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Synthesis and Characterization of Starch Acetates with High Substitution[1]

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ABSTRACT

Acetylation of high-amylose (70%) maize starch to high degree of substitution (DS) was studied by reacting starch with acetic anhydride using 50% aqueous NaOH as the catalyst. DS increased with increasing reaction times and increasing ratios of acetic anhydride to starch. Reaction efficiency (RE) increased with longer reaction times and decreased with increases in the ratios of acetic anhydride to starch for extended reaction times. Increasing the amount of NaOH increased both DS and RE. A series of starch acetates with DS values of 0.57–2.23 were prepared and their crystalline structures, chemical structures, thermal stability, and morphological properties were investigated. After acetylation, and as DS increased from 0.57 to 2.23, the crystalline structures of starch steadily disappeared. The carbonyl group's peak at 1,740 cm^{-1} appeared in the FTIR spectra. The intensity of this peak increased with a decrease in the peak intensity of the hydroxyl groups at 3,000-3,600 cm^{-1}, indicating that the hydroxyl groups on starch were replaced by the acetyl groups. Thermal stability of starch acetates increased. The smooth surface of the starch granules became rough with acetylation. Further acetylation led to the loss of the starch granules and the formation of beehive- and fibrous-like structures.

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In recent years, interest in finding environmentally friendly alternatives to nondegradable plastic material made from petroleum has placed an emphasis on natural macromolecular materials from agricultural sources. Starch has been one of the best choices because of its availability and low cost. However, the strong hydrophilicity and poor mechanical properties of starch prevent its application in the plastic products. As a result, it is logical to chemically modify starch to improve its properties for certain applications.

Of various chemical modifications, starch acetylation can be performed with relative ease to improve significantly the physiochemical and functional properties of the starch, even with a low DS (Moorthy 1985). During acetylation, three free hydroxyl groups on C_2, C_3, and C_6 of the starch molecule can be substituted with acetyl groups. Therefore, the theoretical maximum DS is 3. Starch acetate with DS 0.01–0.2 is approved by the FDA for food use to improve binding, thickening, stability, and texturizing (de Graaf et al 1998). On the other hand, high-DS starch acetates have been prepared since the middle of the last century with the aim of obtaining a replacement for cellulose acetate (Mullen II and Pacsu 1942b; Whistler and Hilbert 1944; Wolff et al 1951). Pyridine was a good catalyst in the preparation of the high-DS starch acetate because it not only led to complete esterification, but also did not cause starch degradation during the reaction. Pretreatment was necessary (Mullen II and Pacsu 1942a; Lohmar and Rist 1950), and the influences of some pretreatments on the reaction rate were compared (Mark and Mehltretter 1970). High conversion efficiencies were obtained when starch was pretreated with DMSO or hot water. However, the high cost, difficult recovery, and volatility of pyridine, along with the inconvenience of pretreatment, limited commercial development of this technology.

Mark and Mehltretter (1972) developed a simple method to prepare relatively undegraded starch triacetate using NaOH as the catalyst without pretreatment. The expected chemical reactions are illustrated in Fig. 1. Reaction 1 is the main rate-controlled reaction involving a base catalyst, where starch is acetylated with acetic anhydride and a base catalyst. This is an example of nucleophilic substitution at an unsaturated carbon atom of acetic anhydride. The substitution takes place by an addition-elimination mechanism (Roberts 1965). Furthermore, the three free OH groups have different reactivities. The primary OH on C_6 is more reactive and is acetylated more readily than the secondary ones on C_2 and C_3 due to steric hindrance. The primary OH located at the exterior surface of the starch molecules reacts readily with the acetic groups, while the two secondary ones located within the interior surface of starch form hydrogen bonds with the OH groups on the neighboring glucose unit. Of the two secondary OH groups, the OH on C_2 is more reactive than the one on C_3, mainly because the former is closer to the hemi-acetal and more acidic than the later (Fedorova and Rogovin 1963). Side reactions 2 and 3 rarely occur because almost no water exists in this reaction system.

Shogren (1996) used this method to prepare starch acetates with DS 1.5, 2.0, and 2.5. However, no research has been published on the influences of reaction conditions on starch acetylation. Therefore, the first part of this study was to investigate the influences of selected reaction conditions on extent of starch acetylation.

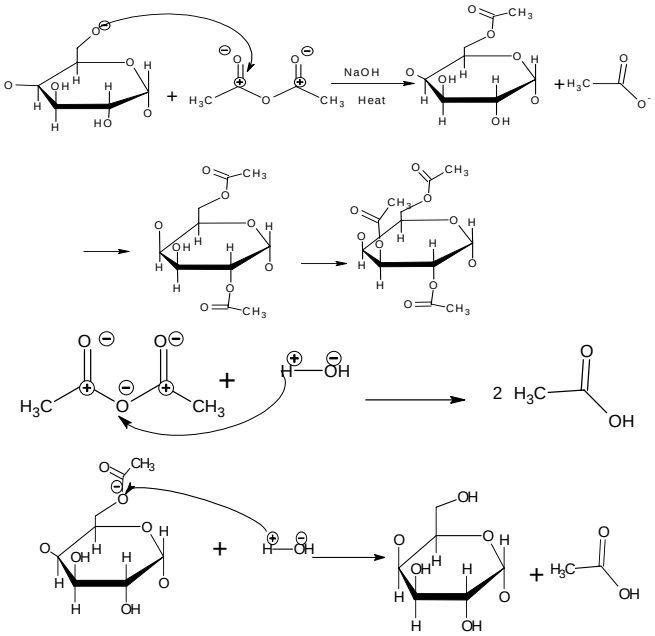

Fig. 1. Chemical reactions during starch acetylation.

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After esterification, the properties of starch esters are changed (Mullen II and Pacsu 1942b; Whistler and Hilbert 1944; Wolff et al 1951), and these changes largely depend on DS and the carbon chain length of the replaced groups (Sagar and Merrill 1995; Shogren 1996; Aburto et al 1999). Hydrophobicity of starch increases with increasing carbon chain length and DS, which further increase the miscibility of starch with other hydrophobic polymers (Thiebaud et al 1997; Zhang et al 1997). Little research has been done on the effects of DS on the functional properties of the high-DS starch acetates. Therefore, the second part of this study was to prepare a series of starch acetates with DS 0.5–3.0 and to investigate their structural properties for potential application as biodegradable thermoplastic materials.

MATERIALS AND METHODS

Synthesis of Starch Acetate

Starch acetylation was conducted by a modification of the procedure of Mark and Mehltretter (1972). Before acetylating, maize starch with 70% amylose (American Maize Products Co., Hammond, IN) was dried in an oven for 24 hr at 40–50°C. Dried starch (30 g) was mixed with acetic anhydride (Aldrich Chemical Co., Milwaukee, WI) at weight ratios of 1:4, 1:3, and 1:2 in a mini reactor with a 600 controller (Parr Instrument Co., Moline, IL). After stirring for 5 min, 50% aqueous NaOH solution was added. The temperature was increased to 123°C within 15 min, and held at this temperature for the designated times of 30, 60, 90, 120, 150, 180, and 240 min. The NaOH was added at levels of 0.15, 0.22, 0.27, and 0.34 g/g, of starch to study the effects of amount of catalyst. Excess cold water was added to the reactor to terminate the reaction and to thoroughly rinse the reaction products. The white acetylated starch was dried at 50°C. The dried products were ground before testing.

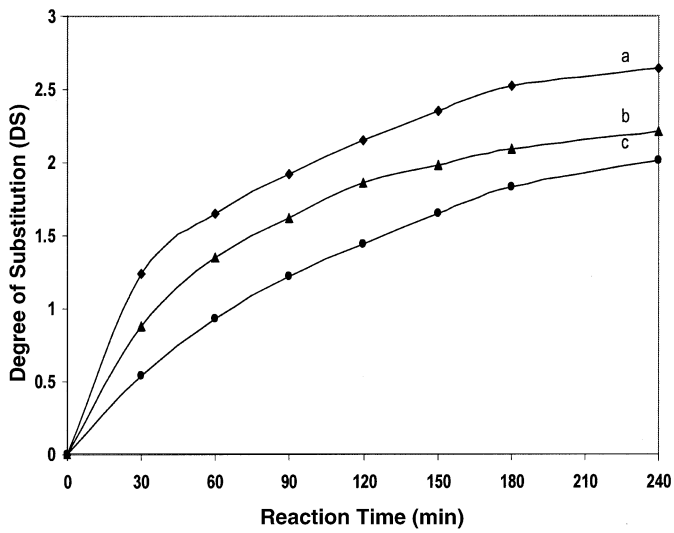

Fig. 2. Degree of substitution (DS) of starch acetates as functions of reaction times and ratios of acetic anhydride (AA) to starch (S). Curves for AA/S 4 (a), AA/S 3 (b), and AA/S 2 (c).

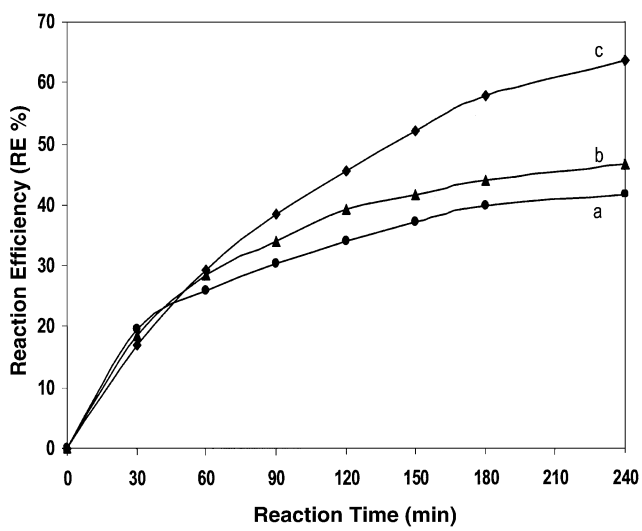

Fig. 3. Reaction efficiency (RE) (%) of the acetylation reaction as functions of reaction times and ratios of acetic anhydride (AA) to starch (S). Curves for AA/S 4 (a), AA/S 3 (b), and AA/S 2 (c).

Determination of Degree of Substitution (DS)

DS value was determined according to the method of Miladinov and Hanna (2000) with some modifications. Powdered acetylated starch was weighed exactly (0.5 g) and placed in a 250-mL conical flask. Distilled water (50 mL) was added and adjusted to pH 7.0 with 0.02*N* HCl. After that, 25 mL of 0.5*N* NaOH was added and the sample was heated on a hot plate until a transparent solution was obtained. Excess NaOH was titrated with HCL back to pH 7.0. Triplicate preparations were performed to obtain a mean value. DS was calculated as:

$$DS = \frac{162 \times (N_{NaOH} \times V_{NaOH} - N_{HCL} \times V_{HCL})}{1{,}000 \times W - 42 \times (N_{NaOH} \times V_{NaOH} - N_{HCL} \times V_{HCL})}$$

where N_{NaOH} was the normality of NaOH, V_{NaOH} was the volume of NaOH, N_{HCL} was the normality of HCl used to back titrate, V_{HCL} was the volume of HCl used to back titrate, and W was the sample weight (g).

Determination of Reaction Efficiency (RE)

RE (%) was calculated according to Khalil et al (1995) as DS × anhydroglucose (mol)/acetic anhydride (mol) × 100%.

X-ray Diffraction

X-ray patterns of native starch and starch acetates with different DS values were analyzed between $2\theta = 3°$ and $2\theta = 40°$ using an X-ray diffractometer (Rigaku D/Max-B, Tokyo, Japan) with Cu-Kα radiation at a voltage of 40 kV and 30 mA.

Fourier Transform Infrared (FTIR) Spectroscopy

IR spectra of native starch and starch acetates were measured using an FTIR spectrometer (Nicolet Avatar 360, Madison, WI) with an Analect FXA-530B diffuse/specular reflectance accessory for DRIFTS. Samples were diluted 1:20 with KBr before acquisition. A background of pure KBr was acquired before the sample was scanned. For each spectrum, the DRIFTS were set with an angle of 5° and 128 scans were run.

Thermal Stability Analysis

Thermogravimetry analyses (TGA) were completed with an instrument calibrated with nickel (Perkin-Elmer TGA 7, Norwalk, CT). Samples (3–6 mg) were placed in the balance system and heated from 50 to 650°C with a heating rate of 20°C/min in a nitrogen atmosphere. The onset temperature was calculated using TGA7 software.

Scanning Electron Microscopy (SEM)

The morphologies of native starch and starch acetates were observed using SEM (Hitachi S-3000N, Tokyo, Japan). Before testing, the samples were mounted on the SEM stubs with double-sided adhesive tapes and then coated with platinum under vacuum to make the sample conductive. Scanning electron photomicrographs were recorded at various magnifications to assure clear images.

RESULTS AND DISCUSSION

Effects of Reaction Times and the Ratio of Acetic Anhydride to Starch on DS and Reaction Efficiency

Figure 2 shows DS as a function of the reaction times and the ratios of acetic anhydride to starch. DS increased reaction time from 30 to 240 min. This was a consequence of the favorable effect of the time on diffusion and adsorption of the acetyl groups on starch molecules (Khalil et al 1995). However, this increase was nonlinear and characterized by an initial faster rate followed by a slower rate. This can be explained by the fact that as the acetylation reaction proceeded, the acetic anhydride monomer was depleted, and also the reactive sites on starch decreased due to structural modification of the starch backbone (Waly et al 1998).

Regarding the effects of the ratios of acetic anhydride to starch (AA/S), DS increased as AA/S increased from 2 to 4 because high acetic anhydride concentration not only resulted in a high molecular collision rate but also led to greater availability of acetic anhydride molecules in the vicinity of starch. The immobility of the hydroxyl groups made this acetylation reaction essentially dependent on the availability of acetic anhydride molecules in the proximity of the starch molecules (Bayazeed et al 1998). When the AA/S ratio increased further to 5, DS did not increase. This was consistent with the results of Mark and Mehltretter (1972).

Reaction efficiency (RE) is another important parameter in evaluating the acetylation reaction. Figure 3 shows RE as the function of the reaction times and the AA/S ratios. RE increased as reaction time increased from 30 to 240 min. As mentioned above, increasing the reaction time provided an opportunity to ensure a sufficient reaction and thus increased RE. However, the changes in RE with the AA/S ratios relied on reaction times. At the initial reaction time of 60 min, high concentrations of acetic anhydride led to a slightly higher RE, suggesting that there was a great availability of the acetic anhydride molecules in proximity to the starch molecules. Afterwards, higher ratios resulted in lower RE. This may be attributable to the fact that after initial modification, the structural changes in the starch molecules reduced their response to increases in the concentration of acetic anhydride (Khalil et al 1995). It was evident that AA/S 2 resulted in significantly higher RE than AA/S 3 and 4 with longer reaction times.

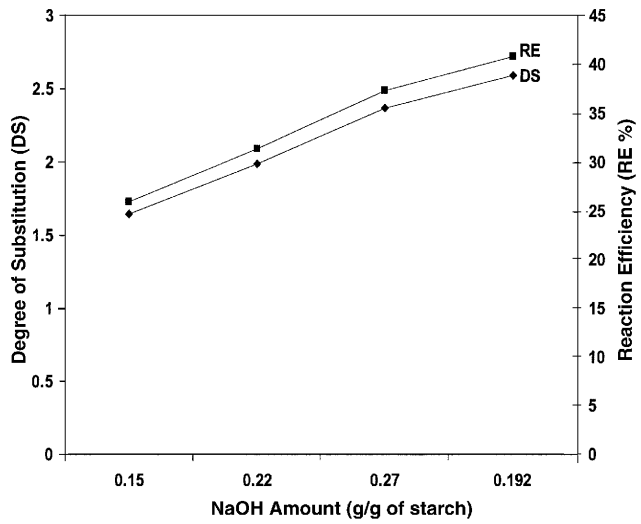

Fig. 4. Effects of NaOH amounts on degree of substitution (DS) and reaction efficiency (RE). Reaction temperature was 123°C; AA/S ratio 4; and reaction time 60 min.

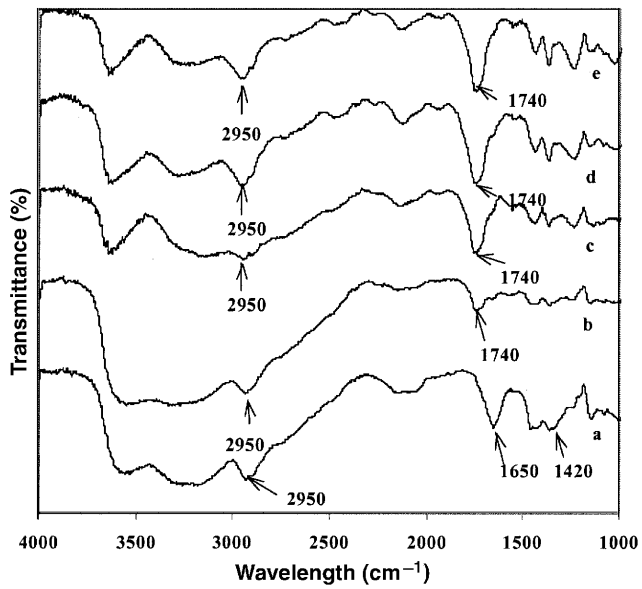

Fig. 6. FTIR spectra of native starch (a) and starch acetates with DS values of 0.57 (b), 1.11 (c), 1.68 (d), and 2.23 (e).

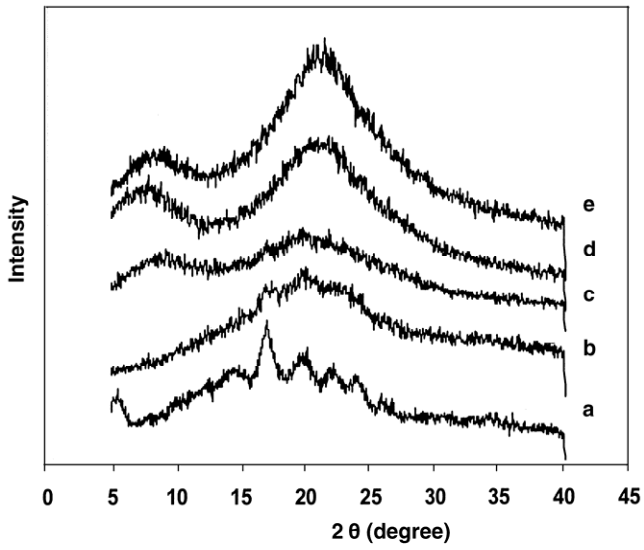

Fig. 5. X-ray patterns of native starch (a) and starch acetates with DS values of 0.57 (b), 1.11 (c), 1.68 (d), and 2.23 (e).

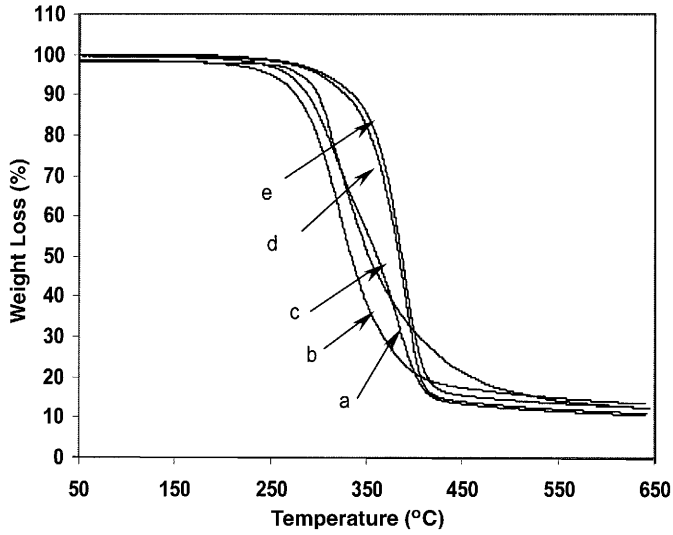

Fig. 7. Thermogravimetry analyses (TGA) curves of native starch (a) and starch acetates with DS values of 0.57 (b), 1.11 (c), 1.68 (d), and 2.23 (e).

Effects of Catalyst on DS and RE

The effects of NaOH (catalyst) on DS and RE are presented in Fig. 4. Both DS and RE increased with increasing amounts of NaOH. When other conditions were constant, DS increased from 1.65 to 2.59 and RE increased from 25.98 to 40.79% with increasing the amounts of NaOH from 0.15 to 0.34 g/g of starch. The increases were approximately linear. The NaOH was a catalyst that affected the reaction by swelling the starch molecules, thereby increasing the diffusability of the acetic anhydride molecules in the vicinity of starch (Bayazeed et al 1998) and by activating the hydroxyl groups of starch to cause nucleophilic attack on the anhydride moieties (Jeon et al 1999).

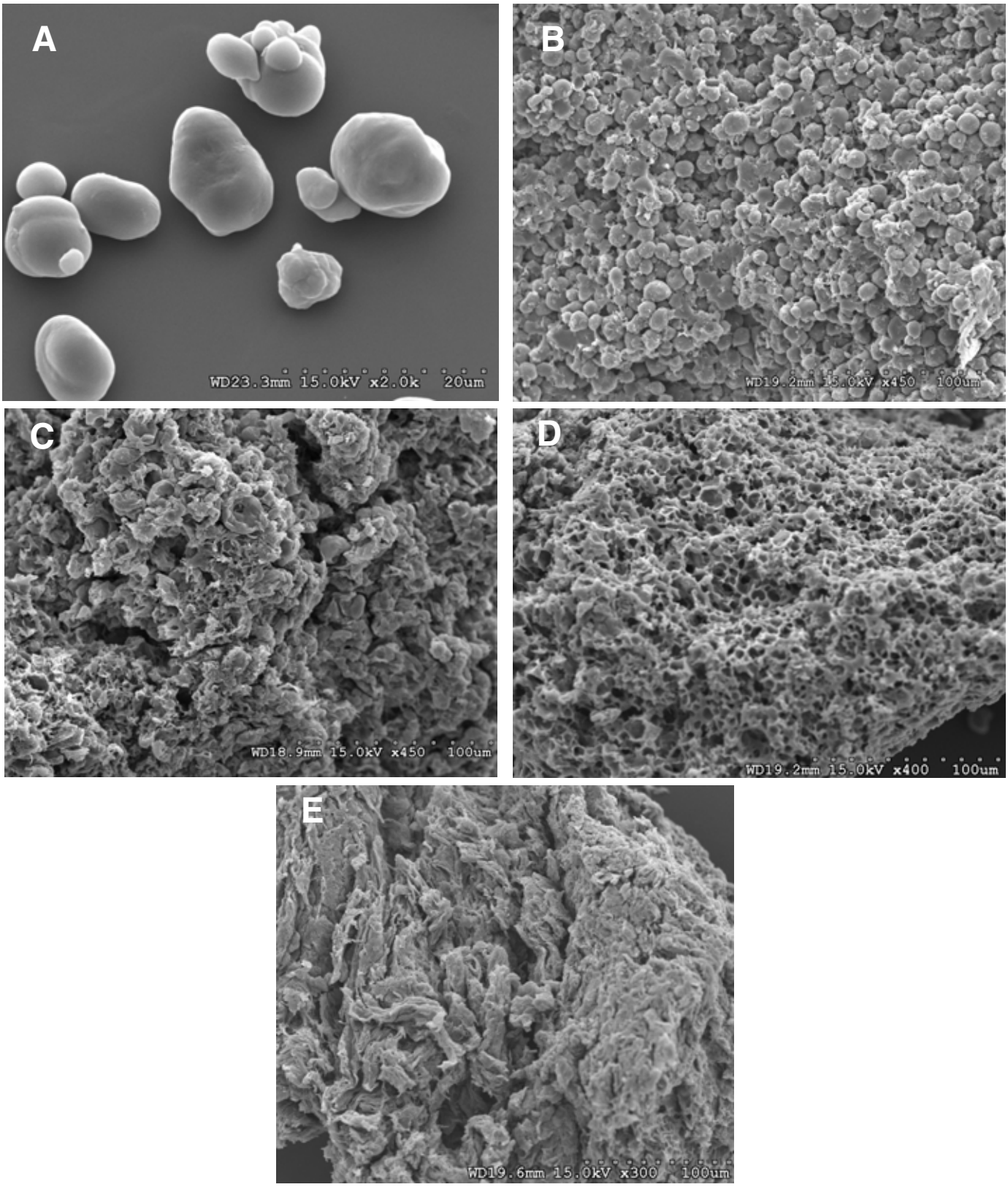

Fig. 8. SEM photographs of native starch (magnification 2,000×) (**A**) and starch acetates with DS values of 0.57 (450×) (**B**), 1.11 (450×) (**C**), 1.68 (400×) (**D**), and 2.23 (300×) (**E**).

Based on the preceding analyses, we optimized the reaction conditions to prepare starch acetates with DS of 0.57, 1.11, 1.68, and 2.23. Selected structural properties and thermal stabilities of the starch acetates were evaluated.

X-ray Diffraction

The X-ray patterns of native starch and starch acetates are shown in Fig. 5. The X-ray pattern for native high-amylose maize starch granules showed a typical B-type crystalline structure because they contained amylose (≈70%) and amylopectin (≈30%) (Zobel 1998). Linear amylose composed of α-1,4-glucopyranose was responsible for the amorphous region, while large amylopectin composed of both α-1,4 and α-1,6-glucopyranose contributed to the crystalline region. The intra- and intermolecular hydrogen bonds were responsible for the highly ordered crystalline structure. When the hydroxyl groups were replaced partially by the acetyl groups (DS 0.57 and 1.11), the remaining hydroxyl groups still had chance to form hydrogen bonds. Therefore, the crystalline peaks existed but the intensities became weak. When DS increased further to 2.23, the acetyl groups replaced most of the hydroxyl groups on starch and no intermolecular hydrogen bonds were formed, which destroyed the ordered crystalline structures. The samples, as expected, gave an amorphous pattern with broad peaks. These broad peaks may have originated from smaller size starch crystals as the acetylation reaction continued (Jandura et al 2000).

FTIR Measurement

FTIR spectroscopy was used to verify the change in the chemical structures of starch molecules resulting from acetylation. The FTIR spectra of native starch and starch acetates are shown in Fig. 6. In the spectrum of native starch, the peaks 3,000–3,600 cm^{-1} and 2,950 cm^{-1} correspond to OH and CH stretchings, while the peaks at 1,650 cm^{-1} and 1,420 cm^{-1} correspond to δ (OH) and δ (CH) bendings (Mano et al 2003). Compared to native starch, starch acetates had a strong absorption band at 1,740 cm^{-1} that was attributed to the stretching of the ester carbonyl C=O and indicated the acetylation of starch. This peak intensity increased as DS increased from 0.57 to 2.23. On the contrary, the intensity of the hydroxyl groups peak at 3,000–3,600 cm^{-1} decreased. The higher DS of the starch acetates, the lower the intensity of this peak. This suggested that the hydroxyl groups in the starch molecules were converted into acetyl groups, which resulted in the loss of starch granule crystallinity. This was consistent with the X-ray diffraction results.

Thermal Stability Analysis

Thermogravimetry analyses (TGA) curves were employed to examine the change of thermal stability caused by the acetylation. The threshold decomposition temperature indicated the highest processing that could be used (Mano et al 2003). Figure 7 shows TGA curves of native starch and starch acetates. Initial degradation of native starch began at 297°C and ended at 326°C with a weight loss of 70.7%. Further heating to 650°C resulted in carbonization and ash formation (Mano et al 2003). For starch acetates, when DS values were 0.57 and 1.11, the onset of degradation was similar to that of native starch but ended at higher temperatures and with lower weight losses. When DS increased to 1.68, thermal stability increased noticeably and the thermal degradation took place at 347°C. When DS increased to 2.23, thermal degradation occurred at 352°C, 5°C higher than that of DS 1.68. The increase in thermal stability with increasing DS was attributed to a small number of hydroxyl groups remaining after acetylation. The decomposition of starch was a result of the inter- or intramolecular dehydration reactions of the starch molecules with water as a main product of decomposition (Thiebaud et al 1997). This condensation reaction was slower after the hydroxyl groups were replaced by acetyl groups. Therefore, a high DS had a beneficial effect on the thermal stability of the sample.

Morphology Study

SEM was performed to observe the morphological modifications of acetylation (Fig. 8). The native starch granules formed clusters with smooth surfaces. A rough surface was observed for DS 0.57. Some small particles were attached to the surface of the starch granules. As DS increased to 1.11, the surface became rougher. The starch granule structures lost completely when DS increased further to 1.68. Instead, a beehive-like structure with uniform porosity was apparent. A fibrous-like structure replaced the beehive-like structure with DS 2.23.

CONCLUSIONS

Starch acetates with a high degree of substitution (DS) were synthesized by a method in which maize starch (containing 70% amylose) reacted with acetic anhydride using NaOH as the catalyst. DS increased with longer reaction times and the higher ratios of acetic anhydride to starch. Reaction efficiency (RE) increased with longer reaction time and decreased with higher AA/S ratios and longer reaction time. Both DS and RE increased with increasing amounts of catalyst. Selected structural properties of starch acetates with DS 0.57–2.23 were investigated. The results showed that, after acetylation and as DS increased, the crystalline structures of native starch gradually were converted to an amorphous structure. The peak of the carbonyl group at 1,740 cm^{-1} appeared in FTIR spectra. The peak intensity increased as DS increased. Thermal stability of starch acetates increased due to the decrease in the number of the hydroxyl groups with acetylation. The smooth surface of the starch granules became rough. Further acetylation led to loss of the starch granules. The measured properties were consistent with each other.

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