

Synthesis, optimization and characterization of acetylated corn starch with the high degree of substitution



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ABSTRACT

Acetylated corn starch (ACS) was synthesized by the reaction of native corn starch (NCS) with acetic anhydride (AA) and acetic acid in an aqueous medium in the presence of p-toluenesulfonic acid (PTSA) as a catalyst. The factors that could affect the degree of substitution (DS) of corn starch were investigated which included the reaction temperature and time, the volume ratio of AA to acetic acid and the usage of the catalyst PTSA. The optimal DS of 2.85 was obtained. Fourier transform infrared (FTIR) spectrometry showed new bands at 1733, 1375 and 1252 cm^{-1} . As DS increased, the bands at 3400 cm^{-1} and 1083 cm^{-1} were gradually weakened. The scanning electron microscopy (SEM) of the ACS indicated that the exterior and interior of native starch were destroyed by the esterification. Wide angle X-ray diffraction revealed that the peaks at 15°, 18°, 20° and 23° were diminished, while the peak at 21° became more distinct as the DS increased. Differential scanning calorimetry (DSC) thermograms exhibited that ACS had some lower gelatinization temperatures and enthalpies than NCS.

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1. Introduction

Starch is a typical biodegradable or environmentally acceptable materials used for energy storage in a variety of plant locations such as seeds, roots and tubers [1]. It is also a semicrystalline polymer comprised of amylose and amylopectin. The unique physical and chemical characteristics and nutritional quality of starch set it apart from all other carbohydrates [2].

In this day and age, starch may be the most prevalent controlled release carrier materials among chitosan, protein and sodium alginate because of its availability, cost-effectiveness, biocompatibility and non-toxicity [3]. Native biodegradable starches are desirable for a range of biomedical applications. However, native starch may not be appropriate in some drug delivery systems, since many bioactive components based on such unmodified starch-based systems release so fast [4]. This is owing to the hydrophilic multi-hydroxyl structure, substantial swelling and rapid enzymatic degradation of native starch. Consequently, native starch is not desirable as the controlled release carrier material for the drug [5,6].

Starch modification which includes physical, chemical, enzymatic and combined modification can be used to alter the starch to be suitable for special goals since it involves the change of

the physical and chemical characteristics of the native starch to develop its functional properties [7,8]. Esterification of native starch imparts great properties which enhance its range of applications. Therefore, it is worth mentioning that acetylated starches with a high DS can have some excellent properties such as hydrophobicity, melt processibility and amounts of non-food applications such as tablet binders, hot melt adhesives, coating, cigarette filters, biodegradable packaging material and pharmaceutical aspects have been suggested [9]. Thus, it is superior to be used as a controlled release carrier material. And its film coatings are used for performing controlled release of an active substance from a pharmaceutical preparation since the films can be seen as a vehicle of improving the efficiency of drug release through a constant but prolonged release with minimum side effects [10]. There have been some reports on the ACS films [11].

The objective of the present study was to synthesize the ACS and optimize the reaction conditions of synthesizing the ACS. And also, starch granules morphology was analyzed by SEM, granules structure was evaluated by XRD and FTIR, gelatinization process was monitored by DSC.

2. Materials and methods

2.1. Materials

NCS (food grade, molecular weight of 1.28×10^6 , viscosity 7200 mPa s of 7% (w/v) gelatinized solution at 25 °C) was

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procured from Xuejing Starch Ltd., Gansu (China). Analytical grade acetic anhydride (AA), sodium hydroxide, hydrochloric acid and p-toluenesulfonic acid (PTSA) were procured from Rionlon Ltd., Tianjin (China). Acetone, acetic acid and chloroform were procured from Guangfu Ltd., Tianjin (China).

2.2. Preparation of acetylated corn starch (ACS)

A series of ACS samples with high DS were prepared. Typically, NCS (5 g) and acetic acid (25 ml) were added to a three-necked flask installed with a condenser on a magnetic stirrer and mixed for 15 min at room temperature. Whereafter the reaction temperature was warmed at 70 °C. AA (25 ml) and PTSA (0.3 g) was added dropwise to the stirred slurry for 15 min. The reaction was allowed to proceed for 2.5 h after the completion of AA addition. At the end of the reaction, the product was washed with excess distilled water, and then oven-dried at 35 °C for 2 days. Finally, the resultant product was milled, sieved and stored in an airtight container for future use.

2.3. Determination of degree of substitution (DS)

Determination of DS of ACS by titration involved complete basic hydrolysis of the ester linkages and titration of the excess alkali [12]. 2.0 g of ACS was weighted accurately and placed in a 250 ml Erlenmeyer flask and 40 ml of acetone was added upon mixing at room temperature. A few drops of 1% (v/v) phenolphthalein indicator was added and the suspension. After addition of 10 ml 0.5 M NaOH, the flask was stoppered loosely with plastic wrap and shaken vigorously for 1 h to complete saponification at room temperature. After shaking, the plastic wrap was removed carefully and washed down. The excess alkali was then back-titrated with a standard 0.5 M HCl to the phenolphthalein endpoint. The solution was stood for 2 h, and any additional alkali, which may have leached from the samples, was then titrated. A blank, using the NCS, was also treated in a similar way [13].

Acetyl content (A) was calculated according to the following equation [14]:

$$A = \frac{(v_1 - v_2) \times 10^{-3} \times M \times 43 \times 100}{W} \quad (1)$$

Acetyl content (A) was used to calculate the DS, according to the following equation:

$$DS = \frac{162A}{[43 \times 100 - (43 - 1) \times A]} \quad (2)$$

where v_1 is the volume of 0.5 M HCl used for titration of NCS, v_2 is the volume of 0.5 M HCl used for titration of ACS, M is the molarity of HCl solution, W is the weight of the ACS, 43 is the molecular weight of the acetyl group, 162 is the molecular weight of anhydroglucose unit [15].

2.4. Fourier transform infrared (FTIR) spectra

Infrared spectra of starch samples were recorded on a FTIR spectrophotometer (American Nicolet Corp. Model 170-SX). The samples were dissolved in deionized water and freeze-dried, then blended with solid potassium bromide (KBr) powder and the blend was made into a pellet. The KBr pellet was dried and subjected to FTIR spectrophotometry. Transmittances were recorded at wave numbers between 4000 and 400 cm^{-1} .

2.5. Scanning electron microscopy (SEM)

The morphology was observed using a scanning electron microscope (SEM). NCS and ACS samples were freeze-dried for

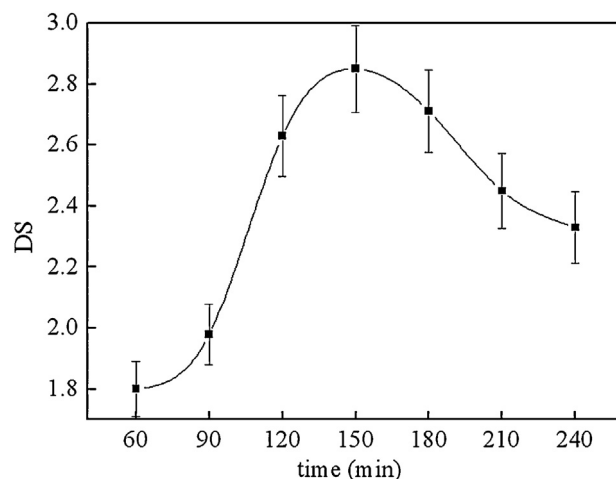


Fig. 1. Effect of the reaction time on DS (reaction conditions: $m_{\text{PTSA}} = 0.3$ g, $V_{\text{AA}}/V_{\text{acetic acid}} = 1:1$ (ml/ml), reaction temperature = 70 °C).

dehydration. The dehydrated samples were sprinkled on double stick tape fixed on circular copper stubs, then coated with gold powder to avoid charging under the electron beam. The granule surface and shape of starch were observed using a scanning electron microscope (Jeol JSM-5600LV, Jeol Ltd., Tokyo, Japan).

2.6. X-ray diffraction (XRD) spectroscopy

The X-ray diffractograms of NCS and ACS were obtained from a X-ray diffractometer (MAC, MXP21VAHF) with $\text{Cu K}\alpha$ radiation detector (tube operating at 40 kV and 100 mA). The starch powders were scanned through the 2θ range of 2–60° with a continuous scan mode to collect data. NCS and ACS samples were equilibrated at 30 °C to a constant weight prior to analysis.

2.7. Differential scanning calorimetry (DSC)

Thermal analysis of NCS and ACS were performed with a differential scanning calorimeter (Perkin-Elmer Corp., Wilton, CT) and the data analyzed using the Pyris software program. Sample (10.0 mg, dry weight) was loaded in aluminum pans and the moisture level adjusted to 10% by adding deionized water. Samples were scanned from 30 °C to 120 °C at a rate of 10 °C/min under a dry N_2 atmosphere, while sealed empty pans were used as reference. The onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and the enthalpy of gelatinization were recorded.

3. Results and discussion

3.1. Optimization of reaction conditions of ACS

ACS with a high DS is commonly prepared by the esterification of NCS with AA in the presence of the PTSA catalyst. DS indicates the average number of hydroxyl groups substituted per anhydroglucose unit. As each anhydroglucose unit has three hydroxyl groups (OH-2, OH-3 and OH-6) available for substitution, the maximum possible DS is 3 [16].

To obtain ACS with the optimum DS, various reaction parameters are optimized, including the reaction time, the reaction temperature, the volume ratio of AA to acetic acid ($V_{\text{AA}}/V_{\text{acetic acid}}$) and the usage of the catalyst PTSA (m_{PTSA}). The details are given below.

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