

Effect of Surface Esterification with Octenyl Succinic Anhydride on Hydrophilicity of Corn Starch Films

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ABSTRACT: Surface of corn starch films was modified through esterification using octenyl succinic anhydride as reactant. Physical properties of the films, moisture absorption, and water contact angle were measured to characterize the effect of the surface esterification modification. The influences of the concentration of alkaline aqueous solution for activating starch, reaction temperature, and time were investigated. It was found that the pretreatments with 1.0% or 2.0% NaOH aqueous solution and reacting at 35°C for 6 h gave rise to films possessing higher water

contact angle, lower equilibrium moisture content, and moisture absorption rate at 95% relative humidity (RH). After the surface esterification modification, the equilibrium moisture content of the starch film decreased up to 29% at 95% RH and the surface water contact angle of the film increased up to 83%. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 940–947, 2009

Key words: starch film; surface modification; esterification; octenyl succinic anhydride (OSA)

INTRODUCTION

Starch is a natural polymer of D-glucose containing amylose and amylopectin. The development of thermoplastic starch (TPS) has received considerable attention over the last two decades because of its biodegradability, renewability, and low cost.^{1–4} However, moisture content in TPS changes with the environment it encounters, and this leads to change in its mechanical properties with ambient humidity, which renders TPS materials unsuitable for many high-humidity applications. The hydroxyl groups on glucose rings in amylose and amylopectin molecules are responsible for the hydrophilicity of TPS.

Surface chemical modification of TPS provides a method to reduce the surface hydrophilic character of TPS products without changing their bulk composition, characteristics, and processing properties. Several reagents, i.e., phenyl isocyanate, a phenol-blocked polyisocyanate, stearoyl chloride, and poly(styrene-co-glycidyl methacrylate), were used to react with the superficial hydroxyl groups of TPS films in the medium of methylene chloride or xylene, and it was found that all the treatments were effective in decreasing the hydrophilic character of the TPS surfaces.⁵ It was reported that the surface energy of

high-amylose potato starch films was lower, and water vapor transmission and water absorption decreased with the degree of starch substitution after surface esterification with octanoyl chloride and pyridine.⁶ In these reported surface modifications, the used organic solvents are usually expensive and toxic.

Modifications of starch to meet requirements of desirable properties for various applications have been of interest for many years in the starch industry. Modifications, such as crosslinking^{7,8} or esterification,^{9–12} can improve water resistance and impart hydrophobicity to starch products. Starch esters with moderate to high degree of substitution (DS) may find applications as substitutes for petroleum-based plastic materials especially in the packaging industry.^{13–15} One of the starch esters prepared by treating the starch with different alkenyl succinic anhydrides (ASAs), alkenylsuccinates, contains both hydrophobic and hydrophilic groups and finds applications as emulsifiers in food system.¹⁶ The length of the alkenyl group and the DS ultimately determine the extent of the hydrophobic character of the modified starch.¹⁷ With increase of the DS and the chain length of the alkenyl group, the hydrophobicity of the modified starch increases. Moreover, the esterification of starch using ASAs can be conducted in aqueous solutions, in media of organic solvents, or even in the powder state of starch with proper moisture content.¹⁸ This opens a route for surface esterification modification of thermoplastic starch products to reduce their surface hydrophilicity.

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Author's previous work showed that surface modification of corn starch films through esterification using dodecenyl succinic anhydride (DDSA) as reactant significantly reduced the moisture sensitivity and surface hydrophilic character of the starch film.¹⁹ The modification was performed at a dry solid state and only ethanol was used for diluting DDSA. In place of DDSA, octenyl succinic anhydride (OSA) may also be used to improve the hydrophobicity of TPS surface. Although a longer chain of the alkenyl group could give rise to higher hydrophobicity at similar DS values, a higher DS may be easily obtained when using the short chain ASAs, which provides another approach to increase the surface hydrophobic character of TPS products.

In this article, the surface of corn starch films was modified through esterification using OSA. The investigation was carried out to examine the effect of surface esterification on moisture absorption behavior and water contact angle of the films and to determine the preferred parameters for surface esterification modification, such as reaction temperature and time as well as concentration of alkaline aqueous solution for activating starch.

EXPERIMENTAL

Materials

The corn starch was supplied by Changchun Jincheng Corn Development, Da Cheng Group (Changchun, China). The reactant, OSA, used in the esterification reaction was 2-octen-1-ylsuccinic anhydride (97%, mixture of cis and trans) purchased from Sigma-Aldrich (Steinheim, Germany). Glycerol, sodium hydroxide, and ethanol were produced by Beijing Beihua Fine Chemicals (Beijing, China). All these chemicals were of reagent grade and used as received without any further purification.

Film preparation

Films were fabricated by solution casting method. Dry starch (25 g) and glycerol (5 g) were mixed and dispersed in 500 g distilled water to make a suspension. Then the temperature of the starch slurry was slowly raised to 90°C and kept at this temperature for 60 min with stirring to gelatinise the starch. The volume of the slurry was maintained by adding water during this period. The mixture was removed from heat, distributed in desired amount into PMMA trays for casting, and dried at 60°C. The prepared films with thickness of about 0.18 mm were peeled from the trays and sealed in zip plastic bags for experimental use.

Surface modification

The sodium hydroxide aqueous solutions with different concentrations were prepared by dissolving sodium hydroxide in distilled water. After conditioning at 11% relative humidity (RH) to moisture equilibrium, small pieces (25 mm × 20 mm) of the starch film were soaked in the sodium hydroxide aqueous solutions for various periods of time. When the films were taken out, the excess solution on the surfaces was absorbed using filter papers. The films treated with the sodium hydroxide aqueous solutions were conditioned at environments with different RH to moisture equilibrium, and then they were dipped in the OSA diluted by ethanol. Later, the samples were taken out and put in an oven for esterification reaction at different temperatures ranging from 25 to 40°C for various time periods. The modified films were removed from the oven and rinsed three times with 70% ethanol aqueous solution to remove all traces of residual reactants.

Characterization

Attenuated total reflectance-FTIR and FTIR

Fourier transform infrared (FTIR) spectra and attenuated total reflectance FTIR (ATR-FTIR) spectra were measured by using Nexus 670 FTIR Spectrometer with an ATR attachment (Nicolet, USA), before and after surface esterification modification, respectively. For FTIR measurements, the specimens were prepared by grinding starch film together with KBr and then pressed into a disc. For ATR-FTIR measurements, the surface of starch films was directly touched to the measuring probe. A spectral resolution of 4 cm⁻¹ was employed and 64 scans were acquired for each spectrum.

Moisture absorption

Moisture absorption was measured by storing the samples at room temperature in desiccators with controlled RHs (11, 33, 57, 75, and 95% RH) which were maintained by saturated salt solutions.²⁰ Briefly, the films were fully dried and weighed in an analytical balance with a precision of 0.1 mg, then exposed to the chosen humidity environment, and weighed again. The moisture content (MC) was calculated using the measured wet weight, W_w , and the dry weight, W_d , by

$$MC = (W_w - W_d)/W_d$$

The moisture equilibrium was considered to be reached when the weight gain was less than 1% since the last weighing.

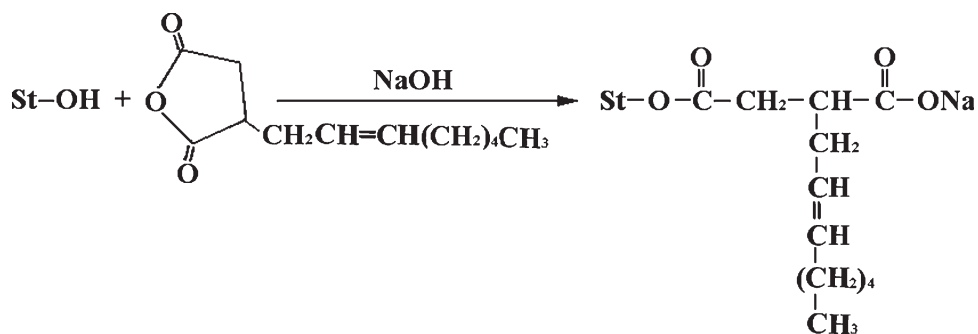


Figure 1 Schematic representation of the esterification reaction between starch and OSA.

Contact angle measurements

Contact angle measurements were carried out by using a contact angle instrument (Contact Angle System OCA20; Dataphysics, Germany). A droplet of distilled water (3 μL) was placed on the film surface. The contact angles were measured on both sides of the drop and averaged. Each reported contact angle was the mean value of at least 10 measurements, taken at different positions on the film. All the samples were conditioned at 75% RH for moisture equilibrium before measurements.

RESULTS AND DISCUSSION

Surface esterification of starch films using OSA

Schematic representation of the esterification reaction between starch and OSA is shown in Figure 1. A comparison of ATR-FTIR spectra for the control film and the ones modified by different esterification treatment conditions is presented in Figure 2(a); Spectrum 1 corresponds to the control film. For the surface-modified films, the esterification reaction took place at 35°C for 6 h, but Spectrum 2 corresponds to the one soaked in 1.0% NaOH aqueous solution for 10 s, conditioned at 75% RH to moisture equilibrium, and then dipped in OSA diluted by five times ethanol (volume); Spectrum 3 corresponds to the one soaked in 0.7% NaOH aqueous solution for 30 s, conditioned at 75% RH to moisture equilibrium, and then dipped in OSA diluted by three times ethanol (volume); Spectrum 4 corresponds to the one soaked in 1.0% NaOH aqueous solution for 30 s, conditioned at 95% RH to moisture equilibrium, and then dipped in OSA diluted by one time ethanol (volume); and Spectrum 5 corresponds to the one soaked in 2.0% NaOH aqueous solution for 10 s, conditioned at 95% RH to moisture equilibrium, and then dipped in OSA diluted by three times ethanol (volume). Comparing the ATR-FTIR spectrum of the control film with those of the modified films, it can be seen that there is a clear new peak located at 1726 cm^{-1} in the spectra of the modified films, which is associated with C=O ester

stretch. This provided the evidence that esterification occurs in the starch film.²¹ Further investigation by the FTIR transmission analysis in the disc prepared from the mixture of ground modified film and KBr powder showed that the absorbance peak at 1726 cm^{-1} became a shoulder or totally disappeared

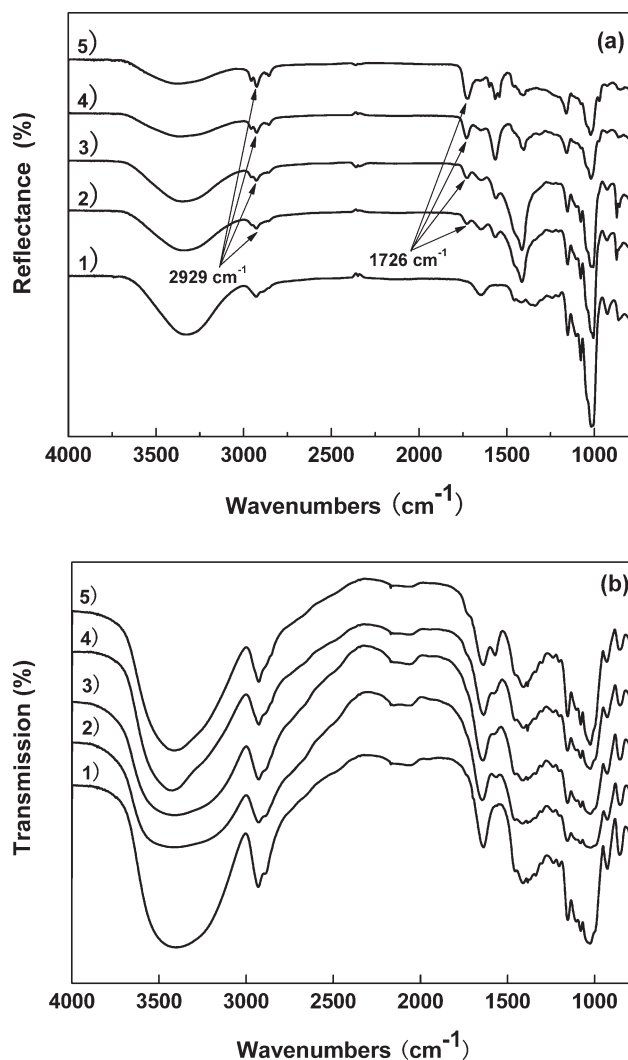


Figure 2 Comparison of ATR-FTIR and FTIR spectra for the control starch film and surface esterification modified ones: (a) ATR-FTIR spectra; (b) FTIR spectra.

as shown in Figure 2(b). This indicated that the esterification was not taking place in the bulk of the starch film and only concentrated on the surface of the film.

It was noted that the intensity of the C=O vibration (1726 cm^{-1}) varied with the esterification treatment condition. This means the surface esterification extent of the starch films was different and dependant on esterification condition. However, it is difficult to quantitatively characterize the surface esterification extent by the ATR-FTIR spectrum. Basically, the characterization of surface esterification extent of a starch film should include two parameters, one is the thickness of surface esterification layer and another is the DS of starch, i.e., the average number of hydroxyl groups substituted per glucose unit in the surface esterification layer. Since ATR-FTIR technique gives a beam penetration of a few micrometers, it implies that the ATR-FTIR spectrum only reflects the esterification at a depth of micrometer order into the film. If the thickness of surface esterification layer is larger than the depth of analysis in ATR-FTIR, the absorbance peak intensity of the C=O vibration located at 1726 cm^{-1} would not correlate to all the DS in the esterification layer. It was reported that, in the FTIR spectra of starch acetate standards, the ratio of absorbance peak intensities of the acetate C=O stretch to the starch CH_2 stretch increases linearly with DS over the range of DS from 0.5 to 2.5.²¹ However, the intensity of the C=O vibration (1726 cm^{-1}) or the ratio of intensities of the C=O vibration (1726 cm^{-1}) to the starch CH_2 vibration (2929 cm^{-1}) in an ATR-FTIR spectrum could only give a qualitative comparison of the surface esterification extent even when the thickness of the surface esterification layer is less than the depth of analysis in ATR-FTIR. A quantitative characterization needs a calibration relationship between the ratio of absorbance peak intensities (A_{1726}/A_{2929}) and DS of surface esterification layer. However, it is difficult to peel off the whole surface esterification layer to measure the DS values.

Compared with the A_{1726}/A_{2929} data of the starch films modified through esterification with DDSA, it was found that using OSA (i.e., decreasing the chain length of the alkenyl group) could give rise to higher values of A_{1726}/A_{2929} , which means a higher DS of starch hydroxyl groups was achieved. This is understandable, because the decrease of the alkenyl group chain length in ASAs enhances diffusivity and mobility of the anhydride which increases the probability of reactive moieties combining.

Effect of surface esterification on moisture absorption

As thermoplastic starch is sensitive to moisture, any improvement in reducing moisture sensitivity and

enhancing water resistance of the materials is highly important. One of the primary aims of the surface esterification modification of starch films is to investigate, how the surface esterification modifications influence the moisture sensitivity of thermoplastic starch.

From initial trials, OSA diluted by three times ethanol (volume) was selected as reactant. The ethanol plays a role, not only as a solvent to dilute the OSA but also as a vehicle to help OSA diffuse into starch film. The selected ratio of OSA to ethanol could provide enough amount of OSA for esterification reaction and allow a deeper diffusion of the reactant into the starch films. The 95% RH environment was used to recondition the films after alkaline treatment, which could lead to higher moisture content in the starch films and in turn enhance starch molecular mobility during the esterification reaction and increase the probability of the reactive moieties combining.

Figure 3 presents the equilibrium moisture contents, in various humidities at room temperature, of the control film and the surface esterification modified ones prepared by soaking the films in 1.0% sodium hydroxide aqueous solution for 10 s, conditioning at 95% RH to moisture equilibrium, then dipping in OSA diluted by three times ethanol (volume), and heating at different temperatures for 6 h. After surface esterification modification, the films showed a notable lower moisture uptake than the control one in the whole relative humidity range. Figure 4 presents the moisture absorption kinetics at 95% RH of the control film and the surface-modified ones. Basically, for all the control and surface-

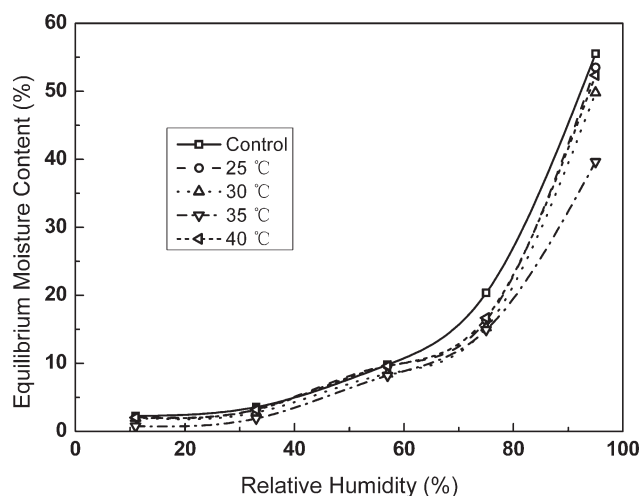


Figure 3 Moisture absorption isotherms at RT of the control film and those modified by soaking in 1.0% NaOH aqueous solution for 10 s, conditioning at 95% RH to moisture equilibrium, then dipping in OSA diluted by three times ethanol (volume), and heating at different temperatures for 6 h.

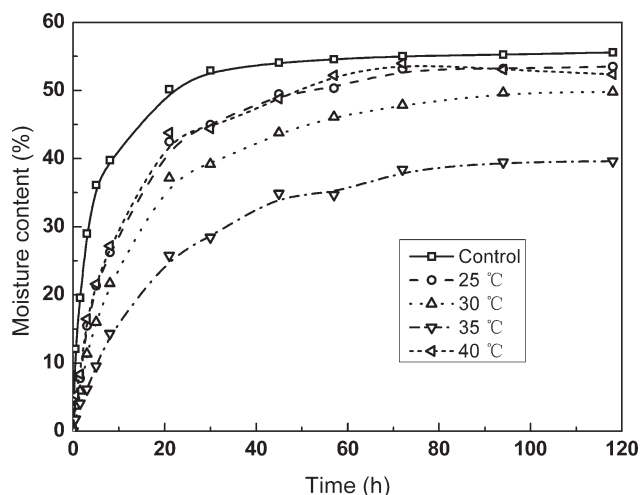


Figure 4 Moisture absorption kinetics at RT and 95% RH of the control film and those modified by soaking in 1.0% NaOH aqueous solution for 10 s, conditioning at 95% RH to moisture equilibrium, then dipping in OSA diluted by three times ethanol (volume), and heating at different temperatures for 6 h.

modified films, moisture absorption was quick in the first 20 h conditioning, and then the curves gradually turned into level. However, surface esterification modification substantially decreased the slope of the initial part of moisture absorption kinetic curves and the final values of moisture uptake. The effects of reaction temperature on the moisture absorption behavior were significant. Reaction at 25°C gave rise to a higher moisture absorption rate (i.e., the slope of the initial part of moisture absorption kinetic curve) and moisture uptake. The moisture absorption rate and moisture uptake decreased with increasing of reaction temperature, and the reaction at 35°C yielded the minimum moisture absorption rate and moisture uptake. Further increase of the reaction temperature resulted in increase of both moisture absorption rate and moisture uptake. The equilibrium moisture content of the starch films modified at 35°C decreased about 29% compared with that of the control one at 95% RH.

It is generally thought that the moisture content of a starch film is related to the available hydroxyl groups which are water-bonding sites. Therefore, the less the hydroxyl groups available to water, the lower will be the equilibrium moisture content in the starch film. The difference in equilibrium moisture content of the films, modified at different temperatures suggested that the DS of starch hydroxyl groups was different, when the esterification temperature was different. A higher temperature would be expected to enhance the diffusion of OSA into the starch films, swelling of the starch films, and mobility of the reactive moieties, and all of these will increase the esterification reaction rate and yield

higher DS. However, if the reaction temperature was too high, more water in the starch films escaped and the films became drier during esterification which could decrease the starch molecular mobility and reduce the probability of the reactive moieties combining. The lower equilibrium moisture content in the films modified at 35°C indicated that more hydroxyl groups have been substituted in the esterification modification under this temperature.

Figure 5 showed the moisture absorption kinetics at 95% RH of the films modified by soaking in NaOH aqueous solutions with different concentrations for 10 s, conditioning at 95% RH to moisture equilibrium, then dipping in OSA diluted by three times ethanol (volume), and heating at 35°C for 6 h. The surface esterification modification significantly reduced the moisture absorption rate and moisture uptake of starch films, i.e., reduced the film's moisture sensitivity. In the investigated range of the concentration of alkaline aqueous solution, the film treated with 1.0% NaOH aqueous solution had a lower moisture absorption rate and moisture uptake. It was reported that the pH values ranged in 8.09.0 gave rise to higher DS and reaction efficiency for the esterification of granular starch with ASAs (OSA and DDSA) in aqueous slurry.^{16,17} For the surface esterification modification of the starch films in this study, the purpose of alkaline treatment is to activate the hydroxyl groups of starch for nucleophilic attack of the anhydride moieties and keep the reaction toward the esterification instead of hydrolysis. Under the condition of fixing soaking time in alkaline aqueous solution, the concentration of alkaline aqueous solution will determine the alkali content in

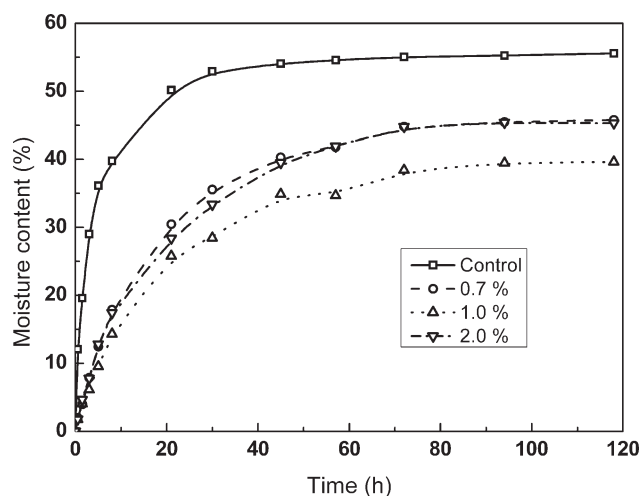


Figure 5 Moisture absorption kinetics at 95% RH of the control film and those modified by soaking in NaOH aqueous solutions with different concentrations for 10 s, conditioning at 95% RH to moisture equilibrium, then dipping in OSA diluted by three times ethanol (volume), and heating at 35°C for 6 h.

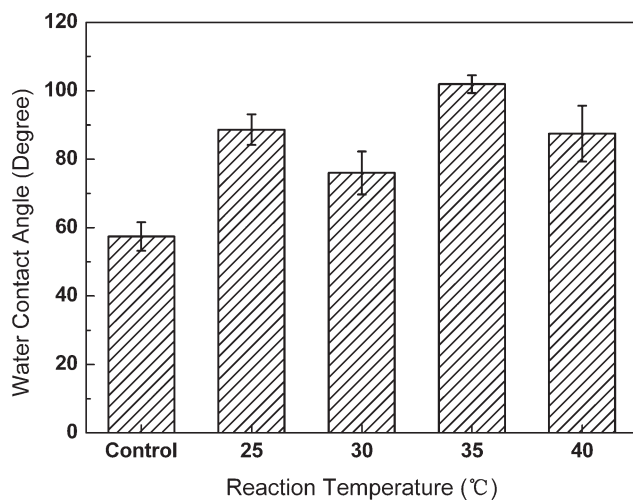


Figure 6 Effect of reaction temperature on water contact angle of the starch films modified by soaking in 1.0% NaOH aqueous solution for 10 s, conditioning at 95% RH to moisture equilibrium, then dipping in OSA diluted by three times ethanol (volume), and heating at various temperatures for 6 h.

surface layer of the starch film and this will affect the esterification efficiency and the DS of starch hydroxyl groups in the surface layer, which eventually impacts the moisture absorption behavior of the films. As shown in Figure 5, a lower moisture absorption rate and moisture uptake obtained for the films treated with 1.0% NaOH aqueous solution indicated that the alkaline condition created by this treatment was favorable to the esterification reaction in the film surface layer to yield higher DS compared with the others.

It was found that the starch films modified through esterification using OSA possessed lower moisture sensitivity than that modified using DDSA.¹⁹ This is probably because a higher DS could be obtained in the surface esterification using OSA so that the hydroxyl groups available to water bonding became less.

Effect of surface esterification on water contact angle

As mentioned earlier, although OSA has shorter alkenyl chain, a higher surface DS of starch hydroxyl groups could be obtained. In other words, the surface of starch films modified through esterification using OSA may have more alkenyl substituents but the chain length of the alkenyl group is shorter. Thus, it is deserved to investigate the effect of surface esterification modification using OSA on the surface hydrophilic character of the starch films. Surface water contact angle is a parameter that provides a quantitative characterization of material surface

energy. An increase in water contact angle indicates an enhancement of hydrophobic character of surface.

Figure 6 shows the effect of reaction temperature on water contact angle of the modified films. For this investigation, the modified films were prepared by soaking the films in 1.0% NaOH aqueous solution for 10 s, conditioning at 95% RH to moisture equilibrium, then dipping in OSA diluted by three times ethanol (volume), and heating at various temperatures for 6 h. Compared with the water contact angle of control film, which is $57.4^\circ \pm 4.2^\circ$, the surface esterification modification significantly increased the water contact angle of the starch films, which indicated the hydrophobic character of starch film surface was enhanced. It can be seen that the reaction at 35°C gave rise to the film having higher water contact angle compared with other investigated reaction temperatures. From the results of the influence of reaction temperature on the moisture absorption behavior of the starch films, it was expected that the water contact angle should increase with reaction temperature, reach a maximum value at 35°C, and then decline. However, the water contact angle at 30°C was lower than that at 25°C. Actually, the measurements were taken at 15 different positions for this condition, and most of data were slightly lower than that of 25°C, but the data from three positions were particularly low which gave rise to a lower water contact angle at 30°C. The reason is not clear at this moment.

Figure 7 presents the effect of concentration of NaOH aqueous solution on water contact angle of the modified films. In this case, the reaction

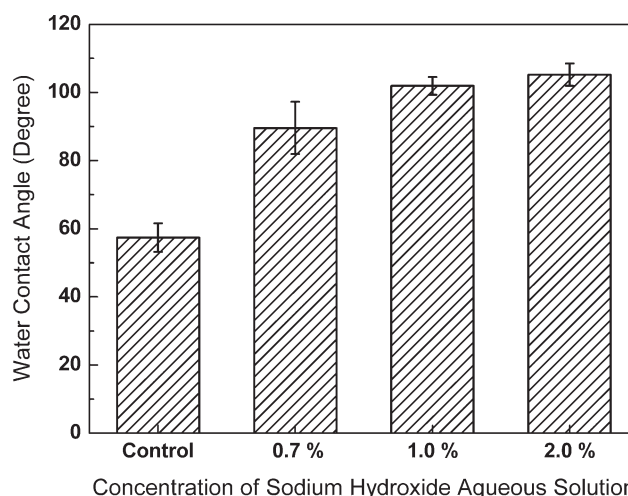


Figure 7 Change of water contact angle with concentration of NaOH aqueous solution for the films modified by soaking in NaOH aqueous solutions for 10 s, conditioning at 95% RH to moisture equilibrium, then dipping in OSA diluted by three times ethanol (volume), and heating at 35°C for 6 h.

TABLE I
Water Contact Angle of the Surface Esterification Modified Films^a

Reaction time (h)	Reaction temperature		
	At 30°C	At 35°C	At 40°C
1	95.0 ± 9.1	90.1 ± 5.9	93.5 ± 7.1
3	99.9 ± 8.4	99.9 ± 5.9	98.4 ± 3.4
6	101.5 ± 7.1	105.2 ± 3.3	105.3 ± 7.8
8	80.5 ± 3.9	94.6 ± 7.2	82.0 ± 7.9

^a Films prepared by soaking in 2.0% NaOH aqueous solution for 10 s, conditioning at 95% RH to moisture equilibrium, then dipping in OSA diluted by three times ethanol (volume), and heating at different temperatures for different time.

parameters were identical to those aforementioned except that the reaction temperature was kept at 35°C and the concentration of NaOH aqueous solutions was changed from 0.7 to 2.0%. The results in Figure 7 show that soaking the films in 2.0% NaOH aqueous solution yielded a higher water contact angle. These were inconsistent with that of the influence of NaOH aqueous solution concentration on the moisture absorption behavior of the starch films. Actually, the effect of concentration of NaOH aqueous solution on water contact angle is a little bit complicated. It is well known that the surface morphology affects the water contact angle and an increase in microroughness is accompanied by hydrophobic properties.⁴ Soaking the films in alkaline aqueous solutions of different concentration could cause film surfaces with different roughness; therefore, the water contact angle of the modified films would be not only dependent on the numbers of superficial alkenyl substituents but also the surface roughness. The dissimilar influences of NaOH aqueous solution concentration on the equilibrium moisture content and water contact angle shown in Figures 5 and 7 may also be explained by the fact that the equilibrium moisture content in the surface esterification modified films is more related to the DS in the whole surface esterification layer, whereas the water contact angle is more related to the DS at the film surface. The treatment with 2.0% NaOH aqueous solution may lead to a higher superficial DS but a lower total DS in the whole esterification layer.

Table I lists the water contact angle data of the surface esterification modified films prepared by soaking in 2.0% NaOH aqueous solution for 10 s, conditioning at 95% RH to moisture equilibrium, then dipping in OSA diluted by three times ethanol (volume), and heating at different temperatures for different time. It can be seen that for the investigated reaction temperatures, the water contact angle increased with increase of reaction time and a 6-h reaction gave the films a maximum water contact

angle. The increasing of water contact angle with reaction time is due to the enhancement of octenyl succinylation, which is a direct consequence of favorable effect of time on diffusion and adsorption of the reactant. However, prolonging the reaction time beyond 6 h resulted in decreased water contact angle. An explanation may be that as the esterification reaction progresses, the OSA was depleted and the reverse reaction of ester hydrolysis became dominant. The results in Table I indicated that 6-h reaction is sufficient to modify the surface layer of starch films and no improvement in water contact angle were observed by further increasing the reaction time in the investigated range.

CONCLUSIONS

The surface of corn starch films was modified through esterification by dipping the films in OSA diluted by three times ethanol (volume) and then heating at 25–40°C for several hours with pretreatments of immersion in sodium hydroxide aqueous solution for 10 s and reconditioning at 95% RH to equilibrium. The surface esterification modification with OSA significantly reduced the moisture sensitivity and surface hydrophilic character of the starch films. The treatments with 1.0% or 2.0% NaOH aqueous solutions and the reaction at 35°C for 6 h gave rise to films possessing higher water contact angle, lower equilibrium moisture content, and moisture absorption rate at 95% RH. After the surface esterification modification, the equilibrium moisture content of the starch film decreased up to 29% (from 55.6% to 39.6%) at 95% RH and the surface water contact angle of the film increased up to 83° (from 57.4° to 105.2°). The surface esterification modification technology using OSA provides a new approach to improve the hydrophilic nature of thermoplastic starch or to produce more moisture resistant thermoplastic starch products without changing their bulk composition and processing properties.

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