

Starch Acetate-Maleate Mixed Ester Synthesis and Characterization¹

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ABSTRACT

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A new starch acetate-maleate mixed ester with different degrees of substitution (DS) for each ester group was prepared. High-amylose (70%) corn starch was first reacted at 123°C with ≈ 4.5 equivalents of acetic anhydride for different times, and then the intermediate products were further reacted at 80°C with 0.27–1.1 equivalents of maleic anhydride for a fixed time. ¹H NMR and alkaline saponification were used to determine DS values of acetyl and maleate groups. Increasing the reaction time from 60 to 120 min for starch and acetic anhydride increased DS of the acetyl group, while DS of the maleate group increased with increasing amounts of maleic anhydride. There was a good agreement between the two

methods for DS determination. The reaction efficiency of acetylation increased from ≈ 30 to 50% with reaction time, and maleation decreased from ≈ 30 to 20% with increasing amounts of maleic anhydride. The mixed esters were characterized by ¹H NMR, ¹³C NMR, FTIR, DSC, and TGA. Characteristic peaks in ¹H NMR, ¹³C NMR, and FTIR spectra indicated the presence of acetyl and maleate groups in starch molecules. The exothermic peak in the DSC curve and the increase in thermal stability from the TGA curve were attributed to thermal cross-linking of the double bond of the maleate group.

Recently, the concern over nondegradable plastic materials made from petroleum has increased the interest in natural macromolecular materials from agricultural sources. Starch is one of the best alternatives because of its availability, low cost, and total degradability after usage. However, starch itself has some disadvantages such as its hydrophilic character, poor mechanical properties, and dimensional stability, especially in an aqueous environment. As a result, it is logical to make starch more hydrophobic by replacing the hydroxyl groups (OH) with ester or ether groups (Mullen and Pacsu 1942; Sagar and Merrill 1995; Jantas 1997; Bayazeed et al 1998; Aburto et al 1999; Neumann et al 2002; Yu and Yang 2003).

Of the diverse chemical modification methods, starch acylation is a promising method because it can be conducted with relative ease. The chemical and physical properties of starch are changed after modification and these changes are largely dependent on the extent of substitution. Acylated starches with degrees of substitution (DS) of 0.01–0.2 are approved by the FDA for use in foods to improve binding, thickening, stability, and texturing (de Graaf et al 1998). Conversely, moderate and highly esterified starches (DS 0.5–3.0) are candidates for engineered materials with suitable mechanical characteristics compared with pure precursors (Sagar and Merrill 1995; Aburto et al 1999; Demirgoz et al 2000; Kiatkamjornwong et al 2001). Preparation of highly esterified starch usually involved pretreatment and use of pyridine as a catalyst. However, the high cost, the difficult recovery, and explosivity of pyridine, as well as the inconvenience of a pretreatment step, limited this technology's commercial development. Mark and Mehlretter (1972) developed a simpler method to prepare undegraded starch triacetate using 50% NaOH and without pretreatment. In recent years, Copinet et al (2000) acetylated starch to DS 1.5 in refluxing acetic anhydride containing sodium acetate.

Many reports have focused on single esters. In fact, mixed esters of starch have been reported to have a broader range of properties than single esters (Wolff et al 1957) because each ester group provided a different functionality. Rudolph and Glowaky (1978)

prepared carboxyl-functional mixed esters of hydrolyzed starch and found that they were a new class of chemically modified polymers with wide application. Maleic anhydride, a cyclic anhydride containing dicarboxylic acid and a double bond, can be grafted onto many polymers to improve the reactivity of polymers and to further increase the compatibility of the polymer with other polymers (Carlson et al 1999; Wu 2003).

Therefore, the objective of this study was to prepare starch acetate-maleate by reacting starch with acetic anhydride and maleic anhydride with NaOH. Their structural properties for potential application as biodegradable thermoplastic materials were investigated.

MATERIALS AND METHODS

Synthesis of Starch Acetate-Maleate

Starch esterification was conducted by a modification of the procedure of Mark and Mehlretter (1972). Corn starch with $\approx 70\%$ amylose (American Maize Products Co., Hammond, IN, USA) was first dried for 24 hr at 40–50°C to decrease the moisture content ($<2\%$). Dried starch (0.185 mol, based on anhydroglucose unit) was mixed with acetic anhydride of 4.73 mol/mol of starch (Aldrich Chemical Co., Milwaukee, WI, USA) in a mini-reactor with a 600 controller (Parr Instrument Co., Moline, IL, USA). After stirring for 5 min, 3 mL of 50% aqueous NaOH solution (0.04 mol) was added. The actual acetic anhydride added to starch was ≈ 4.5 mol/mol of starch because some acetic anhydride was converted to sodium acetate when sodium hydroxide was added. The temperature was increased to 123°C within 15 min, and then held at this temperature for 60, 90, or 120 min. When preparing the acetate-maleate ester, the temperature was decreased to 80°C, and three levels (0.27, 0.55, and 1.10 mol/mol of starch) of maleic anhydride (Aldrich Chemical Co., Milwaukee, WI, USA) were added into the reactor. The mixtures were reacted for 60 min at 80°C. The reaction was terminated by adding cold tap water to the reactor. The white products were obtained by rinsing extensively with water until the filtrate was pH > 5 and then drying at $\approx 50^\circ\text{C}$. The dried products were ground before testing.

Determination of Degree of Substitution (DS)

The degrees of substitution (DS) of each functional group in the mixed esters were determined by proton nuclear magnetic resonance (¹H NMR). Before testing, the ground sample was extracted with ethyl alcohol for 24 hr in a Soxhlet extractor to remove the remaining acids and then air-dried. Starch esters were dissolved in deuterated dimethyl sulfoxide (DMSO-d₆) with a low

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solubility caused by some cross-linking during maleation. The ^1H NMR spectra were acquired at 37°C using a 500 MHz DRX spectrometer (Bruker Avance, Billerica, MA, USA). Scans (64) were acquired for each sample with relaxation times of 1.0 sec. Seven methylene protons of starch were used as the internal reference. The peak chemical shifts were expressed in parts per million from tetramethyl silane and integrations were performed. The calculated DS values were compared with the results of alkaline saponification in Rudolph and Glowaky (1978). Briefly, total acid

content was obtained by completely hydrolyzing ester linkages of mixed esters with aqueous KOH containing 1% pyridine. The acid content due to free carboxyl acid of maleate ester was measured by titration in aqueous solution containing pyridine. Modified starch suspended in water was usually pH 5–6. The difference between the above two acid contents was attributed to acetyl groups. The DS analyses and all following tests were performed as triplicates.

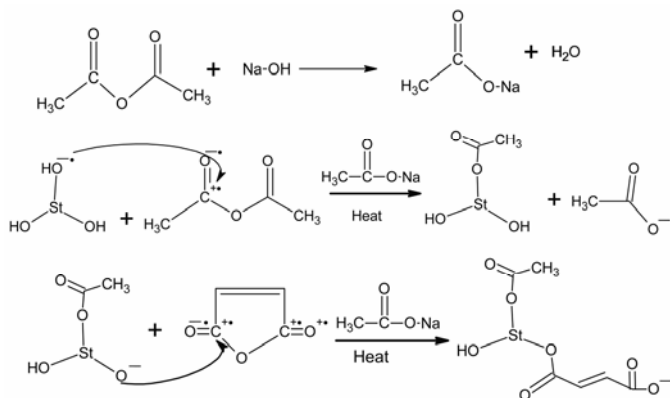


Fig. 1. Chemical reactions during starch acetylation and maleation.

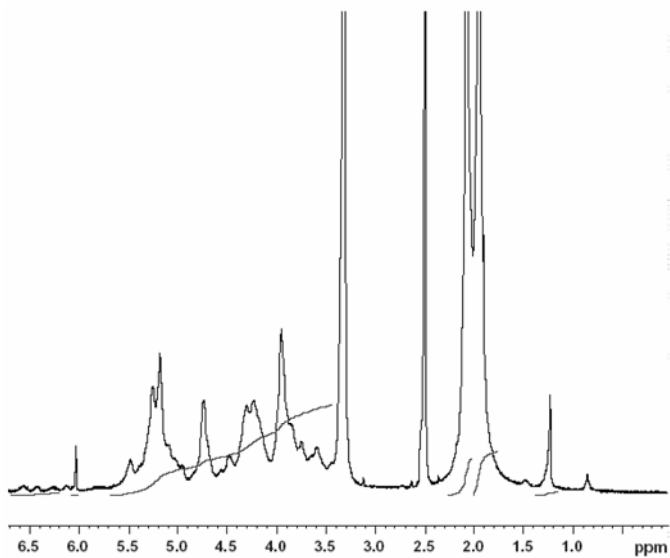


Fig. 2. ^1H NMR spectrum of starch acetate-maleate.

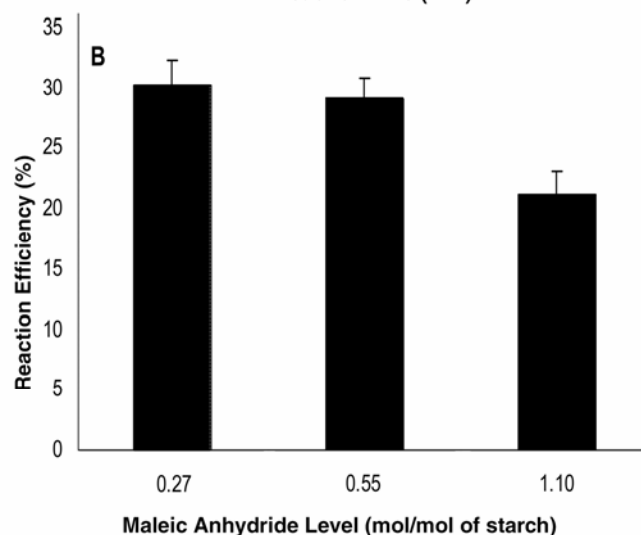
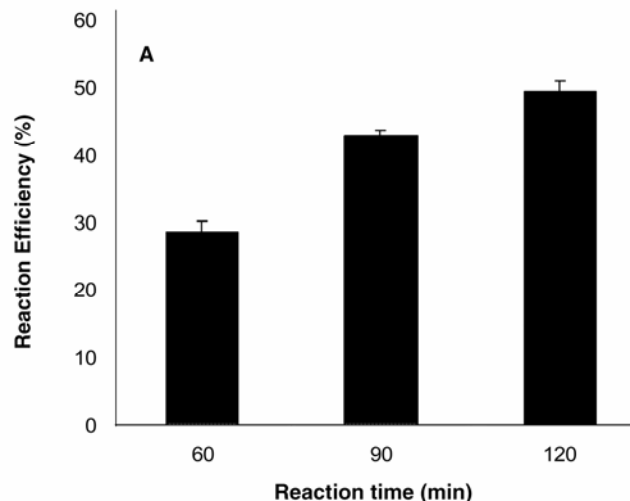


Fig. 3. Reaction efficiencies (RE) (%) for (A) acetylation as a function of the reaction time at reaction temperature of 123°C and 4:1 acetic anhydride-to-starch (w/w) and (B) maleation as a function of maleic anhydride level.

TABLE I
Reaction Conditions and Degree of Substitution (DS) of Starch Acetate-Maleate Mixed Esters as Determined by ^1H NMR and Titration Methods

Sample	Reaction Time for Starch and Acetic Anhydride ^a (min)	Level of Maleic Anhydride (mol/mol of starch)	DS of Acetyl Group		DS of Maleate Group	
			NMR	Titration	NMR	Titration
1	60	0.27	1.34	1.39	0.05	0.09
2	90	0.27	1.64	2.05	0.06	0.08
3	120	0.27	2.10	2.40	0.10	0.08
4	60	0.55	1.20	1.39	0.14	0.17
5	90	0.55	1.89	1.98	0.18	0.16
6	120	0.55	1.92	2.35	0.19	0.15
7	60	1.10	1.18	1.26	0.26	0.25
8	90	1.10	1.72	2.04	0.23	0.21
9	120	1.10	1.97	2.26	0.27	0.24

^a All reactions contained ≈ 4.5 mol of acetic anhydride and 0.2 mol of sodium acetate/mol of starch

Determination of Reaction Efficiency (RE)

Reaction efficiencies for acetylation and maleation processes were calculated according to Khalil et al (1995). The DS used in the calculation was determined by titration

$$\text{RE (\%)} = [\text{DS} \times \text{Anhydroglucose (mol)}/\text{anhydride (mol)}] \times 100\%$$

Carbon Nuclear Magnetic Resonance (^{13}C NMR) Spectrum

^{13}C NMR spectrum of starch acetate-maleate was measured using a 600 MHz Bruker AVANCE magic-angle spinning (MAS) solid-state NMR at 8 kHz MAS spin speed and 90° pulse with high-power decoupling (Billerica, MA, USA). Before testing, the sample was finely ground with a mortar and pestle and packed into a zirconium rotor. A 4-mm MAS solids probe was used and delay time was 20.0 sec. The spectra were acquired at room temperature with 2,048 scans.

Fourier Transform Infrared (FTIR) Spectroscopy

IR of the native starch, starch acetate, and starch acetate-maleate were measured using an FTIR spectrometer (Nicolet Avatar 360, Madison, WI, USA) with an Analect FXA-530B diffuse/specular reflectance accessory. Ground samples were diluted 1:20 with KBr

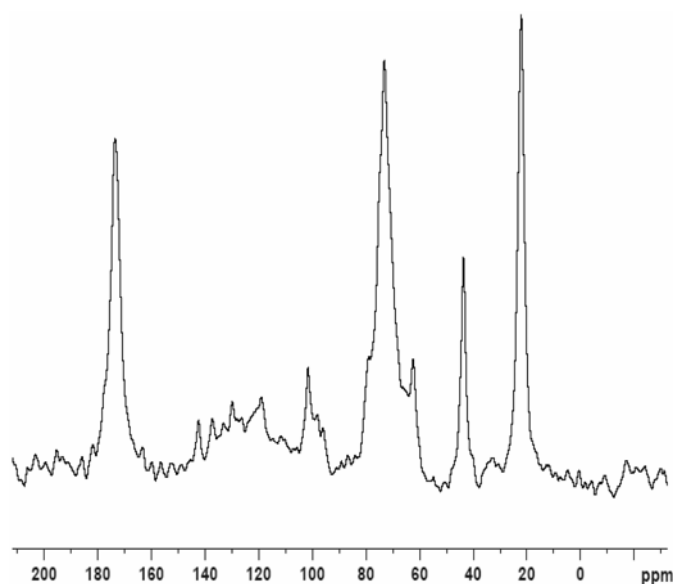


Fig. 4. Solid-state ^{13}C NMR spectrum of starch acetate-maleate.

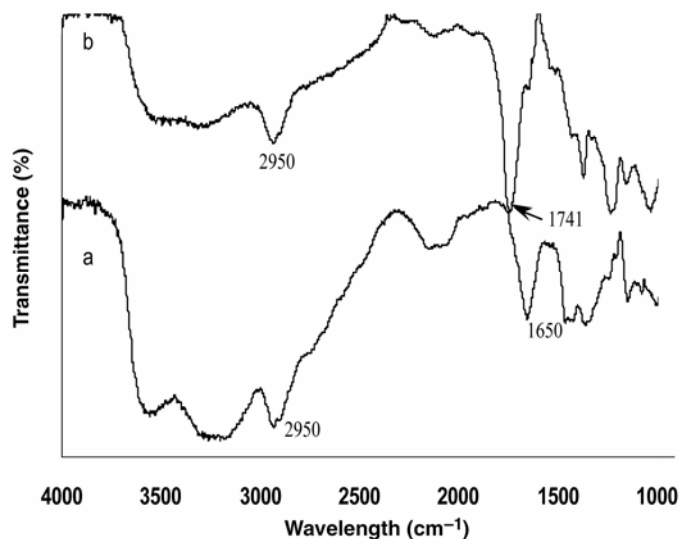


Fig. 5. FTIR spectra of (a) native starch and (b) starch acetate-maleate.

(1 mg of ground sample diluted with 20 mg of KBr) before scanning. A background for pure ground KBr was acquired before scanning samples. For each spectrum, the diffuse reflectance angle was set at 5° , and 128 scans were acquired at a resolution of 4 cm^{-1} .

Differential Scanning Calorimetry (DSC)

DSC measurement was performed with a Perkin-Elmer DSC7 (Norwalk, CT, USA). Dried ground samples ($\approx 15\text{ mg}$) ($<2\%$ moisture) were placed in stainless steel DSC pans (Perkin Elmer). The samples were heated from 40 to 250°C with a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere.

Thermal Stability Analyses

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

RESULTS AND DISCUSSION

Mechanism of Synthesis of Starch Acetate-Maleate

During the preparation of the starch acetate-maleate, the addition sequence of the two anhydrides played an important role in the final product. The results of preliminary tests showed the maleic anhydride seemed to be more reactive than the acetic anhydride. Therefore, when these two anhydrides were introduced simultaneously at the beginning of the reaction, the reaction temperature was hard to control and led to burning of the reactants. As a result, it was required to first add acetic anhydride and to let it react with starch for a period of time, and then add maleic anhydride. The catalyst NaOH first reacted with acetic anhydride to form sodium acetate as real catalyst for acetylation and maleation. The expected chemical reactions are shown schematically in Fig. 1.

Determination of DS and RE

A representative ^1H NMR spectrum for starch acetate-maleate is shown in Fig. 2. The peaks from 3.5 to 5.5 ppm were assigned to the seven C-H protons on the $\alpha\text{-D-glucopyranosyl}$ unit (Laignel et al 1997). The peak at 6.4–6.6 ppm was the two protons on the C=C of maleate (Chong et al 2001). The peak at 1.9–2.1 ppm corresponded to the methyl protons of the acetyl groups (de Graaf et al 1995). DS for the acetyl group was quantitated as $1/3$ of the area of the acetyl protons divided by $1/7$ of the sum of the areas of the starch C-H proton peaks, while DS for maleate group was estimated as $1/2$ of the area of CH=CH peak divided by $1/7$ of the starch CH areas (Shogren 2003; Elomaa et al 2004). Table I summarizes the DS values of each ester measured by two different methods. DS of acetyl groups increased when reaction time increased from 60 to 120 min regardless of the measurement method. This was a consequence of the favorable effect of the time on diffusion and addition of the acetyl groups to starch molecules (Khalil et al 1995). DS of maleate groups also increased with increasing amounts of maleic anhydride from 0.27 mol/mol of starch to 1.10 mol/mol of starch. High maleic anhydride concentration not only resulted in a high molecular collision rate but also led to greater availability of maleic anhydride molecules in the vicinity of starch.

There were good agreements in DS values for both acetyl and maleic groups as determined by titration and NMR, with $R^2 = 0.9208$ for the acetyl group and $R^2 = 0.9036$ for the maleic group, respectively. The slightly higher deviation between the two methods for the maleate group was attributed to the effect of a low level of free acid in the titration. The free acid residue consumed the base that was supposed to neutralize the free carboxyl acid of maleate.

Reaction efficiency (RE) is an important parameter in describing the acetylation and maleation reactions. Figure 3 shows RE of

acetylation as a function of reaction time and that of maleation as a function of mole amounts of maleic anhydride. RE of acetylation increased from 28.5 to 49.4% as reaction time increased from 60 to 120 min. This was because increasing the reaction time provided an opportunity to ensure sufficient reaction of excess acetic anhydride. In contrast, RE of maleation decreased with increasing maleic anhydride amounts. This may have been attributable to the fact that after initial acetylation, the structural changes in the starch molecules reduced their response to increases in the concentration of maleic anhydride. It was evident that the RE was significantly lower for 0.204 mol of maleic anhydride.

Solid-State ^{13}C NMR

A representative solid ^{13}C NMR spectrum, instead of a solution ^{13}C NMR due to low solubility of starch acetate-maleate in organic solvent, was acquired as shown in Fig. 4. Two peaks at 22.2 and 173.7 ppm were assigned to methyl carbon and carbonyl carbon in the acyl group, respectively, which verified that acetylation occurred. The peaks at 137.4 and 129.9 ppm were attributed to the carbon of $\text{C}=\text{C}$ in the maleate group, which had a low intensity and indicated a low degree of substitution for maleation. For anhydroglucose unit, C_1 and C_6 had chemical shifts at 101.7 and 62.5 ppm, respectively, while C_2 , C_3 , and C_5 had unresolved chemical shifts peaking at 73.2 ppm, and C_4 was a small shoulder to the left of this peak (Nilsson et al 1996). The peak at 43.7 ppm might have been from the KEL-F sample holder.

Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of native starch and starch acetates-maleate are shown in Fig. 5. In the spectrum of native starch, the peaks between $3,000$ and $3,600\text{ cm}^{-1}$ and $2,950\text{ cm}^{-1}$ corresponded to OH and CH stretchings, while the peak at $1,650\text{ cm}^{-1}$ was assigned to δ (OH) bending (Mano et al 2003). Compared with native starch, a strong absorption band at $1,740\text{ cm}^{-1}$, attributed to the stretching of the ester carbonyl $\text{C}=\text{O}$, appeared in the spectrum for starch acetate-maleate and indicated that esterification of starch occurred (Xu et al 2004). The peak corresponding to double bond of $\text{CH}=\text{CH}$ ($\approx 1,630\text{ cm}^{-1}$) could not be found. This is due to a low number of maleate groups in the molecules, and the corresponding peak may have overlapped with the peak at $1,650\text{ cm}^{-1}$.

Differential Scanning Calorimetry (DSC)

DSC thermograms of native starch, starch acetate, and starch acetate-maleate mixed ester are shown in Fig. 6. As can be seen, native starch with 5% moisture content had a T_g of 176.9°C . After acetylation, the T_g value decreased and DS 1.11 starch acetate had a T_g of 153.9°C , which was 23°C lower than native starch. This agreed with the results of Shogren (1996). The decrease in T_g with acetylation was due to the fact that the replacement of hydroxyl groups by acetyl groups decreased the intermolecular hydrogen bonds and increased chain mobility (Aburto 1999). In starch acetate-maleate, T_g did not significantly change compared with its starch acetate counterpart because the degree of substitution of the maleate group in the molecules was only 0.14. However, the tiny exothermic peak between 163 and 166°C was attributed to the thermal cross-linking of the double bond of the maleate group (Jantas 1997).

Thermal Stability Analysis

The changes in thermal stability caused by esterification were studied using TGA. Representative TG curves of native starch, starch acetate, and starch acetate-maleate mixed esters with two levels of DS for the maleate group are shown in Fig. 7. For native starch, thermal degradation was initiated at 297°C . The acetylated sample had an initial decomposition temperature of 318°C . The decomposition of unmodified starch is a result of the inter- or intramolecular dehydration reactions of starch molecules with

water as a main product of decomposition (Thiebaud et al 1997). When the remaining hydroxyl groups in starch acetate were substituted further by maleate group, thermal degradation of the samples occurred at a higher temperature; thermal degradation started at 362 and 377°C for starch acetate-maleate with maleate DS 0.14 and DS 0.26, respectively. The greater thermal stability with addition of the maleate group was due to the thermal cross-linking of double bonds in maleate molecules. This was consistent with the results of Jantas (1997) for acryloyloxystarch. The higher molecular weight due to cross-linking increased the decomposition temperature, resulting in a more thermally stable product (Carlson et al 1999).

CONCLUSIONS

Starch acetate-maleate mixed esters were synthesized by reacting high-amylose (70%) corn starch with excess acetic anhydride for different times, and further reacting with different amounts of maleic anhydride for a fixed time. The degree of substitution (DS) of acetyl groups increased with longer reaction times, while DS of maleate groups increased with increasing amounts of maleic anhydride. The reaction efficiency of the acetylation process increased

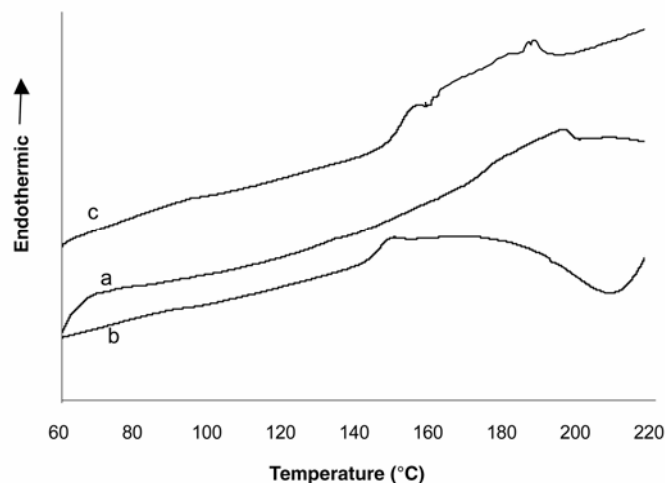


Fig. 6. DSC thermographs of (a) native starch with moisture content of 5%, (b) starch acetate with DS 1.1, and (c) starch acetate-maleate mixed ester with DS 1.3.

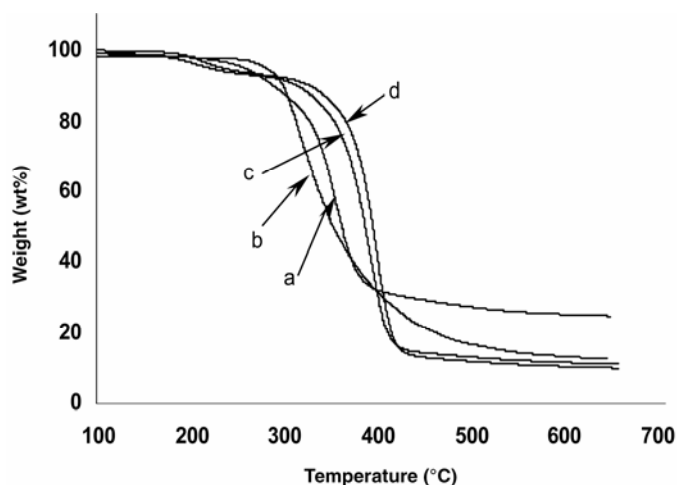


Fig. 7. TG curves of (a) native starch, (b) starch acetate with DS 1.1, (c) starch acetate-maleate with DS 1.1 for acetyl group and 0.14 for maleate group and (d) starch acetate-maleate with DS 1.1 for acetyl group and 0.26 for maleate group.

with increasing reaction time, whereas that of maleation decreased with increasing amounts of maleic anhydride. The occurrence of esterification was demonstrated by characteristic peaks in ^1H NMR, ^{13}C NMR, and FTIR spectra. Thermal cross-linking of the double bond of the maleate group resulted in an exothermic peak in the DSC curve and an increase in thermal stability.

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