Surface esterification of corn starch films: Reaction with dodecenyl succinic anhydride

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ABSTRACT

Surface of corn starch films was modified through esterification using dodecenyl succinic anhydride (DDSA) as reactant. The effects of reaction temperature and time, concentration of alkaline aqueous solution for activating starch, concentration of ethanol diluted DDSA, and time of alkaline aqueous solution treatment on the physical properties related to material's hydrophilic nature, such as moisture absorption and surface water contact angle, were investigated. It was found that the surface esterification modification significantly reduced the moisture sensitivity and surface hydrophilic character of starch film. Due to the hydroxyl groups in the film surface layer were reacted with DDSA, the equilibrium moisture content of the starch film under 95% RH declined 22% and the surface water contact angle increased up to 82% after surface esterification modification.

1. Introduction

Thermoplastic starch (TPS), a homogeneous starch melt obtained through disrupting the starch granular structure by mechanical and thermal energy with presence of water or other plasticizers, can be processed with existing plastic processing technologies (Lorcks, 1998; Shogren, Fanta, & Doane, 1993). TPS has attracted significant interest in recent years because of its biodegradability, renewability and low cost (Chandra & Rustgi, 1998; Gandini, 2008; Mohanty, Misra, & Hinrichsen, 2000; Yu, Dean, & Li, 2006) and has found its applications in the plastic market to replace non degradable petrochemical-based materials especially in packaging industry. Loose-fill (foamed chips for filling space around goods within a packing box) and packaging trays made from TPS are commercially available. However, the hydrophilic nature of TPS, mainly due to the hydroxyl groups on starch molecules, renders TPS unsuitable for many high humidity applications.

On the other hand, modifications of starch to meet requirements of desirable properties for various applications have been of interest for many years in the starch industry. Esterification is one of the modifications which can impart hydrophobicity to starch products (Aburto et al., 1999; Neumann, Wiege, & Warwel, 2002; Sagar & Merrill, 1995; Shogren, 2003; Tessler & Billmers, 1996). Starch esters with moderate to high degree of substitution (DS, 3 is the highest) may find applications as substitutes for petroleum-based plastic materials especially in the packaging industry

(Albertsson & Karlsson, 1995; Bisws et al., 2008; Riward, Moens, Roberts, Brigham, & Kelley, 1995; Xu, Dzenis, & Hanna, 2005). However, the market penetration has been low due to relatively high production costs of starch esters (Bisws et al., 2008). Several studies have been done in an attempt to prepare starch esters more rapidly and environmentally friendly (Bisws, Shogren, Kim, & Willett, 2006; Bisws et al., 2008; Miladinov & Hanna, 2000; Shogren, 2003).

Surface chemical modification is a promising method to reduce the surface hydrophilic character without changing their bulk composition and properties of TPS products. The superficial hydroxyl groups of TPS can be substituted with hydrophobic groups or react with cross-linking agents to form starch molecule networks, so that the surfaces of TPS products become less sensitive to moisture.

It was reported that surface hydrophobicity of TPS samples was improved greatly when the TPS surface has been treated with pre-polymers having —NCO groups (Yu & Liu, 2002). Bengtsson, Koch, and Gatenholm (2003) reported that after surface esterification with octanoyl chloride and pyridine, 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. Carvalho, Curvelo, and Gandini (2005) used several reagents, i.e., phenyl isocyanate, a phenol blocked polyisocyanate, stearoyl chloride and poly(styrene-co-glycidyl methacrylate) to react with the superficial hydroxyl groups of TPS films in the medium of methylene chloride or xylene, and found that all the treatments were effective in decreasing the hydrophilic character of the TPS surfaces. Cross-linking technology was also used for surface modification of thermoplastic starch. Surface of corn starch sheets was modified by cross-linking through ultra violet (UV) irradiation

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by using sodium benzoate as photosensitizer, the results showed that surface photo-cross-linking modification significantly reduced the hydrophilic character of the starch sheet surface and enhance the water resistance of the starch sheets (Zhou, Zhang, Ma, & Tong, 2008).

Compared to the esterification modification of native granular starch, surface esterification of thermoplastic starch should be easier. Since starch crystalline structure has been disrupted in TPS, the reactant reagents can diffuse into material and combine with the hydroxyl groups on starch molecules more easily. In addition, the amounts of reactant reagents used in a surface modification would be significantly lower than that in a bulk modification. Moreover, as surface modification can be carried out after the formation of TPS products, it will not affect the processing properties of TPS.

In this study, surface of corn starch films was modified through esterification using dodecenyl succinic anhydride (DDSA). Investigation was carried out to determine the preferred parameters such as esterification reaction temperature and time, concentration of alkaline aqueous solution for activating starch, concentration of ethanol diluted DDSA, and treating time in alkaline aqueous solution. The influence of surface esterification on some physical properties, such as moisture absorption behavior and water contact angle, of the films was presented.

2. Experimental

2.1. Materials

The corn starch was supplied by Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (Changchun, China). The reactant used in the esterification reaction was DDSA (dodecenyl succinic anhydride, 90% purity) purchased from Sigma–Aldrich (St. Louis, USA). Glycerol, sodium hydroxide and ethanol were from Beijing Beihua Fine Chemicals Co. Ltd. (Beijing, China). All these chemicals were of reagent grade and used as received without any further purification.

2.2. Film preparation

Films were fabricated by solution casting method. Mixture of 25 g dry starch and 5 g glycerol was dispersed in 500 ml distilled water to make a suspension. Then the temperature of the starch slurry was slowly raised to 90 °C with stirring and kept at this temperature for 60 min and maintained stirring to gelatinise the starch. The volume of the slurry was maintained by adding water during this period. The mixture was removed from heat and was 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.

2.3. Surface modification

The sodium hydroxide aqueous solutions with different concentrations were prepared by dissolving sodium hydroxide in distilled water. After conditioned at 11% RH to moisture equilibrium, small pieces (25 × 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 by using filter papers. The films treated with the sodium hydroxide aqueous solutions were conditioned in 95% RH environments for moisture equilibrium, and then they were dipped in ethanol diluted DDSA. Afterwards, the samples were placed in an oven at different temperature ranged from 30–40 °C for various times to finish the esterification reaction. The modified films were removed

from the oven and rinsed three times with 70% ethanol aqueous solution to remove all traces of residual reactants.

2.4. Characterization

2.4.1. FTIR and ATR-FTIR

Fourier transform infrared (FTIR) spectra and attenuated total reflectance FTIR spectra were measured by using a 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 sample together with KBr and then pressed into a disc. For ATR-FTIR measurements, the measuring probe directly touched the surface of starch films. A spectral resolution of 4 cm^{-1} was employed and 64 scans were acquired for each spectrum.

2.4.2. Moisture absorption

Moisture absorption was measured by storing the samples at room temperature in desiccators with controlled relative humidities (11%, 33%, 57%, 75% and 95% RH) which were maintained by saturated salt solutions (Zhou et al., 2008). 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 less than 1% since the last weighing.

2.4.3. 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 ten measurements taken at different positions on the film. All the samples were conditioned at 75% RH for moisture equilibrium before measurements.

3. Results and discussion

3.1. Surface esterification of starch film

The starch films were surface modified through esterification using DDSA as reactant. Fig. 1 showed the schematic representation of the esterifiation reaction. The esterification of starch with dodecenyl succinic anhydride could take place in an aqueous slurry system or even in its powder state under temperature of 25–40 °C, and the reaction could last several hours (Chen, Zhang, Zhang, & Wu, 2000; Jeon, Viswanathan, & Gross, 1999). For the surface esterification in a solid state starch film, a reaction condition at 35 °C for 6 h was firstly tried. Fig. 2 presented a comparison of FTIR spectra and ATR-FTIR spectra for control starch film and one modified by soaking in 1.0% sodium hydroxide aqueous solution for 30 s and
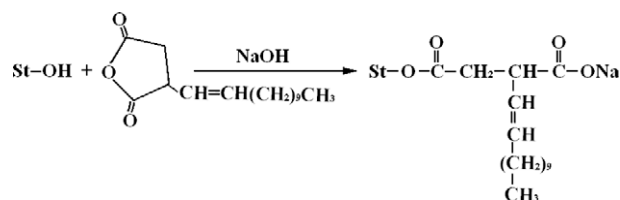

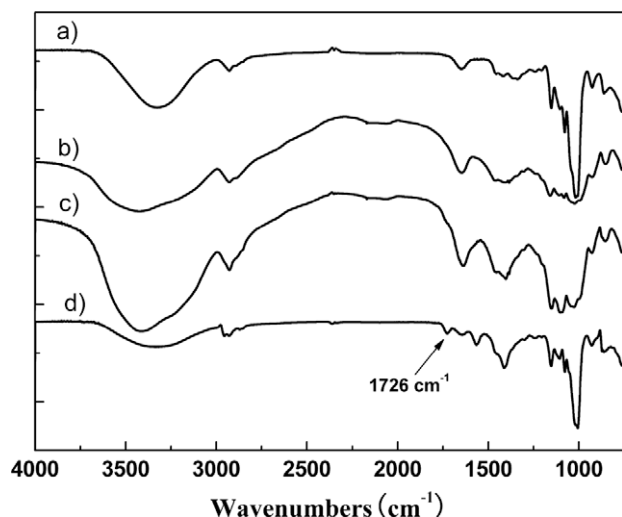**Fig. 1.** Schematic representation of the esterification reaction.

Fig. 2. Comparison of FTIR spectra and ATR-FTIR spectra for the control starch film and a surface esterification modified one: (a) ATR-FTIR spectrum of the control film; (b) FTIR spectrum of the powder from the whole modified film; (c) FTIR spectrum of the powder scraped from surface of the modified film; (d) ATR-FTIP spectrum of the modified film.

conditioned at 95% RH to moisture equilibrium, then dipping in 1/10 (v/v) DDSA/ethanol and heating at 35 °C for 6 h. The spectrum A was obtained by the ATR-FTIR method from surface of the control film. The spectrum B was obtained from a specimen prepared by grinding a small piece of the modified film together with KBr and then pressed into a disc. The spectrum C was obtained from a specimen prepared by mixing and grinding the powder scraped from surface of the modified film with KBr and then pressed into a disc. Spectrum D was obtained by the ATR-FTIR method from surface of the modified film. Comparing these spectra, it can be seen that there is a clear new peak in the ATR-FTIR spectrum of the modified film located at 1726 cm^{-1} (spectrum D) which is associated with C=O ester stretch. This is evidence that esterification occurs in the starch film (Shogren, 2003). Inspection of Fig. 2, it was found that, in the FTIR spectrum of the surface powder (spectrum C), the absorbance at 1726 cm^{-1} significantly reduced and only a shoulder could be seen, while this peak totally disappeared in the FTIR spectrum of the modified film (spectrum B). These observations indicated that the esterification was not taking place in the bulk of the starch film and only concentrated to the surface of the film. Since ATR technique gives a beam penetration of a few micrometers, this implied that the esterification at least occurred at a depth of micrometer order into the film.

For the surface esterification modification of starch films in this study, several factors could influence the extent of the esterification of starch films. These factors include the reaction temperature and time, concentration of sodium hydroxide aqueous solution, concentration of DDSA in ethanol, soaking time in the alkaline aqueous solution, and moisture content of the specimen. Investigation of the surface esterification kinetics could provide an efficient route to reach a desired extent of surface esterification. 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 degree of substitution (DS) of starch, i.e., the average number of hydroxyl groups substituted per glucose unit in the surface esterification layer. The general titration method for determining DS in starch ester (Bhosale & Singhal, 2006; Jeon et al., 1999), which could give DS value corresponding to the whole bulk of involved starch sample, is not suitable to characterize the extent of surface esterification which only takes place in

surface layer of starch film. Although AFT-FTIR spectra could be used to characterize the surface esterification extent of the starch films, it can only give a qualitative result instead of a quantitative one. Moreover, since the depth of analysis in the AFT-FTIR method is dependant on the wavelength, the refractive index of the sample and the angle of incidence, it can be imagined that if the thickness of the surface esterification layer is less than the depth of analysis in AFT-FTIR, the absorbance peak intensity of the C=O vibration located at 1726 cm^{-1} should be increase with the DS of the esterification layer. However, if the thickness of surface esterification layer is larger than the depth of analysis in AFT-FTIR, the absorbance peak intensity of the C=O vibration located at 1726 cm^{-1} would not correlate to the DS of the whole esterification layer. Thus, characterization of surface esterification extent by AFT-FTIR has limitation when the thickness of surface esterification layer can not be determined. Some other methods are being considered to characterize the surface esterification extent of starch films, further work will be under investigation.

3.2. Effect of surface esterification on moisture absorption

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 the material. Although precise characterization of the surface esterification extent in starch films is difficult, the effect of surface esterification modification on moisture absorption of starch films could be characterized easily by examining the moisture absorption isotherms at room temperature and the moisture absorption kinetics at 95% relative humidity using the control film and surface modified ones.

Fig. 3 presented the equilibrium moisture contents, in various humidities at room temperature, of the control film and the surface esterification modified films prepared by soaking the films in 1.0% sodium hydroxide aqueous solution for 30 s and conditioned at 95% RH to moisture equilibrium, then dipping in 1/5 (v/v) DDSA/ ethanol and heating at 35 °C for different time. It can be seen that, after surface esterification modification, the films showed a notable lower moisture uptake than the control one in the whole relative humidity range. At 95% RH, the equilibrium moisture content of the surface esterification modified films decreased about 22% compared to that of the control one.
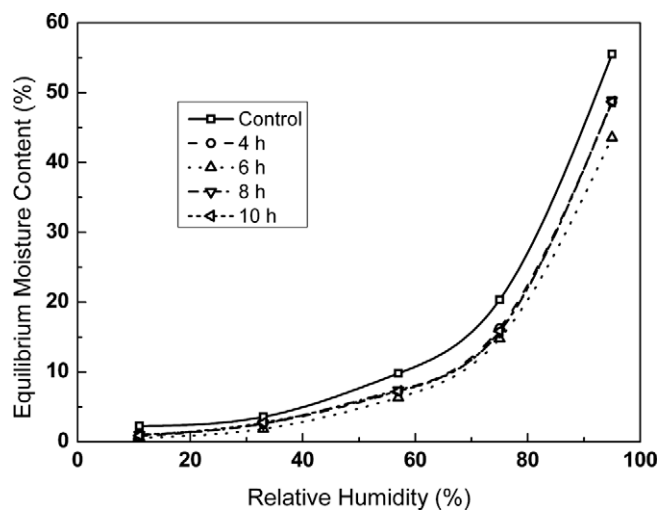

Fig. 3. Moisture absorption isotherms at RT of the control and modified films by heating different time at 35 °C (in 1.0% NaOH for 30 s, 95% RH conditioned, 1/5 (v/v) DDSA/ethanol).

Moisture absorption kinetics of the films were examined at 95% RH, the data were presented in Fig. 4. Basically, for all the control and surface modified films, moisture absorption was quick in the first 10 h conditioning, afterwards the curves gradually turned into level. The influence of surface esterification modification on the initial part of moisture absorption kinetic curves was not marked. However, the final values of moisture uptake for the surface modified films decreased. These results suggested that although surface esterification modification under the described conditions did not give the starch films a noticeable change in moisture absorption rate, it did dramatically reduce the moisture uptake ability of the films. Other reaction temperatures (30 and 40 °C) were also investigated, the results were similar and showed that the influence of the reaction temperature was not markedly and 6 h reaction was better than others (4, 8 and 10 h).

It was reported that the pH values ranged in 8.0–9.0 gave rise to higher DS and reaction efficiency for the esterification of granular starch with alkenyl succinic anhydrides in aqueous slurry (Bhosale & Singhal, 2006; Jeon et al., 1999). 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. Thus, the concentration of alkaline aqueous solution and the soaking time, which will determine the alkali content and distribution thickness in the film's surface layer, are important parameters to affect the surface esterification extent (i.e., the thickness of esterification surface layer and the degree of substitution in the layer) which in turn impacts the moisture absorption behavior of the films. Fig. 5 showed the moisture absorption kinetics at 95% RH of the films modified by soaking in NaOH aqueous solutions with different concentrations for 60 s and conditioned at 95% RH to moisture equilibrium, then dipping in 1/10 (v/v) DDSA/ethanol and heating at 35 °C for 6 h. The effect of the concentration of alkaline aqueous solution on the moisture absorption was markedly. Compared to the control film, the surface modified films showed lower moisture uptake ability and moisture absorption rate as well. In the investigated range, the 0.7% sodium hydroxide aqueous solution gave rise to the film possessing a lower equilibrium moisture content and slower moisture absorption kinetics. It is general thought that the moisture content of starch film is related the available hydroxyl groups which are water bonding sites. Therefore, the less the
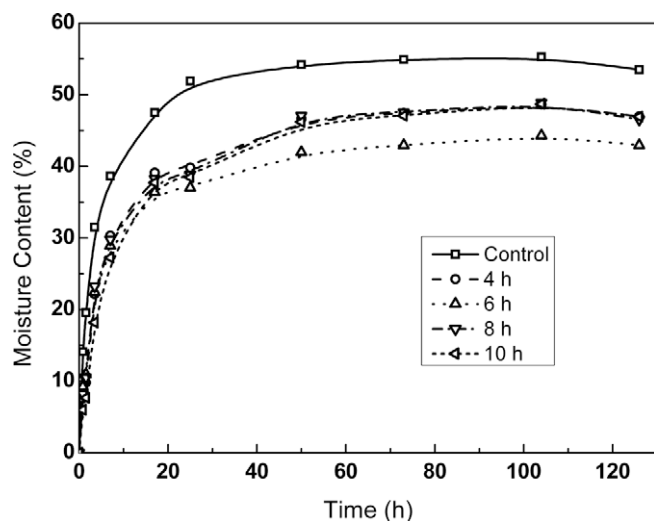

Fig. 5. Moisture absorption kinetics at RT and 95% RH of the control and modified films by soaking in different concentration NaOH aqueous solutions for 60 s (95% RH conditioned, 1/10(v/v) DDSA/ethanol, 35 °C for 6 h).

hydroxyl groups available to water is, the lower the equilibrium moisture content in the film. The lower equilibrium moisture content in the surface modified films indicated that more hydroxyl groups have been substituted in the surface esterification modification. In the modification process wherein the films were soaked in NaOH aqueous solutions with different concentrations for same time, the thickness of esterification surface layer should be same. The difference in equilibrium moisture content suggested that the DS is different in the surface esterification layer. This may be because the alkaline condition created by soaking in 0.7% sodium hydroxide aqueous solution is favorable to the esterification reaction occurred at the film surface compared to the others. The effect of soaking time in sodium hydroxide aqueous solutions with various concentrations on the moisture absorption was also examined. In the investigated range, 10–120 s, the influence was not significantly (data not shown). This is probably due to the effect of DDSA diffusion depth because the thickness of surface esterification layer is not only dependant on the soaking time in sodium hydroxide aqueous solution but also the DDSA diffusion depth.

The ethanol plays a role not only a solvent to dilute the DDSA but also a vehicle to help the DDSA diffuse into starch film. Obviously, concentration of ethanol diluted DDSA will determine the amount of DDSA available to esterification and the depth that the DDSA could diffuse into the films. Although a lower concentration of ethanol diluted DDSA will provide less DDSA for esterification at the surface, it can give rise to a deeper diffusion of DDSA into films which will lead to more starch hydroxyl groups involved in the esterification reaction. Therefore, the concentration of ethanol diluted DDSA will influence the depth that esterification takes place and the DS of hydroxyl groups in surface esterification layer which in turn impacts the moisture absorption behavior of the films. Fig. 6 showed the moisture absorption kinetics at 95% RH of the films modified by soaking in 1.0% NaOH aqueous solution for 30 s and conditioned at 95% RH to moisture equilibrium, then dipping in ethanol diluted DDSA with different volume ratios and heating at 35 °C for 6 h. It can be seen from Fig. 6, modification with 10 times ethanol diluted DDSA gave rise to the films a higher equilibrium moisture content at 95% RH compared to that modified by other ethanol diluted DDSA, this is probably because the 10 times ethanol diluted DDSA could not provide enough DDSA for esterification reaction to substitute the starch hydroxyl groups. However, there is no marked difference in equilibrium moisture content for the films modified by one, three and five times ethanol diluted DDSA. This suggested that the concen-

Fig. 4. Moisture absorption kinetics at RT and 95% RH of the control and modified films by heating different time at 35 °C (in 1.0% NaOH for 30 s, 95% RH conditioned, 1/5 (v/v) DDSA/ethanol).
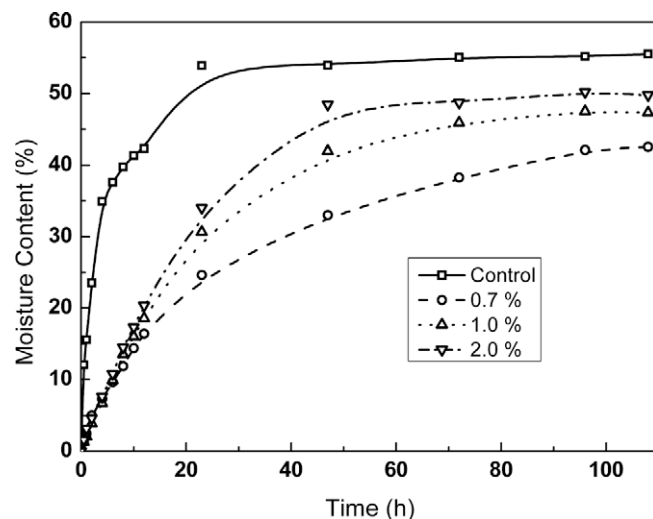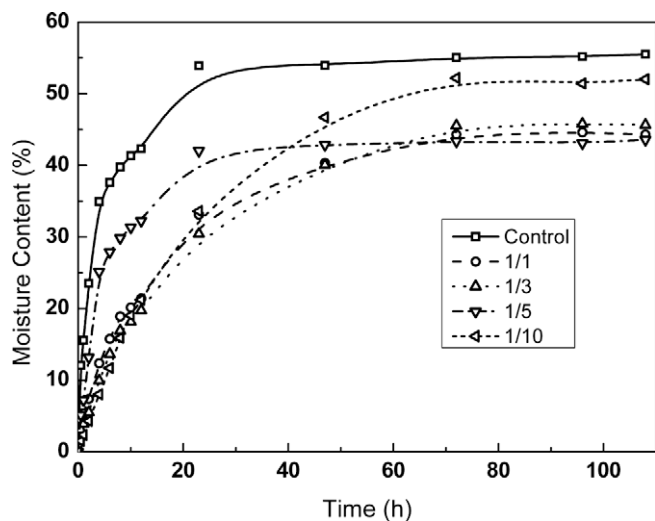
Fig. 6. Moisture absorption kinetics at RT and 95% RH of the control and modified films by dipping in DDSA/ethanol with different volume ratios (in 1.0% NaOH for 30 s, 95% RH conditioned, 35 °C for 6 h).

tration of five times ethanol diluted DDSA is sufficient for the surface esterification reaction in starch films and further increase of the concentration of DDSA in ethanol could not lead to a higher surface esterification extent.

The moisture content of starch film should also have influence on the extent of surface esterification. Although no reconditioning after soaking in NaOH aqueous solution is easier, more convenient and saving time in practical applications, it is difficult to evaluate and control the water content in the surface layer containing sodium hydroxide for the studied cases. Therefore, all the specimens were conditioned at 95% RH to moisture equilibrium before dipping in the ethanol diluted DDSA and heating for esterification. Thus, the effect of moisture content of film on surface esterification should be negligible. Actually, the specimens conditioned at 75% and 95% RH after soaking in NaOH aqueous solution were compared, and the results showed that the specimens conditioned at 95% RH had more intense absorbance peak of C=O vibration located at 1726 cm^{-1} in AFT-FTIR spectra and their moisture absorption behavior suggested a higher extent of esterification was yielded after surface modification.

3.3. Effect of surface esterification on water contact angle

One of the parameters which reflect the hydrophilic nature of the material is the surface water contact angle. Since the two surfaces of the starch films prepared by casting method have different morphologies (the surface contacting with PMMA plate was smoother) and surface contact angle correlates with not only the surface polarity but also surface roughness, the water contact angle was only measured at the air contact surface in this study.

Table 1 presented the water contact angles of the surface esterification modified films prepared by soaking in 1.0% NaOH aqueous

Table 1
Water contact angles of the surface esterification modified films prepared at different temperatures for different time (in 1.0% NaOH for 30 s, 95% RH conditioned, 1/5 (v/v) DDSA/ethanol).

Reaction time (h)	30 °C	35 °C	40 °C
4	97.0 ± 5.9°	104.0 ± 5.7°	103.1 ± 2.7°
6	100.3 ± 3.4°	93.6 ± 8.7°	76.0 ± 5.9°
8	102.2 ± 5.5°	94.3 ± 5.1°	100.5 ± 4.6°
10	109.3 ± 10.5°	94.9 ± 4.1°	103.3 ± 3.6°

solution for 30 s and conditioned at 95% RH to moisture equilibrium, then dipping in 1/5 (v/v) DDSA/ethanol and heating at different temperatures for different time. Compared to the water contact angle of control film, which is 57.4 ± 4.2°, the surface esterification modification significantly increased the water contact angle of the films, an up to 82% jump of water contact angle was observed. An increase in water contact angle indicates an enhancement of hydrophobic character of surface and a lower value for the polar component of the surface energy. The enhancement of surface hydrophobic nature of the starch film can be explained by the inference that, after the esterification reaction, some hydroxyl groups in the surface layer have been consumed and are never available to water.

Fig. 7 showed the change of water contact angle with concentration of NaOH aqueous solution when the surface modifications were carried out by soaking the films in NaOH aqueous solutions with different concentrations for 60 s and conditioned at 95% RH to moisture equilibrium, then dipping in 1/10 (v/v) DDSA/ethanol and heating at 35 °C for 6 h. Since soaking the films in alkaline aqueous solutions of different concentration could cause the film surface having different surface roughness, therefore the difference in the water contact angle of the modified films treated with NaOH aqueous solutions of different concentration may be not only dependent on the extent of surface esterification but also the surface roughness. Fig. 8 showed the change of water contact angle with concentration of DDSA in ethanol when the surface modifications were carried out by soaking the films in 1.0% NaOH aqueous solution for 30 s and conditioned at 95% RH to moisture equilibrium, then dipping in ethanol diluted DDSA with different volume ratios and heating at 35 °C for 6 h. The results showed that when the 1/5 (v/v) DDSA/ethanol was used, the surface modification gave rise to a higher value of surface water contact angle compared to the others.

The relationship between the water contact angle and the equilibrium moisture content at 95% RH is complicated. A modified film with lower equilibrium moisture content at 95% RH was not always corresponding to the one having a higher water contact angle. This is understandable. The equilibrium moisture content may be more related to the DS in the whole surface esterification layer of the film, while the water contact angle probably is more related to the DS of superficial hydroxyl groups
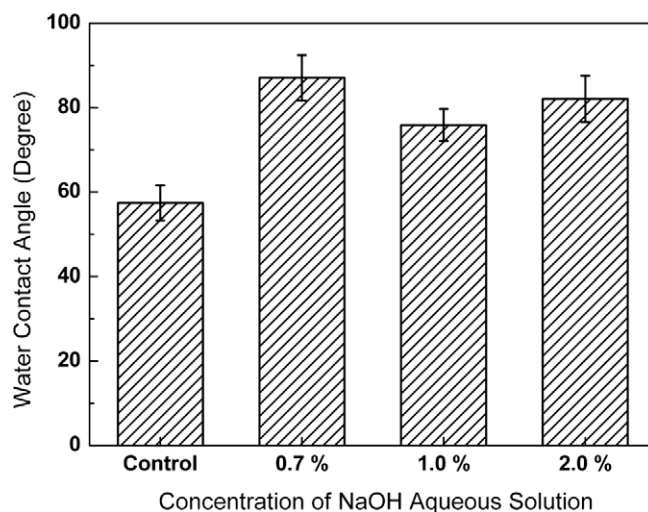

Fig. 7. Change of water contact angle with concentration of NaOH aqueous solution for the films soaked in NaOH aqueous solutions for 60 s (95% RH conditioned, 1/10 (v/v) DDSA/ethanol, 35 °C for 6 h).
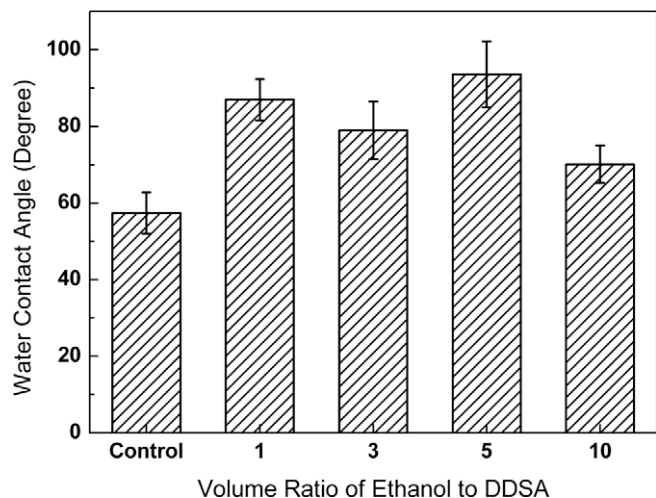
Fig. 8. Change of water contact angle with concentration of DDSA in ethanol for the modified films (in 1.0% NaOH for 30 s, 95% RH conditioned, 35 °C for 6 h).

of the starch film and the surface roughness. Shorter soaking in NaOH aqueous solution and dipped in denser DDSA/ethanol solution would give rise to a thinner surface esterification layer due to less of starch macromolecules involved in the esterification reaction, but the DS in the esterification layer could reach a relative higher value if reaction conditions were optimum. The effect of surface esterification modification on moisture absorption and water contact angle is dependent on the total DS of the hydroxyl groups in the esterification layer and the DS of superficial hydroxyl groups of the film.

4. Conclusions

The surface of thermoplastic starch films can be modified through esterification by dipping the films in ethanol diluted DDSA and then heating at 30–40 °C in air for several hours with pretreatments of immersion in sodium hydroxide aqueous solution for a while and reconditioning at 95% RH to equilibrium. The surface esterification modification with DDSA significantly reduced the moisture sensitivity and surface hydrophilic character of the starch films. After surface esterification modification, the equilibrium moisture content of the starch film at 95% RH decreased up to 22% and the surface water contact angle of the film increased up to 82%. The surface esterification modification technology using DDSA provide a new approach to improve the hydrophilic nature of thermoplastic starch and to produce more moisture resistant thermoplastic starch products without changing their bulk composition and properties. This modification technology will extend the possible applications of thermoplastic starch materials.

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