Characterization and Solvent Free-Synthesis of Modified Potato Starch

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Abstract- This paper reports the synthesis of higher fatty acid esters (C8, C12, C16) of potato starch in the absence of organic solvents. The synthesis process is interesting and very convenient in which water is utilized as a nontoxic and a low-priced solvent. Starch dispersed in the reaction medium was alkali treated and then alkaline starch was esterified with using octanoyl, lauroyl and palmitoyl chloride. Esterification was readily carried out under an air atmosphere for reaction duration of 5–10 min. The results indicated that the degree of substitution of the starch esters diminishes with increase in fatty acid chain length. The chemical structural characteristics were investigated by FTIR. Surface morphology of modified starch was studied using scanning electron microscopy (SEM). Also X-ray diffraction studies showed that the starch crystalline structure has changed during reaction.

Keywords- Modified Starch; Fatty Acid; Esterification; Without Organic Solvents

I. INTRODUCTION

Starch with basic chemical formula (C6H10O5)n is a natural, biodegradable, renewable, high polyol, no toxicity, available in plenty and low-cost biopolymer which has found wide application in diverse areas of polymer science. It usually has two major components and appears: linear polymer amyllose (normally 20-30%) consisting of a-(1-4)-linked D-glucopyranose and amylopectin (normally 70-80%), having the same backbone as amyllose but with a large number of a-(1-6)-linked branch points. By far the largest source of starch is corn (maize) with other commonly used sources being wheat, potato, tapioca and rice [1-3]. Recently, there has been a growing interest in hydrophobically modified derivatives of polysaccharides for different applications. The amphiphilic nature imparted upon polysaccharides after hydrophobic modification gives them a wide and interesting applications spectrum, for instance as rheology modifier, emulsion stabilizer, surface modifier and as drug delivery vehicles [4, 5].

The hydrophilic nature of the native starch due to the hydroxyl groups is a major limitation for development of starch-based materials. Chemical modification of starch has been widely studied for producing hydrophobic and water-resistant material by way of chemical reaction with hydroxyl groups in the starch molecule. The esterified starch ester is a kind of modified starches that are synthesized with various reactants such as acid anhydrides (octenyl succinic anhydride (OSA) [6-8], dodecenyl succinic anhydride (DDSA) [9], fatty acids [10-12], and fatty acid chlorides [13-18].

A number of hydrophobic fatty acid esters have been synthesized from both maize, and potato starch. Hydroxyethyl starch was esterified with the long chain fatty acids under mild reaction conditions using DCC and DMAP [11]. The synthesis of modified hydrophobic starch using fatty acids was done by means of potassium persulphate as catalyst in dimethyl sulfoxide (DMSO) [12]. Several substituted starches were prepared by acylation of starch with fatty acid chlorides in organic solvents, such as pyridine or dimethylacetamide (14). However, the utilization of an organic solvent is prohibited for industrial applications, especially in food sector. There are also economical, environmental, and safety problems involved and also in some of these reactions, a problem of waste, corrosive atmosphere, and purification of the products was a task. Thus, an efficient method of synthesizing fatty acid esters of starch without organic solvents has been described during modification of starches with OSA [6].

In this paper, we have discussed the modification of potato starch using different long-chain fatty acid chlorides. This reaction is a simple and convenient method for esterification of starch using fatty acid chlorides and has several benefits in comparison of previous classic methods including utilizing water as green solvent instead of organic solvents. In this reaction hydrophobically modified products precipitate in water and separate without need to any non-solvent because they are low soluble in water. Also the reaction time is very short and it is complete just during several minutes. The aim of this research was the esterification of inexpensive, naturally potato starch with convenient method. To this end, the properties of esterified starches in aqueous media instead of using organic solvents such as toluene, pyridine or dimethylacetamide were investigated.

II. MATERIALS AND METHODS

A. Materials

Potato starch was purchased from Fluka and was dried at 110°C for about 10 h to remove absorbed moisture. Octanoyl, lauroyl, palmitoyl chloride were of reagent grade and were purchased from Sigma Chemical. All other chemicals and solvents were reagent grade and used as received, except DMSO which was stored over 3Å molecular sieves for drying.
B. Methods

1) Fourier Transformation Infra-red (FTIR) Spectra:

The FTIR analysis was performed using a FTIR Bruker-Tensor 270 spectrometer. The modified starch was mixed with analytical grade KBr at a weight ratio of 5/200 mg.

2) X-ray Diffraction (XRD):

The pattern of X-ray diffraction of the samples was obtained by Siemens diffractometer with Cu-K radiation at 35 kV in the scan range of 2θ from 2θ to 30°.

3) Scanning Electron Microscopy (SEM) Observation:

Scanning electron micrographs were obtained with a LEO 440i scanning electron microscope under vacuum at an operating voltage of 10 kV. The morphology of the starch, grafted with fatty acid chlorides was observed using a scanning electron microscope. Dried modified starch samples were gold coated by sputtering for 15 s.

4) Preparation of Acylated Potato Starch:

Starch esterification was carried out in two steps. In the first step, starch dispersed in the reaction medium was alkali treated and in the second step, the alkaline starch was esterified by the addition of fatty acid chlorides. The starch was dried at 100°C for 2 h before reaction was accomplished. Starch (1 g) was added to NaOH solution (10 ml, 0.25 M) at room temperature, then starch and water alkaline were mixed under low speed conditions for approximately 10 minutes. The selected amount of fatty acid chlorides (see Table 1) was added dropwise to the reaction container under stirring at 300 rmp and room temperature. Upon completion of the reaction, the mixture was neutralized to pH 7 with acetic acid, then modified products precipitate in water and it was ended by filtering the precipitated esterified starch, and finally extracted with MeOH in a soxhlet extractor for 1 day to completely remove unreacted fatty acid chlorides from the esterified starch. Esterified starch was then washed with water and ethanol and dried under vacuum at 40°C. Precipitated time was very short and it was completed just during several minutes (3-5 minutes). The above process was repeated once again. The filtrates were collected together and dried in vacuum, weighed and were kept in a desiccator. Table 1 includes a list of the materials used during synthesis and their amounts. The recuperation yield of the fatty starch ester was calculated according to the following Equation (1): This formula is for 1 gram of starch.

\[
\text{Yield} \% = \frac{m \times 162}{DS(M-1)+162}
\]

Where DS, M and m correspond to the degree of substitution, molecular mass of the corresponding fatty chain grafted onto starch and mass of modified starch. The molecular mass of the anhydroglucose unit is 162.

<table>
<thead>
<tr>
<th>Alkyl chain</th>
<th>Potato starch (0.006 mol)</th>
<th>Fatty acid</th>
<th>Acid chloride (mol)</th>
<th>Yield, % (DS-value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>acetyl</td>
<td>0.42 ml (0.006 mol)</td>
<td>n.r</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>propionyl</td>
<td>0.53 ml (0.006 mol)</td>
<td>n.r</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>pentaoyl</td>
<td>0.72 ml (0.006 mol)</td>
<td>n.r</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>octanoyl</td>
<td>1 ml (0.006 mol)</td>
<td>50 % (0.51)</td>
<td></td>
</tr>
<tr>
<td>C12</td>
<td>lauroyl</td>
<td>1.5 ml (0.006 mol)</td>
<td>75 % (0.30)</td>
<td></td>
</tr>
<tr>
<td>C16</td>
<td>palmitoyl</td>
<td>2 ml (0.006 mol)</td>
<td>85 % (0.15)</td>
<td></td>
</tr>
</tbody>
</table>

5) Determination of Degree of Substitution (DS):

As glucose monomer contains three free hydroxyl groups that can be substituted, the average degree of substitution (DS) can range from 0 up to 3.0. The degree of substitution was estimated according to Aburto et al [13]. The samples were dried at 105°C for 2 h before analysis. The degree of substitution (DS) was determined by proton NMR (1HNMR). For NMR determination the sample was dissolved in DMSO-d6. The peaks between 3.100 and 5.120 ppm corresponded to the signals from the seven protons of the glycoside structure. The three protons of CH3 terminal of the acyl chain were observed as a triplet at 0.865 ppm. The DS was obtained from the ratio of the area of the proton peak at 0.865 ppm to that of the proton peak between 3.100 and 5.1.

III. RESULTS AND DISCUSSION

A. Esterification of Starch

Esterified starch was prepared in NaOH solution (0.25 M) at room temperature in the presence of fatty acid chlorides (Fig. 1). The introduction of hydrophobic groups by esterification significantly decreases the hydrophilicity of starch and the
hydrophobicity depends on the degree of substitution. To this reaction were added the starch and fatty acid chloride in the molar ratio 1:1 respectively. Indeed, recent work by Fang has demonstrated the suitability of the method for the aqueous esterification of Four starches (corn, Hylon VII, Hylon, Amioca) [19]. They reported successful esterification reaction of starch with fatty acids that was limited to acid chlorides containing 6–10 carbon chains because below that range, the acyl chlorides were hydrolyzed under the reaction conditions and converted to their salt. We succeeded in carrying out the esterification reaction of potato starch even with longer carbon chain acid chlorides with some modification such as decreasing the NaOH concentration, reaction temperature and reaction time in this method. The reaction time is very short and it is completed just during several minutes and the hydrophobically modified products precipitated from water and separated without need to non-solvent. It is clear that a competition between acyl group substitution and acid chloride hydrolysis (or product saponification) occurred, particularly for those acyl chlorides (propionyl, pentanoyl) that were water-miscible. Also this reaction cannot be for higher of degree substitution (2, 3) as with choosing starch and fatty acid chloride in the molar ratio 1:2 and 1:3. It is noteworthy that the only successful esterification occurred in the case of reaction with long chain fatty acid chlorides. Only unreacted starch was isolated when acetyl, propionyl and pentanoyl chlorides were used as acylating agents.

Fig. 1 Scheme for reaction of starch with fatty acid chlorides (palmitoyl chloride)

B. FTIR Measurements

The FTIR spectra of native and modified potato starches are shown in Fig. 2. In the spectrum of pure starch (Fig. 2a), three characteristic peaks appear between 938-1157 cm\(^{-1}\), these peaks are the most characteristic band for a polysaccharide. It was attributed to the C–O stretching vibrations. This band was also observed in the spectra of starch esters. Relevant three peaks were better resolved manifesting cancellation of certain hydrogen bonds in starch. Another characteristic peak occurred at 1642 cm\(^{-1}\) is due to the presence of bound water in starch. An extremely broad band was observed between 3100 and 3500 cm\(^{-1}\). It was assigned to the hydroxyl group stretching vibrations. The maximum of that peak moved from original 3388 cm\(^{-1}\) for pure starch, and to over 3440 cm for starch esters (Fig. 2b). These changes could be interpreted in terms of decrease in the concentration of hydrogen-bonded hydroxyl groups, as they were converted into ester groups. These spectra provide evidence of octanoylation, lauroylation and palmitoylation by the presence of the ester carbonyl group stretch at 1738-1742 cm\(^{-1}\). The appearance of the band above 1735 cm\(^{-1}\) could be considered as an argument for the esterification of fatty chloroacids with starch, because the vibrations of the carbonyl group in ester used to reside in this region. The band at 2850 cm\(^{-1}\) was assigned to the aliphatic C–H stretching vibrations.

Fig. 2 FTIR spectra of native starch (a) esterified potato starch (b)

C. X-ray Diffraction

X-ray diffraction measurements were performed to check if the chemical modification altered the crystallinity of starch. The X-ray diffraction spectra of native starch and esterified starches are presented in Fig.3. Starch was composed of amylose and amylopectin. Amylose is located mainly in the amorphous domain of starch granule. In contrast, amylopectin makes up the
framework of the crystalline lamellae, and branching points are located in the disordered amorphous domains between the crystallites, which leads to the crystal diffractions. Regarding the crystalline structure of fatty acid potato starch esters, a complete loss of native crystallinity after substitution situation of hydroxyl groups by a fatty acid chain is observed (Fig. 3). Potato starch is a kind of cereals starch exhibiting an A-type pattern, with strong reflection at 15°, 17°, and 23°. This observation showed that esterification mainly occurred in crystalline domain. It reacted with the hydroxyl groups in the crystalline domain, and destroyed the crystalline structures of the starch and new structure of acylated starch was formed. The large diffraction peak between 9.9° and 10.5° increases when the length of the fatty acid chains grafted onto starch is increased up to 16 carbons atoms. These two diffraction angles have been attributed to the fatty acid-amylose complex corresponding to the hydrated (Vh) and anhydrous (Va) structures, respectively. In our case, the anhydrous structure is favored when a bulky chain, e.g. a palmitoyl group, is grafted onto starch, which is in agreement with previous reports [20].

![X-ray diffraction patterns of native potato and its esters (C8 and C16)](image)

**D. Scanning Electron Microscopic (SEM)**

Surface morphological analysis of starch and modified starch was confirmed by scanning electron microscopy (SEM) and is presented in Fig. 4. SEM of native potato starch showed typical granules of spheroid forms of size 10–20 μm. Smaller particles of damaged starch granules were also seen. Fig. 4b shows SEM micrographs of potato starch that are modified with (acyl chain: C8, DS: 0.41). Images revealed that the granularity of the products was retained partly and granules suffered essential damage. The SEM micrographs exhibited that granules somewhat were agglutinated. Also the modified potato starch showed morphological changes, indicating that the condition for acylation caused detectable change in the structural characteristics.

![Scanning electron microscopic (SEM) micrographs of the:](image)

(a) native potato starch (b) modified potato starch with (with c8, DS: 0.41)

**IV. CONCLUSIONS**

In summary, hydrophobically modification of potato starch was successfully carried out by mild esterification using acyl chlorides (octanoyl, lauroyl, palmitoyl chloride) in aqueous media and without any solvent, which gave good yields. The evidence of occurrence of chemical modification was checked by FT-IR. Surface morphological analysis of starch and modified starch was confirmed electro microscopic observation using (SEM) and finally X-ray diffraction studies show that starch crystalline structure has changed during reaction.

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