

# Physical Properties of Chemically Modified Starch(RS4)/PVA Blend Films—Part 1

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**Abstract** In this paper, we report on the physical properties of films that have been synthesized by using native corn starch (NS) and chemically modified starch (RS4). NS or RS4/PVA blend films were synthesized by using the mixing process and the casting method. Glycerol (GL), sorbitol (SO), and citric acid (CA) were used as additives. The chemically modified starch (RS4) was synthesized by using sodium trimetaphosphate (STMP) and sodium triphosphate (STPP) as a crosslinker. Then, the RS4 thus synthesized was confirmed by using the pancreatic-gravimetric method, swelling power and an X-ray diffractometer (XRD).

Tensile strength (TS), elongation (%*E*), swelling behavior (SB), and solubility (*S*) of the films were measured. The result of the measurements indicated

the RS4-added film was better than the NS-added film. Especially, the RS4/PVA blend film with CA as an additive showed the physical properties superior to other films.

**Keywords** Additives · Chemical modified starch(RS4) · Film · Physical properties

## Introduction

There is currently a revival of worldwide interest in the use of biopolymers for applications in which synthetic polymers have traditionally been the materials of choice. Materials of interest include different synthetic or biosynthetic polymers, as well as plant-based polymers such as starch and pectin. Such polymers may be biodegradable and recyclable and, therefore, may help satisfy the increasing consumer and regulatory demands for materials with these properties. Physical incorporation of granular starch as a functional additive or filler into synthetic polymers by plastic processing is well known as the first generation of starch compounds. In the 1990s, biodegradable plastic manufacturing technology began to focus on thermoprocessing of starch-based compounds without using any petrochemical polymers with the conventional equipment. Thus, thermoplastic starch (TPS), cited as the second generation of starch plastics, has been developed. Commercially available products of this kind of plastics include Novon and Mater-Bi (about 60% starch, 40% modified PVA and plasticizers) [1, 2]. In addition to starch, the latter serial products marketed by Novamont may contain polycaprolactone, poly (ethylene vinyl alcohol), as

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well as cellulose acetate, depending on the specific application [3–6].

Starch is renewable and biodegradable polysaccharides [3]. Native starch usually contains about 30% amylose, 70% amylopectin and less than 1% lipids and proteins from plant. Biodegradable starch-based plastics such as starch/cellulose, starch/PVA (polyvinyl alcohol), etc., 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 [7–10].

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 bond that is absolutely biodegradable. PVA samples with number average molecular weights as high as 100,000 have been reported to be completely degraded by soil bacteria, especially by Pseudomonads [3].

In most studies, films have been synthesized from corn starch [11–13], wheat starch [14, 15], rice starch [16], potato starch [17], and cassava starch [18, 19], and the investigations of their mechanical properties

revealed that amylose content of starch affected the properties of films. Starch-based films have an effect on physical properties because of linear structure of amylose and branch structure of amylopectin of starch. Especially, these films are soluble in water because of the amylopectin of branch structure. Thus, many studies are being conducted on starch-based film based on chemically modified starch [20–21].

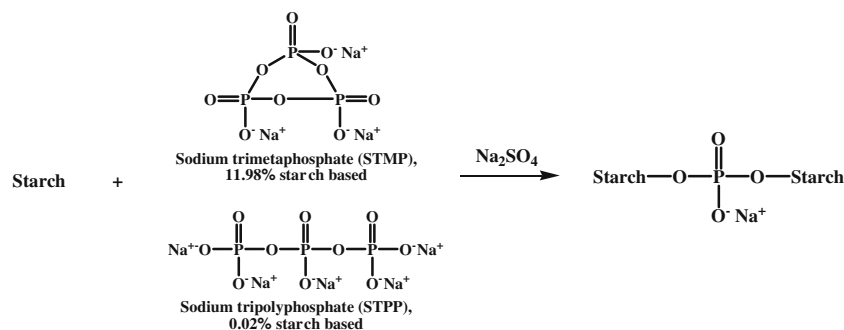
In this work, films were synthesized with chemically modified starch (RS4) and native starch (NS) and their physical properties were investigated.

Chemical modification has long been known to inhibit the in vitro digestibility of starch, the extent of which is related to the type and degree of modification, the extent of gelatinization, and the choice of enzyme. In particular, because cross-linking of starch stabilizes the granule structure and restricts swelling, highly cross-linked starch is very difficult to hydrolyze by  $\alpha$ -amylase, and the starch's solubility in dimethyl sulfoxide or NaOH is reduced. The Cross-linked starch that is difficult to hydrolyze by  $\alpha$ -amylase is called resistant starch type 4 (RS4) [22, 23]. Chemically modified

**Table 1** Composition of native starch or RS4/PVA blend films

Sample name	NS	RS4	PVA	GL	SO	CA
NSP	5%	–	5%	–	–	–
RS4P	–	5%	5%	–	–	–
NSPGL10	5%	–	5%	10 wt. %	–	–
NSPGL20	5%	–	5%	20 wt. %	–	–
NSPGL30	5%	–	5%	30 wt. %	–	–
NSPGL40	5%	–	5%	40 wt. %	–	–
NSPGL50	5%	–	5%	50 wt. %	–	–
RS4PGL10	–	5%	5%	10 wt. %	–	–
RS4PGL20	–	5%	5%	20 wt. %	–	–
RS4PGL30	–	5%	5%	30 wt. %	–	–
RS4PGL40	–	5%	5%	40 wt. %	–	–
RS4PGL50	–	5%	5%	50 wt. %	–	–
NSPSO10	5%	–	5%	–	10 wt. %	–
NSPSO20	5%	–	5%	–	20 wt. %	–
NSPSO30	5%	–	5%	–	30 wt. %	–
NSPSO40	5%	–	5%	–	40 wt. %	–
NSPSO50	5%	–	5%	–	50 wt. %	–
RS4PSO10	–	5%	5%	–	10 wt. %	–
RS4PSO20	–	5%	5%	–	20 wt. %	–
RS4PSO30	–	5%	5%	–	30 wt. %	–
RS4PSO40	–	5%	5%	–	40 wt. %	–
RS4PSO50	–	5%	5%	–	50 wt. %	–
NSPCA10	5%	–	5%	–	–	10 wt. %
NSPCA20	5%	–	5%	–	–	20 wt. %
NSPCA30	5%	–	5%	–	–	30 wt. %
NSPCA40	5%	–	5%	–	–	40 wt. %
NSPCA50	5%	–	5%	–	–	50 wt. %
RS4PCA10	–	5%	5%	–	–	10 wt. %
RS4PCA20	–	5%	5%	–	–	20 wt. %
RS4PCA30	–	5%	5%	–	–	30 wt. %
RS4PCA40	–	5%	5%	–	–	40 wt. %
RS4PCA50	–	5%	5%	–	–	50 wt. %

**Fig. 1** Synthesis of chemically modified starch (RS4)



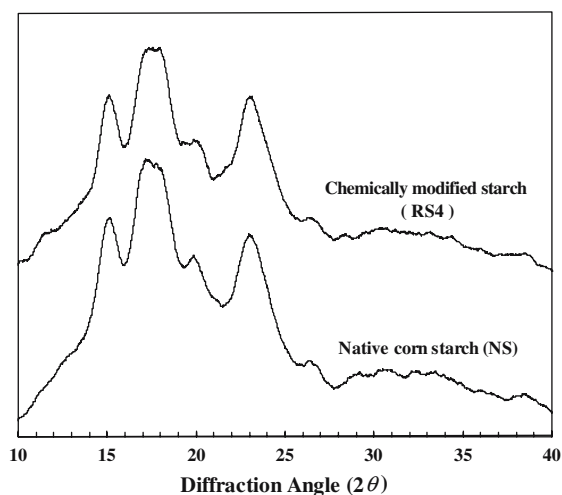
starch (RS4) was synthesized using the method of Shin, Song and Seib [24].

The films were prepared by casting method. Starch/PVA blend films synthesized by using GL, SO and CA as additives were investigated for their mechanical properties (TS and %E) with %RH, swelling behavior and solubility.

## Experimental

### Materials

Starch (corn starch) was obtained from Doosan Corn Products Korea, Inc.(Korea). Polyvinyl alcohol (PVA), reagent grade glycerol (GL), citric acid (CA), sodium trimetaphosphate (STMP), sodium triphosphate (STPP), and sodium sulfate were purchased from Aldrich Chemical Company, Inc. (Milwaukee, USA). PVA was 99% hydrolyzed with a molecular weight average of 89,000–98,000. The water used to prepare starch/PVA blend films was redistilled after deionization.



**Fig. 2** X-ray diffractograms of native corn starch (NS) and RS4

### Preparation and Determination of Chemically Modified Starch (RS4)

Chemically modified starch (RS4) was prepared using the method of Shin, Song and Seib [24]. Briefly, RS4 starches were prepared from starch (50 g, dry basis, db), cross-linked with sodium trimetaphosphate (STMP, 5.94 g) and sodium tripolyphosphate (STPP, 0.06 g) under alkaline condition (pH 11.5) at 45 °C for 3 h. Cross-linked RS4 starch was ground and passed through a 100 mesh sieve (under  $\Phi 150 \mu\text{m}$ ).

RS4 was synthesized and then measured by the pancreatin-gravimetric method, swelling power, and an X-ray Diffractometer (D/MAX Ultima III, Rigaku, Japan) [25].

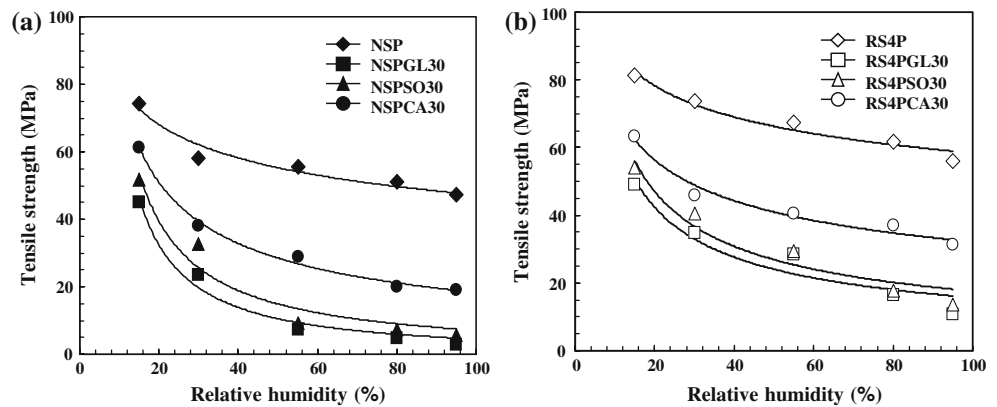
### Starch/PVA Blend Films Preparation

Films were obtained by the casting method. First, PVA solution was prepared by dissolving PVA in hot water (95 °C). Native corn starch (NS), cross-linked starch (RS4) and additives (GL, SO and CA) were mixed together with water using a Kitchen Aid® mixer for 10 min. Formulations contained 10, 20, 30, 40 and 50% GL, SO and CA (weight basis). PVA solution and mixed NS or RS4/additives were kept at 95 °C for 5 min. Then, the mixture was blended to form homogeneously gel-like solution with a mechanical stirrer (1,200 rpm) at room temperature for 50 min. The total polymer amount was

**Table 2** Swelling power of native corn starch and RS4

Temperature	Swelling power	
	Native corn starch(NS)	RS4
20 °C	2.6	1.81
30 °C	3.41	2.28
50 °C	5.16	2.86
80 °C	7.63	3.5
95 °C	9.56	4.0

**Fig. 3** Tensile strength (TS) of starch/PVA blend films, stored for 7 days at different relative humidities. **(a)** Tensile strength (TS) of NS/PVA blend films with/without additives versus different relative humidities. **(b)** Tensile strength (TS) of RS4/PVA blend films with/without additives versus different relative humidities



100 g. NS, RS4 and PVA had the same mass ratio, and the content of additives was expressed as mass percent ratio of additives to total NS, RS4 and PVA weight, respectively. Bubbles, the by-product of preparation, were removed by using an aspirator. The mixing composition is shown in Table 1. The gel-like solution thus prepared was poured on a pre-warmed (75 °C) Teflon<sup>®</sup> mould (200 × 200 × 2 mm). Water was evaporated from the moulds in a ventilated oven at 50 °C for 12 h. Dried films were put in open polyethylene bags and stored at 25 °C and at RH 52% for one week before the measurements were performed.

Japan) at 10 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.

TS and %*E* of each film were evaluated after storage in different relative humidity (%RHs) for 7 days. Constant %RHs were obtained by using saturated salt solutions of Na<sub>2</sub>SO<sub>4</sub> (~93% RH), Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (~1% RH), CaCl<sub>2</sub> (~33% RH) and LiCl (~15% RH). Films were stored in desiccator chambers over the salt solutions at 25 °C. The tests were carried out at 25 °C and 54% RH in a constant temperature and humidity room.

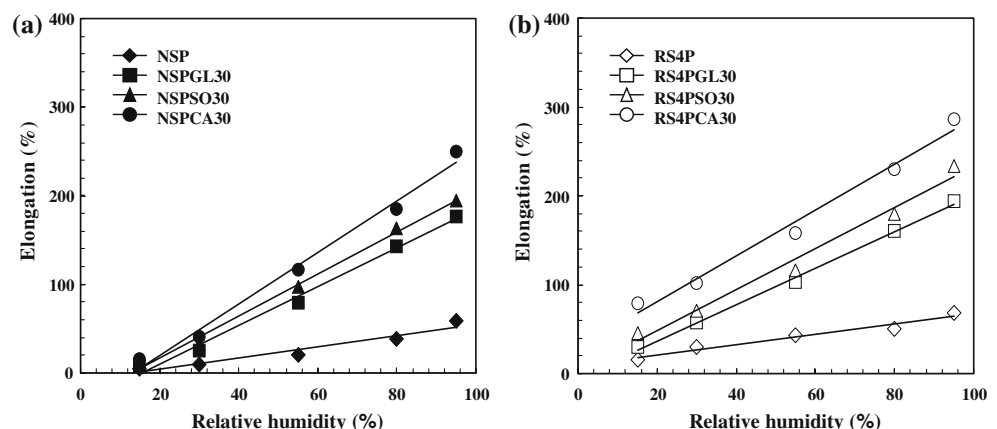
### Mechanical Properties of Films

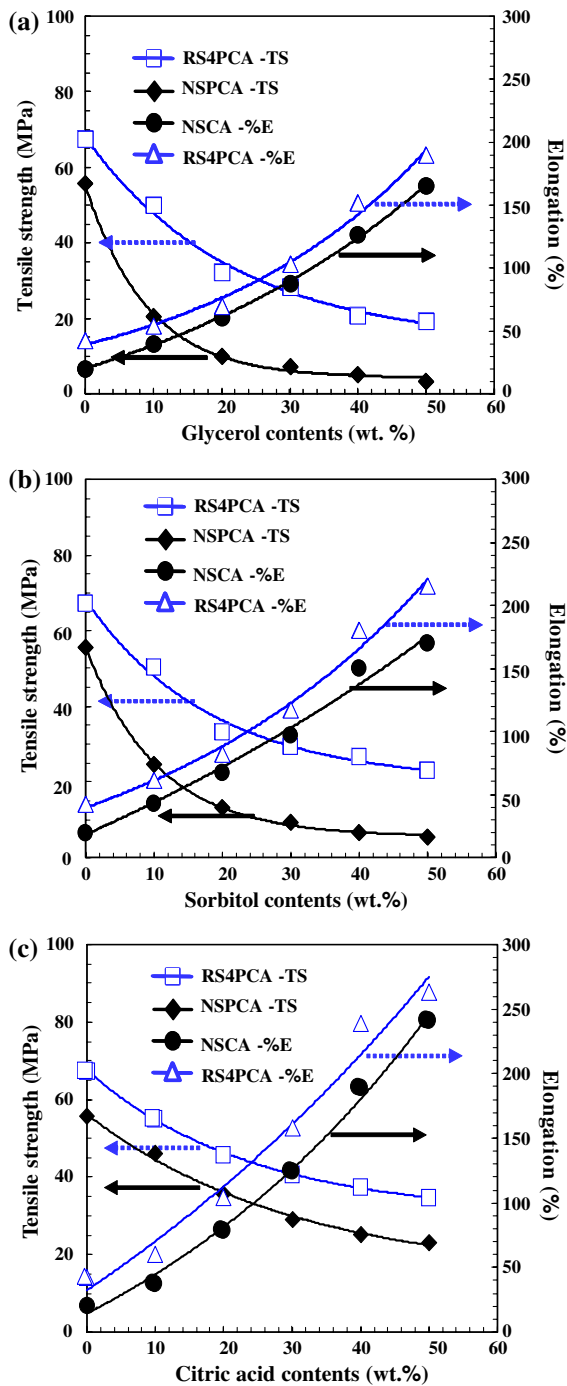
Tensile strength (TS) and elongation (%*E*) were evaluated for each film using an Instron 6012 testing machine. Three dumbbell shaped specimens (ASTM D-412) were cut from each film. Each specimens had a width of 12 mm. The specimens average thickness was about 0.2 mm. The thickness of the films was measured with a mechanical scanner (digital thickness gauge 'Mitutoyo', Tokyo,

### Swelling Behavior and Solubility of 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 swelling behavior (SB) in starch/PVA blend film was calculated as (1):

**Fig. 4** Elongation (%*E*) of starch/PVA blend films, stored for 7 days at different relative humidities. **(a)** Elongation (%*E*) of NS/PVA blend films with/without additives versus different relative humidities. **(b)** Elongation (%*E*) of RS4/PVA blend films with/without additives versus different relative humidities





**Fig. 5** Tensile strength (TS) and Elongation (%E) of NS or RS4/PVA blend films. Where films were stored at 25 °C at RH 52% for 7 days. **(a)** Tensile strength (TS) and Elongation (%E) of NS or RS4/PVA blend films added glycerol (GL). **(b)** Tensile strength (TS) and Elongation (%E) of NS or RS4/PVA blend films added sorbitol (SO). **(c)** Tensile strength (TS) and Elongation (%E) of NS or RS4/PVA blend films added citric acid (CA)

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

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 equation (2) :

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

where  $W_0$  is the first dry weight of starch/PVA blend film, and  $W_d$  is the dry weight of swelled starch/PVA blend film.

### Results and Discussion

#### Determination of Chemically Modified Starch (RS4)

RS4 was synthesized and the characterization of RS level was verified by using the pancreatin-gravimetric method, swelling power, XRD as reported by Shin et al. [25]

RS level of chemically modified corn starch was about 11%, when measured by the pancreatin-gravimetric method.

Crosslinkage was molded by covalent bond between starch molecules. Figure 1 illustrates the reaction mechanism of RS4 using STMP. Figure 2 shows the result of XRD analysis of native corn starch (NS) and chemically modified starch (RS4).

NS and RS4 exhibited peaks at  $2\theta = 15^\circ, 17^\circ, 20^\circ,$  and  $23^\circ$  because only crosslinkage occurred without the change of starch structure [25].

Table 2 presents the result of swelling power of NS and RS4. As the temperature increased from 20 °C to 95 °C, the swelling power of NS increased faster than RS4 and NS. NS was gelatinized above 60 °C.

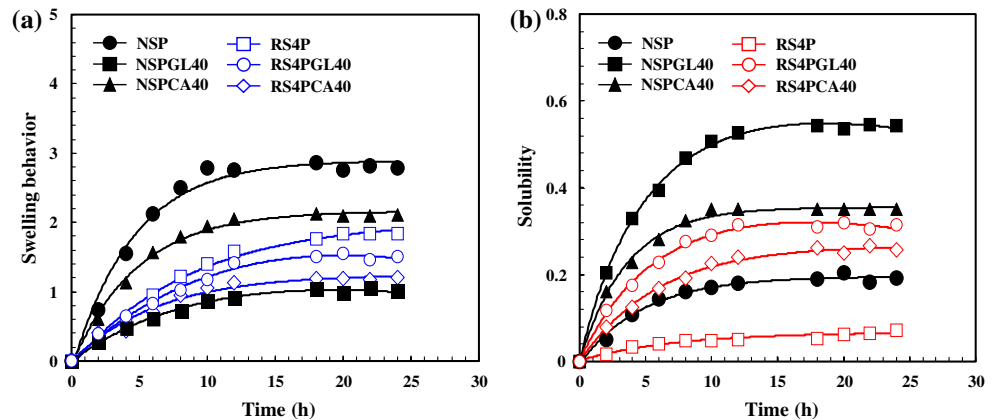
#### Mechanical Properties of Films

Films were prepared using the method developed in our previous work [26].

Figures 3 and 4 show the effect of percent relative humidity on films containing NS or RS4 in which GL, SO and CA were used as additives.

TS of the films decreased because RH increases, when plasticizer is added to polymers.

**Fig. 6** Swelling behavior (SB) and solubility (*S*) of NS or RS4/PVA blend films versus time. (a) Swelling behavior (SB) of NS or RS4/PVA blend film with/without additives versus time. (b) Solubility (*S*) of NS or RS4/PVA blend film with/without additives versus time



Figures 3a and b show that there was a large decrease in TS in all the films tested as the storage RH increased from 15 to 33%. Especially, films with additives showed that TS was exponentially changed. There was a large decrease in TS between 15 and 33% RH probably because water was absorbed by solubility to GL, SO and CA as additives. And TS change was smaller in films using NS than RS4.

Figures 4a and b show the change of %*E* with percent relative humidity. The %*E* of the films increased as %RH increased in the films tested. Starch is hygroscopic and will gain or lose water to achieve equilibrium with the ambient air. Water is also a plasticizer for starches. By placing the starch-based films in different RHs, the films will either lose or gain water to be in equilibrium with the air in the humidity chamber. Since water is plasticizer, changing the water content in the film will change the properties of the films. Increasing plasticizer levels in synthetic plastic has been shown to increase %*E*. This is consistent with other work done with starch-based films and is consistent with systems where the plasticizer is increasing.

The slopes of the regression line for films using RS4 seem parallel to each other and different from the other films tested. The slopes for RS4P, RS4PGL30, RS4PSO and RS4PCA30 were 0.59, 2.05, 2.31 and 2.58, respectively, while the slope for films using NS was higher than films using RS4. The slope for NSP, NSPGL30, NSPSO30 and NSPCA30 were 0.64, 2.19, 2.36 and 2.92, respectively. Ideally, films with good properties should not change with humidity or change very little.

Figures 5a, b and c present the result of TS and %*E* on films to which GL, SO and CA were added with increasing content of 10, 20, 30, 40 and 50 wt.% on films using NS and RS4. As the wt.% of GL (a), SO (b), and CA (c) increased from 10 wt.% to 50 wt.%, TS decreased while %*E* increased. And we observed that

TS and %*E* of films with the addition of SO or CA were higher than the plasticizer using GL. And films using RS4 was higher than NS.

Starch, PVA and additives were combined too easily because branch structure of amylopectin in NS was crosslinked.

#### Swelling Behavior and Solubility of Starch/PVA Blend Films

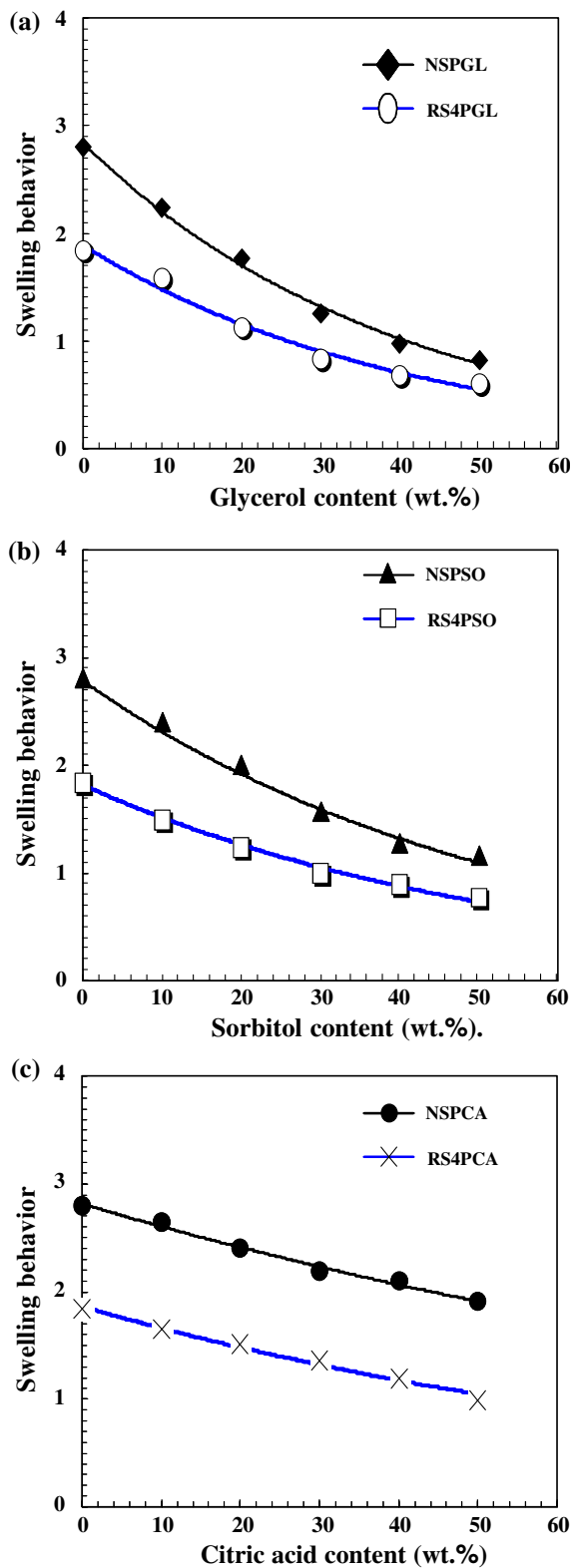
SB and *S* of the film that used NS or RS4 and PVA with/without additives are shown in Figs. 6a and b.

In conformity with time, SB and *S* was increased and equilibrated over 20 h.

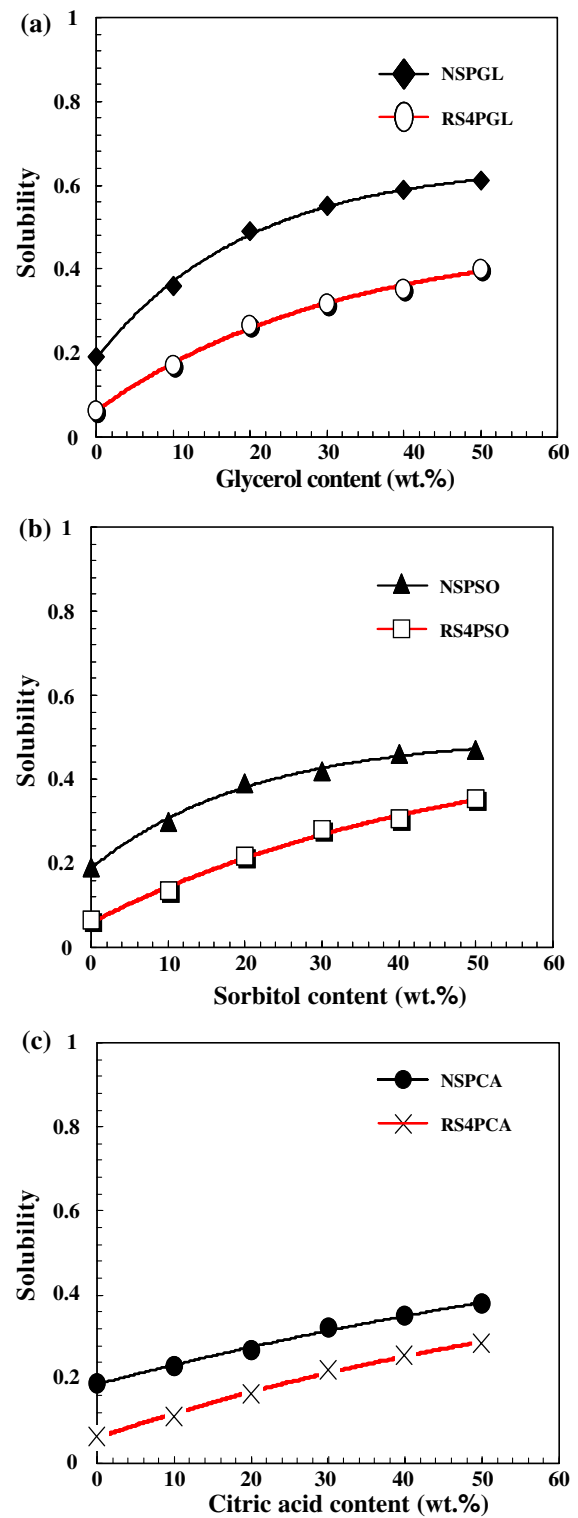
In Fig. 6a, except for the film using NS and added GL as additive, SB of films using NS was higher than that using RS4. The SB of the NS-based film that used GL as an additive was the lowest because the functional group capable of hydrogen bonding was weaker than the SO- or CA-added film.

As shown in Fig. 6b, film using NS and added GL had the highest *S* value. But SB of the film using RS4 and added GL was lower than the film using NS and added GL because hydrogen bond of hydroxyl group in GL with RS4 and PVA easily occurred due to crosslinkage between starch molecules. In Figs. 7a, b and c, with the increase in the content of GL (a), SO (b) and CA (c) as additives, SB of the films using NS and RS4 decreased slightly and *S* increased (see Figs. 8a, b and c).

GL-added film using NS showed a low SB value, but it had a high *S* value. The degree of combination related to hydrogen bonding on GL-added film was weaker than SO- or CA-added film. In Figs. 7 and 8, we were able to observe that films using RS4 and added GL, SO and CA were lower than the films using NS and added GL, SO and CA.



**Fig. 7** Swelling behavior (SB) of NS or RS4/PVA blend films. (a) Swelling behavior (SB) of NS or RS4/PVA blend films added glycerol (GL). (b) Swelling behavior (SB) of NS or RS4/PVA blend films added sorbitol (SO). (c) Swelling behavior (SB) of NS or RS4/PVA blend films added citric acid (CA)



**Fig. 8** Solubility (*S*) of NS or RS4/PVA blend films. (a) Solubility (*S*) of NS or RS4/PVA blend films added glycerol (GL). (b) Solubility (*S*) of NS or RS4/PVA blend films added sorbitol (SO). (c) Solubility (*S*) of NS or RS4/PVA blend films added citric acid (CA)

## Conclusions

Native corn starch (NS) film and chemically modified starch(RS4) / PVA blend film were synthesized by using the mixing process and the casting method. The calculation results of TS, %E, SB, and S of the synthesized films using RS4 added GL, SO and CA as additives demonstrated that the films gained superior physical properties because amylopectin, which has the branch structure of NS, was crosslinked by sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP). As a result, RS4, PVA and additives were combined easily.

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