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The mechanism of starch granule reacted with OSA by phase transition catalyst in aqueous medium

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ABSTRACT

The reactivity of octenyl succinic anhydride (OSA) with starch by phase transition catalyst (PTC) was investigated. The effects of two types (quaternary ammonium salt and non-ionic surfactant) and concentrations of PTC on the degree of substitution (DS) and reaction efficiency (RE) of OS-starch were examined. In aqueous medium, the use of a PTC, polyoxyethylene lauryl ether (AEO) produced derivatives with higher DS than others. The DS of OS-starch reached 0.0195 with 0.1% AEO, significantly higher than that (0.0182) without the use of PTC. As the concentration of AEO increased, the DS of OS-starch did not increase. The structural of AEO was investigated by nuclear magnetic resonance (NMR) spectroscopy. Conductivity measurement and Fourier transform infrared (FT-IR) spectroscopy confirmed that AEO could form complexes with Na^+. The complex of AEO and Na^+ could combine with starch-O^-, it should be possible to improve the transport of anion starch-O^- to the hydrophobic reagents.

1. Introduction

Native starch is modified, physically or chemically, to improve its functional properties. One of the modifications is to substitute the hydroxyl groups of starch with dicarboxylic acid anhydride. It was found that starch could be modified by octenyl succinic anhydride (OSA) in an aqueous suspension (Caldwell & Wurzburg, 1953). By substitution reaction with OSA, esters containing both hydrophilic and hydrophobic groups, starch acquires emulsifying (Trubiano, 1986). Amongst the alkenyl succinic anhydrides, octenyl succinic anhydride has been permitted for use in foods in many countries at a level of 3.0% (Bhosale & Singhal, 2007). The foods and industrial products with OS-starch include salad dressings, creams, paints, adhesives, biodegradable plastics, etc. and the functions of OS-starch include beverage emulsifiers, clouding agents, flavour stabilizer, coatings, etc. (Bhosale & Singhal, 2007; Jane, Robert, Nidolov, & Roque, 1991). Recent studies have shown that OS-starch could be used as dietary fibre because of its resistance to digestive enzymes, and thus to increase the resistant starch (RS) contents (Zhang et al., 2011). Up to now, the materials, reaction parameters, distribution of OS groups, physical and chemical properties and industrial applications of OS-starch had been reported (Bhosale & Singhal, 2006, 2007; Huang et al., 2010; Hui, Chen, Fu, Xu, & He, 2009; Jane et al., 1991; Shogren, Viswanathan, Felker, & Gross, 2000; Song, He, Ruan, & Chen, 2006; Zhang et al., 2011).

Generally, OS-starch is produced by starch and an OSA reagent in aqueous alkaline slurry system. The reaction parameters such as pH, temperature, starch concentration, weight percentage of OSA and reaction time were proved to affect the degree of substitution (DS) and reaction efficiency (RE) of OS-starch (Bhosale & Singhal, 2006; Hui et al., 2009; Song et al., 2006). However, the aqueous reaction has disadvantages because it was carried out in heterogeneous systems. The starch granules have many narrow channels leading from the surface to a central cavity; only the particles at least as large as 50 nm can access the channels. The solubility of OSA in water is low, there is probably a mixture of OSA droplets and OSA dissolved in water. The droplets could react with the granular surface or, depending on their size, travel into the channels and interior cavity. Presumably only OSA which is molecularly dissolved or extremely finely dispersed could penetrate into the bulk of the granule (Shogren et al., 2000). The DS and RE of OSA with starch in aqueous suspension was about 0.016–0.019 and 69–82%, respectively, under these reaction conditions: pH 8–9, reaction temperature of 25–35 °C, starch concentration of 35%, OSA concentration of 3% (based on the weight of starch), and reaction time of 3–6 h (Bai, Shi, & Wetzel, 2009; Hui et al., 2009; Song et al., 2006; Zhang et al., 2011). Some researchers have investigated that to increase the reaction efficiency by using organic solvents

Abbreviations: AEO, polyoxyethylene lauryl ether; BTMAB, benzyltrimethyl ammonium bromide; CTAB, cetyltrimethyl ammonium bromide; DS, degree of substitution; EO, ethylene oxide; FT-IR, Fourier transform infrared spectroscopy; ^1H NMR, ^1H nuclear magnetic resonance; OSA, octenyl succinic anhydride; PTC, phase transition catalyst; RE, reaction efficiency; TBAB, tetrabutylammonium bromide.

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(Bhandari & Singhal, 2002; Viswanathan, 1999). Another method of increasing the RE and reducing the reaction time is to put the OS-starch under high temperature or pressure conditions (Kim et al., 2010; Shogren, 2003). Though those methods could increase the DS and reduce the reaction time, the operation was complex and resource (energy) consuming.

Phase transfer catalysis (PTC) is now a well established technique in organic synthesis. PTC has also been recognized as a useful tool which is an environmentally friendly and economically feasible approach to achieve process efficiency in multiphase reactions (Yadav & Bisht, 2004). Phase transfer agent, acting in catalytic amounts, facilitates interphase transfer of species. The catalytic action is based on the condition that the catalyst–nucleophile ion-pair (Q^+Y^-) is favourably partitioned into the organic phase, so that the nucleophilic substitution reaction $Q^+Y^- + RX \rightarrow RY + Q^+X^-$ in the organic phase is fast and that the Q^+X^- ion-pair is favourably partitioned into the aqueous phase (Nelson & Benjamin, 2011). It is reported that the use of a PTC produced cross-linked starches with higher degrees of cross-linking starch than the control in an aqueous medium (Jyothi, Moorthy, & Rajasekharan, 2006). By using PTC such as quaternary ammonium or non-ionic surfactants, it should be possible to improve the transport of anion starch-O^- to the hydrophobic reagents.

In recent years, the phase transfer catalytic method in organic synthesis has been rapidly adopted and applied. However, to the best of our knowledge, there were few reports about the application of PTC in the modification of starch, especially, the mechanism of preparation of modified starch by PTC. Therefore, the objective of this work was to find an effective type of PTC, and investigate the effect of concentration of PTC on the degree of substitution (DS) and reaction efficiency (RE) of OS-starch, and deduce the mechanism of preparation of OS-starch by phase transition catalyst.

2. Materials and methods

2.1. Materials

Native cornstarch (13.5% moisture content) was obtained from DACHENG Company (Changchun, China). OSA was obtained from Nanjing Golden Chemical Co., Ltd (Nanjing, China). AEO was obtained from Guangzhou City XinGuan Trading Co., Ltd (Guangzhou, China). Other chemicals used in the study were all analytical grade.

2.2. Preparation of OS-starch

Cornstarch (100 g, dry starch basis, dsb) was suspended in distilled water (35%, w/w). The weighed quantity of PTC was adjusted at 0.05%, 0.1%, 0.25% and 0.5% of the dry starch base. The pH of the suspension was adjusted to 8.0–9.0 with a pH meter by adding 3% NaOH solution. OSA (3.0% dsb) was added with a burette over 1 h while maintaining the temperature at 35 °C. After the reaction, the pH was adjusted to 6.5 with 6% HCl solution. The mixture was centrifuged and washed two times with distilled water and two times with ethanol. The OS-starch was oven-dried at 40 °C for 24 h, and passed through a 100 mesh nylon sieve (Zhang et al., 2011).

2.3. Determination of the degree of substitution

The OS-starch sample (5 g, dsb) was accurately weighed and suspended by stirring for 30 min in 25 mL of HCl–isopropyl alcohol solution (2.5 M). Then 100 mL of aqueous isopropyl alcohol solution (90%, v/v) was added and stirred for an additional 10 min. The suspension was filtered through a glass filter, and the residue was washed with 90% isopropyl alcohol solution until Cl^- could be detected no longer (using 0.1 M $AgNO_3$ solution). The starch was re-dispersed in distilled water (300 mL) and heated in a boiling water-bath for 20 min with stirring. The starch dispersion was titrated with standard NaOH solution (0.1 M), using phenolphthalein as an end-point indicator. A blank was simultaneously titrated with native starch as a control (Zhang et al., 2011):

$$DS = \frac{0.162 \times (A \times M)/W}{1 - [0.210 \times (A \times M)/W]} \quad (1)$$

where A is the titration volume of NaOH solution (mL), M is the molarity of NaOH solution, and W is the dry weight (g) of the OS-starch.

The reaction efficiency (RE) was calculated as follows:

$$RE = \frac{ActualDS}{TheoreticalDS} \times 100\% \quad (2)$$

The theoretical DS was calculated by assuming that all the added OSA reacted with starch to form the ester derivative.

2.4. Surface tension measurement

The interfacial tensions were measured at temperatures of 25 °C (±1°C) by the Wilhelmy plate method using a Data Physics DCAT11 (Beijing, China) interfacial tensiometer. The concentrations of AEO were 0.01, 0.03, 0.05, 0.08, 0.1, 0.25, 0.5, 0.75, and 1 g/L (Bachmann et al., 2006).

2.5. Conductivity measurement

AEO (0.5 g) was accurately weighed and suspended in distilled water (100 mL). Standard NaOH solution (0.1 mM) was added to the solution; after each addition, the solution was stirred to ensure the homogeneous mixing, and then was subjected to a conductivity measurement (DD-307, Shanghai, China). Distilled water was measured as the blank.

2.6. ^1H NMR spectra

The ^1H NMR spectra were recorded on a Bruker AV400 NMR spectrometer (Ettlingen, Germany) at the frequency of 400 MHz. The sample (AEO) was measured after being dissolved in methanol-d_4, using tetramethylsilane as an internal standard.

2.7. Fourier transform infrared spectroscopy of the complexes of AEO and Na^+

The AEO sample (0.5 g) was accurately weighed and suspended in methyl alcohol (100 mL). The NaOH (0.341, 0.171, 0.085 g) was added and stirred to dissolve. The solvent was evaporated under reduced pressure in a rotary evaporator (RE-2000B, Shanghai, China) and the complexes were extracted. The FT-IR spectra were obtained from the samples in KBr pellets using a Vector 33 FT-IR spectrophotometer (Bruker, Ettlingen, Germany). A spectral resolution of 4 cm^{-1} was employed and 64 scans were acquired for each spectrum.

2.8. Statistical analysis

All experiments were performed with at least three repetitions, and results hereto are expressed as their means ± the standard deviation (SD). When necessary, the number of repetitions is noted in the text. The significance of the differences between groups was tested using t-test analysis. A probability level (p value) of <0.05 was considered to be statistically significant unless stated