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Study on the synthesis and physicochemical properties of starch acetate with low substitution under microwave assistance

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ABSTRACT

In this study, synthesis and physicochemical properties of starch acetate with low substitution under microwave were studied. A three-level-three-factorial Central Composite Design using Response Surface Methodology (RSM) was employed to optimize the reaction conditions. The optimal parameters are as follows: amount of acetic anhydride of 12%, radiation time of 11 min, and microwave power of 100 W. These optimal conditions predicted by RSM were confirmed that the degree of substitution (DS) of acetate starch is 0.0691 mg/g and the physical and chemical properties of natural corn starch (NCS) and corn starch acetate (ACS) were further studied.The transparency, water separation, water absorption, expansion force, and solubility of ACS low substitution are better than NCS, while the NCS's hydrolysis percentage is higher than ACS, which indicate that the modified corn starch has better performance than native corn starch. The surface morphology of the corn starch acetate was examined by scanning electron microscope (SEM), which showed that it had a smooth surface and a spherical and polygonal shape. However, samples' shape is irregular. Crystal structure was observed by X-ray diffraction, and the ACS can determine the level of microwave technology that can destroy the extent of the crystal and amorphous regions. Fourier transform infrared (FTIR) spectroscopy shows that around 1750 cm^{-1} carbonyl signal determines acetylation bonding successfully.

1. Introduction

In recent years, the people environmental protection consciousness. Non-degradable, oil, water soluble polymer - ester compounds, polyacrylamide and polyethylene cellulose acetate is widely used in applications, such as thickener, paper, paint, etc. [1], in order to reduce pollution, are considering changing use some biopolymers, such as biodegradable, renewable, corn starch, etc. [2].

Starch acetate, also known as acetylated starch, is an esterified starch produced by the reaction of hydroxyl groups of starch macromolecules and acetic acid or other acid derivative under certain conditions [3]. Depending on the degree of substitution of the hydroxyl hydrogen atom on the starch glucose units, the starch is divided into low degree of substitution of starch acetate and high degree of substitution of starch acetate [4]. Starch acetate with low substitution which degree of substitution (DS) is 0.2 or less, and it has stable chemical properties, good transparency and gloss, low gelatinization temperature, not gel, flexibility, extensibility, folding and high wear resistance, etc. Starch acetate with low substitution is mainly used in the food industry [5]. According to the rules of U.S. Food and Drug Administration (FDA), only 2.5% or less of the acetylated starch acetate can be used for food processing [6].

After the de Graaf was first synthesized the acetylated starch in the laboratory by using acetic anhydride as the esterifying agent in 1865, the number of studies on starch acetate have reached to a large amount [7]. De Graaf studied that starch acetate with DS 0.01–0.2 is approved by the PDA for food use to improve stability, texturizing, thickening and binding [8]. Starch acetates with high substitution have been prepared with the aim of obtaining a replacement for cellulose acetate [9–11]. Pyridine is a good cat-

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alyst in the preparation of starch acetate with high substitution, because it not only lead to complete esterification, but also doesn't cause starch degradation. Pretreatment is necessary [12,13], and the influences of some pretreatments on the reaction rate were compared [14]. Mark and Mehltretter [15] developed a simple method to prepare relatively undegraded starch triacetate using NaOH as the catalyst without pretreatment. Shogren [16] used this method to prepare starch acetates with DS 1.5, 2.0, and 2.5.

Currently, most methods of heating synthesising starch acetate use a water bath or heating units, which will consume a long time and may damage the structure of starch [17]. To avoid such shortcomings, a new method is adapted in heating synthesis. In recent years, the method of microwave heating has been extensively studied and applicated in the field of organic synthesis. The technology of microwave is applicated in the fields of chemistry, chemical analysis and environmental protection. And the advantages of microwave technology are to save energy and time, simplify procedures, reduce the use of organic solvents, improve the reaction rate and significantly reduce the waste of hazardous on the environment by the chemicals reaction producing, etc [18]. However, no research has been published on the influences of reaction conditions on starch acetylation under microwave assistance. Therefore, the first part of this study was to investigate the influences of selected reaction conditions on extent of starch acetylation, and optimized the synthesis by using response surface.

The application of microwave radiation to starch modification technology is still in experimental studies and exploratory stage. From a number of research results, there is a certain prospect. And microwave radiation will become a hot topic [19]. In the microwave field, starch, water, and polar molecules such as hydroxyl exist frequency vibration, friction, and then heat is produced. The structure of morphology of starch granule is influenced by this heating. The rheology, regenerative resistance and starch gel properties of starch are changed. Lastly the starch properties are changed [20]. Lewandowicza et al. [21] studied the effect of microwave on the crystallization characteristics natural corn starch. After microwave treatment, the diffraction peak position of starch did not change corresponding to the increase of diffraction intensity. Ndife et al. [22] studied that when, wheat, corn and rice starch were placed in a microwave reactor, heated for 15–25 s, the rate of corn starch was significantly lower than that of wheat and rice. The time is over 25s, and there is no significant difference. Hong et al. studied, microwave technology for modified starch has became a new technical mean [23]. The application of microwave technology in the modified starch is still in the basic stage. It is urgent to further study various physical and chemical properties of starch under microwave action. The modified starch is obtained, which the character is clearer, and function is more perfect. Little research has been done on the effects of DS on the functional properties of starch acetate with low substitution. Therefore, the second part of this study was to prepare a series of starch acetates with low substitution under microwave assistance and to investigate their structural properties for potential application as biodegradable thermoplastic materials.

This experiment used corn starch as raw materials, acetic anhydride as esterification agent and NaOH as catalyst. This study aimed at investigate the main variables (irradiation power, irradiation time and the amount of acetic anhydride) for synthesis of starch acetate with low substitution under the reaction condition of microwave-assisted heating, and optimized the synthesis by using response surface. The different DS of starch acetate's particle morphology, crystallization characteristics, chemical structure, physical transparency, and freeze-thaw stability were analyzed. Information obtained in this work is essential to provide experimental and theoretical basis for potential application as biodegradable thermoplastic materials.

2. Materials and methods

2.1. Materials and reagents

The native corn starch was supplied by Guowei Starch Co., Ltd. (Xi'an City, Shanxi Province, China). Acetic anhydrides were purchased from Xilong Chemical Co., Ltd. (China). Sodium hydroxide, hydrochloric acid, Anhydrous sodium carbonate, absolute ethanol, methyl orange indicator, and phenolphthalein indicator were purchased from Kelong Chemical Reagent Factory (Chengdu city, Sichuan Province, China). All chemicals and reagents used in experiments have reached to the purity of A.R (Analytical Reagent).

2.2. Preparation of starch acetate

A certain amount of corn starch was weighted. Starch emulsion (40%, mas.%) was made by adding water, and transferred into 250 mL beaker, and then stirred constantly about 10 min under a middle of speed on a magnetic stirrer. The pH was adjusted by adding NaOH solution (3%, mas,%), and controlled at 8.0-9.0. Then a few drops of acetic anhydride were slowly dropped by the dropper for a few moments. The pH value was adjusted by plusing a few drops of NaOH solution, and maintained at 8.0-9.0. So repeatedly, acetic anhydride was dropped about 20 min. The reaction was continued a certain time by placing in a microwave reactor and setting power. The pH value was controlled at 4.5-6.5 by adding the hydrochloric acid (0.5 mol/L) when the reaction was stopped. The product was absorbed by vacuum suction filter.Cleaning the filter cake with distilled water until the washing liquid was not acidic. The filter cake was dried in a thermostatic oven (45 °C, 12 h) and then storaged backup by smashing and sieving through a 100 mesh or 120-mesh sieve [24].

2.3. Determination of DS of starch acetate

5 g samples were weighted approximately after having been ground and sufficiently dried. The quality of sample was accurated to 0.001 g. The samples which were constant weight was placed in 250 mL conical flask, added 50 mL of distilled water and was kept shaking. Then add two or three drops (phenolphthalein indicator (10 g/L) into them, then which was titrated to reddish with NaOH solution (0.1 mol/L).

When a saponification by adding 25.0 mL NaOH solution (0.45 mol/L) and vibrating 30 min on a magnetic stirrer, it was time to stop stirring. The product remained on the stirred rod, stopper and the flask wall on the opening was carefully rinsed with distilled water. And excess alkali was titrated until the phenomenon of red was disappeared by HCl standard solution (0.2 mol/L). When the color change was kept 30 s and not changed, we can regard it as the titration end point. Volume of hydrochloric acid standard solution (0.2 mol/L) was spent as V_1 (mL). In addition, alkali was consumed by causing a small amount of degradation in the alkaline saponification process. To eliminate this impact, starch was used in the blank titration. It was time to calculate the content of acetyl and DS [25].

Blank test: a kind of absolute dry native starch was weighted accurately about 5 g (same as sample weight). Measuring steps were same as above. Recording the elapsed volume of hydrochloric acid standard solution (0.2 mol/L) as V_2 (mL).

$$B = \frac{(V_2\text{-}V_1) \times d \times 0.043}{m} \times 100\% \quad (1)$$

$$DS = \frac{162B}{43 \times 100 - (43\text{-}1)B} \quad (2)$$

In the formula, B stands for acetyl content,%; m stands for the weight of the weighing sample,g; d stands for the standard solution