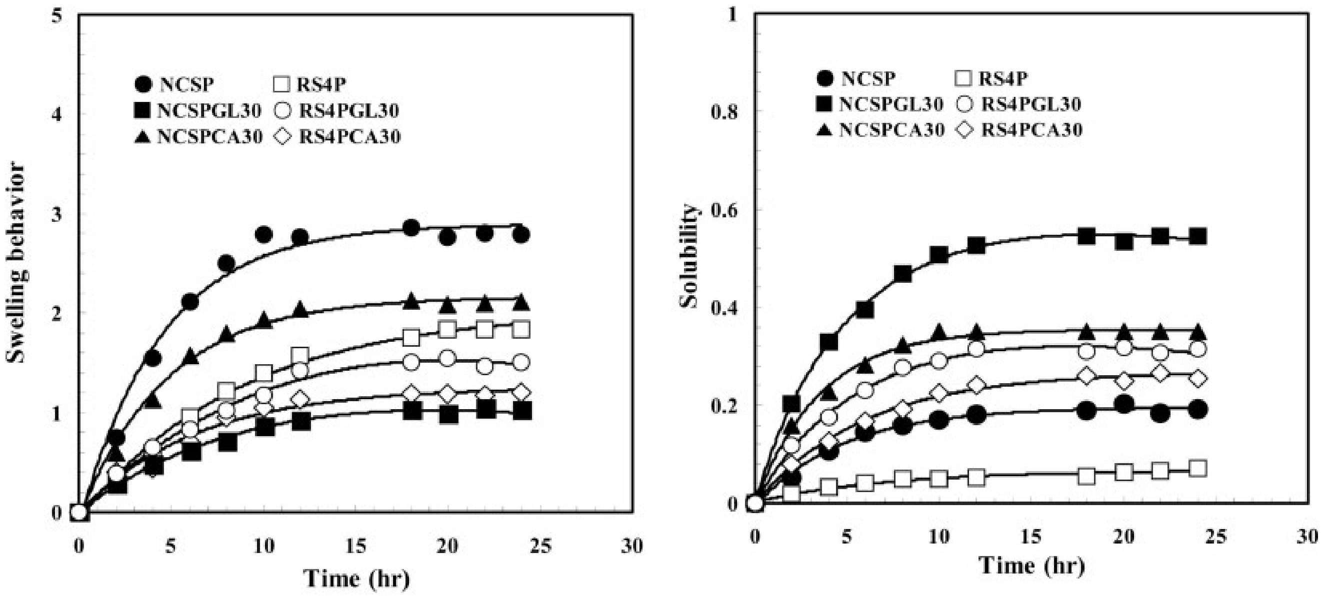


(a) (b)

Figure 7 Tensile strength and elongation of NCS and RS4/PVA blend films stored at 25°C and 52% relative humidity for 7 days: (a) NCS and RS4/PVA blend films with GL added and (b) NCS and RS4/PVA blend films with CA added.

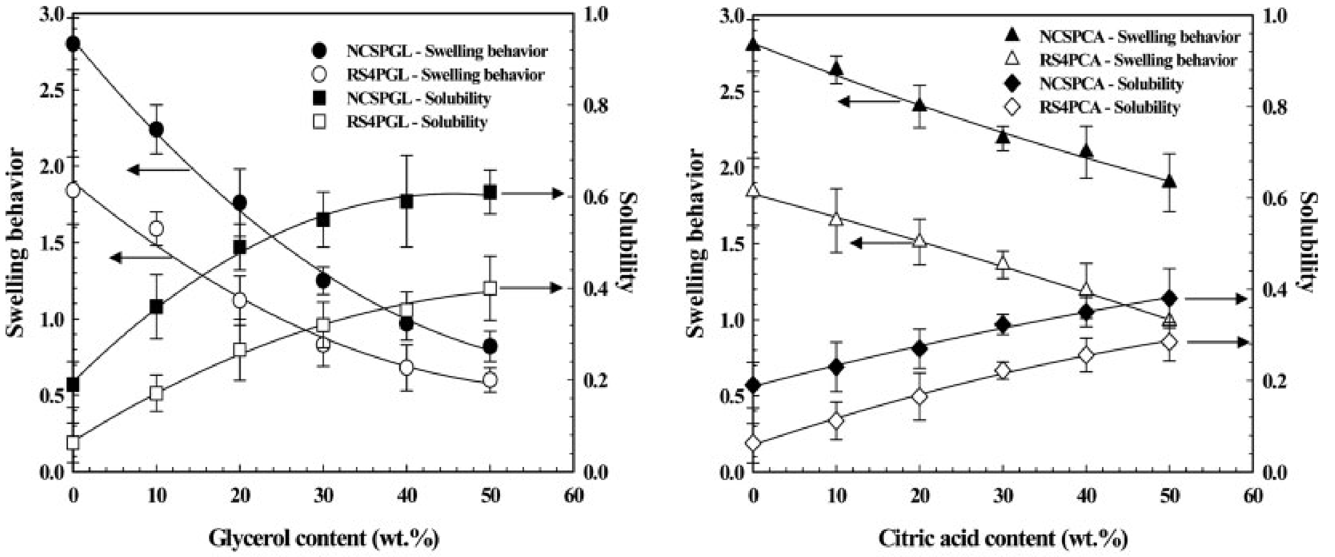
for films using NCS were higher. The slopes for NCSP, NCSPGL30, and NCSPCA30 were 0.6427, 2.1901, and 2.9209, respectively. Ideally, films with good properties should not change with the humidity or should change very little.

Figure 7(a,b) presents the result of the tensile strength and elongation for films using NCS and RS4 to which GL and CA were added with increasing contents of 10, 20, 30, 40, and 50 wt % (starch and PVA weight bases). As the weight percentage of GL and CA increased from 10 to 50 wt %, the tensile strength decreased, whereas the elongation increased. We observed that the tensile strength and elongation of the CA-added films were higher than those of the plasticizer using GL. Films using RS4 had higher values than films using NCS.



(a) (b)

Figure 8 (a) Swelling behavior and (b) solubility of NCS and RS4/PVA blend films with or without additives versus time.



(a)

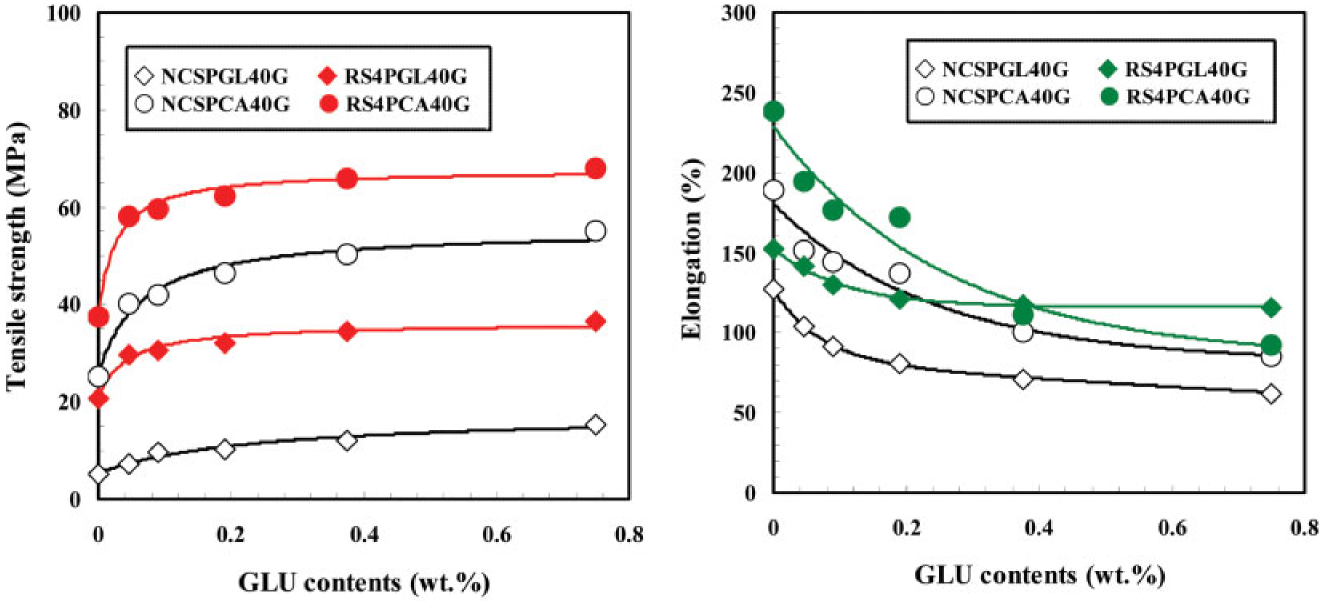
(b)

Figure 9 Swelling behavior and solubility of NCS and RS4/PVA blend films: (a) NCS and RS4/PVA blend films with GL added and (b) NCS and RS4/PVA blend films with CA added.

Swelling behavior and solubility of the starch/PVA blend films

The swelling behavior and solubility of the films that used NCS or RS4 and PVA with or without additives are shown in Figure 8(a,b). In conformity with the time, the swelling behavior and solubility increased and equilibrated over 20 h.

In Figure 8(a), except for the film using NCS to which GL was added as an additive, the swelling behavior of the films using NCS was higher than that of the films using RS4. The swelling behavior of the NCS-based film that used GL as an additive was the lowest because the functional group capable of hydrogen bonding was weaker than that of the CA-added film. As shown in Figure 8(b), the film using



(a)

(b)

Figure 10 (a) Tensile strength and (b) elongation of NSPGL40, NSPCA40, RS4PGL40, and RS4PCA40 films with GLU added as a crosslinking agent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

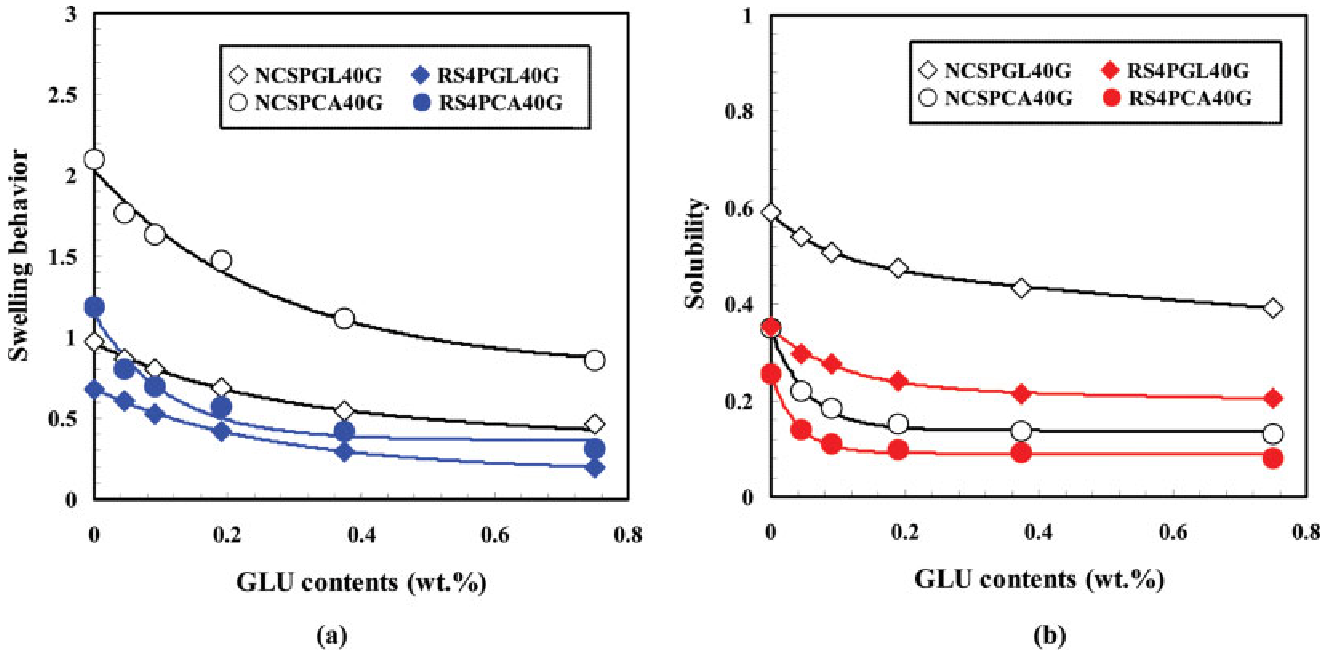


Figure 11 (a) Swelling behavior and (b) solubility of NSPGL40, NSPCA40, RS4PGL40 and RS4PCA40 films with GLU added as a crosslinking agent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

NCS to which GL was added had the highest solubility value. However, the swelling behavior of the film using RS4 to which GL was added was lower than that of the film using NCS to which GL was added because hydrogen bonding of the hydroxyl group in GL with RS4 and PVA easily occurred on account of crosslinkage between starch molecules. In Figure 9(a,b), with an increase in the contents of GL and CA as additives, the swelling behavior of the films using NCS and RS4 decreased slightly, and the solubility increased.

The GL-added film using NCS showed a low swelling behavior value, but it had a high solubility value. The degree of combination related to hydrogen bonding for the GL-added film was weaker than that for the CA-added film. In Figure 9, we can observe that the films using RS4 with GL and CA added had lower values than the films using NCS with GL and CA added.

Effect of the crosslinking agent

Figures 10 and 11 show the tensile strength, elongation, swelling behavior, and solubility of starch/PVA blend films with GLU added as a crosslinking agent.

In this work, the mechanical properties due to the addition of GLU to NCSPGL40, NCSPCA40, RS4PGL40, and RS4PCA40 were investigated.

Figure 10(a,b) shows the tensile strength and elongation of films with increasing contents of GLU added. As the concentration of GLU increased from 0.045 to 0.75 wt %, the tensile strength increased, whereas the elongation decreased. It was verified that a sudden change in the tensile strength and elongation happened in the GLU-added NCSPCA40 and RS4PCA40 films. This phenomenon took place because of the superior reactivity of CA and GLU.

Figure 11(a,b) shows the swelling behavior and solubility values of films with GLU added. With increasing GLU contents, the swelling behavior and solubility values of the NCSPGL40, NCSPCA40, RS4PGL40, and RS4PCA40 films decreased. In particular, films using RS4 with CA as an additive and GLU as a crosslinking agent showed physical properties superior to those of other films.

CONCLUSIONS

NCS and RS4/PVA blend films were synthesized with a mixing process and casting method. The results for the tensile strength, elongation, swelling behavior, and solubility of the synthesized films using RS4 with GL and CA as additives demonstrated that the films gained superior physical properties because amylopectin, which has a branch structure for NCS, was crosslinked by STMP. As a result, the RS4, PVA, and additives were combined easily.

To verify the effect of the crosslinkage of starch/PVA blend films, films were prepared with GLU as a crosslinking agent. With an increasing concentration of GLU as a crosslinking agent, we confirmed that the swelling behavior and solubility values decreased for the starch/PVA blend films. In particular, the RS4/PVA blend film with CA as an additive showed the effect of crosslinkage superior to that of other films.

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