# Edible Starch Sodium Octenyl Succinate Film Formation and its Physical Properties

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**ABSTRACT:** Edible starch sodium octenyl succinate (SSOS) films, with or without glycerol as plasticizer, were prepared by solution-casting method. The effect of SSOS concentration, degree of substitution (DS) of octenyl group, as well as glycerol content, on the properties of SSOS films was studied including tensile strength, water vapor permeability (WVP), and oil permeability (OP). The results indicated that the tensile strength of SSOS film was up to $39.4 \pm 1.9$ MPa when the concentration of SSOS was 0.05 g/mL and DS was 0.05. The increase of glycerol content resulted in a decrease of film tensile strength. WVP of SSOS films was relatively low. Meanwhile, study in OP showed that SSOS films were oilproof. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

## INTRODUCTION

Edible films may prevent mass transfer of water or other compounds, such as oxygen, carbon dioxide, oil, and aroma compounds, between a product and surroundings or between different layers of a product.[1] Thus, these films can protect foods from the exposure to moisture and oxygen.[2] In addition to the biodegradability, the films can be consumed along with food, can provide additional nutrients, may enhance sensory characteristics, and may include antimicrobials.[3,4] Edible films can be prepared from biomaterials such as polysaccharides and proteins with suitable mechanical properties[5,6] and can be plasticized by low molecular weight compounds, such as polyols.[7,8] But they are highly sensitive to moisture and show poor water vapor barrier properties.[9,10] In contrast, films composed of lipids have better water vapor barrier properties, but are usually relatively inflexible.[11] Thus, multicomponent films with either polysaccharides/lipids or proteins/lipids have been made with the combining advantages of the individual film-forming materials.[12]

Starch has been an attractive film-forming material, because it is a renewable and abundant resource.[13] Nevertheless, starch

exhibits strong hydrophilic character and poor mechanical properties,[14] which make it unsatisfactory for some applications such as packaging purposes. Starch sodium octenyl succinate (SSOS), a starch derivative produced by esterification of native starch,[15] has been approved for the use in foods by FDA and within EU[16,17] because of its nontoxicity and degradability.[18,19] It has been used in food products such as sauces, puddings, and infant foods for more than 30 years.[20] Through this esterification, the hydrophobicity of octenyl group is introduced while the hydrophilicity of starch backbone is retained,[21] which means that the molecule is amphiphilic. As a result, film prepared from this starch derivative may be similar to the multicomponent films. Furthermore, the film-forming procedure can be simplified, and phase separation will not occur because that only a single material is used. 2-Octenyl succinic anhydride (OSA), one of the raw material SSOS, has been used as plasticizers in starch acetate film formation,[22] but film-forming ability of SSOS has not been investigated before. This article aims to prepare SSOS films, study the physical properties, water vapor, and oil permeability (OP), and to suggest eventual applications.

## EXPERIMENTAL

### Materials

SSOS with the DS ranging from 0.02 to 0.07 was synthesized using corn starch (Huanglong Food Industry Co., Changchun, China) and OSA (Wei-hua Spices Chemical Co., Hangzhou, China) according to the report.[15] Glycerol was purchased from Dalian Traditional Chinese Medicine Group (Liaoning, China). Calcium chloride was purchased from Beipiao Jingta Calcium Hydroxide Factory (Liaoning, China). The other chemicals used in the study were purchased locally. All these chemicals were of analytical reagent and used as received.

### Preparation of SSOS and Determination of the Degree of Substitution

Corn starch was suspended in distilled water (40%, w/w) with agitation. The pH of the suspension was adjusted to 8.5–9 with a pH meter (Cole-Parmer, American) by adding 3% NaOH (w/w) solution. About 0.05–0.22 mL (/g starch) OSA was dissolved in absolute alcohol (v/v) and then added slowly into starch solution over 2 h. The reaction was continued for a further hour. Then, the pH was adjusted to 6.5–7 with 3% HCl solution, the mixture was filtered under vacuum, washed twice with distilled water and three times with 95% aqueous alcohol, and the solid was vacuum dried at 60°C for 24 h and then passed through a nylon sieve of 120 mesh (60 mm opening).

The DS is the average number of hydroxyl groups substituted per glucose unit. It was determined by titration.[23] A starch sodium octenyl succinate (SSOS) sample (5 g, dry weight) was accurately weighed and dispersed by stirring for 30 min in 25 mL of $2.5M$ HCl isopropyl alcohol solution. One hundred milliliters of 90% (v/v) aqueous isopropyl alcohol solution were added, and the slurry stirred for an additional 10 min. The suspension was filtered through a glass filter, and the residue was washed with 90% isopropyl alcohol solution until no $Cl^-$ could be detected any longer (using $0.1M$ $AgNO_3$ solution). The SSOS was redispersed in 300 mL of distilled water, and then the dispersion was heated in a boiling water-bath for 20 min. The starch solution was titrated with $0.1M$ standard NaOH solution, using phenolphthalein as an indicator. A blank was simultaneously titrated with native corn starch as a sample. The DS was calculated by the following equation:

$$DS = \frac{0.162 \times V \times c}{m - 0.210 \times V \times c} \qquad (1)$$

where $V$ is the titration volume of NaOH solution (mL), $c$ is the molarity of NaOH solution, and $m$ is the dry weight (g) of the SSOS.

### Preparation of SSOS Films

Starch sodium octenyl succinate (SSOS) films were prepared by solution-casting method. About 0.03–0.055 g/mL aqueous suspension of SSOS, with or without glycerol as plasticizer, was gelatinized at 100°C for 30 min, and then films were prepared by casting on polypropylene trays and evaporating at room temperature, followed by drying at 50°C for 24 h in an oven. The films were then carefully peeled off and placed in chambers over salt solutions with relative humidity (RH) of 70%. When glycerol was added as plasticizer, the mass ratios between glycerol and SSOS were 1/12, 1/6, and 1/4, respectively.

### Measurement of Film Thickness

SOSS film thickness was measured using an outside micrometer 701-01 (Harbin Measuring & Cutting Tool Works, China). Measurements were taken at three different locations on the film. The film thickness was presented as mean ± standard deviation and used for calculating tensile strength and water vapor permeability (WVP).

### Measurement of Tensile Strength

Three strip specimens of 15 mm × 250 mm were cut from each SSOS film sample, and then the strips were conditioned at 25°C and 70% RH for 24 h. ZLL-10 paper tensile strength tester (Yibin Paper Industry Co., Sichuan, China) was used for determining the tensile strength of the film. Distance between gripper of the tester was set at 150 mm and the tensile speed at 1 mm/s. Tensile strength of the film was calculated as follows[24]:

$$\sigma = F/S \qquad (2)$$

where $\sigma$ is tensile strength (MPa); $F$ is breaking force (N); $S$ is cross-sectional area of the film ($m^2$), calculated from the thickness and width of the film.

### Measurement of WVP

The water vapor permeability (WVP) of SOSS films was measured by standard method according to GB/T1037-1988[25] at 25°C and 100% RH using cylindrical cup. Circular film samples at about 10 mm of diameter were placed over the mouth of the test cup and sealed by melt paraffin. The cup was prefilled with anhydrous calcium chloride leaving 3 mm to the top as suggested by GB/T1037-1988. After the film specimens were equipped, the assembly was weighed and placed in a chamber conditioned at 25°C and 100% RH. Weight increments of the cup were measured and plotted at intervals. The slope of the straight line was calculated with a linear regression. The WVP was calculated as follows:

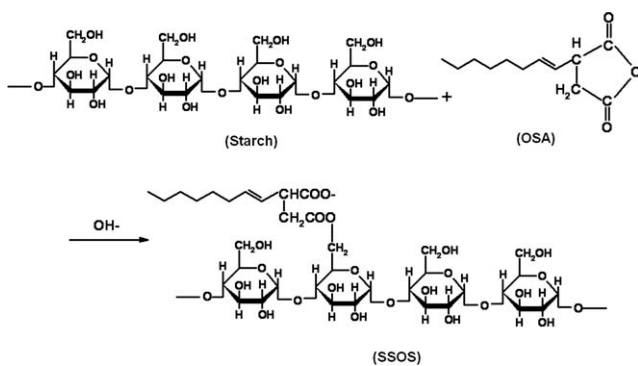$$WVP = \Delta m \times d/(A \times \Delta t \times \Delta P) \qquad (3)$$

where $d$ is film thickness measured as described in section "Measurement of Film Thickness" (m), $\Delta m$ is the weight increment of the cup (g), $A$ is the area exposed ($m^2$), $\Delta t$ is the time lag for permeation (s), and $\Delta P$ is water vapor partial pressure difference across the film (Pa). All specimens were tested in triplicate.

### Measurement of OP

A tube filled of ∼ 15 mL of oil was covered with a film sample attached with tape. It was hung upside down for 5 days. The total weight variation was measured, and oil permeability (OP) was calculated as follows:

$$OP = \Delta m \times d/(A \times t) \qquad (4)$$

where $\Delta m$ is weight variation of the tube (g), $d$ is film thickness (m), $A$ is the area exposed ($m^2$), and $t$ is standing time, 5 days in this work.

Scheme 1. Synthesis procedure of SSOS.



Figure 2. Effects of DS and glycerol content on the tensile strength of SSOS film. Concentration of SSOS being 0.05 g/mL.

## Observation of Films with Scanning Electron Microscopy

The microstructure of the SSOS films was studied using scanning electron microscopy (SEM). Small pieces (5 × 5 mm) of the film were cut and fixed onto sample holders with conducting glue and then sputtered with a layer of gold. The samples were then examined by SEM (JSM-6460LV, JEOL, Japan).

## X-ray Diffraction Studies

After being stored for a week at 20°C and 70% RH, X-ray diffraction patterns of starch and SSOS films were analyzed using an X-ray diffractometer (D/max3B, Rigaku Corp., Japan) in the angular range of 5–50 (2θ) with Nickel-filtered Cu Kα radiation ($\lambda = 0.154$ nm) at a voltage of 40 kV and current of 30 mA.

From the scattering spectrum, the relative crystallinity of films was determined as the ratio of the integrated crystalline intensity to the total intensity according to Nara and Komiya[26] using the software Origin 7.5 (Microcal, Northampton, MA).

## RESULTS AND DISCUSSION

### Preparation of SSOS with Different DS

Starch sodium octenyl succinate (SSOS) with different DS was prepared by adding different amount of OSA (0.05–0.25 mL/g starch) into aqueous slurry of corn starch. The synthetic reac-
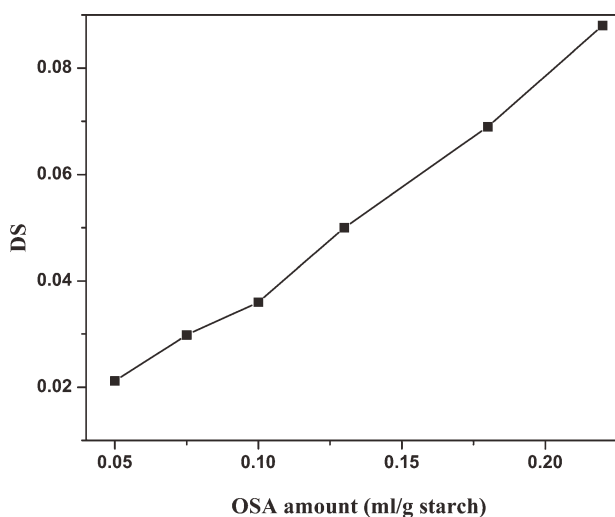


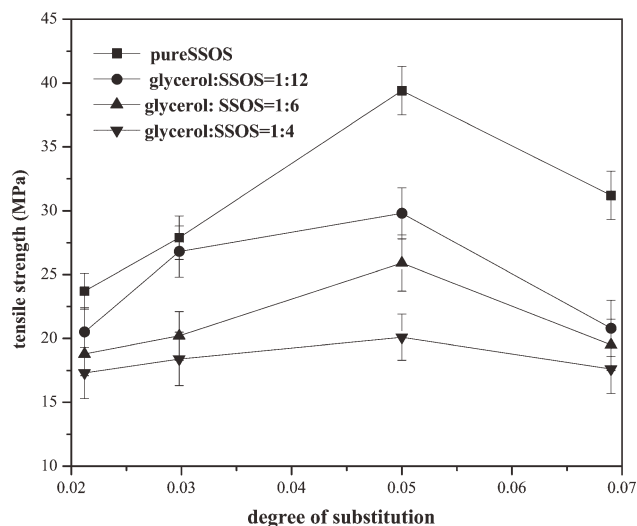Figure 1. Effect of OSA amount on the degree of substitution.

tion of SSOS is presented in Scheme 1. The effect of OSA amount on the DS of SSOS is shown in Figure 1, which indicated that the DS increased with the increment of OSA amount in the range of our study. In this article, SSOS with the DS of 0.021, 0.030, 0.050, and 0.069 was used to investigate the effect on film performance.

### Tensile Strength

**Effect of Degree of Substitution and Glycerol Content.** The effect of degree of substitution (DS) of octenyl succinate group and glycerol content on tensile strength of SSOS film was tested, and the results were shown in Figure 2. With the increase of DS of octenyl succinate group, the tensile strength of the film increased when DS was less than 0.05, but decreased with DS beyond 0.05. Reaction of OSA introduced octenyl groups and free carboxyl groups onto starch molecule (as shown in Scheme 1), which was thought to affect the tensile strength of the film. Ghanbarzadeh et al.[27] reported that interaction could take place between the carboxyl groups of citric acid and the hydroxyl groups on the starch, with the increase of carboxyl groups, the tensile strength increased, and the maximum strength could be reached at 10% (w/w starch) content of citric acid. Similar cross-linking of starch and chitosan by ferulic acid was obtained by Mathew and Abraham,[28] where the optimized content of ferulic acid is about 5% (w/w polysaccharide). SSOS with higher DS means a larger content of carboxyl groups, which can be cross-linked more efficiently, and thus the film has a higher strength. DS 0.05 is equivalent to a cross-linker amount of 5% (mol/mol glucose residue) or 6.7% (w/w starch), which is in the same order of magnitude in the above studies. Nevertheless, octenyl succinate groups, especially the octenyl groups, can also act as plasticizer; thus, with a further increase of DS, tensile strength of the film declines as a result of the decrease of intermolecular force. The tensile strength of SSOS film without any added plasticizer was 39.4 ± 1.9 MPa, and it decreased as the concentration of glycerol increased. This behavior could be related to the structural modifications of starch network when
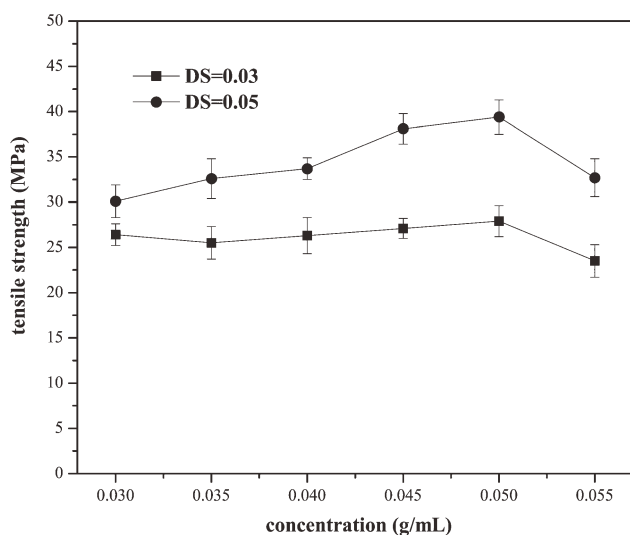
**Figure 3.** Tensile strength of films prepared form different concentrations of SSOS.



**Figure 5.** X-ray diffractograms of starch film and SSOS (DS = 0.05) film.

glycerol was incorporated. Glycerol reduced the interactions among the macromolecules and made the film matrix less dense; thus, understress movements of polymer chains were facilitated and the tensile strength decreased. This effect of glycerol was also demonstrated by other authors.[29–31]

**Effect of SSOS Concentration.** The effect of starch sodium octenyl succinate (SSOS) concentration on tensile strength of the film was shown in Figure 3. It can be seen that the tensile strength of SSOS film increased slightly at first and then decreased with the increase of concentration. The maximum tensile strength was 39.4 ± 1.9 MPa when the concentration of SSOS was 0.05 g/mL. SSOS film exhibited fairly good strength. As we have known, carboxyl group of octenyl succinate could act as cross-linker. At low-SSOS concentration, the film was
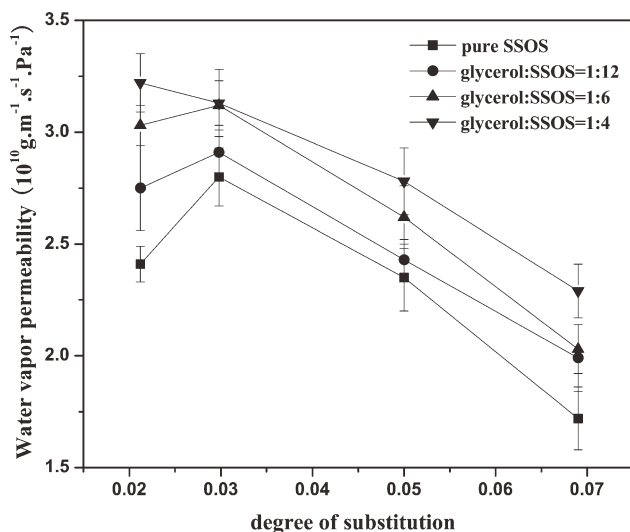
thinner (e.g., 0.019 ± 0.002 mm with concentration of 0.03 g/mL), which meant that carboxyl groups per unit area were less. Although increasing the concentration, film thickness increased (e.g., 0.031 ± 0.003 mm with concentration of 0.05 g/mL), and carboxyl groups per unit area increased and thus strengthen the film. Nevertheless, the solution became too sticky to flow freely beyond 0.05 g/mL, which means that the molecules could not extend enough, and the film became uneven, thus reduced the tensile strength.

**Water Vapor Permeability**
**Effect of DS and Glycerol Content.** Water vapor permeability (WVP) of the film is important when it is applied as edible packaging materials. Figure 4 showed the effect of DS of octenyl group on WVP of SSOS films. It was observed that with the increase of DS, WVP values increased first and then decreased. This tendency is probably due to the balance of crystallinity and hydrophobicity of the film. X-ray diffraction patterns of starch



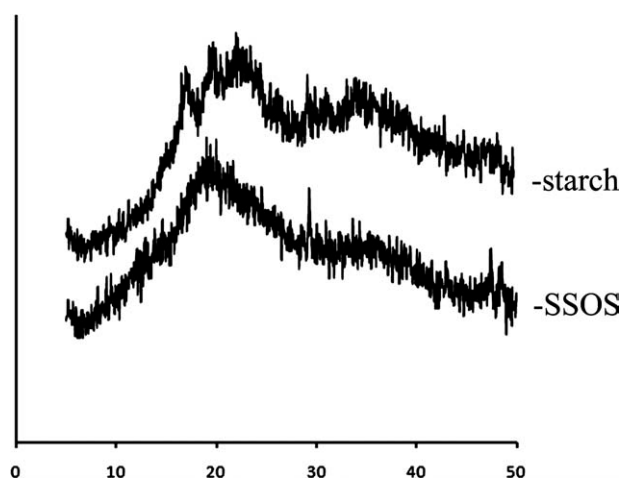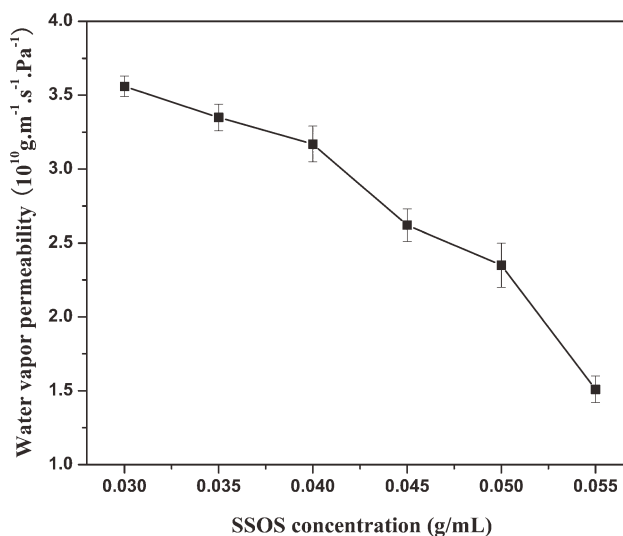**Figure 4.** Effects of DS and glycerol content on water vapor permeability. Concentration of SSOS being 0.05 g/mL.



**Figure 6.** Effects of concentrations of SSOS on water vapor permeability of the film. DS = 0.05.
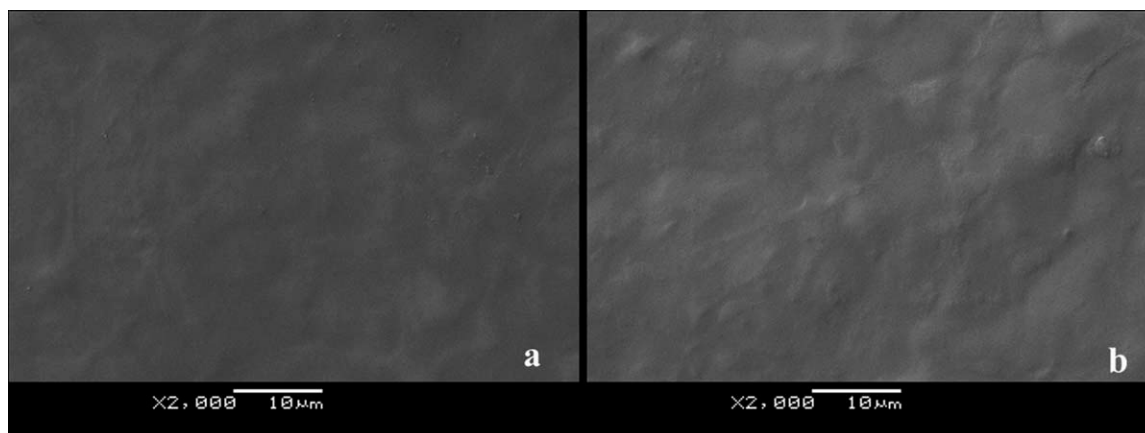
**Figure 7.** Scanning electron micrographs of the surface of SSOS films (DS = 0.03). Concentrations of SSOS being 0.03 (a) and 0.05 g/mL (b), respectively.

and SSOS films were shown in Figure 5. The relative crystallinity was 11.86% for starch film and 2.16% for SSOS (DS = 0.05) film, respectively, which suggested the introduction of octenyl groups decreased the crystallinity. Therefore, water vapor can hardly get through the film of SSOS with low DS, because the film is more regular and crystallized, which increases the barrier properties of the material.[30] Although DS increased to some extent, the crystallinity decreased accordingly contributing to the increase of WVP. However, further increase of DS also enhance the hydrophobicity of SSOS film, which might become the dominant factor resisting the diffusion of water vapor through the film and lowered down the WVP.

Figure 4 also shows the effect of glycerol content on WVP of SSOS films. The WVP of SSOS film without any plasticizer was $2.80 \pm 0.13 \times 10^{-10}$ g m$^{-1}$ s$^{-1}$ Pa$^{-1}$, and it increased up to $3.13 \pm 0.15 \times 10^{-10}$ g m$^{-1}$ s$^{-1}$ Pa$^{-1}$ as the glycerol content increased to 1/4 (mass ratio) of SSOS. Plasticizers are expected to decrease intermolecular forces between polymers chains, imparting increased film flexibility while decreasing barrier properties. Thus, the films matrix became less dense. Moreover, the hydrophilic character of glycerol is favorable to adsorption and desorption of water molecules.[30] As a result, glycerol contributes to the increase of WVP, which is disadvantageous in terms of moisture barrier properties.

**Effect of SSOS Concentration.** The effect of starch sodium octenyl succinate (SSOS) concentration on WVP (Figure 6) showed that WVP of SSOS films decreased from $3.56 \times 10^{-10}$ to $1.51 \times 10^{-10}$ g m$^{-1}$ s$^{-1}$ Pa$^{-1}$ with increasing of SSOS concentration. The reason perhaps is not only the hydrophobicity of octenyl groups, but also their compact structure due to the relative increase of molecular framework in the casting solution (see also in Figure 7). Thus, SSOS films are good barriers for water vapor.

**Oil Permeability**

When SSOS was used as edible film, its permeability of oil would affect the application; thus, oil permeability (OP) of the film made from SSOS with different DS and concentration had been studied. The results (Table I) showed that both of DS of

octenyl group and concentration of SSOS had almost no effect on OP within the scope of this study. The possible reason was that the film was more hydrophilic as a whole, because DS of octenyl group was relatively low (no more than 0.07), and the hydrophobic octenyl groups sporadically distributed in the film. That is to say, the film was almost oilproof. Another reason, perhaps, was that SSOS films were prepared on a hydrophobic surface, which led to the unsymmetrical distribution of octenyl groups between the two sides. The existence of hydrophilic side prevented the oil from getting through. Furthermore, SEM micrographs of SSOS films (Figure 7) showed that the films, either with low (0.03 g/mL) or high (0.05 g/mL) concentration, were fully compact, which can provide higher mass transfer resistance than that of films with loose structure. As a result, both water and oil are hardly permeable. Thus, it is reasonable to conclude that the film will protect the core material in it well.

## CONCLUSION

Edible SSOS films were produced in the present study. The effects of concentration of SSOS, DS of octenyl group, and glycerol content on the film properties were studied. The tensile strength of the film was up to $39.4 \pm 1.9$ MPa. The increase of glycerol content resulted in a decrease of film tensile strength. WVP of SSOS films was low. Glycerol can contribute to the increase of WVP of the film. Meanwhile, study in OP showed that the film was oilproof. Overall, SSOS films are good barriers for water vapor and oil and are suitable for low-moisture foods.

**Table I.** Oil Permeability [g/(m d) $\times 10^3$] of SSOS Film with Different Concentrations and DS

| | Concentration (g/mL) | | | |
|---|---|---|---|---|
| DS | 0.040 | 0.045 | 0.050 | 0.055 |
| 0.021 | 0.1 | 0 | 0 | 0.1 |
| 0.030 | 0 | 0 | 0.1 | 0 |
| 0.050 | 0 | 0.1 | 0 | 0.2 |
| 0.068 | 0.1 | 0 | 0.2 | 0 |

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