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Rapid preparation of starch esters by high temperature/pressure reaction☆

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Abstract

This study was undertaken to determine if starch esters of moderate to high degree of substitution (DS) could be prepared more rapidly, efficiently and with fewer byproducts. The method selected was to heat mixtures of dry corn starch, glacial acetic acid and anhydrides under pressure in small (60 μl) stainless steel sealed pans. Starch acetates of DS 0.5–2.5 were prepared at temperatures of 160–180 °C in 2–10 min. Reaction efficiencies were essentially 100%. Reaction rates increased with increasing acetic acid concentration and decreased with increasing acetic anhydride concentration. The acetic acid remaining in the samples could be completely removed by vacuum stripping at 120–190 °C. Starch succinates of DS 1.0–1.5 were prepared at temperatures and times similar to those for starch acetates above. Longer reaction times (20–60 min) were required for the preparation of starch octenylsuccinates and dodecenylsuccinates having moderate DS values (~0.5). Significant acetylation due to esterification of starch with acetic acid also occurred in these systems for long heating times (>20 min). This results in release of water and probably accounts for some of the apparent degradation (reduction in viscosity, browning) seen at long heating times.
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Keywords: Starch; Starch acetate; Starch succinate; Synthesis

1. Introduction

Most starch esters currently being made commercially are low (<0.1) degree of substitution (DS) starch acetates, alkenylsuccinates, phosphates and adipates and are used in the form of aqueous solutions/suspensions for food applications (Jarowenko (1986) and Lower (1996), and Tessler & Billmers 1996). These are normally prepared by adding the desired anhydride to an aqueous starch/water slurry at room temperature along with NaOH solution to neutralize the acid formed and maintain pH of about 8. Reaction times are several hours and reaction efficiencies are typically about 70% depending on the type of anhydride and reaction conditions (Jarowenko, 1986; Jeon, Viswanathan, & Gross, 1999).

Starch esters of moderate to high degree of substitution (DS 0.5–2.5) can have very different properties such as hydrophobicity/melt processibility and a number of non-food applications such as tablet binders, hot melt adhesives, coatings, cigarette filters, biodegradable plastics and metal ion absorbants have been suggested. Jarowenko (1986), Lower (1996) and Tessler and Billmers (1996) have reviewed some of the work in this area.

In early work, Mullen and Pacsu (1942) and Wolff, Olds, and Hilbert (1951) prepared fully substituted fatty acid esters of starch using fatty anhydrides and pyridine as the solvent/catalyst. The preparation of starch succinates (Bhandari & Singhal 2001), dodecenylsuccinates (Assempour, Koenig, & Huang, 1994), and propionate/phthalates (Rudolph & Glowaky, 1978) using similar methods have been described. Other solvents used for the synthesis of starch esters have included *N*-methyl pyrrolidone (Reinisch, Radics, & Roatsch, 1995), dimethyl formamide (Shimoozono & Shiraishi 1997) and dimethylacetamide/LiCl (Fang, Fowler, Tomkinson, & Hill 2002). However, many organic solvents are expensive, toxic and difficult to remove from starch so an alternative method would be desirable. Mark and Mehltretter (1972) prepared starch triacetates by refluxing starch, acetic anhydride and 50% NaOH solution for 2–5 h. Shogren, (1996) used a similar method to prepare starch acetates of DS 1.5–2.5 in 10–50 min. Large quantities of sodium acetate byproduct were produced and

☆ Product names are necessary to report factually on available data; however the USDA neither guarantees nor warrants the standard of the product, and the use of the name USDA implies no approval of the product to the exclusion of others that may also be suitable.

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reaction efficiencies were relatively low (45–65%) due to hydrolysis of acetic anhydride by water and sodium hydroxide. Billmers and Tessler (1994) prepared starch acetates, propionates and butyrates of DS 1–2 by mixing an aqueous suspension of starch with anhydride and 25% NaOH for about 4 h at 0–40 °C. Reaction efficiencies were 50–90% and large amounts of sodium fatty acyl byproduct were produced. Sulfuric acid (Lepeniotis & Feuer 1997) and methanesulfonic acid (Feuer, 1997) have been used as catalysts for the acetylation of starch in acetic acid/acetic anhydride. Reaction conditions have to be controlled carefully as molecular weight degradation occurs readily in the presence of strong mineral acids (Mullen & Pacsu, 1942). Fatty acid esters of starch were prepared by gelatinization of starch by formic acid followed by treatment with fatty acid chlorides (Aburto et al., 1999). Cellulose and starch were activated in concentrated NaOH followed by acylation with fatty acid chlorides (Kwatra, Caruthers, & Tao, 1992).

Recently, the preparation of starch esters using high temperature, pressure, intensive mixing methods have been claimed. Vaca-Garcia, Borredon, and Gaset (2000) used reactive extrusion at 180–230 °C to prepare starch esters from starch, fatty acid methyl esters and transesterification catalysts (NaOH). Lammers, Tiitola, and Vuorenpaa (1998) prepared medium-high DS starch acetate using a procedure similar to that of Shogren (1996) but at higher temperatures (130–180 °C) and pressures (0.1–50 bar). Runkel, Stoye, Rapthel, and Kakuschke (1999) prepared starch acetates of DS 1.2–2.6 by heating moist starch with acetic anhydride at 180 °C and 5 bar pressure for 30 min. Few details of the effects of reaction conditions were included in these patents, however.

In this paper, the reaction of dry starch with anhydrides in the presence of acetic acid at high temperatures and pressures was studied in order to design a process to synthesize starch esters more efficiently and at lower cost. Acetic acid was chosen since previous work has shown that starch/acetic acid mixtures will melt at 180 °C (Shogren, 2000) and thus should render the starch amorphous and more reactive. It is also inexpensive, non-toxic and naturally produced by the acetylation reaction. The effects of acetic acid concentration, type and concentration of anhydride, and reaction temperature on the reaction rates were studied. Micro-size reaction vessels were used to conduct experiments in parallel, thus reducing time and the amount of chemicals required.

2. Experimental

2.1. Materials

Normal corn starch was either Buffalo 3401 from CPC International, Englewood Cliffs, NJ or pure food grade starch from Staley, Decatur, IL. High (70%) amylose corn starch was Amylomaize VII from American Maize-Products (now Cargill, Hammond, IN). All starches contained about 11% water. Glacial acetic acid and sodium acetate were reagent grade from Fisher and Aldrich, respectively. Acetic anhydride was 99 + % from Aldrich, octenylsuccinic anhydride (mixture of *cis* and *trans*) was 97% from Aldrich and dodecenylsuccinic anhydride was 95% from Sigma. Deuterium oxide, 99.96% D, sodium deuteroxide, 99.9% D and sodium 3-(trimethylsilyl) propionate 2,2,3,3-d_4, 98% D were from Aldrich.

2.2. Methods

Starches were first dried at 120 °C in a vacuum oven for 2 h. Dried starches were mixed with glacial acetic acid and anhydride in glass stoppered flasks and then a small portion (50 μl) was pipetted into the bottom half of a stainless steel DSC pan. These pans were Large Volume Capsules (60 μl), Perkin Elmer part number 0319-0218, Norwalk, CT. The top and bottom capsule parts seal together using a Viton o-ring and can withstand pressures up to 350 psi. Pans were quickly sealed and placed in between preheated 1/2 inch thick steel plates (10 in × 6 in.) in an oven (model 19, Precision Scientific, Chicago, IL). The bottom steel plate had 20 1/2 inch diameter, 1/4 inch deep holes drilled in it, each of which holds one pan. Temperatures were measured inside the wells in the plate with a 0.02 inch diameter wire type-K thermocouple, time constant 0.13 s (Cole Parmer, Vernon Hill, IL). After the desired heating time, pans were removed from the oven and allowed to cool. Pans were opened by striking the edge with a hammer and the contents of 2–3 pans were scooped out and placed in a beaker containing 50 ml of ethanol (starch acetates and succinates) or hexane (starch alkenylsuccinates). After magnetic stirring for several hours, the supernatant was decanted off, more ethanol (starch acetates and succinates) or ethanol/water 1/1 (starch alkenylsuccinates) was added and the extraction repeated. Samples were air dried overnight. Reactions of starch/acetic acid/acetic anhydride 1/1/1 by weight were repeated on 4 separate occasions and the standard deviations are shown in the figures. Some reactions were scaled up using a stainless steel, 450 ml pressure reactor equipped with a mechanical stirrer blade and heating mantle (Model 4562, Parr Instrument Co., Moline, IL.)

Degree of substitution (DS) values for some starch acetates were determined by FTIR spectroscopy using a Nicolet Impact 410 spectrometer (Madison, WI). KBr pellets were prepared from 1 mg of sample and 200 mg KBr. Intensities of the C=O vibration (1743 cm^{-1}) relative to the starch CH_2 vibration (2929 cm^{-1}) were compared to a standard curve of A_{1743}/A_{2929} versus D.S for starch acetate standards. The standards were prepared and DS values measured by titration as reported earlier (Shogren, 1996). DS values for succinate, alkenylsuccinate and some acetate esters were determined by ^1H NMR using a Bruker

(Billerica, MA) Avance 400 MHz NMR spectrometer equipped with a Z-gradient, inverse detection, 5 mm broadband probe. Approximately 10 mg of sample was added to 0.6 ml of 0.5 M NaOD in D_2O and allowed to sit with occasional shaking for 5–10 days. Sodium 3-(trimethylsilyl) propionate 2,2,3,3-D_4 was added to some samples as an internal standard. Some of the hydrolyzed starch alkenylsuccinates were not soluble at room temperature and hence the NMR spectra of these were obtained at 70 °C where clear solutions were obtained. Acetate DS was quantitated by 1/3 of the area of acetyl proton resonance at 1.92 ppm divided by 1/7 of the sum of the areas of the starch C–H proton peaks at approximately 3.3–4.1 ppm and 5.1–5.3 ppm. Succinate DS was estimated by 1/4 of the area of the succinate CH_2 resonance at 2.41 ppm divided by 1/7 of the starch CH proton areas. Alkenylsuccinate DS was measured by the area of the alkenyl C=CH peak at approximately 5.5–5.6 ppm divided by 1/7 of the starch CH areas. DS values of starch acetates determined by the NMR method were within 5% of values determined by titration for starch acetate standards of DS 2.0 and 0.52. Reaction efficiencies were calculated as the ratio of measured DS to theoretical DS (mole anhydride/mole glucose residue).

3. Results and discussion

FTIR spectra of starch acetate standards prepared as described earlier are shown in Fig. 1. Intensities of the acetate C=O stretch at 1743 cm^{-1} relative to the starch CH_2 stretch at 2929 cm^{-1} versus acetate DS are plotted in Fig. 2. The calibration curve was linear over the range of DS from 0.5 to 2.5. Representative ^1H NMR spectra of starch acetate, succinate, octenylsuccinate and dodecenylsuccinate are shown in Fig. 3.

The effect of temperature on the acetylation of dry normal corn starch in glacial acetic acid/acetic anhydride (GAA/AA) 1/1 for 5 min is shown in Fig. 4. Temperatures given are those measured inside the steel well rather than in the small pan. However, the pan is so small and light (0.32 g) that temperatures within the pan probably rise to near the indicated temperature fairly quickly. The reaction at 178 °C was repeated on four separate occasions with the standard deviation given by the error bar in the figure. The rate of reaction increases rapidly at 150 °C and is essentially complete at 170 °C, giving starch acetate of D.S 1.5. The reaction efficiency is 100% or slightly higher, probably due to some esterification of starch with acetic acid (see also Fig. 5).

The effects of acetic acid and sodium acetate on the reaction of dry starch with acetic anhydride at 178 °C are shown in Fig. 5. There is essentially no reaction between starch and acetic anhydride after 10 min of heating, indicating that the presence of acetic acid is required for acetylation to occur. The acetic acid probably swells the starch and disrupts hydrogen bonding, allowing starch hydroxyl groups freedom to react. It should also be noted that the melting temperature of dry starch in excess acetic acid is approximately 180 °C (Shogren, 2000), so

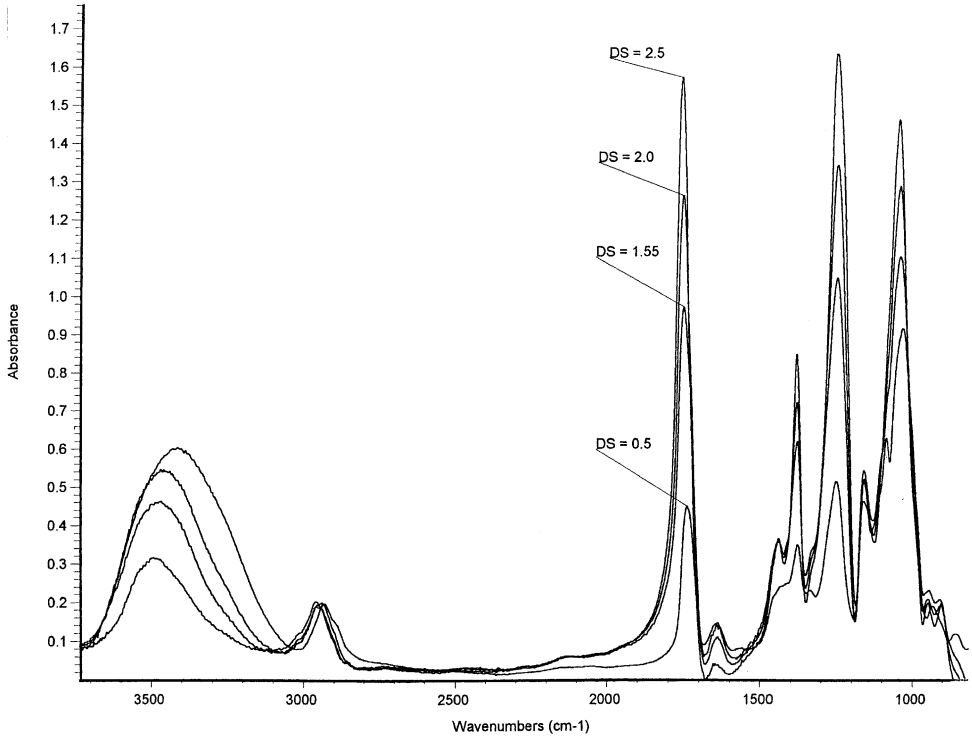

Fig. 1. FTIR spectra of starch acetate standards having degree of substitution (DS) of 0.52, 1.55, 2.0 and 2.5.

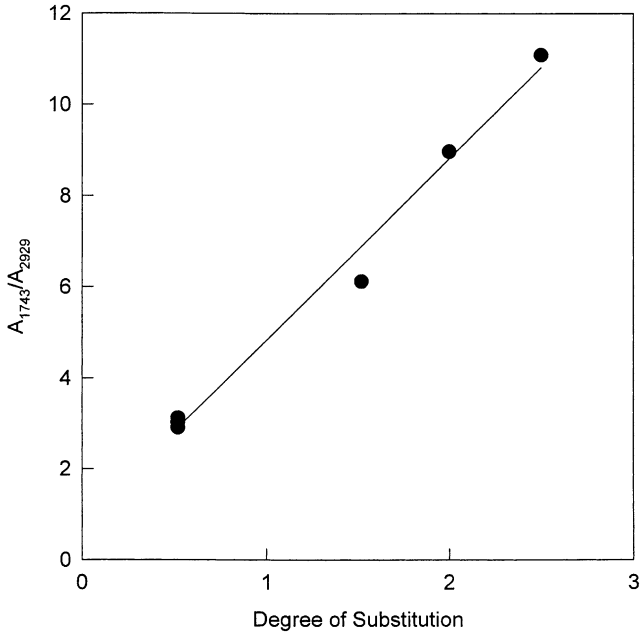

Fig. 2. Calibration of the ratio of FTIR absorbancies at 1743 cm^{-1}/2929 cm^{-1} versus acetyl DS.

that the segmental mobility of starch at these temperatures probably also enhances reaction rates. Addition of sodium acetate, a commonly used acetylation catalyst, increases the initial reaction rate slightly, but has little effect on the DS after 5 min. Reactions are mostly complete after 2 min, suggesting that the internal temperature of the pans rises rapidly over that time. The acetylation of high (70%) amylose starch in a ratio of starch/GAA/AA of 1/1/1 at 179 °C was also studied. Results were very similar to those obtained for normal corn starch, with DS values of 1.54 and 1.63 obtained after 5 and 10 min of heating, respectively. The appearance of starch acetates of DS 1.5 after removal from the pans was a clear to light tan, highly viscoelastic polymer which became a white solid after adding ethanol.

The effect of acetic acid concentration on the rate of reaction of dry starch/acetic anhydride 1/1 at 180 °C is shown in Fig. 6. The rate of acetylation is very slow at an acetic acid level of 10% based on starch weight. The rate increases considerably at 30% acetic acid and, although slower than with 100% acetic acid, the DS reaches the theoretical value after 10 min.

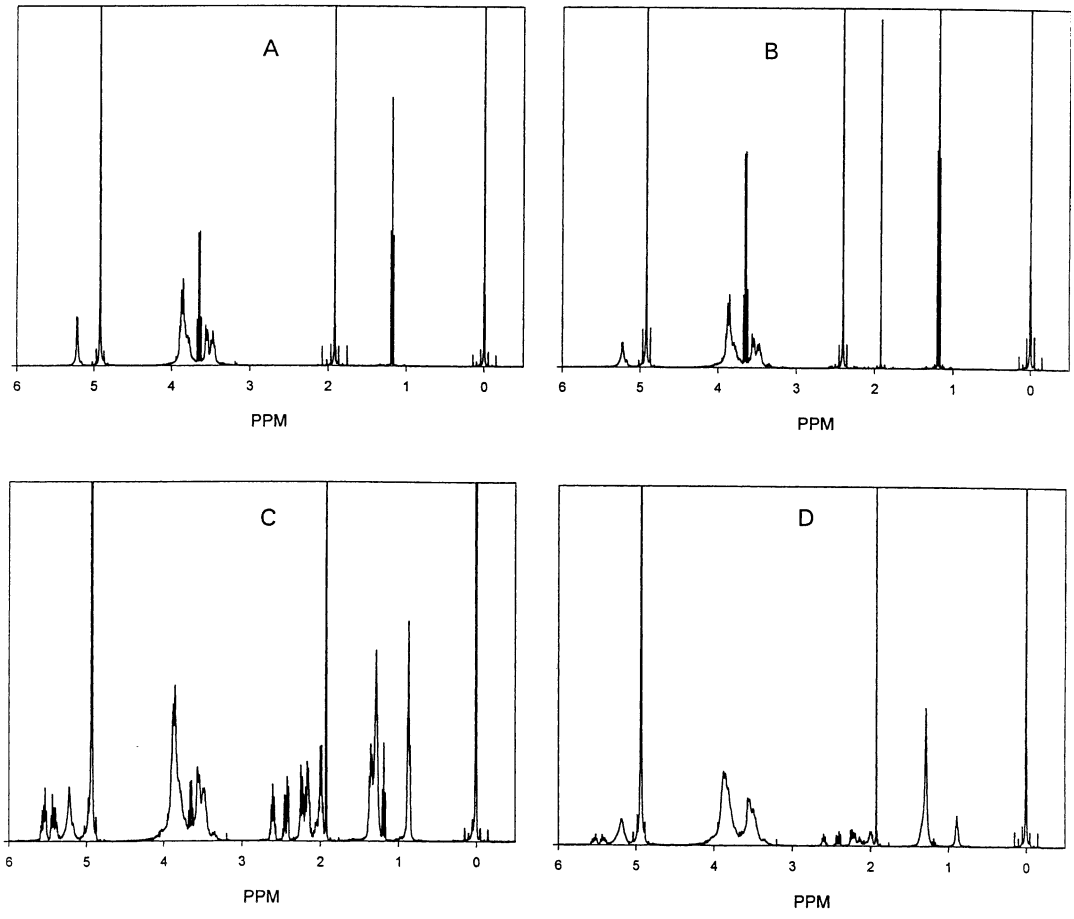

Fig. 3. ^{1}H NMR spectra of starch/acetic acid/acetic anhydride 1/1/1 sample after heating for 5 min (A); Starch/acetic acid/succinic anhydride 1/1/1 sample after heating for 5 min (B); starch/acetic acid/octenylsuccinic anhydride 1/1/1 sample after heating for 20 min (C); starch/acetic acid/dodecenylsuccinic anhydride 1/1/1 sample after heating for 20 min (D). Temperatures were 178–180 °C.

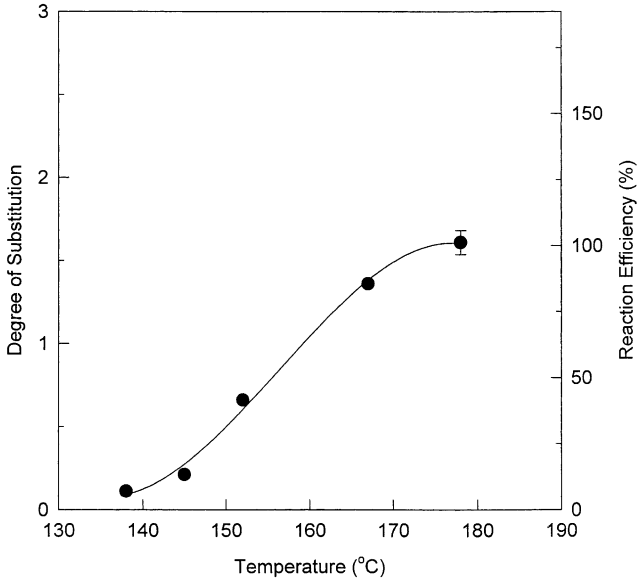

Fig. 4. Effect of reaction temperature on acetylation of corn starch/acetic acid/acetic anhydride 1/1/1 for 5 min.

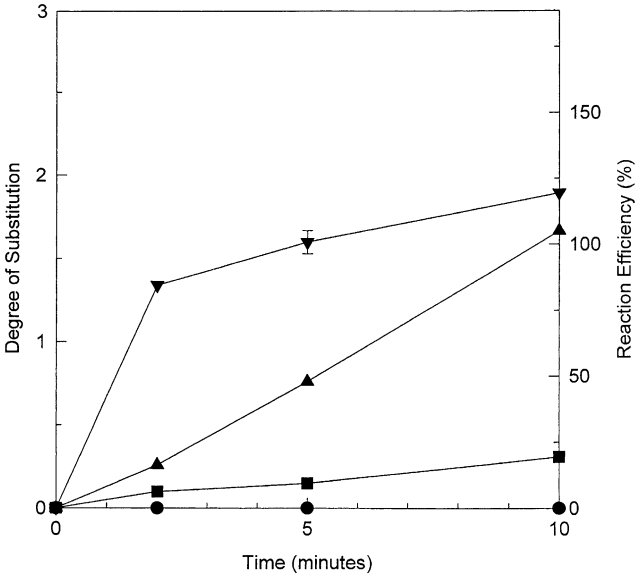

Fig. 6. Effect of acetic acid concentration on the acetylation of corn starch at 180 °C: starch/acetic acid/acetic anhydride 1/0/1 (●); starch/acetic acid/acetic anhydride 1/0.1/1 (■); starch/acetic acid/acetic anhydride 1/0.3/1 (▲); starch/acetic acid/acetic anhydride 1/1/1 (▼).

The effect of acetic anhydride concentration on the acetylation of starch/acetic acid 1/1 mixtures at 178 °C is shown in Fig. 7. Initial rates of acetylation are not greatly affected by acetic anhydride concentration but longer times are required for complete reaction as acetic anhydride level rises. This is probably due to greater dilution of reactants at the higher anhydride levels as the reaction proceeds. Interestingly, the reaction efficiency for the CS/GAA/AA 1/1/0.3 mixture reached 149% after 10 min while mixtures having higher AA levels had efficiencies near 100% or lower. The higher acetylation than expected was presumably due to direct esterification with acetic acid. The effect of acetic acid esterification on reaction efficiency is magnified at low DS levels since the amount of esterification contributed by acetic acid (DS 0.1–0.2 after 10 min) is significant compared to that from the anhydride (DS 0.47 for CS/GAA/AA 1/1/0.3). Data calculated from a second order

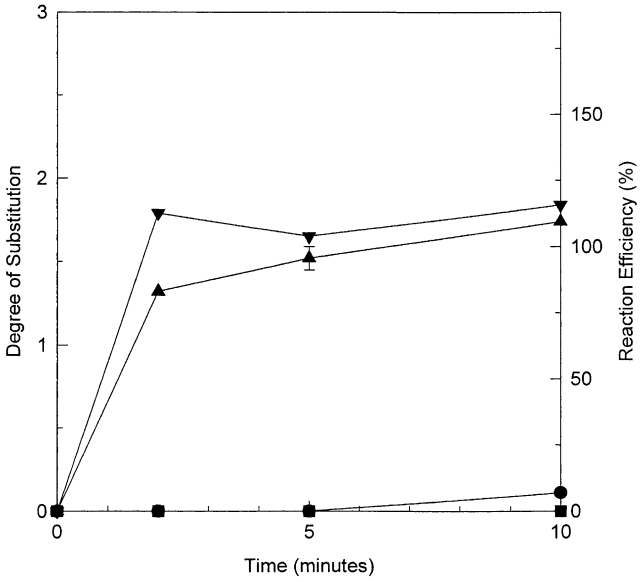

Fig. 5. Effect of addition of acetic acid and sodium acetate on the acetylation of corn starch at 178 °C: starch/acetic acid 1/1 (●); starch/acetic anhydride 1/1 (■); starch/acetic acid/acetic anhydride 1/1/1 (▲); starch/acetic acid/acetic anhydride/sodium acetate 1/1/1/0.05 (▼).

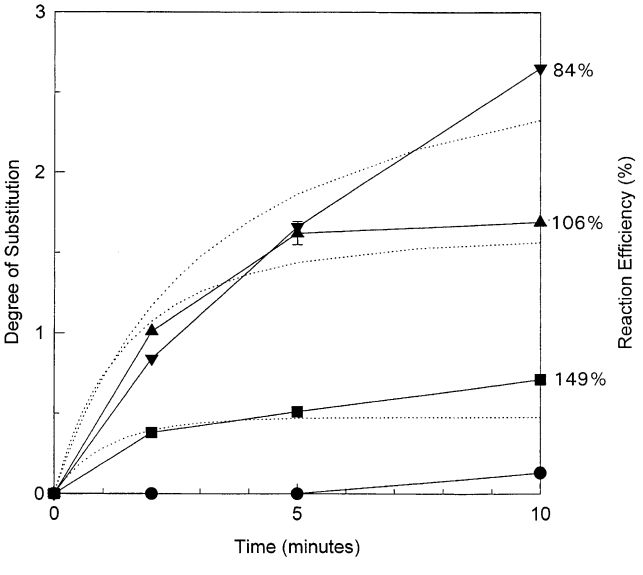

Fig. 7. Effect of acetic anhydride concentration on the acetylation of corn starch at 178 °C: starch/acetic acid/acetic anhydride 1/1/0 (●); starch/acetic acid/acetic anhydride 1/1/0.3 (■); starch/acetic acid/acetic anhydride 1/1/1 (▲); starch/acetic acid/acetic anhydride 1/1/2 (▼). Dashed lines are calculated from a second order kinetic model (see text).

kinetic model (Kwatra, et al., 1992) using a single rate constant of 0.10 l/mol min (dashed lines in Fig. 7) fit the experimental results fairly well for CS/GAA/AA 1/1/0.3 and 1/1/1 but predict higher initial rates than those seen for 1/1/2 sample. The implies a lower initial rate constant for the 1/1/2 sample, perhaps due to initial dilution of the acetic acid by acetic anhydride and lessening the rate of activation of the starch. Thus, gradual addition of acetic anhydride might be one way to accelerate acetylation, especially when high DS starch esters are desired.

It would be of interest to determine if excess acetic acid present after reaction could be removed by vacuum stripping in order to facilitate recycling of acetic acid. After heating a mixture of starch/GAA/AA 1/1/1 in sealed pans at 180 °C for 5 min, the pans were opened and placed in a vacuum oven for different times and temperatures. The measured weight losses and those calculated based on the composition expected after reaction completion are compared in Table 1. The excess acetic acid was completely removed by heating in vacuo at 125 °C for 20 min or 190 °C for 2 min. Previous work (Shogren, 2000) had shown that acetic acid tightly binds to starch due to the formation of amylose V-type inclusion complexes and was difficult to remove even by heating. In the present case, however, the presence of the acetyl groups at a DS of approximately 1.6 probably prevents the formation of any V-type complex.

The rate and extent of reaction of starch with succinic anhydride (SA) at a ratio of starch/GAA/SA 1/1/1 and temperature of 178 °C is shown in Fig. 8. Samples appeared white and rubbery after removal from the pan and were white powders after extraction and drying. The reaction is rather fast, comparable to that of starch and acetic anhydride but did not go to completion, reaching a DS of 1.23 (reaction efficiency of 77%). Part of the reason for this may be that water released during the esterification of starch and acetic acid could react with succinic anhydride to form succinic acid or hydrolyse the starch succinate ester bond. Also, the succinate group is bulkier than the acetate and may tend to interfere with succinic anhydride molecules as they approach the higher DS starch succinates, thus slowing the reaction. The starch succinate swelled but did not dissolve in 0.1 M $NaHCO_3$ buffer (pH 8.4) suggesting that some cross-linking may have occurred due to esterification of the free succinic carboxylic acids with starch hydroxyls. A small degree of cross-linking on dry heating of starch and succinic acid has been noted previously (Seidel et al., 2001).

Table 1
Volatilization of acetic acid from a starch/GAA/AA 1/1/1 reaction mixture

Heating temperature (°C)	Heating time (min)	Measured weight lost (%)	Theoretical weight loss[a] (%)
125	2	47	53
125	5	48	53
125	20	53	53
125	60	55	53
190	2	55	53

Starch/GAA/AA 1/1/1 was heated in sealed pans for 5 min at 180 °C then opened and heated in vacuo for the indicated times and temperatures
[a] Calculated from reaction stoichiometry.

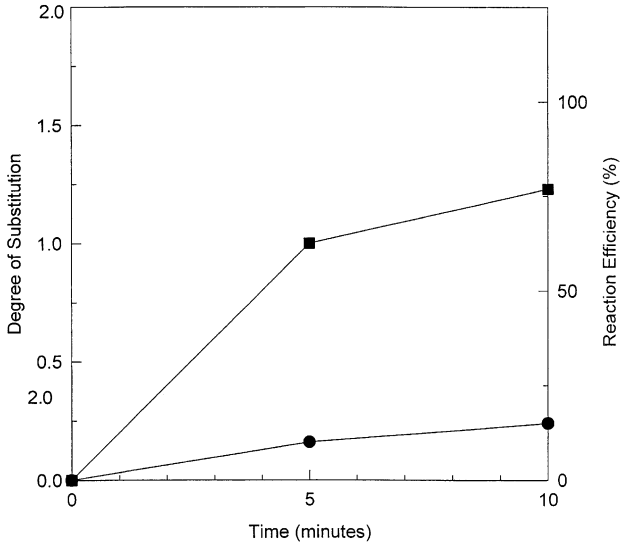

Fig. 8. Reaction of corn starch/acetic acid/succinic anhydride 1/1/1 at 178 °C: DS of succinate (■); DS of acetate (●). Reaction efficiency scale refers to succinate.

The rates of reaction of octenylsuccinic anhydride (OSA) and dodecenylsuccinic anhydride (DDSA) with starch are slower as shown in Figs. 9 and 10, respectively. Starch octenylsuccinate/acetate of OSA DS 0.49 and acetate DS of 0.34 was obtained after 20 min at 180 °C. This represented an OSA reaction efficiency of 65%; no further increase in DS occurred on further heating for

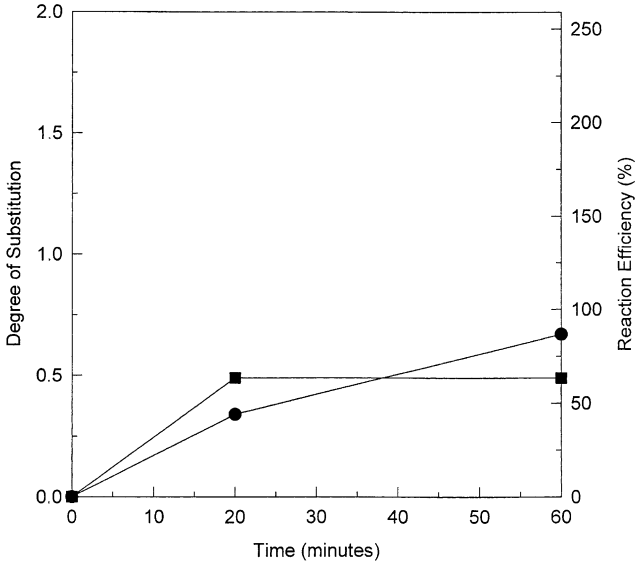

Fig. 9. Reaction of corn starch/acetic acid/octenylsuccinic anhydride 1/1/1 at 180 °C: DS of octenylsuccinate (■); DS of acetate (●). Reaction efficiency scale refers to octenylsuccinate.

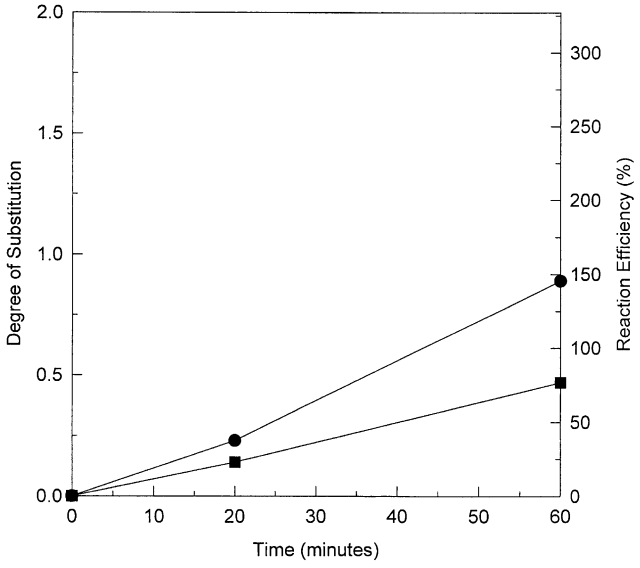

Fig. 10. Reaction of corn starch/acetic acid/dodecenylsuccinic anhydride 1/1/1 at 180 °C: DS of dodecenylsuccinate (■); DS of acetate (●). Reaction efficiency scale refers to dodecenylsuccinate.

a total of 60 min. The DS of starch dodecenylsuccinate/acetate increased gradually over the entire 60 min heating time, giving a DDSA DS of 0.49 and acetate DS of 0.89 after 60 min. at 180 °C. This represented a reaction efficiency of 78% (82% if the 95% purity of the starting DDSA is taken into account). However, the materials obtained after 60 min heating were dark reddish-brown in color, sticky in consistency and likely degraded. In contrast, materials heated for 20 min were light tan in color and had a solid consistency. The starch alkenylsuccinate/acetate esters either were either highly swollen or soluble in polar solvents such as ethanol, THF, acetone and toluene but were hardly swollen by water or hexane. The slow reaction of long chain hydrocarbon anhydrides with polysaccharides has been often observed in the past and is thought to be due to steric effects (Aburto et al., 1999; Gedon & Fenge, 1992).

To determine the feasibility of scale-up of the micro-scale esterifications, a reaction mixture of 50 g each of dry starch, glacial acetic acid and acetic anhydride were heated in a sealed 450 ml stainless steel Parr stirred reactor. In the first experiment, the reaction mixture was heated to 176 °C over 15 min followed by cooling to 100 °C over an additional 15 min after which the bomb was opened. The resulting starch acetate was light brown in color and had a DS of 1.68. In the second experiment, the reaction mixture was heated to 165 °C over 11 min followed by cooling to 100 °C over an additional 6 min after which the bomb was opened. The resulting starch acetate was white in color and had a DS of 1.21. There may have been some inhomogeneities in temperature distribution in these experiments due to the highly viscous nature of the reaction mixture and consequent difficulties in stirring.

The preparation of moderate to high DS starch esters by the method described here has several potential advantages over aqueous batch processes currently used. Reactions are fast, reaching completion in a few minutes for acetylations and succinylations and hence would be candidates for continuous reactive processing such as reactive extrusion or microwave tube heating. The esterification reaction is quite exothermic so this can be taken advantage of to reduce heating energy requirements. Byproducts are minimized since reaction efficiencies are high and no catalyst is used. In the case of starch acetates, the sole byproduct is acetic acid, which can be removed and recycled by vacuum stripping, thus reducing or eliminating the need for large quantities of wash water. In the case of starch succinates and alkenylsuccinates, reaction efficiencies might possibly be increased by venting off acetic acid during the later stages of the reaction and thus reducing the water formed during the esterification of starch with acetic acid. Water probably competes with starch for reaction with the anhydride and also hydrolyses the starch backbone and lowers molecular weight. Another potential advantage is that water soluble starches could be easily esterified while this would be difficult in the aqueous method due to the difficulty of extracting the byproducts from the starch.

Further work remains to be done in terms of characterizing the molecular weight, side chain distribution, physical properties and potential applications of starch esters prepared as described here. The distribution of ester groups along the starch chain could very well be different than that obtained from aqueous slurry procedures since starch is probably swollen or even dissolved in hot acetic acid during reaction rather than being in the semi-crystalline granular state. Relatively little work on the physical properties of different types of high DS starch esters has been reported, presumably due to the difficulty of making these. Also, moderate to high DS cellulose esters have received more attention and more commercial success probably due to their superior mechanical and viscous properties. Amylose and amylopectin from starch are, however, more flexible macromolecules than cellulose and thus may have some advantage in areas such as adhesives, coatings and thermoplastic extrudates. New genetically modified amyloses of higher molecular weights and purities rivaling those of cellulose may also become available and costs may also be lower than cellulose.

In summary, starch acetates, succinate/acetates and alkenylsuccinate/acetates of low to high DS have been prepared rapidly and efficiently by simply heating starch, acetic acid and the appropriate anhydride at elevated temperatures and pressures. Little or no byproducts are formed since no catalyst or neutralization base is required. Acetic acid solvent can be easily removed from the starch esters by heating under vacuum. Future work will involve characterizing the effects of substitution and molecular weight on starch ester physical properties, developing

catalysts to give substitution at specific sites and developing continuous reactive processing schemes.

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