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Rapid Starch Acetylation at Low Temperature Using Iodine as Catalyst

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Summary: A method to prepare starch acetate using acetic anhydride (AA) is presented. The process was carried out at temperatures below 100 °C using iodine (I) as a catalyst. The effect of reaction temperatures, as well as AA/starch and I/starch weight ratio was analyzed. The results show that high degrees of substitution can be reached by this method and the initial amount of acetic anhydride has a substantial effect on reaction efficiency. For a weight ratio of acetic anhydride to native starch (AA/AN) equal to two, a substitution degree of 3 was reached for 30 min and 70 °C.

Keywords: acetylation; iodine; starch acetate; substitution degree

Introduction

Starch is a material that can be used as a biodegradable polymer because of its large natural abundance and low cost. However, the hydrophilic nature of starch granules limits its possible applications. Starch, as a polyalcohol, may form esters with organic and inorganic reagents[1] and it is well known that the hydrophobicity of starch increases with molecular weight, but also with its degree of substitution (DS). Furthermore, an increment in DS increases its miscibility with hydrophobic polymers.[2] High DS acetylated starches can be melt process and have various applications such as hot melt adhesives, coating, biodegradable packaging materials and drug delivery among others.[3–7] Thus, chemical modification through esterification is one of the most interesting options to produce biodegradable polymers from starch and for blending with other polymers. Several papers have reported on starch esterification with acetic anhydride or vinyl acetate using different methods.[8–11] Tomasik and Schilling[1] published an extensive review of the chemical modification of starch and described several methods of starch acetylation.

Xu et al.[9] followed a simple acetylation method described for the first time by Mark and Mehltretter[12] with acetic anhydride and using NaOH as a catalyst. They reported values of DS between 1 and 2 for different AA/starch ratios at 123 °C and a reaction time of 2 h. Another acetylation method using acetic anhydride in alkaline media was reported by Jarowenko.[13] Shogren[14] managed to prepare starch esters rapidly using a high temperature/pressure method and reported DS values between 0.5 and 2.5 for 2–10 min. Recently, Chi et al.[15] used a mixture of glacial acetic acid and acetic anhydride obtaining $DS = 2.89$ after 3 hours of reaction at 75 °C using methanesulphonic acid as catalyst.

It has been demonstrated that iodine is an excellent acylating reagent for the acetylation of alcohols.[16] An alternative method for starch acetylation was developed by Biswas et al.[17] in which iodine (I) was used as a catalyst. They proposed the reaction scheme as presented in Figure 1 in

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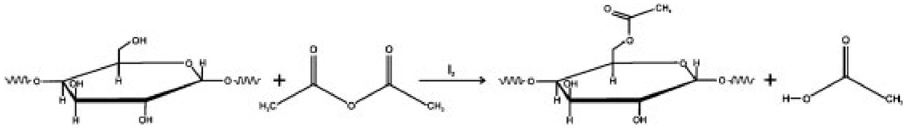

Figure 1.
Reaction for acetylation of starch with acetic anhydride using iodine as a catalyst.

which iodine activates the carbonyl group of acetic anhydride making the latter more reactive. This method is solvent-free and for a short time (just 10 minutes). However, they did not carried out a complete analysis for the effect of reaction conditions on the substitution degree.

The interactions between starch and iodine have been extensively studied, and the blue complex that amylose forms with iodine is well known. The structure of the complex has been established by Rundle and Baldwin[18] assuming a six-fold helical conformation. More recently, the bonds between amylose and iodine have been questioned by Calabrese and Khan.[19] In such complexes, amylose took well ordered rigid structure, with the hydroxyl groups oriented to outside of helical and it could facilitate acetylation. In the present work, a study of the reaction conditions (time, temperature and catalyst amount) for the acetylation of starch using acetic anhydride and iodine is presented.

Experimental Part

Synthesis of Starch Acetate

Before the acetylation reaction, the native corn starch (S) from Almidones Mexicanos S.A. de C.V. (Guadalajara, México) was dried for 24 h in a vacuum oven at a temperature of 60 °C to reduce its moisture content below 2%. The acetylation reaction was carried out by mixing the required amounts of dried corn starch, acetic anhydride (AA) and iodine (I) from Golden Bell Reactivos (México) in a 500 mL Erlenmeyer flask open to the atmosphere. The temperature was fixed using a glycerol bath on an electrically heated hot plate with a magnetic stirrer with constant stirring. The composition of the reaction system was varied to study the effect of AA and I amounts on DS (Table 1). Reaction mixture samples were taken at given times and rapidly cooled in a saturated sodium thiosulfate solution (20 mL) at 20 °C while stirring until the dark blue color solution changed to white. This confirmed that all the iodine was converted to iodide. The samples were then washed with 20 mL of methanol from Golden Bell Reactivos (México) and stirred for 20 min. After this time, the samples were filtered and washed with distilled water. Finally, the samples were dried at 60 °C for 24 h in a vacuum oven.

Determination of the Substitution Degree (DS)

The substitution degree was obtained according to the method proposed by Xu et al.[9] with some modifications. First, 0.5 g of starch acetate was placed in a 750 mL flask. Then, 50 mL of distilled water was added and finally, 25 mL of 0.5 M NaOH was added. The mixture was heated until the solution became clear (approximately 5 h) and the excess of NaOH was titrated with HCl (0.02 M) until a pH of 7 was obtained. Simultaneously, a blank sample with native starch was processed. The DS

Table 1.
Reaction system composition.

S [g]	AA/S [-]	I/S [-]	I/AA [-]	Reaction temperature [°C]
50[a]	1	3.3/50	3.3/50	25, 60, 70, 80
50	2	6.6/50	3.3/50	25, 60, 70, 80
50	2	3.3/50	1.67/50	70, 80

[a] Equivalent to 308 mmol of anhydroglucose units.

was calculated according to the modified Xu et al.[9] equation as:

$$SD = \frac{162 \times M_{HCl} \times (V_{HCl_0} - V_{HCl})}{1000 \times W - 42 \times M_{HCl} \times (V_{HCl_0} - V_{HCl})} \quad (1)$$

where M_{HCl} is the molarity of the HCl solution used in the titration, V_{HCl_0} and V_{HCl} are volumes of HCl solution used in the titration of the blank and starch acetate samples, respectively. W is the sample weight in g. The DS determination was performed in triplicate and the average value was reported.

Determination of the Reaction Efficiency (RE)

The reaction efficiency was calculated according to Khalil et al.[20] with a small modification as follows:

$$RE(\%) = SD\frac{n_{AGU}}{2n_{AA}} \times 100 \quad (2)$$

where n_{AGU} and n_{AA} are the number of moles of anhydroglucose units and acetic anhydride, respectively. The number 2 in the denominator takes into account that each molecule of acetic anhydride may substitute two OH groups. In the reaction scheme presented in Figure 1, Biswas et al.[17] proposed that only one ester is created from each AA molecule. However, it has been reported in different works that RE values higher than 100% are possible when acetic acid is used for the starch acetylation with acetic anhydride.[21] This can be due to direct esterification by the acetic acid. It is possible that an additional ester group by each AA molecule may be produced by the reaction scheme showed in Figure 2.

FTIR analysis

The spectra of native starch and starch acetate were obtained by a Perkin-Elmer Spectrum One spectrophotometer. The method of KBr pellet was used and the spectra were obtained using 100 scans and a resolution of 4 cm^{-1}.

Results and Discussion

Effect of Reaction Temperature on DS and RE

Figure 3 shows the substitution degree as a function of reaction time for a system prepared with an acetic anhydride/starch ratio equal to one (AA/S = 1) and 3.3 g of iodine for each 50 g of starch. The results show that the substitution degree increases rapidly in the first few minutes and then the reaction rate slows down due to decreasing

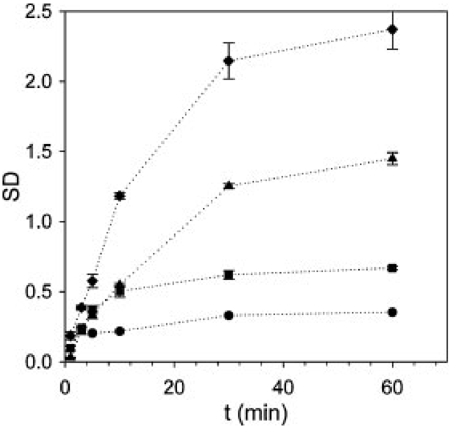

Figure 3.
Substitution degree as a function of reaction time for AA/S = 1, using 3.3 g of iodine for each 50 g of starch. Reaction temperatures are: ●: 25, ■: 60, ▲: 70, and ◆ 80 °C.

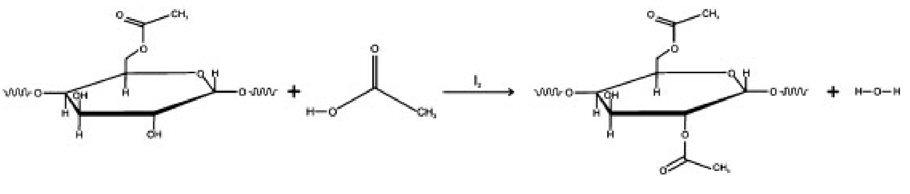

Figure 2.
Reaction scheme for acetylation of starch with acetic acid using iodine as a catalyst.

acetic anhydride and available reaction sites (hydroxyl groups) concentrations.[9] On the other hand, it is very interesting to observe that acetylation is achieved even at relatively low temperatures and that the substitution degree increases as the reaction temperature increases. In previous studies,[17] it was suggested that temperatures above 100 °C were required for acetylation to take place. However, this work shows that a high DS value (2.3) can be reached at 80 °C and 1 h of reaction.

The substitution degree as a function of time for a system prepared with a ratio of AA/S = 2, using twice the amount of iodine (6.6 g of I for each 50 g of starch) to keep constant the acetic anhydride/iodine ratio is presented in Figure 4. A similar behavior as observed in Figure 3 is obtained: the substitution degree increases as temperature increases. However, DS values are lower than the ones reached at AA/S = 1.

In Figure 5, the reaction efficiency as a function of time is presented for two cases AA/S = 1 (Figure 5a) and AA/S = 2 (Figure 5b). It can be clearly seen that the efficiency increases as the reaction temperature increases, in agreement with the results presented in Figures 3 and 4. However, it is also observed that an increase in acetic anhydride concentration results in a lower reaction efficiency. According to equation (2), the reaction efficiency is a function of both the substitution degree and the molar ratio between the anhydride of the anhydroglucose units (corresponding to the starch) and the amount of acetyl groups added to the reaction mixture. From this, even if a similar substitution degree are reached for both cases presented (AA/S = 1 and AA/S = 2), the reaction efficiency decreases with an increase in the amount of acetic anhydride.

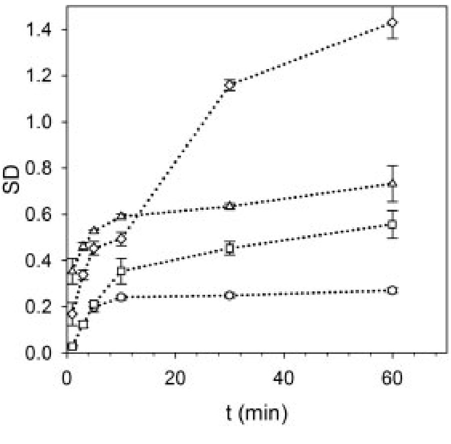

Figure 4.
Substitution degree as a function of reaction time for AA/S = 2, using 6.6 g of iodine for each 50 g of starch. Reaction temperatures are: ○: 25, □: 60, Δ: 70, and ◇: 80 °C.

Effect of the Amount of Iodine on DS

Biswas et al.[17] reported the effect of the amount of iodine and acetic anhydride on starch acetylation at 100 °C. They reported no changes in DS (DS = 1.6 reaction time = 10 min) when the weight ratio S/AA decreased (at constant AA/I ratio). Additionally, they found a small decrease in DS (DS = 1.3) when the AA/I ratio was tripled at constant S/AA ratio. In a recent work,[22] it was found that in cellulose acetylation, DS increases with the weight percent of iodine with respect to glucane in the reaction media until 15% weight is reached. If a large amount of iodine is used (20% weight), the reaction yield and DS decreased. In our work, the trends on the effect of I and AA amounts on the DS are different probably due to the different reaction conditions. Figure 6 presents a comparison between the esterification reactions carried out at 70 °C (Figure 6a) and 80 °C (Figure 6b). These plots show the strong effect of the amount of iodine on DS. The DS for a ratio AA/S = 1 (3.3 g of I/50 g starch) is higher than the value for the system with AA/S = 2 (6.6 g of I/50 g starch). However, when the ratio of native starch and iodine was kept constant increasing only the amount of AA, the reaction was faster with a higher final value of DS. Constant DS values were reached after only 30 minutes at 70 or 80 °C.

During the reaction, the stages taking place can be directly observed because iodine addition leads to color changes in the

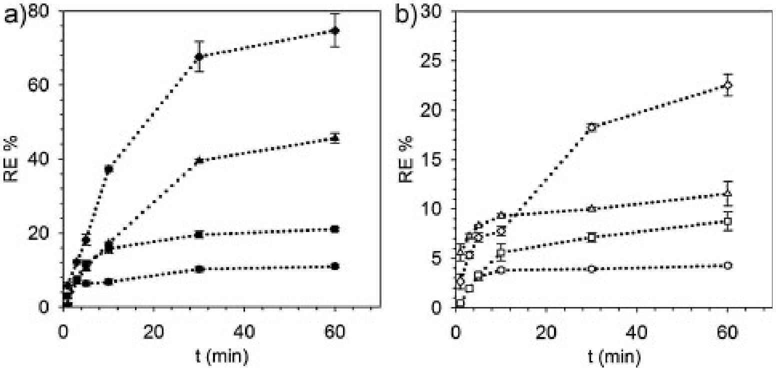

Figure 5.

Reaction efficiency as a function of reaction time for: (a) AA/S = 1 and 3.3 g of iodine for each 50 g of starch, and (b) AA/S = 2 and 6.6 g for each 50 g of starch (b). Reaction temperatures are: ○: 25, □: 60, Δ: 70, and ◇: 80 °C.

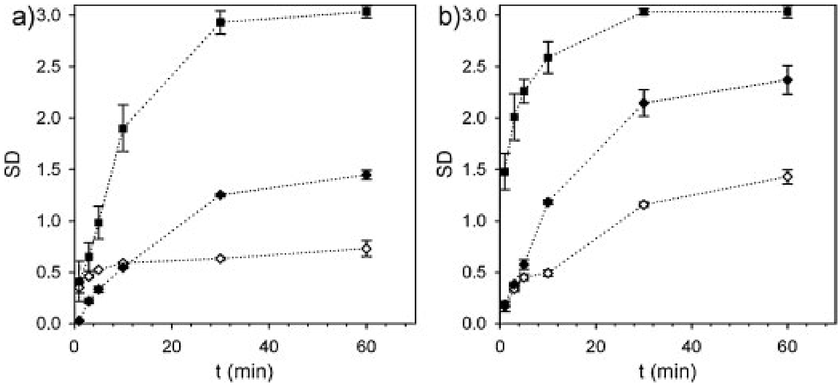

Figure 6.

Effect of iodine on acetylation reaction at (a) 70 °C and (b) 80 °C, The different conditions used are: ◆: AA/S = 1 (3.3 g of I/50 g starch); ◇: AA/S = 2 (6.6 g of I/50 g starch), and ■: AA/S = 2 (3.3 g of I/50 g starch).

solution from white to blue, which is an indication of starch-iodine complex formation. According with Rundle and Baldwin,[18] the amylose sorbed 26% of its own weight in iodine. This indicates the presence of one I_2 molecule per 6 anhydroglucose units in each helical turn of the amylose chain. Murdoch[23] concludes that the maximum iodine content should be 30 wt% assuming that the entire amylose molecule was helical and able of accommodating the maximum number of I_2 molecules. It is possible that I_5 or I_3 anions were formed from I^- and $2I_2$ or I_2, respectively. It was then enveloped with amylose forming well known blue complex. In such complexes, amylose took well ordered rigid structure with the hydroxyl groups oriented to outside of the helical. It could facilitate acetylation as the helical amylose in the blue complex is acetylated, the complex deteriorated liberating iodine into solution. Iodine liberation probably causes formation of iodidric acid with the acetic acid and may cause inhibition of acetylation because it is a very strong nucleophile and may compete for stabilization with the carboxylic acid. After approximately 10 minutes of reaction (depending of temperature), there is also a sudden change in viscosity,[9] changing from a thin solution to a viscous paste (stirring becomes difficult). This observation is also a clear indication that acetylation is taking place.

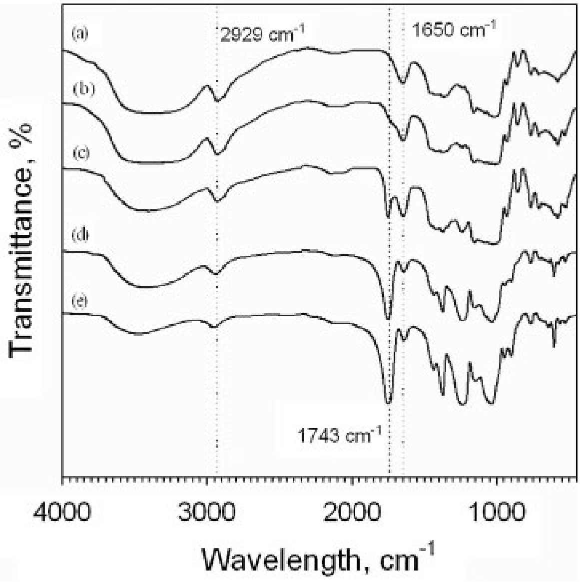

Figure 7.
FTIR spectra of native starch (a) and starch acetates with different DS: (b): 0.1, (c): 0.5, (d): 1.1, and (e): 2.9.

FTIR Analysis

FTIR spectroscopy was used to evaluate the changes in starch chemical structure due to acetylation. Figure 7 shows the spectra of native starch and starch acetate with different DS values. The bands at 3000–3600 cm^{-1} correspond to the stretching of OH groups and the band at 2950 cm^{-1} belongs to the stretching vibrations of the aliphatic C–H bonds. The bands at 1650 cm^{-1} and 1420 cm^{-1} correspond to the bending of δ(OH) and δ(CH), respectively. In the case of starch acetate, a band appears at 1740 cm^{-1} which corresponds to the ester group due to the stretching of the carbonyl bond (C=O). It is possible to appreciate a decrease in the intensity of the band corresponding to OH groups as well as an increase in the carbonyl group band as DS increases. Also, the bands at 1238 and 1372 cm^{-1} (the other two major ester bands) increased with changes in DS from 0 to 2.9 as the samples where dried in the same conditions, which can confirm that starch acetylation took place. Moreover, it is possible to see the changes in the ratio between intensities of C=O and CH_2, and Shogren[14] reported a calibration curve involving this ratio and DS.

Conclusions

In summary, starch acetate was synthesized from corn starch using acetic anhydride and iodine as a catalyst. The acetylation was carried out at temperatures below 100 °C and it was found that the acetylation reaction takes place from 25 °C obtaining $\mathrm{DS} \approx 0.25$ in 60 min. As expected, the substitution degree increases with temperature and reaction times. Under an optimum reaction conditions ($\mathrm{AA/S} = 2$; 3.3 g of I/ 50 g starch at 70–80 °C), $\mathrm{DS} = 3$ was obtained in just 30 minutes. It was also found that the reaction efficiency was substantially affected by the amount of AA used in the reaction, thus an increment of AA/S ratio reduces the RE. FTIR spectroscopy also confirms that acetylation took place by the apparition of the 1740 cm^{-1} band and the increasing ratio between the intensities of this band and the 2950 cm^{-1} band when DS increases. Nevertheless, an optimum amount of iodine is critical to use in order to get the desired DS by this acetylation method.

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