

# Succinoylation of Wheat Straw Hemicelluloses with a Low Degree of Substitution in Aqueous Systems

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**ABSTRACT:** The reaction of wheat straw hemicelluloses with succinic anhydride in aqueous alkaline systems was studied. The products showed a rather low degree of substitution, ranging from 0.017 to 0.21. The effects of reaction times of 0.5–16 h, temperatures of 25–45°C, and molar ratios of succinic anhydride to anhydroxylose units in hemicelluloses of 1:5–1:1 on the succinoylation yield and degree of substitution were examined. With the reaction kept within a pH range of 8.5–9.0, a temperature range of 25–28°C, a reaction duration of 1–2 h, and a 1:1 molar ratio of succinic anhydride to hemicelluloses were preferred. The structure of the resulting polymers was determined with Fourier transform infrared and <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy, which indicated monoester substitution. The thermal stability of the esterified polymer increased with chemical modification. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 757–766, 2002

**Key words:** hemicelluloses; succinoylation; aqueous system; thermal stability

## INTRODUCTION

Wheat straw is one of the main agricultural residues and is produced in large quantities worldwide every year. In developing countries such as China and India, some quantities of these fibrous crop residues are currently underused as raw materials for paper making. However, large amounts of these byproducts are not used as industrial raw materials on a significant scale because most of the straw is discarded as waste or is burned on the farm. Pollution, therefore, becomes a major problem in these areas.

Although straw is known to be a natural composite material made basically of three biopolymers (cellulose, hemicelluloses, and lignin), it can not be molded because it lacks plasticity. This is due to the chemical bonds between its main components, the crystalline nature of cellulose, and the three-dimensional molecular structure of lignin.<sup>1</sup> Hemicelluloses are the major constituents of wheat straw and account for approximately 32% of dry material. They are commonly isolated from straw by extraction with dilute alkali solutions or 2% H<sub>2</sub>O<sub>2</sub> at pH 11.5 and are separated by precipitation of the neutralized extracts in ethanol.<sup>2</sup> Similar to starch<sup>3–6</sup> and cellulose,<sup>7,8</sup> hemicelluloses through chemical modification<sup>9–11</sup> (e.g., esterification) are improved with respect to their thermoplastic properties. In other words, hemicelluloses with one or two free hydroxyl groups are hydrophilic, whereas synthetic polymers are usu-

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ally hydrophobic; this reduces their usefulness in industrial applications. However, these shortcomings can be overcome by modifications such as esterification with fatty acid chlorides. Until now, the preparation of hemicellulosic derivatives, especially hydrophobic derivatives, has been conducted with organic solvents such as *N,N*-dimethylacetamide, *N,N*-dimethylformamide, and pyridine.<sup>10,11</sup> The esterification agents generally used are fatty acid chlorides.<sup>10</sup> These derivatives have been approved to impart water resistance to products.<sup>10,11</sup> Conversely, the formation of polysaccharide succinates increases the hydrophilicity of modified polysaccharides because carboxylic acids are known to improve water absorption in polymers.<sup>12</sup> For example, starch succinates (polyanions) offer a number of very desirable properties, such as high viscosity, low-temperature viscosity stability, high thickening power, low gelatinization temperature, cook clarity, and good filming properties. Thus, such succinate derivatives of polysaccharides have been recommended as binders and thickening agents in foods, tablet disintegrants in pharmaceuticals, surface-sizing agents, and coating binders in paper.<sup>13,14</sup> Furthermore, high densities of starch side-chain carboxylate groups have been found to provide useful properties such as metal chelation.<sup>12</sup>

In 1953, Caldwell and Wurzburg<sup>15</sup> patented the modification of starch with octenyl succinic anhydride in aqueous systems under alkaline conditions. More recently, a systematic study of the succinylation of starch was performed to determine how changes in the starch concentration, starch/anhydride ratio, pH, temperature, and reaction time affect the efficiency of esterification under mild alkaline conditions. The modified starches, containing relatively longer alkenyl substituents and carboxylic acid groups that further interact with paper by the formation of esters with cellulose, have been used as paper-sizing agents.<sup>12</sup> This groundbreaking work of conducting starch reactions in aqueous systems is also environmentally friendly because organic solvents are avoided during both the reaction process and the product separation. However, the chemical modification of hemicelluloses with succinic anhydride (SA) to produce novel materials for industry has not been exploited yet, particularly in aqueous systems.

During the last 10 years, our research group has been involved mainly in the isolation, characterization, and modification of hemicelluloses from cereal straws as novel materials for indus-

trial use.<sup>2,10,11</sup> We found that esterified hemicelluloses prepared under homogeneous reaction conditions in the system *N,N*-dimethylformamide/lithium chloride by reaction with native hemicelluloses with various acyl chlorides (C<sub>3</sub>–C<sub>18</sub>) in the presence of 4-dimethylaminopyridine as a catalyst and triethylamine as a base are considerably more hydrophobic than natural hemicelluloses.<sup>10</sup> This increasing hydrophobic capacity may lead to the use of esterified hemicelluloses in the production of plastics, especially biodegradable and/or environmentally degradable plastics, resins, films, and coatings in the food industry. In contrast, to increase the hydrophilicity of modified hemicelluloses and improve water absorption in polymers, with this research overall we intend to establish an environmentally friendly chemical modification procedure such as the succinylation of hemicelluloses in aqueous systems. In this work, the influence of the SA concentration, temperature, and reaction duration on the yield and degree of substitution (DS) of the hemicellulosic succinate, which enabled us to optimize reaction conditions for an efficient succinylation of hemicellulose ester, was studied. The modified hemicelluloses were further characterized with Fourier transform infrared (FTIR), <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy, and thermal analysis.

## EXPERIMENTAL

### Materials

Wheat straw was obtained from the experimental farm of the North-Western University of Agricultural and Forest Sciences and Technology (Yangling, China). The hemicelluloses were isolated from holocellulose with 10% KOH at 22°C for 16 h with a liquor ratio of 1:18 and recovered by precipitation of the neutralized hydrolysate in four volumes of ethanol. The method for their sugar analysis is described in a previous article.<sup>11</sup> SA was purchased from Shaanxi Chemical Co. (Xian, China).

### Succinylation of Hemicelluloses

Typical procedures for the reactions of SA with hemicelluloses in aqueous alkaline systems are as follows. Hemicellulosic powder [3.30 g, equaling 0.025 mol of anhydroxylose (AX) units and 0.05 mol of hydroxyl functionality in the hemicelluloses] was dissolved in 30 mL of distilled water at

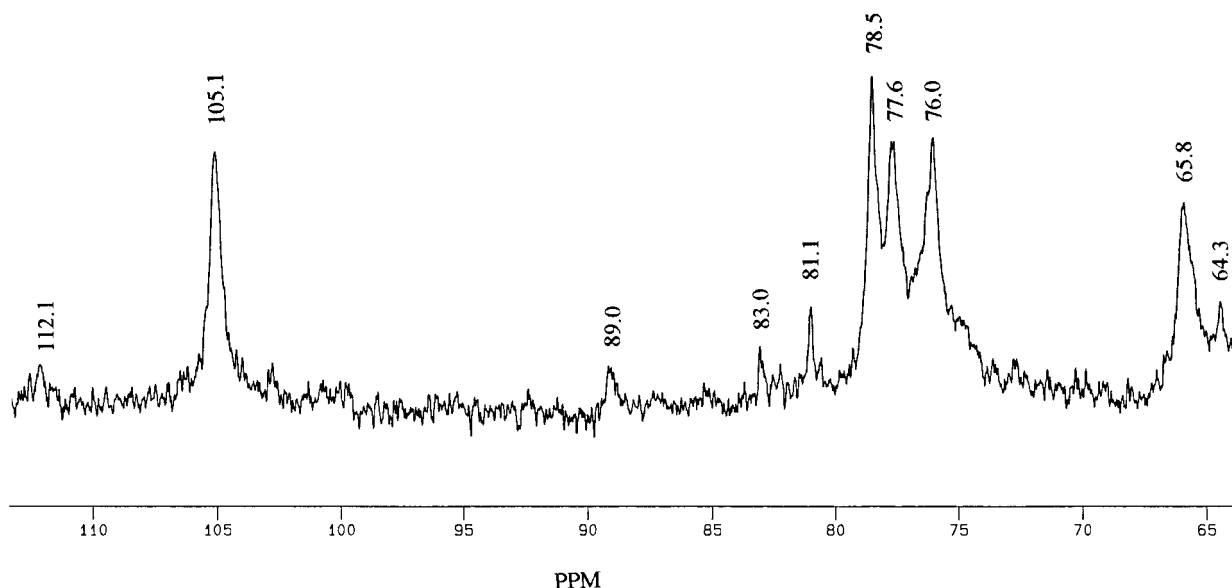


Figure 1  $^{13}\text{C}$ -NMR spectrum of native wheat straw hemicelluloses.

25–45°C under stirring until it was completely dissolved (approximately 10 min). The pH was adjusted to 8.5–9.0 with a 2% NaOH solution. Then, SA (1.00 g, equaling 0.01 mol of SA and 0.01 mol of carboxyl functionality, a molar ratio of 1:2.5; 0.5 g, equaling 0.005 mol of carboxyl functionality, a molar ratio of 1:5; 1.25 g, equaling 0.0125 mol of carboxyl functionality, a molar ratio of 1:2; 1.67 g, equaling 0.0167 mol of carboxyl functionality, a molar ratio of 1:1.5; or 2.5 g, equaling 0.025 mol of carboxyl functionality, a molar ratio of 1:1) was added slowly over 20 min. The reaction was allowed to proceed at pH 8.5–9.0 for a total of 0.5, 1, 2, 3, 5, 7, 10, 12, and 16 h, respectively, with stirring. Isolation and purification of the product were obtained by resuspension of the reaction mixture in 120 mL of ethanol with stirring. The resulting hemicellulosic derivative precipitate was filtered off and washed thoroughly with ethanol and acetone to remove any color impurities and residual reagents. The purified product was first air-dried for 12 h and then further dried in an oven for 15 h at 50°C.

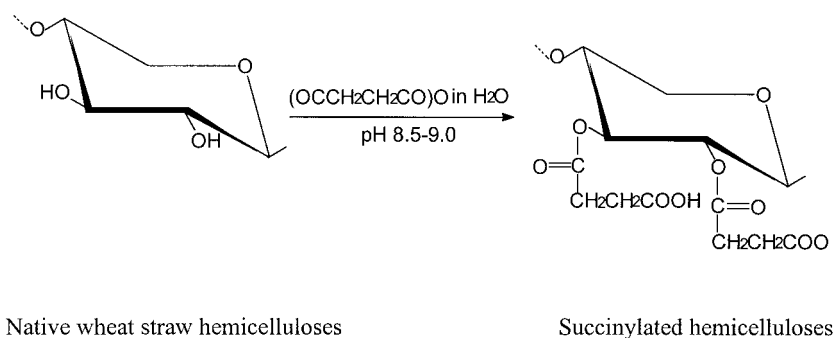
#### Characterization of the Succinylated Hemicelluloses

The yield percentages were calculated under the assumption that all of the hemicelluloses were converted into diesterified hemicelluloses (Fig. 1). In that case, the yield percentage and DS would be 100% and 2.0, respectively. The unreacted SA in a reaction mixture was separated from the product by dissolution in ethanol and acetone. If

no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 39.7% with a DS value of 0.0.

The chemical structure of the succinylated hemicelluloses was evaluated with FTIR and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy. A Nicolet 510 spectrophotometer (Warwick, England) was used for recording FTIR spectra with a KBr disc containing 1% finely ground samples. The solution-state  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of both native hemicelluloses and succinylated derivatives were collected on a Bruker MSL-300 spectrometer (Oxford, England) at 300 and 74.5 MHz. The  $^1\text{H}$ -NMR spectra were recorded at 25°C from a 20-mg sample dissolved in 1.0 mL of  $\text{D}_2\text{O}$  for a total of 152 scans. Solution  $^{13}\text{C}$ -NMR spectra were recorded at 25°C from a 150-mg sample dissolved in 1.0 mL of  $\text{D}_2\text{O}$  after 15,000 scans. A 60° pulse flipping angle, a 3.9- $\mu\text{s}$  pulse width, and a 0.85-s delay time between scans were used.

The thermal stability of the hemicellulosic derivatives was performed with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (Netzsch STA-409; Hamburg, Germany). The sample weighed between 10 and 15 mg. The scans were run from room temperature to 600°C at a rate of 10°C/min under a dry air atmosphere. All the experimental results represent the mean of at least a triplicate, and each sugar analysis was chromatographed twice. The standard errors or deviations were lower than 6.3%.



**Figure 2** Scheme for the succinylation of wheat straw hemicelluloses.

## RESULTS AND DISCUSSION

### Characterization of the Isolated Native Hemicelluloses

On the basis of the dry weight of wheat straw, treatment of the holocellulose with 10% KOH at 22°C for 16 h yielded 31.5% hemicellulose. Xylose ( $78.7 \pm 1.3\%$ ) was a predominant sugar component. Arabinose ( $9.2 \pm 0.4\%$ ) appeared as the second major sugar constituent. Glucose ( $4.0 \pm 0.2\%$ ), galactose ( $2.2 \pm 0.1\%$ ), and rhamnose ( $1.0 \pm 0.1\%$ ) were present as minor sugar constituents. The uronic acids, mainly 4-*O*-methyl-*D*-glucuronic acid, were present in a noticeable amount ( $4.2 \pm 0.2\%$ ). The amount of associated lignin in isolated hemicelluloses was insignificant ( $\sim 1.0 \pm 0.1\%$ ). Gel permeation chromatography showed the native hemicelluloses had a weight-average molecular weight of 28,100 Da with a polydispersity of 5.3. As shown in the  $^{13}\text{C}$ -NMR spectrum of the native hemicelluloses in Figure 1, the main 1,4-linked  $\beta$ -*D*-xylopyranosyl (Xylp) units were obviously characterized by the signals at 105.1, 78.5, 77.6, 76.0, and 65.8 ppm, which were attributed to C<sub>1</sub>, C<sub>4</sub>, C<sub>3</sub>, C<sub>2</sub>, and C<sub>5</sub> of the  $\beta$ -*D*-Xylp units, respectively. The signals at 112.1, 89.0, 83.0, 81.1, and 64.3 ppm were assigned to C<sub>1</sub>, C<sub>4</sub>, C<sub>2</sub>, C<sub>3</sub>, and C<sub>5</sub> of the  $\alpha$ -*L*-arabinofuranosyl (Araf) residues, respectively. These signals with further methylation analysis clearly showed that the main polysaccharide chain consisted of *D*-xylopyranose units linked glycosidically by  $\beta$  (1 $\rightarrow$ 4) bonds. Side chains consisted of *L*-Araf units linked by  $\alpha$  (1 $\rightarrow$ 3) bonds. The uronic acid, mainly 4-*O*-methyl-*D*-glucuronic acid, was bound to *D*-xylosyl units of the main chain by  $\alpha$  (1 $\rightarrow$ 2) bonds.<sup>16</sup>

### Yield and DS

Hemicellulose derivatives containing free carboxylic groups were prepared by the reaction of the

polysaccharides with SA to yield the monoesterified dicarboxylic acid with a low DS in aqueous alkaline systems. A scheme for the succinylation of the polymers is shown in Figure 2. The side reactions are the hydrolysis of SA and starch succinate. Furthermore, crosslinking (in the form of the full ester) and other complex formations may also occur but are not significant because the final product is actually produced in the form of the sodium of the acid ester, which limits its further reaction to forming diesters.<sup>17</sup> In other words, in the diagrammatic formula in Figure 2, the carboxylic group COOH is originally present in the form of its salt. If it is undesirable to have the acid ester in the form of its salt, the final product may be washed with a dilute mineral acid so that the salt of the carboxylic group might be changed to the normal carboxyl form COOH, except that the final reaction pH is adjusted to 5.5–6.0 with a dilute mineral acid such as HCl.<sup>15</sup>

Table I gives the yield and DS of the succinylated hemicelluloses obtained under various conditions. As expected, because of the freedom of associated unreacted SA in the isolated products, the DS values of the hemicellulosic derivatives were calculated from the yield percentages of succinylated hemicelluloses under the assumptions of each AX unit in the polymer containing two free hydroxyl groups and each SA molecule reacting with one free hydroxyl group in one carboxylic acid. Obviously, as can be seen in Table I, the yield and DS of the products depended mainly on the reaction duration, molar ratio of reactant agents, and temperature used. In all cases, the reaction pH was adjusted to 8.5–9.0 through the addition of a 2% NaOH solution. The reaction of the hemicelluloses and anhydride reagent was initiated by the adjustment of the pH to alkaline media or greater than 7.0. After the system reached the desired pH and the reaction was begun, the reaction was continued by the addition of

**Table I** Yield<sup>a</sup> of Succinylated Wheat Straw Hemicelluloses and DS

Succinylation Condition				Succinylated Hemicelluloses		
Molar Ratio <sup>b</sup>	Temperature	Time (h)	pH <sup>c</sup>	Preparation Number	Yield (%)	DS
1 : 2.5	28	0.5	8.5–9.0	1	41.1	0.045
1 : 2.5	28	1	8.5–9.0	2	44.3	0.15
1 : 2.5	28	2	8.5–9.0	3	45.5	0.19
1 : 2.5	28	3	8.5–9.0	4	42.2	0.083
1 : 2.5	28	5	8.5–9.0	5	40.9	0.040
1 : 2.5	28	7	8.5–9.0	6	40.9	0.040
1 : 2.5	28	10	8.5–9.0	7	40.5	0.026
1 : 2.5	28	12	8.5–9.0	8	40.4	0.023
1 : 2.5	28	16	8.5–9.0	9	40.4	0.023
1 : 2.5	25	2	8.5–9.0	10	45.1	0.18
1 : 2.5	35	2	8.5–9.0	11	42.0	0.086
1 : 2.5	40	2	8.5–9.0	12	41.6	0.063
1 : 2.5	45	2	8.5–9.0	13	40.2	0.017
1 : 5	28	1	8.5–9.0	14	40.7	0.033
1 : 2	28	1	8.5–9.0	15	44.8	0.17
1 : 1.5	28	1	8.5–9.0	16	45.0	0.18
1 : 1	28	1	8.5–9.0	17	46.0	0.21

<sup>a</sup> Based on the assumption that all of the hemicelluloses were converted to diesterified hemicelluloses (yield = 100%; DS = 2.0). If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 39.7% for succinylation with a DS value of 0.0.

<sup>b</sup> Molar ratio represents the moles of SA/moles of AX units in hemicelluloses.

<sup>c</sup> pH represents the reaction pH.

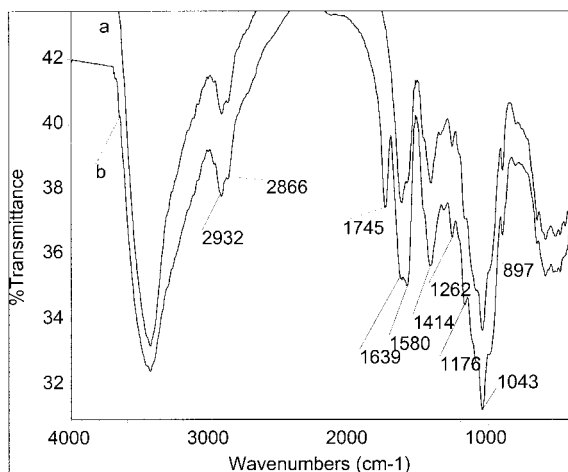
enough alkali to maintain the pH between 8.5 and 9.0. On the basis of studies of starch succinylation in aqueous slurry systems, Jeon et al.<sup>12</sup> stated that the highest reaction efficiency was obtained for the pH range 8.5–9.0. An increase or decrease in the reaction pH above or below this range had significant effects on the DS. This observation may be explained by the fact that pH values greater than 9.0 favor anhydride hydrolysis, whereas pH values less than 8.5 do not sufficiently activate the hydroxyl groups of hemicelluloses for nucleophilic attack of the anhydride moieties. Thus, the pH range of 8.5–9.0 was used in all our experiments.

The first reaction parameter studied was the reaction duration. For this investigation, the following parameters were fixed: the pH was 8.5–9.0, the molar ratio of SA to AX units in hemicelluloses was 1:2.5, and the reaction temperature was 28°C. As can be seen in Table I, an increase in the reaction time from 0.5 h in sample 1 to 1 h in sample 2 and to 2 h in sample 3 resulted in a significant increase in the reaction yield from 41.1 to 44.3 and 45.5% and in the DS from 0.045 to 0.15 and 0.19, respectively. Prolonging the reaction times beyond 2 h led to a substantial decrease in the yield and DS. An explanation is that

as the reaction progresses, the anhydride is depleted because of the succinylation and hydrolysis reactions. As a result, the reverse reaction of ester hydrolysis becomes dominant.<sup>12</sup>

The reaction temperature is another important parameter. From the results listed in Table I, it can be seen that for temperatures between 25 and 28°C, a good yield (45.1–45.5%) of the esterified product and a good DS (0.18–0.19) were obtained. A further increase in the reaction temperature from 28 to 35, 40, and 45°C resulted in a significant decrease in the DS by 0.10, 0.13, and 0.17, respectively. The reason for this slight increase in the yield of esterification was probably that an increase in the reaction temperature enhanced the anhydride diffusion into the hemicellulosic granules, which increased succinylation reaction rates. However, a higher temperature would be expected to increase the solubility of SA in aqueous media, which would increase hydrolysis. This would lead to a decrease in the DS of the hemicellulosic succinates. Thus, a temperature of 28°C was used in the studies described later because the product with the highest DS was obtained at this temperature.

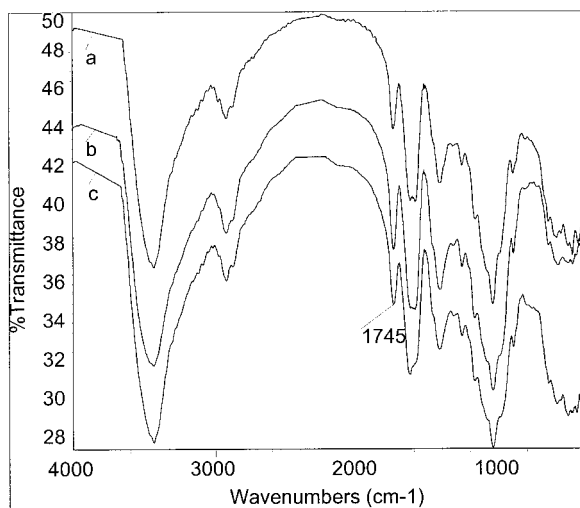
Besides the reaction time and temperature, the molar ratio of SA to AX units in hemicelluloses



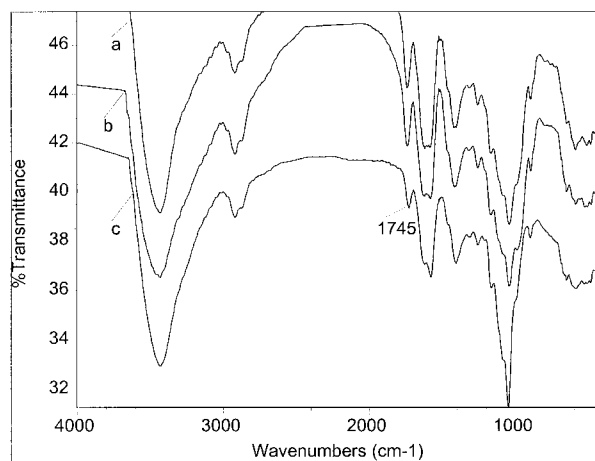
**Figure 3** FTIR spectra of (a) natural wheat straw hemicelluloses and (b) succinylated hemicellulosic preparation 10.

was another important reaction parameter affecting the reaction efficiency. The data for samples 14–17 in Table I indicate that as the molar ratio of SA to hemicelluloses increased from 1:5 to 1:2, 1:1.5, and 1:1, the reaction DS increased from 0.033 to 0.17, 0.18, and 0.21, respectively. This increase in the DS with increases in the reactant concentration could be interpreted in terms of the greater availability of succinic molecules in the proximity of the hemicellulosic molecules at relatively higher concentrations of the esterifying agent.

As discussed previously, the reaction yield and DS depended strongly on the reaction time and

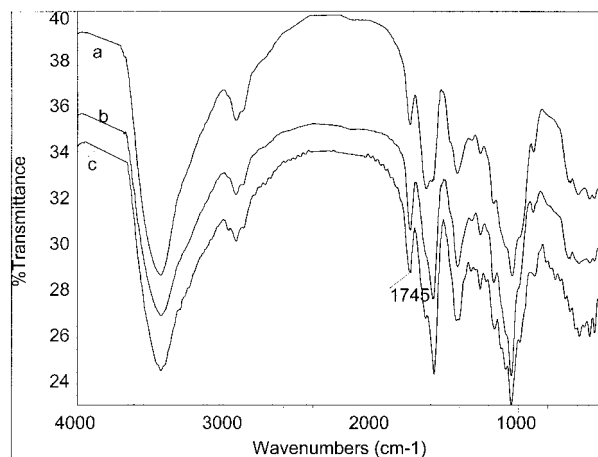


**Figure 4** FTIR spectra of succinylated hemicellulosic preparations (a) 1, (b) 3, and (c) 5 obtained in aqueous systems.

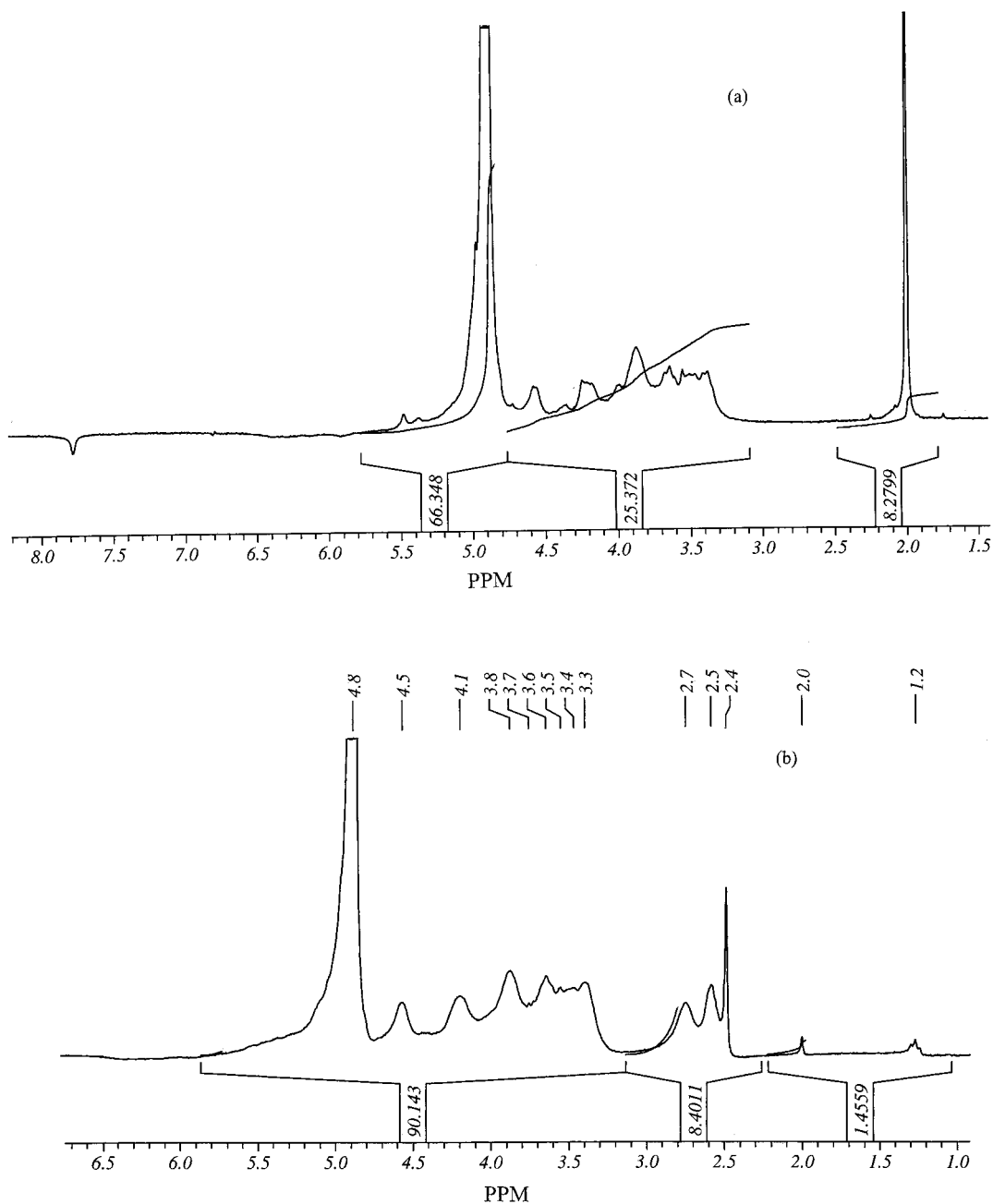


**Figure 5** FTIR spectra of succinylated hemicellulosic preparations (a) 11, (b) 12, and (c) 13 obtained in aqueous systems.

temperature, pH, and molar ratio of SA to hemicelluloses. The preferred reaction conditions that led to the highest reaction yield (46.0%) and DS (0.21) were as follows: the pH was 8.5–9.0, the temperature was 28°C, and the reaction time was 1 h, and the molar ratio of SA to hemicelluloses was 1:1. However, compared with the results of the succinylation of hemicelluloses with an *N,N*-dimethylformamide/lithium chloride system as the solvent and pyridine and/or 4-dimethylaminopyridine as the catalyst (DS ≤ 1.67),<sup>18</sup> a much lower yield or DS was achieved in the aqueous phase in this study. This suggests that the side reactions of the hydrolysis of SA and hemicellulosic succinate were also dominant, except for suc-



**Figure 6** FTIR spectra of succinylated hemicellulosic preparations (a) 14, (b) 15, and (c) 16 obtained in aqueous systems.



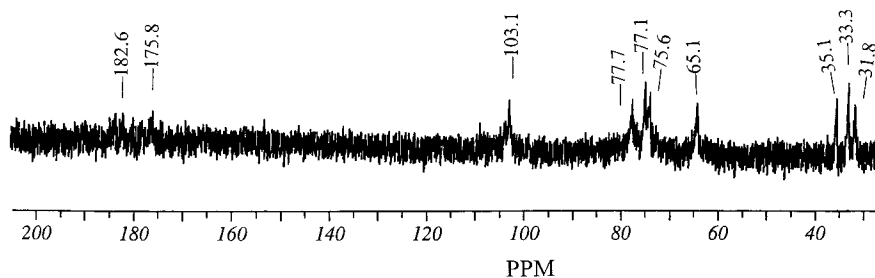
**Figure 7**  $^1\text{H-NMR}$  spectra of (a) native hemicellulose and (b) succinylated hemicellulosic preparation 10.

cinoylation in aqueous alkaline systems. A similar phenomenon was observed during the succinylation of starch in aqueous media by Caldwell and Wurzburg,<sup>15</sup> Jeon et al.,<sup>12</sup> and Billmers and Mackewicz.<sup>19</sup> With a systematic study of starch esterification with alkenyl succinates in aqueous slurry systems, Jeon et al. reported that the maximum achievable DS after 6 h under aqueous conditions was only about 0.04. Similarly, another DS up to 0.09 was documented by reactions

being conducted under harsh acidic conditions followed by mild alkaline conditions.<sup>19</sup>

### FTIR Spectra

The FTIR spectra of native hemicelluloses [Fig. 3(a)] and succinylated hemicelluloses [Fig. 3(b), sample 10] confirm the extent of esterification, depicting some representative spectra of hemicellulosic esters. In the spectrum of native hemicel-



**Figure 8**  $^{13}\text{C}$ -NMR spectrum of succinylated hemicellulosic preparation 2.

luloses, a strong band at  $1043\text{ cm}^{-1}$  is the most characteristic band for a polysaccharide, and it originates from C—O stretching in C—O—C glycosidic linkages. This band is also observed in succinylated hemicelluloses [Fig. 3(b)]. This band was not significantly affected by succinylation due to low substitution. Another characteristic band is the one at  $3445\text{ cm}^{-1}$  (data not shown) due to hydroxyl bond stretching. The intensity of this peak decreased slightly in the succinylated derivatives, indicating a low DS. Figure 3(b) provided evidence of succinylation by showing the presence of two important ester bands at  $1745$  and  $1176\text{ cm}^{-1}$ . The former band at  $1745\text{ cm}^{-1}$  is attributed to the absorption by carbonyl bonds in esters. The latter band at  $1176\text{ cm}^{-1}$  is assigned to C—O stretching in esters ( $\text{O}=\text{C}-\text{O}-\text{CHCH}_2-$ ).<sup>6</sup> The stretching of carbonyl groups in carboxylic acids was not observed or overlapped with carbonyl bonds in esters at  $1745\text{ cm}^{-1}$  in Figure 3(b). This lack of a carboxylic acid absorption band at  $1712\text{ cm}^{-1}$  is also probably due to the formation of the salts of the acid ester with sodium ion in aqueous systems.<sup>20</sup> The methyl and methylene C—H stretching gives bands between  $2932$  and  $2866\text{ cm}^{-1}$ , and their intensity increased in the succinylated polymers. As expected, the disappearance of peaks at  $1850$  and  $1780\text{ cm}^{-1}$  [in Fig. 3(b)] of succinylated polymers confirmed that the products were free of unreacted SAs.<sup>21</sup>

The influence of the reaction time, temperature, and reactant molar ratio of SA to hemicelluloses on the intensity of the absorption bands in FTIR spectra was also comparatively examined, and their spectra are given in Figures 4–6, respectively. Figure 4(a–c) provides FTIR spectra of succinylated hemicellulosic preparations 1 (0.5 h), 3 (2 h), and 5 (5 h), respectively. As illustrated, the intensity of the ester band at  $1745\text{ cm}^{-1}$  increased with an increase in the reaction time from 0.5 h in Figure 4(a) to 2 h in Figure 4(b) and then decreased to 5 h in Figure 4(c), corresponding to the reaction yield and DS. Similar phenomena of

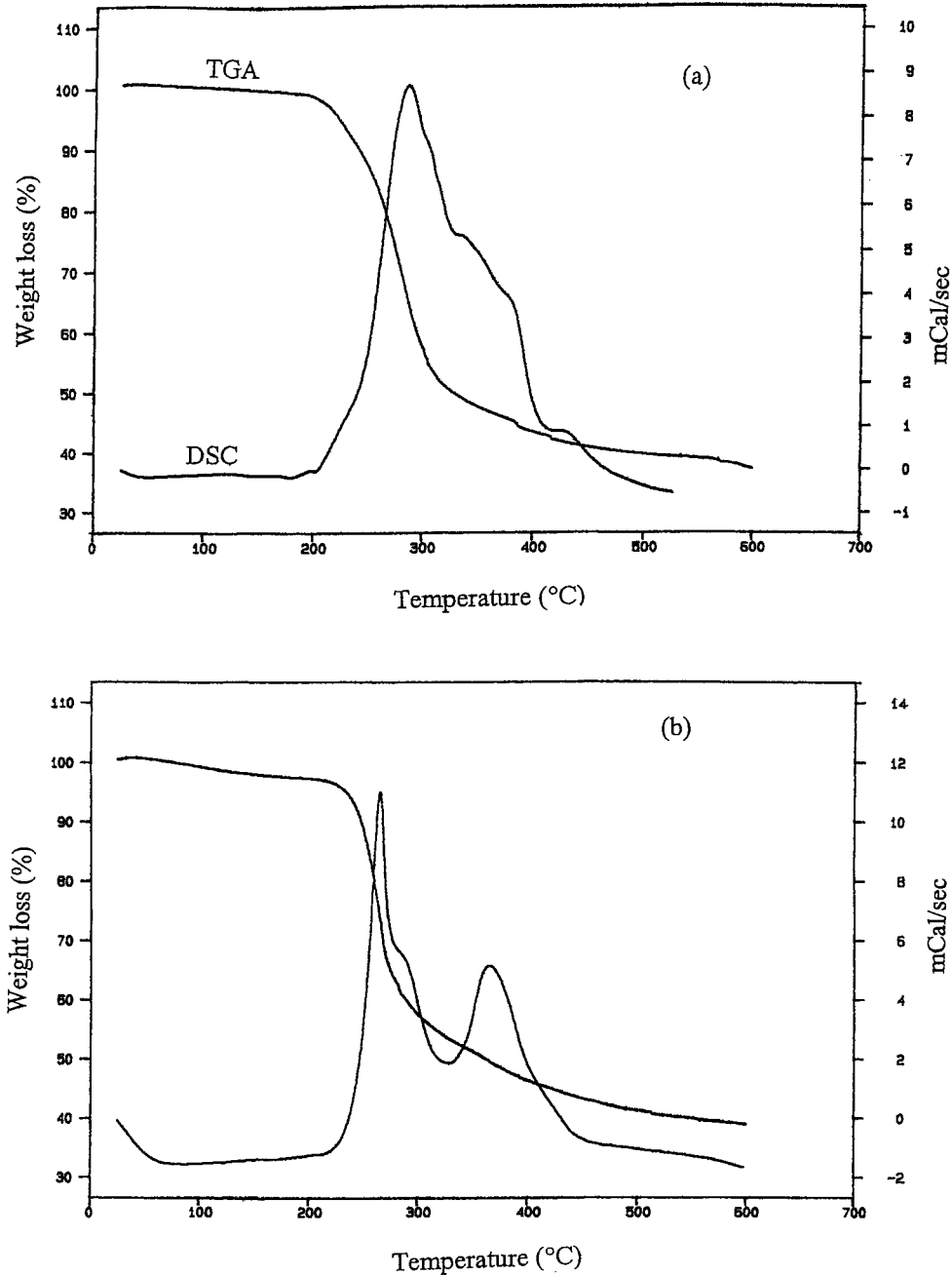
increasing or decreasing intensity of the ester bond at  $1745\text{ cm}^{-1}$  with increments of the reaction temperature between  $35$  and  $45^\circ\text{C}$  (samples 11–13) and reactant molar ratio of SA to hemicelluloses from 1:5 to 1:1.5 (samples 14–16) were also observed in the spectra given in Figures 5 and 6.

#### $^1\text{H}$ - and $^{13}\text{C}$ -NMR Spectra

The chemical changes in the structures of hemicelluloses were verified by both  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy. Figure 7 shows the  $^1\text{H}$ -NMR spectra of native hemicelluloses and monosuccinate ester sample 10. Figure 7(a) (native hemicelluloses) gives the peak of the equatorial proton of the AX unit in hemicelluloses at  $4.8$ – $5.0\text{ ppm}$ , whereas the other protons of the AX unit in hemicelluloses are located at  $3.3$ – $4.5\text{ ppm}$ . The peak at  $2.0\text{ ppm}$  may arise from protons that are on a carbon adjacent to an acid group ( $\text{CH}-\text{COOH}$ ), such as 4-*O*-methylglucuronic acid in native hemicelluloses. For Figure 7(b) (succinylated polymer sample 10), the peaks at  $4.8$ – $5.0$  and  $3.3$ – $4.5\text{ ppm}$  are due to the equatorial proton and other protons of the AX unit in hemicelluloses, respectively, that were found in the NMR spectrum of the native hemicelluloses as well. The new peaks at  $2.7$ ,  $2.5$ , and  $2.4\text{ ppm}$  are indicative of the methylene proton connecting the carboxylic acid and ester group of the hemicellulosic succinate.<sup>21</sup>

The  $^{13}\text{C}$ -NMR spectrum of esterified polymer sample 2 with a DS value of 0.15 is shown in Figure 8. From the spectrum of native hemicelluloses given in Figure 1, it can be seen that the presence of three signals between  $31.8$  and  $35.1\text{ ppm}$  and two small peaks at  $175.8$  and  $182.6\text{ ppm}$  is characterized by the methylene carbon atoms and carbonyl ester and carboxylic acid groups, respectively, corresponding to the formed monosuccinate groups. The occurrence of five signals at





**Figure 9** Thermograms of (a) native hemicelluloses and (b) succinylated hemicellulosic preparation 2.

103.1, 77.7, 77.1, 75.6, and 65.1 ppm relates to carbon atoms of C<sub>1</sub>, C<sub>4</sub>, C<sub>3</sub>, C<sub>2</sub>, and C<sub>5</sub> in the  $\beta$ -D-Xylp units of hemicelluloses.

#### Thermal Analysis

The thermal stability of both native polymers and their derivatives was studied with TGA. Figure 9 illustrates the TGA curves of native hemicellulo-

ses and succinylated polymer sample 2. As observed, native hemicelluloses and modified polymer sample 2 are stable up to 207 and 227°C, respectively. Beyond these temperatures, thermal degradation took place, depending mainly on the water content of the samples.<sup>22</sup> A previous study<sup>23</sup> on starch degradation has shown that the water is the main product of decomposition at temperatures below 300°C, formed by intermolec-

ular or intramolecular condensation of starch hydroxyls. A similar product could be produced during the decomposition of hemicelluloses and their derivatives in this study. As depicted in Figure 9, at 90 and 50.0% weight losses, the decomposition temperatures of native hemicelluloses and succinylated polymer sample 2 occurred at 238 and 328°C and 250 and 362°C, respectively. This indicated that the succinylated polymer had higher thermal stability than unmodified hemicelluloses. This greater thermal stability of the modified esters is probably due to the lower amounts of remaining hydroxyl groups after succinylation.<sup>5</sup>

DSC was used to investigate the possibility of interaction between the native hemicelluloses and SA.<sup>6</sup> The unmodified hemicelluloses showed only one large exothermic peak at about 286°C, whereas esterified polymer sample 2 with a DS value of 0.15 displayed two noticeable exothermic peaks centered at 270 and 362°C and one small endothermic peak at 326°C. This endothermic peak resulted from the melting of the crystallized part of the polymer, and its intensity increased with the DS (thermograms not shown). This observation supported the results obtained by FTIR and NMR spectroscopy and confirmed again that the reactions between hemicelluloses and SA occurred.

## CONCLUSIONS

In short, the esterification of hemicelluloses with SA in aqueous alkaline systems is an elegant method for obtaining polymers with carboxylic groups and low DSs. The preferred reaction conditions were as follows: pH 8.5–9.0, 28°C, 1 h, and 1:1 molar ratio of SA to hemicelluloses. An increase in the reaction time from 0.5 to 2 h between samples 1 and 3 resulted in a significant increase in the DS from 0.045 to 0.19, whereas the further extension of the reaction duration to 16 h led to a substantial decrease in the DS to 0.023. Increasing the molar ratio of the anhydride to hemicelluloses from 1:5 to 1:1 between samples 14 and 17 resulted in an enhancement of the DS from 0.033 to 0.21. Increasing the reaction temperature from 28 to 45°C led to a drastically declining DS value from 0.19 to 0.017. The thermal

stability of the products was also increased by chemical modification. These hemicellulosic succinates could be used as thickening agents and metal-ion binders.

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