SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF ACETYLATED HIGH-AMYLOSE CORN STARCH

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High-amylose corn starch (HACS) is very attractive due to its peculiar physico-chemical characteristics associated with its high amylose content. The aim of this work was to obtain acetylated high-amylose corn starch (AHACS) under optimum acetylation parameters, using HACS as a raw material, acetic anhydride as an acetylating agent and sodium hydroxide as a catalyst. The acetylation parameters were optimized by the orthogonal test. Acetylated high-amylose corn starch (AHACS) was characterized by infrared spectroscopy, DSC and TGA. Its freeze-thaw stability, swelling power, blue value and retrogradation were measured and compared with those of HACS and corn starch (CS). The best conditions for preparing AHACS were: reaction temperature of 40 °C, reaction time of 2 h and pH 8.5. The thermal stability of HACS was poor because of the high amylose content. The effect of acetylation on the crystalline region of HACS was not obvious. HACS was more easily acetylated by acetic anhydride than corn starch. Acetylation had a positive influence on the freeze-thaw stability and retrogradation of HACS, and significantly increased its swelling ability. However, acetylation did not change the blue value of HACS. Also, acetylation led to a reduction of the onset temperature, peak temperature and end temperature, but to an increase in the melting enthalpy. When the temperature was higher than 600 °C, the amylose starch was easily broken down, compared with the amylopectin starch. The acetylation was capable of obviously improving the thermal stability of HACS.

Keywords: high-amylose corn starch, acetylation, acetic anhydride, synthesis, property

INTRODUCTION

Starch may be sourced from many different agricultural products, such as potato, corn, cassava, wheat and others. It is a mixture of amylose, a linear polymer of α-1,4-linked glucose units, and amylopectin, a highly branched, high molecular weight polymer of short α-1,4 chains joined by α-l,6 bonds.[1] It has been found that high-amylose starch is more suitable for forming films, due to its processing ability and mechanical properties,[2-4] related to amylose, which has fewer branched points. As a result, it has a nearly linear structure, which makes its behavior resemble that of conventional synthetic polymers.[5,6] In addition, high-amylose starches require higher temperatures than normal starches to adequately gelatinize, as well as pressurized heating for complete cooking.[7,8]

Native starch is an excellent raw material, but its use is limited in industrial applications because of some undesirable properties. Often, the desired functional characteristic, such as texture stability, solubility in cold water or thickening power after cooking can not be achieved by native starch. However, these limitations can be overcome by physically, chemically, or enzymatically modifying the starch to achieve improved functional properties.[9] The chemical modification of starch can be performed by oxidation, esterification, etherification *etc*.[10-12] The introduction of acetyl groups into starch chains results in structural reorganization due to the steric hindrance and repulsion of the starch molecules, which facilitates the percolation of water in the amorphous regions

of the starch granules and increases the swelling power of the granules.[13]

The objective of this research was to optimize the acetylation parameters of high-amylose corn starch (HACS) and evaluate the effect of acetylation on its technological properties in order to enhance its properties, enlarge its applicability and improve its production up to an industrial level.

EXPERIMENTAL

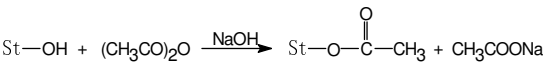
Materials

High-amylose corn starch (amylose content = 69%) was purchased from Shandong Huanong Special Corn Development Co. Ltd. (China). Corn starch was acquired from Liaoning Province Military Ningguan Agriculture Sideline Base Starch Factory (China). Sodium hydroxide was obtained from Shenyang Xinhua Reagent Factory (China). Acetic anhydride was purchased from Tianjin Chemical Reagent One Factory (China). Hydrochloric acid was received from Shenyang Paier Fine Chemical Factory (China). Potassium bitartrate was acquired from Shenyang Xinxing Reagent Factory (China). Iodine was obtained from Shenyang Reagent One Factory (China). Potassium iodide was purchased from Shenyang Xinhua Reagent Factory (China). All the above reagents were of analytical grade.

Methods

Acetylation of high-amylose corn starch

An amount of 34.7 g of HACS (water content = 12.08%) was mixed with 50 mL of distilled water. The suspension was placed into a 250 mL three-neck round bottom flask, stirred under heating in a water bath to a required temperature. After the pH of the suspension was adjusted to a desired value by the sodium hydroxide solution with a mass concentration of 4%, the required amount of acetic anhydride was added dropwise into the suspension within 20 minutes. At the same time, the pH of the suspension was maintained constant by the above sodium hydroxide solution. The acetylation was carried out for a certain time. After the reaction was completed, vacuum filtration of the slurry was conducted by a SHZ-C vacuum pump with a circulated water system (Henan Province Gongyi City YingYuHua Instrument Factory, China). The obtained filtered cake was washed several times by distilled water. The resultant cake was dried at 110 °C for about 3 h in a 1010-2 electrothermal constant-temperature dry box (Jintan City Dadi Automation Instrument Factory, China) to a moisture content of less than 12%. Finally, the dried cake was ground and screened. Acetylated high-amylose corn starch (AHACS) was thus obtained.[14,15] The formula of the high-amylose corn starch reacting with acetic anhydride is as follows:



Determination of acetyl content

An amount of 2 g of the AHACS (dry basis) was weighed, transferred into a 250 mL conical flask with 40 mL of distilled water. After a few drops of phenolphthalein as an indicator were added, the mixture was titrated with 0.1 mol/L sodium hydroxide to permanent pink color. Then, we added 25.0 mL of 0.15 mol/L NaOH into the mixture again, and shook it vigorously for half an hour. Afterwards, the stopper and the neck of the flask were flushed with a little distilled water, and the excess alkali was titrated by 0.10 mol/L HCl until the pink color of the mixture disappeared. 25.0 mL of 0.15 mol/L NaOH as blank was titrated according to the above described method. The content of acetyl groups and the degree of substitution (DS) were calculated as follows:[16,17]

$$W_{AC} = \frac{(V_2 - V_1) \times C_{HCl} \times 0.043 \times 100}{m \times (1 - H)} \quad (1)$$

$$DS = \frac{162 \times W_{AC}}{4300 - 42W_{AC}} \quad (2)$$

where W_{AC} is the acetyl content (%), V_2 is the volume of 0.10 mol/L HCl used to titrate the blank (mL), V_1 is the volume of 0.10 mol/L HCl used to titrate the samples (mL), C_{HCl} is the normality of 0.10 mol/L HCl, m is the mass of the samples (g), H is the moisture content.

Freeze-thaw stability

The paste of the sample was prepared by mixing 4 g of HACS or AHACS (dry basis) with 100 g of distilled water. The suspension was heated in the water bath to 95 °C until the paste was evenly formed, and then cooled to the ambient temperature. Precisely weighed 10 g of the paste was added into each of the pre-weighed 10 mL centrifuge tubes, and placed in a freezer at -18 °C for 24 h. Then, all the tubes were removed from the freezer and thawed at 30 °C in the water bath for 2 h. These tubes were centrifuged at 3000 r/min for 15 min by a TDL80-2B desk centrifuge (Shanghai Anting Scientific Instrument Factory, China). Syneresis was determined at the freeze-thaw cycling up to five cycles. The separated water percentage was then calculated as the mass ratio of the decanted liquid to the total paste before centrifugation and multiplied by 100. A low separated water percentage means high freeze-thaw stability.[18,19]

Blue value

An amount of 100 mL of 0.5 mg/mL starch slurry was gelatinized by heating in the water bath, and then cooled to room temperature. 2 mL of the paste was sucked and placed into a 100 mL volumetric flask. We added about 0.2 g of potassium bitartrate and 1 mL of iodine potassium iodide solution (iodine concentration of

2 mg/mL, potassium iodide concentration of 20 mg/mL) into the paste, and then diluted it to the total volume of 100 mL by distilled water. After the paste was allowed to rest for 60 minutes, the absorbance of the paste was measured at 680 nm by a VI-1501 spectrophotometer (Tianjin Gangdong Sci. & Tech. Development CO., LTD, China). The blue value was determined by the following formula:[20,21]

$$\text{Blue value} = \frac{4 \times \text{absorbance value}}{10 \times \text{sample concentration}} \quad (3)$$

where the unit of the sample concentration is mg/L.

Swelling power

We added 0.4 g of the sample weighed precisely (dry basis) and 99.6 g of distilled water into a 200 mL conical flask, and placed it in the water bath at the temperature of 90 °C for 20 min. Meanwhile, the total mass of the paste was kept constant during the heating. Precisely weighed 10 g of the paste was taken and added into each of six pre-weighed 10 mL centrifuge tubes, and then centrifuged at 3000 r/min for about 15 min by a TDL80-2B desk centrifuge (Shanghai Anting Scientific Instrument Factory, China). The supernatant from each of the centrifuge tubes was carefully poured out, and transferred into an evaporating Petri dish, and dried at 105 °C overnight in a 1010-2 electrothermal constant-temperature dry box (Jintan City Dadi Automation Instrument Factory, China). The dried residue was then cooled in a desiccator and weighed for the soluble substance. The sediment paste from each of the centrifuge tubes was then weighed to give the mass of the swollen sample granules. The result was expressed by the calculation as:[22,23]

$$\text{Solubility}(\%) = \frac{\text{mass of dried residue of supernatant} \times 100}{\text{mass of sample on dry basis}} \quad (4)$$

$$\text{Swelling power}(\%) = \frac{\text{mass of sediment paste} \times 100}{\text{mass of sample on dry basis} \times (100 - \%\ \text{solubility})} \quad (5)$$

Retrogradation

An amount of 50 mL of the slurry with a concentration of 1.0% by dry mass was produced using distilled water, and then put into a 100 mL beaker and gelatinized for 10 min in a boiling bath, keeping its volume unchanged. After that, the paste was cooled to 25 °C, the transparency of the supernatant was measured by a VI-1501 spectrophotometer (Tianjin Gangdong Sci. & Tech. Development CO., LTD, China) at different standing times. The more transparent the supernatant was, the stronger the retrogradation of the samples, and *vice versa.*[24]

Fourier transform infrared spectroscopy (FTIR)

An IR Prestige-21 infrared spectrometer (Shimadzu Corporation, Japan) was used to record the FTIR spectra within the range of 4000-400 cm^{-1}. The FTIR spectra were recorded in the solid state using the KB pellet method. Sample and potassium bromide were mixed in a ratio of 1:100, and the blend was pressed to obtain a tablet.[25]

Thermal analysis

The thermal analysis of HACS and its derivatives was carried out with a TGA Q50 V20.10 Build 36 thermogravimeric analyzer and a DSC Q20 V24.4 Build 116 differential scanning calorimeter (TA Instruments, US) in a nitrogen atmosphere. To properly characterize the thermal characteristics, HACS and its derivatives had to be analyzed in a sealed pan in order to prevent loss of water from the formulation during heating.

DSC analysis was performed under the following conditions: sample mass of 4.0-5.0 mg, heating rate of 10 °C/min, temperature range of 10-250 °C, nitrogen flow rate of 50.0 mL/min.[26]

TGA analysis was carried out under the following conditions: sample mass of 6.0-7.0 mg, heating rate of 10 °C/min, temperature range of 10-800 °C, nitrogen flow rate of 60.0 mL/min.[27,28]

Particle morphology

Particle morphology was observed by a XPL-2 transflective polarizing microscope (Nanjing Jiangnan Yongxin Optics Company LTD., China). About 5 mg of the samples was placed on a clean slide. A cover glass was used to cover the sample particles, and then moved back and forth until the particles could be uniformly dispersed on the slide. The cover glass was removed. The lighting power of the polarizing microscope was opened. The appropriate magnification was selected, and then the light source was adjusted and focused. The slide with the sample particles was put and moved under the object lens of the polarizing microscope. The appropriate viewing area was selected to observe the size and the shape of the sample particles.[29]

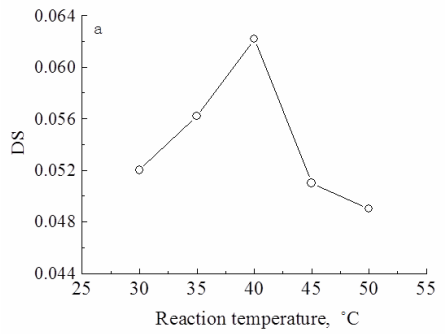
RESULTS AND DISCUSSION

Effects of reaction temperature, reaction time, pH and amount of acetic anhydride on DS of AHACS

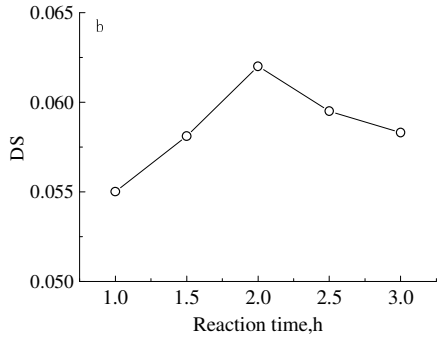
The effects of reaction temperature, reaction time, pH and amount of acetic anhydride on the DS of AHACS are illustrated in Figure 1. Because the HACS has high gelatinization temperature, compared with that of common starch, during the acetylation of HACS no swelling inhibitor was added into the slurry to facilitate the post-treatment. The reaction temperature was varied from 30 to 50 °C to examine the reaction temperature effects (Fig. 1a). Within this temperature range, the DS of AHACS ranged from 0.049 to 0.0622, and its

variation was of 0.0132. When the reaction temperature was less than 40 °C, the DS of AHACS increased with increasing reaction temperature. When the reaction temperature was higher than 40 °C, however, the DS of the AHACS decreased with further increasing reaction temperature. It is possible that the variation of the reaction temperature influenced the swelling, the pore numbers on the surface of starch particles, and the thermal motion of acetic anhydride molecules, as well as the side reaction of acetic anhydride. As a result, the reaction temperature influenced the esterification. Thus, the most suitable reaction temperature for the acetylation was considered to be 40 °C.

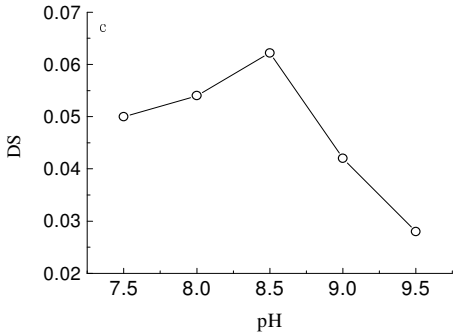
As may be noted in Figure 1b, the reaction time was varied from 1 to 3 h to examine the reaction time effects. Within the reaction time range, the DS of the AHACS had values from 0.055 to 0.0622, and its variation was of only 0.0072.



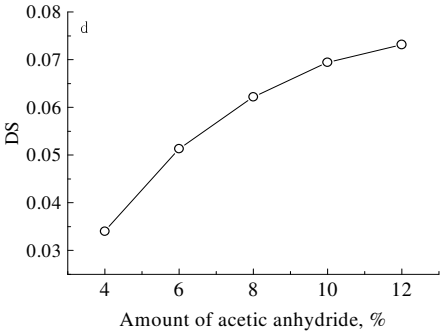
Reaction conditions: pH 8.5, amount of acetic anhydride 8.0%, reaction time 2.0 h



Reaction conditions: pH 8.5, amount of acetic anhydride 8.0%, reaction temperature 40 °C



Reaction conditions: reaction temperature 40 °C, amount of acetic anhydride 8.0%, reaction time 2.0 h



Reaction conditions: pH 8.5, reaction temperature 40 °C, reaction time 2.0 h

Figure 1: Effects of reaction temperature, reaction time, pH and amount of acetic anhydride on the DS of AHACS

Table 1
Comparison of acetylation between HACS and CS

Samples	DS
Acetylated high amylose corn starch	0.062
Acetylated corn starch	0.053

The influence of the reaction time on the DS of AHACS was obviously smaller than that of the reaction temperature. When the reaction time was less than 2 h, the DS of the AHACS increased with increasing reaction time. When the reaction time exceeded 2 h, the DS of the AHACS decreased with increasing reaction time. It proved that the ester bonds in the AHACS molecules were unstable under the weak alkaline environment. However, it was only slightly influenced by the alkalinity. Consequently, the most suitable reaction time for the acetylation was considered to be 2 h.

To examine the effects of pH, it was varied from 7.5 to 9.5 (Fig. 1c). When the pH was below 8.5, the DS of the AHACS increased with increasing pH. When the pH was higher than 8.5, however, the DS of the AHACS decreased with increasing pH. Also, the variation of the DS of AHACS in the pH range from 7.5 to 8.5 was lower than that in the pH range from 8.5 to 9.5. It suggested that the acetyl groups in AHACS particles were easily deacetylated under the alkaline environment. Thus, the optimum pH for the acetylation was considered to be 8.5.

The amount of acetic anhydride was varied from 4% to 12% to examine its effects on the DS of AHACS (Fig. 1d). The DS of AHACS ranged from 0.034 to 0.073 as the amount of acetic anhydride was varied from 4% to 12%. The DS of AHACS increased with increasing amount of acetic anhydride when the acetylation reaction was conducted in the aqueous suspension. Considering the practical use of AHACS, the amount of acetic anhydride was selected to be of 8%.

Comparison of acetylation between HACS and corn starch (CS)

The comparison of HACS and corn starch as regards their acetylation is shown in Table 1. The following reaction conditions were used: amount of high-amylose corn starch or corn starch of 34.7 g, mass concentration of slurry of 36%, reaction time of 2.0 h, reaction temperature of 40.0 °C, pH 8.5 and amount of acetic anhydride of 8.0%.

It may be noted from Table 1 that, under the same reaction conditions, the DS of AHACS was higher than that of acetylated corn starch. This indicated that the HACS was more easily acetylated than CS by acetic anhydride, which suggested that the number of hydroxyl groups on the surface of HACS was greater than that for CS.

Optimization of processing parameters

An orthogonal test with 4 factors and 3 levels was designed to optimize the acetylation conditions on the basis of the single-factor experiments. These factors included the reaction temperature, reaction time, and pH. The DS was as used as a criterion in each test. The amount of acetic anhydride was held at 8%. The design and results of the L_9 (3^4) orthogonal test are shown in Table 2. However, the best conditions for preparing AHACS could not be selected only based on the results in Table 2, and needed to be further analyzed. Thus, the k and R values were calculated and listed in Table 2. The greater the R was, the greater the influence of the factor on the DS, and the more important the factor was. The formulas for calculating the k and R were as follows:[30]

$$k_1 = \frac{1}{3}\left(DS_{A,\text{level }1} + DS_{B,\text{level }1} + DS_{C,\text{level }1}\right) \quad (6)$$

$$k_2 = \frac{1}{3}\left(DS_{A,\text{level }2} + DS_{B,\text{level }2} + DS_{C,\text{level }2}\right) \quad (7)$$

$$k_3 = \frac{1}{3}\left(DS_{A,\text{level }3} + DS_{B,\text{level }3} + DS_{C,\text{level }3}\right) \quad (8)$$

$$R = k_{max} - k_{min} \quad (9)$$

where $DS_{A,\text{level }1}$, $DS_{A,\text{level }2}$ and $DS_{A,\text{level }3}$ are the DS at the i^{th} level of factor A; $DS_{B,\text{level }1}$, $DS_{B,\text{level }2}$ and $DSB_{B,\text{level }3}$ are the DS at the i^{th} level of factor B; $DS_{C,\text{level }1}$, $DS_{C,\text{level }2}$ and $DS_{C,\text{level }3}$ are the DS at the i^{th} level of factor C (i = 1, 2, 3), R is the difference between the maximum and the minimum of the k for the same factor.

From the results of the orthogonal experiment (Table 2), we could find that the different conditions yielded AHACS with different DS, ranging from 0.034 to 0.058. In addition, the influence of the factors on the DS of AHACS decreased in the order of pH > reaction temperature > reaction time according to the R value. The pH was found to be the most important determinant of the DS. For each factor, if the k_i value of i^{th} level was maximum, this level was the most suitable reaction condition. Therefore, the optimum conditions were as follows: pH 8.5, reaction

temperature of 40 °C and reaction time of 2 h. Under these optimum conditions, the DS of AHACS reached 0.062.

Freeze-thaw stability, swelling power and blue value of CS, HACS, AHACS

The freeze-thaw stability, swelling power and blue value of CS, HACS and AHACS are presented in Table 3. It may be noted that the separated water percentage of HACS was higher than that of CS. It suggested that the amylose in starch could reduce the freeze-thaw stability of starches. However, the acetylation did improve the freeze-thaw stability of HACS. The freeze-thaw stability of AHACS increased with its increasing substitution degree. The swelling power of HACS was less than that of CS.

The acetylation resulted in significantly higher swelling power than that of the native starch. Also, the swelling power of AHACS increased with increasing DS. Besides, the blue value of HACS was much higher than that of CS. However, the acetylation did not change the blue value of HACS. According to these data, obviously, the properties of HACS were different from those of CS, owing to the high amylose content.

Retrogradation of CS, HACS, AHACS

The retrogradation of CS, HACS and AHACS (DS = 0.0622) is shown in Figure 2. It is clear from Figure 2 that the retrogradation of HACS was stronger than those of CS and AHACS. The retrogradation of AHACS was intermediate between those of HACS and CS. It proved that the amylose content in starches could change the retrogradation of starch. The amylose molecules' chains settled easily. The acetylation reduced the retrogradation of HACS owing to the introduction of the acetyl groups into the molecules of HACS. It indicated that the acetyl groups could prevent the chains from aggregating.

Table 2
Design and results of L_9 (3^4) orthogonal test

Test numbers	Reaction temperature (A), °C	Reaction time (B), h	pH (C)	DS
1	35	1.5	8.0	0.043
2	35	2.0	8.5	0.056
3	35	2.5	9.0	0.034
4	40	1.5	8.5	0.058
5	40	2.0	9.0	0.042
6	40	2.5	8.0	0.040
7	45	1.5	9.0	0.032
8	45	2.0	8.0	0.038
9	45	2.5	8.5	0.034
k_1	0.044	0.044	0.041	
k_2	0.047	0.045	0.049	
k_3	0.035	0.036	0.036	
R	0.012	0.009	0.013	

Table 3
Freeze-thaw stability, swelling power and blue value of CS, HACS and AHACS

Samples	Separated water percentage, %	Swelling power, %	Blue value
CS	46.2	15.7	0.282
HACS	52.7	6.4	0.637
AHACS (DS=0.043)	33.2	13.6	0.635
AHACS (DS=0.062)	22.3	17.2	0.638

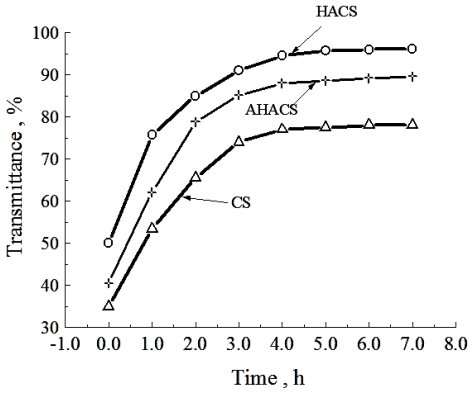


Figure 2: Retrogradation of CS, HACS and AHACS

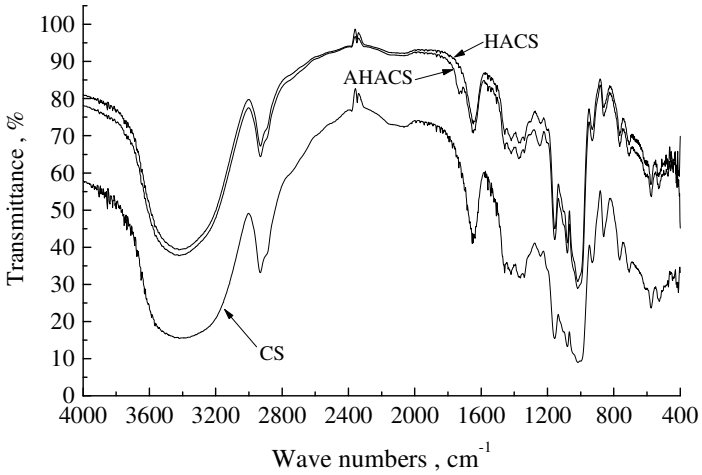


Figure 3: FTIR spectra of CS, HACS and AHACS

FTIR analysis

The FTIR spectra of CS, HACS and AHACS (DS = 0.0622) are shown in Figure 3. The absorption peak of CS, HACS and AHACS at the wavenumber of 1640 cm^{-1} belong to H-O-H bending vibration. The absorption peaks at 2930 cm^{-1} and 1075 cm^{-1} in the spectra of CS, HACS and AHACS are assigned to the stretching vibration of the C-H bond and C-O bond, respectively. The absorption peak at 3420 cm^{-1} in all the three spectra corresponds to the stretching vibration of the -OH bond. The stretching vibration peak of the -OH bond of CS is wider, but its intensity is weaker, compared with the same peaks in the spectra of HACS and AHACS. This suggests that the number of -OH groups was higher on the surface of HACS particles than on the CS particles. This finding is in accordance with the results of the acetylation comparison between HACS and CS discussed earlier. In addition, the absorption peak at 1740 cm^{-1} in the spectrum of AHACS can be attributed to the characteristic peak of the carbonyl groups. This proves that carbonyl groups were introduced into the molecules of HACS owing to the acetylation.

TGA and DSC analyses

The TGA and DSC curves of CS, HACS and AHACS (DS = 0.0622) are presented in Figure 4. The thermal degradation mechanism of starch was a multiple-step mechanism.[31] From Figure 4, it is clear that the dehydration and decomposition are two separate processes, which could be observed

clearly during the thermal degradation of starch. The first step was observed below 150 °C, which was related to the moisture content of the samples. The mass of the samples decreased dramatically as the temperature ranged from about 250 to 350 °C. The DSC and TGA curves of HACS were different from the ones of CS and AHACS, especially the variation of the DSC curves was significant. The acetylation changed the thermal stability and melting process of HACS. When the temperature was below 500 °C, the TGA curve of HACS was close to that of AHACS. When the temperature increased above 500 °C, however, the difference between the TGA curves of HACS and AHACS gradually enhanced. The TGA curves of HACS and AHACS overlapped at the temperature of about 440 °C. Similarly, the TGA curves of CS and HACS overlapped at about 600 °C. It suggested that when the temperature exceeded 600 °C, the amylose starch was easily broken down, compared with the amylopectin starch. The endothermic peak of AHACS was strengthened after HACS was acetylated. Finally, the values for the relevant thermodynamic parameters were calculated and listed in Table 4 and Table 5, in order to further analyze the thermal behavior of CS, HACS and AHACS.

From Table 4, it may be noted that the onset decomposition temperature of HACS was greater than that of CS, but the end decomposition temperature of HACS was lower than that of CS. The acetylation reduced the onset decomposition temperature of AHACS, but increased its end decomposition temperature. The rate of mass loss of HACS was the least among the three samples. It proved that the acetylation was capable of obviously improving the thermal stability of HACS.

From Table 5, it is clear that the onset temperature, peak temperature, end temperature and melting enthalpy of HACS were higher than those of CS. The acetylation led to a decrease in the onset temperature, peak temperature and end temperature, but to an increase in the melting enthalpy.

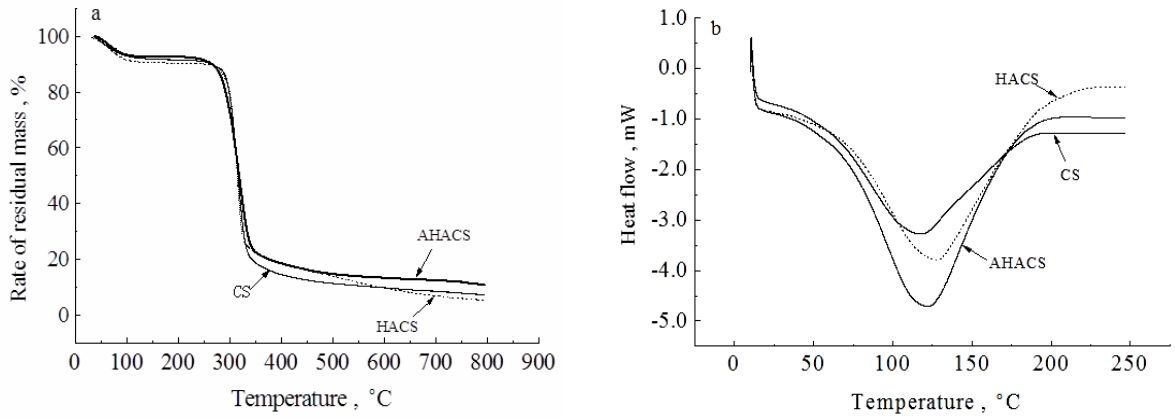


Figure 4: TGA (a) and DSC (b) curves of CS, HACS and AHACS

Table 4
Onset decomposition temperature, end decomposition temperature and mass loss rate

Samples	Onset decomposition temperature, °C	End decomposition temperature, °C	Rate of mass loss, %
CS	291.3	331.3	61.0
HACS	300.4	326.7	34.2
AHACS (DS=0.062)	287.0	346.2	63.2

Table 5
Onset temperature (T_o), peak temperature (T_p), end temperature (T_e) and melting enthalpy (ΔH)

Samples	T_o, °C	T_p, °C	T_e, °C	ΔH, J•g^{-1}
CS	60.5	116.5	187.9	239.3
HACS	73.6	127.5	194.6	265.7
AHACS (DS=0.062)	71.1	121.7	186.0	298.1

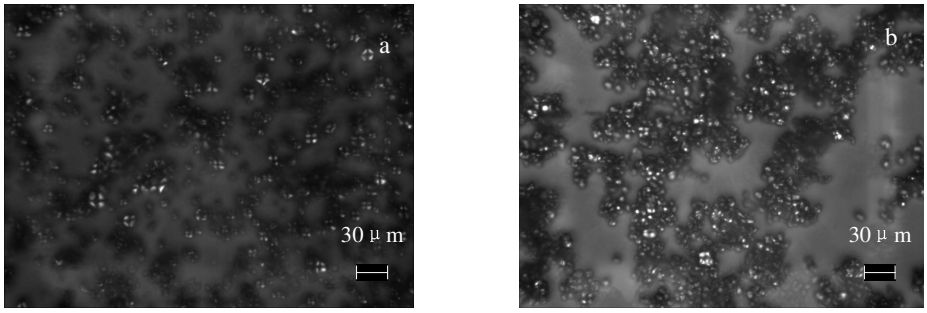


Figure 5: Polarizing microscope images of HACS (a) and AHACS (b)

Particle morphology

The particle morphology is illustrated in Figure 5. Polarization crosses on the HACS and AHACS particles can be obviously observed. The HACS and AHACS particles displayed an irregular shape, and their size ranged from about 10 to 30 μm. The appearance of HACS particles was still similar to that of AHACS ones. The effect of the acetylation on the crystalline region of HACS was not obvious.

CONCLUSION

The DS of AHACS was influenced by factors such as the reaction temperature, reaction time, pH and amount of acetic anhydride. HACS was more easily acetylated by acetic anhydride, compared with CS. The influence of the acetylation factors on the DS of AHACS decreased in the following order: pH > reaction temperature > reaction time. The optimum conditions for preparing AHACS were as follows: pH 8.5, reaction temperature of 40 °C and reaction time of 2 h. The acetylation could improve the freeze-thaw stability of HACS, and significantly increased its swelling power. On the other hand, the acetylation did not change the blue value of HACS. The properties of HACS were different from those of CS, owing to the high amylose content. The number of the -OH groups on the surface of the HACS particles was higher than that on the CS particles. The acetylation reduced the retrogradation of HACS, but increased the onset temperature, peak temperature, end temperature, and melting enthalpy. The thermal stability of HACS was poor, owing to its amylose content, when the temperature was higher than 600 °C. Also, the acetylation was capable of improving the thermal stability of HACS. The crystalline region of HACS was little influenced by the acetylation.

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