Preparation and Characterization of Wheat Straw Hemicellulosic Succinates

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*Hemicellulosic succinates with a degree of substitution ranging from 0.28 to
1.67 were prepared by modification with succinic anhydride using pyridine
as catalyst and N, N-dimethylformamide/lithium chloride system as sol-
vent. Variations in reactant molar ratio from 1:1 to 6:1 and reaction time
from 1 to 12 h resulted in an increase in a degree of substitution from 0.28
to 1.03 and 0.87 to 1.67, respectively. However, it should be noted that the
reaction efficiency decreased as the molar ratio of anhydride to hemi-
celluloses increased from 6:1 to 8:1. Also, extending the reactions beyond
12 h at 80°C led to products of lower substitution. The thermal stability of
the esterified polymers decreased by chemical modification, but a thermal
stability of the succinylated hemicelluloses over to 200°C is satisfactory.*

In the past few years, studies concerning the total or partial substitution of synthetic plastics by biodegradable materials such as natural ligno-cellulosic fibers from agroresource have been increasing steadily[1]. Among these natural materials, agricultural by-products such as straws are attractive from the standpoint of providing biodegradation properties to the end products. Wheat straw, one of the most abundant renewable materials, is composed mainly of cellulose ($\sim 38\%$) and hemicelluloses ($\sim 32\%$)[2]. The latter are commonly extracted from the straw by dilute alkali and isolated by precipitation of the neutralized extract in ethanol. The main hemicellulosic chain consists of D-xylopyranose units linked glycosidically by β $(1 \rightarrow 4)$ bonds. Side chains comprise L-arabinofur-anosyl units linked by α $(1 \rightarrow 3)$ bonds. The 4-*O*-methyl-D-glucuronic acid is bounded to D-xylosyl units of the main chain by α $(l \rightarrow 2)$ bonds[3].

One very attractive feature of hemicelluloses is their chemical com-position, with large amounts of relatively easily accessible hydroxyl units that can be used for the attachment of a variety of functional groups. Chemical modification of hemicelluloses with long chain acyl chlorides impart water resistance to the product[4]. Conversely, the formation of hemicellulosic succinates and adipates increases the hy-drophilicity of modified hemicelluloses. Furthermore, high densities of hemicelluloses side-chain carboxylic groups provide useful properties such as metal chelation[5]. Chemical modification of dextran[6], pull-ulan[7], starch[8,9] with succinic anhydride have been extensively studied under highly variable reaction conditions. Such polysaccharide succi-nates offer a number of very desirable properties such as high viscosity, low-temperature viscosity stability, high thickening power, low gelati-nization temperature, clarity of cooks and good filming properties. Therefore, succinate derivatives have been recommended as binders and thickening agents in foods, tablet disintegrants in pharmaceuticals and surface sizing agents and coating binds in paper[9]. Similarly, modi-fication of cellulose and wood with dicarboxylic acid anhydrides such as succinic, maleic or phthalic anhydrides has been pointed out as a way of introducing new material properties[10,11]. Furthermore, by addition reaction of the esterified cellulose or wood with epoxide and anhydride, oligoesterified materials are obtained. These chemically modified ma-terials could be molded, by hot pressing, into plasticized sheets with decreased hygroscopicity[12–15]. In spite of the large interest in starch and cellulose modification with dicarboxylic acid anhydrides, the succi-noylation of hemicelluloses has not been reported. It was therefore of interest to study the effect of such modification with the aim of ex-ploiting the reactive chemistry of hemicellulosic succinates as novel materials for use in many industries.

The present work is part of a more extended work undertaken for chemical modification of wheat straw hemicelluloses by our

laboratories, intended to study the effect of reactant molar ratio and reaction time on the succinoylation efficiency in N, N-dimethylformamide (DMF)/lithium chloride (LiCl) systems. The modified hemicelluloses were then characterized by Fourier-transform infrared (FT-IR), and ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopies, as well as 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). It was dried in sunlight and then cut into small pieces. The cut straw was ground to pass a 1.0-mm size screen. The methods for extraction of hemicelluloses from the ground straw and their sugar analysis have been described in a previous paper[4]. The sugar analysis showed that xylose was present as the predominant sugar component, comprising 82.9% of the total sugars. Arabinose (9.7%) occurred as the second major sugar constituent. Glucose (4.0%), galactose 2.2%, and rhamnose (1.1%) were present as minor sugar constituents. The uronic acids, mainly 4-O-methyl-D-glucuronic acid, were present in a noticeable amount (4.6%). DMF solvent was dried prior to use according to conventional methods. Anhydrous LiCl was dried at 130°C for 2 h before use. Other reagent grade chemicals such as succinic anhydride (SA) and pyridine were purchased from Sigma Chemical Company (Xiam, China).

Succinoylation of Hemicelluloses

The succinic derivatives of hemicelluloses containing free carboxylic groups were prepared by reaction of the wheat straw hemicelluloses with succinic anhydride in DMF/LiCl systems to yield the mono-esterified dicarboxylic acid (figure 1). The details of the succinoylation of the hemicelluloses were as follows: dry hemicelluloses powder (0.66 g, equal to 0.005 mol of anhydroxylose unit and 0.01 mol of hydroxyl functionality in hemicelluloses) in 30 mL distilled water were heated to 80°C under stirring until completely dissolved (approximately 5 min). A 20 mL volume of DMF was added and the reaction was stirred for another 5 min. The water was removed from the swollen gel by re-peated distillation under reduced pressure at 50°C. To this mixture, 0.10 g LiCl and 15 mL pyridine were added, and the temperature was raised to 80°C. Then 0.5 g (equal to 0.005 mol of succinic anhydride
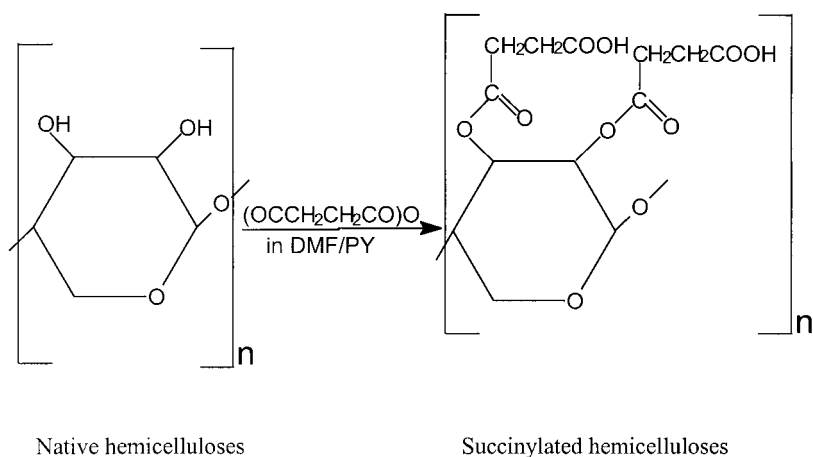
FIGURE 1 Scheme for succinoylation of wheat straw hemicelluloses.

and 0.005 mol of carboxyl functionality, molar ratio 1:1), 1.0 g (0.01 mol of carboxyl functionality, molar ratio 2:1), 1.5 g (0.015 mol of carboxyl functionality, molar ratio 3:1), 2.0 g (0.02 mol of carboxyl functionality, molar ratio 4:1), 2.5 g (0.025 mol of carboxyl function-ality, molar ratio 5:1), 3.0 g (0.03 mol of carboxyl functionality, molar ratio 6:1), 3.5 g (0.035 mol of carboxyl functionality, molar ratio 7:1) and 4.0 g (0.04 mol of carboxyl functionality, molar ratio 8:1) succinic anhydride, previously dissolved in 10 mL DMF, were added over a time period of 10 min, respectively, while stirring the reaction mixture at 80°C. The reaction was stopped at a required period (1–16 h) by cooling the resulting mixture to room temperature. Then the homogeneous re-action mixture was slowly poured into 120 mL of ethanol with stirring. The white product that separated from the solution was filtered off and collected. The filtrate was washed thoroughly with ethanol and acetone to eliminate any color impurities and by-products. Finally, the product was first air-dried for 12 h and then further lyophilized overnight under reduced pressure.

Characterization of the Succinylated Hemicelluloses

The yield percentages were calculated based on the assumption that all of the hemicelluloses were converted to di-esterified hemicelluloses (Figure 1). In that case the yield percentage and the degree of substitution (DS) would be 100% and 2.0, respectively. The unreacted succinic an-hydride in a mixture of reaction was separated from the product by

dissolving 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 hemicellulosic derivatives was evaluated by FT-IR, and ^{1}H and ^{13}C NMR spectroscopies. A Nicolet 510 spectrophotometer was used to record FT-IR spectra using a KBr disc containing 1% finely ground samples. The solution-state ^{1}H and ^{13}C-NMR spectra were obtained on a Bruker MSL-300 spectrometer at 300 and 74.5 MHz. ^{1}H NMR spectrum was recorded at 25°C from 20 mg of sample dissolved in 1.0 mL DMSO-d_6 for a total of 152 scans. The ^{13}C-NMR spectrum was recorded at 25°C from 120 mg of sample dissolved in 1.0 mL D_2O after 15,000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width and a 0.85 μs delay time between scans were used.

Thermal stability of succinylated hemicelluloses was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (NETZSCH STA-409). 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.

RESULTS AND DISCUSSION

Yield and Degree of Substitution

It is well known that the reaction of anhydride with alcohol is a rapid and irreversible reaction. Usually succinic anhydride reacts with poly-saccharides to form the half-ester (mono-ester). This is particularly true when the reaction is performed in homogeneous system[9]. In contrast to acetic anhydride, succinic anhydride is not able to swell the hemicellulosic structure. Therefore, a pre-swelling step and a suitable solvent or catalyst should be added to the reaction system to increase the accessibility of the reactive hydroxyl groups of the hemicelluloses to the reactions. Similar observations were found in the reaction of wood with succinic anhydride by Marchetti et al.[16]. Furthermore, to obtain ester-ified hemicelluloses bearing carboxyl groups, the anhydride should be used in the liquid state by dissolving in DMF solvent since succinic anhydride has a mp of 119–120°C. In this study, the succinylated hemi-celluloses containing free carboxylic groups were prepared by reaction of the polysaccharide with succinic anhydride to yield the mono-esterified dicarboxylic acid using pyridine as catalyst and DMF/LiCl system as solvent, since DMF/LiCl is suitable for this mono-esterification and the reaction in DMF/LiCl system proceeds smoothly at 80°C. Nonpolar solvent like hexane leads to poor grafting efficiency, whereas polar sol-vent like DMF gives satisfactory result, although DMF is a expensive solvent for esterification reactions.

The yield and degree of substitution of the succinylated hemicelluloses under the experimental conditions are given in Table I, and the scheme for succinoylation is displayed in Figure 1 based on the assumption that one attached succinic acid will result in one carboxylic acid. In this case, DMF/LiCl acts as a solvent for both the starting hemicelluloses and the final products. By using different amounts of succinic anhydride or controlling the reaction for various durations, it is possible to prepare esters with different degrees of substitution (DS, defined as the moles of substituents of hydroxyl groups per anhydroxylose unit in hemicelluloses). The theoretical maximum degree of substitution is two since each repeating anhydroxylose unit contains two hydroxyl groups. Due to

TABLE I The yield[a] of succinylated hemicellulose and the degree of substitution (DS).

Succinoylation conditions				Succinylated hemicelluloses		
Molar ratio[b]	Temperature (°C)	Time (h)	(DMF/PY[c])	Sample no.	Yield (%)	DS[d]
1:1	80	2	2/1	1	48.1	0.28
2:1	80	2	2/1	2	61.3	0.72
3:1	80	2	2/1	3	64.9	0.83
4:1	80	2	2/1	4	68.5	0.95
5:1	80	2	2/1	5	7.03	1.01
6:1	80	2	2/1	6	70.9	1.03
7:1	80	2	2/1	7	69.1	0.97
8:1	80	2	2/1	8	68.5	0.95
6:1	80	1	2/1	9	66.1	0.87
6:1	80	4	2/1	10	73.4	1.12
6:1	80	6	2/1	11	78.2	1.27
6:1	80	8	2/1	12	84.2	1.47
6:1	80	10	2/1	13	86.8	1.56
6:1	80	12	2/1	14	90.2	1.67
6:1	80	16	2/1	15	84.2	1.47

[a] Based on assumption that all of the hemicelluloses are converted to di-esterified 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 succinoylation with a DS value of 0.0.

[b] Molar ratio represents the mol of succinic anhydride/mol of anhydroxylose units in hemicelluloses.

[c] Abbreviation for *N,N*-dimethylformamide/pyridine (v/v).

[d] Degree of substitution.

the isolated products being free of associated unreacted succinic an-
hydride, the DS values of the hemicellulosic derivatives were calculated
from the yield percentage of succinylated hemicelluloses on the as-
sumption of each anhydroxylose unit in the polymer containing two free
hydroxyl groups, and each succinic anhydride molecule reacting with
one free hydroxyl group in one carboxylic acid. Obviously, as can be
seen from Table I, the yield and DS of the products depended on the
molar ratio of the reactant agents and reaction duration. Increasing the
molar ratio of the anhydride/hemicelluloses from 1:1 in sample 1 to 6:1
in sample 6 resulted in a significant yield increase from 48.1 to 70.9%
and a DS value increase from 0.28 to 1.03. These increases in yield and
DS by an increment of the reactant concentration could be interpreted
in terms of greater availability of succinic anhydride molecules in the
proximity of the hemicellulosic molecules at higher concentration of the
esterifying agent[17]. In contrast, as the molar ratio of the anhy-
dride/hemicelluloses was further increased from 6:1 in sample 6 to 8:1 in
sample 8, the yield and DS decreased from 70.9 to 68.5% and 1.03 to
0.95, respectively. This may result from insufficient mixing between SA
and hemicellulose phases. Also, sufficient time may not have been given
for large extents of anhydride succinoylation at the higher SA con-
centrations. This phenomenon was consistent with the studies of starch
succinoylation in aqueous slurry systems[5]. In addition, variations in the
reaction time and its effect on the yield and DS of succinylated polymers
were studied at reactant molar ratio of 6:1. As seen from Table I, in-
creasing the reaction time from 1 h in sample 9 to 4 h in sample 10, 6 h
in sample 1l, 8 h in sample l2, 10 h in sample 13 and l2 h in sample l4
resulted in a growth of yield from 66.1 to 73.4, 78.2, 84.2, 86.8 and
90.2%, respectively, together with an increment of DS value from 0.87 to
1.12, l.27, 1.47, l.56 and 1.67, respectively. Prolonging the reaction times
beyond 12 h led to a decrease in the yield and DS as shown between
samples 14 and 15 with a yield decreasing from 90.2 to 84.2% and a DS
value decreasing from 1.67 to 1.47. An explanation is that as the reaction
progresses, the anhydride is depleted due to succinoylation and hydro-
lysis reactions. As a result, the reverse reactions such as hydrolysis of
hemicellulosic succinate become dominant. A similar decreasing trend
with increasing reaction time was observed during the succinoylation of
waxy corn starch[5].

Based on modification reaction of dextran with SA using pyridine as
catalyst and DMF/LiCl system as solvent, Arranz[6] demonstrated that
the acylation reaction is more efficient in the presence of pyridine and the
reaction rate depends on the amounts of pyridine added. In this study,
it was found that pyridine was a useful catalyst, while the effect of
temperature on the DS of the products was not straightforward. With
pyridine as catalyst, a temperature of 80°C led to satisfactory DS values
between 0.28 and 1.67. Under an optimum reaction condition in sample

14 (molar ratio 6:1, DMF/PY 2:1, 80°C, 12 h), over 90% hydroxyl groups in native hemicelluloses (a maximum DS = 1.85)[4] were succinylated. In order to gain a complete substitution (DS = 1.85), addition of more mole of succinic anhydride per mol of free OH groups or raising reaction temperature is needed.

FT-IR Spectra

The FT-IR spectra of native hemicelluloses (spectrum 1) and succinylated hemicelluloses (spectrum 2, sample 4) are illustrated in Figure 2. As expected, the disappearance of peaks at 1850 and 1780 cm^{-1} in spectrum 2 of succinylated polymers confirmed that the products are free of the unreacted succinic anhydride[10]. In the two spectra the characteristic broad peak at 1050 cm^{-1} is attributed to C-O-C bond stretching, which was negligibly affected by succinoylation[18]. This indicated that the β-glucosidic linkages between the sugar units were not modified by the succinoylation reaction. A strong broad band at 3450 cm^{-1} is assigned to the hydroxyl groups in both native and succinylated hemicelluloses, and its intensity decreased in the esterified derivatives. The symmetric C-H vibrations or methylene group deformation exhibit bands between 2986 and 2880 cm^{-1}, and their intensity increased in succinylated polymers. In particular, the spectrum of succinylated
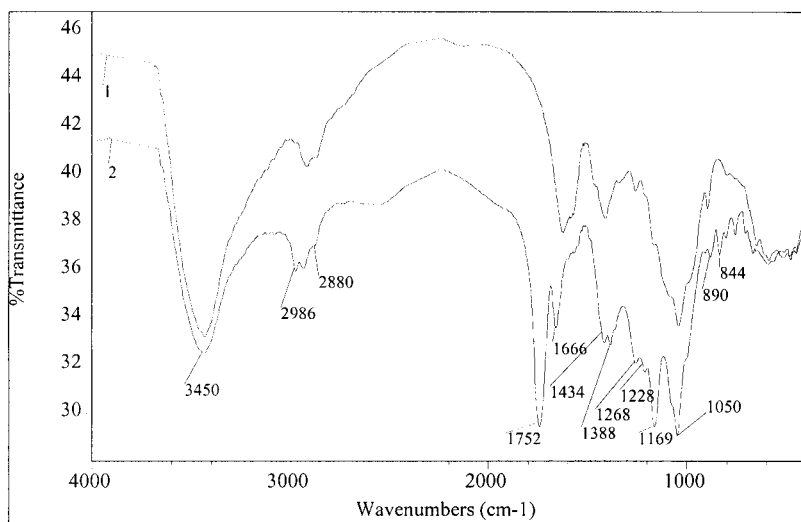
FIGURE 2 FT-IR spectra of natural wheat straw hemicelluloses (spectrum 1) and succinylated hemicelluloses (spectrum 2, sample 4).

sample is characterized by two important ester bands at 1752 and 1169 cm^{-1}. The former band at 1752 cm^{-1} is indicative of absorption by carbonyl bonds in esters. The latter band at 1169 cm^{-1} is characterized by the C-O stretching in the esters (OC-O-CHCH$_{2^-}$)[19]. The stretching of the carboxylic acids forming intermolecular hydrogen with pyridine bonding occurs at 1666 cm^{-1}[20]. These results revealed that the formation of the monoester of succinylated hemicelluloses in the homogeneous DMF/LiCl system was dominant. However, it should be noted that with longer reaction time, hemicellulose-attached succinic acid may continue to react with hydroxyl groups in the nearby surrounding crosslinks. In this study, however, it is possible that pyridine can reduce crosslinking since it is capable of forming salts with carboxylic groups. Another band for supporting the monoester appears at 1268 cm^{-1}, which arises from carbon single bonded hydroxyl group (O=C-OH) stretching vibration in carboxylic acid.

Figure 3 illustrates the FT-IR spectra of succinylated hemicellulose preparations 1 (spectrum 1), 3 (spectrum 2) and 6 (spectrum 3). The presence of two ester bands at 1745 and 1162 cm^{-1} and two carboxylic acid bands at 1646 and 1282 cm^{-1} indicated that only one carboxylic group had reacted, and the peak intensities increased with an increment of the DS from 0.28 (spectrum 1) to 0.83 (spectrum 2) and to 1.03 (spectrum 3). In contrast, the intensity of the band at 3448 cm^{-1} for hydroxyl group stretching decreased with the increase of DS from sample 1 to sample 3 and to sample 6. This decreasing OH trend corresponded to the increasing level of the esterification. The new absorption band that appeared at 1574 cm^{-1} was the result of the conversion of carboxylic groups to their amine salts with pyridine[15]. Similar trends were also observed between samples 9, 12, and 15, and their spectra are illustrated in Figure 4.

^{1}H and ^{13}C NMR Spectra

Sample 11 was analyzed by ^{1}H NMR spectroscopy, and its spectrum is given in Figure 5. As compared to the native hemicelluloses (spectrum not shown), the new peaks at 2.5 and 2.4 ppm are attributed to the methylene proton connecting the carboxylic group (-CH$_2$-COOH) and ester group (-CH2-COOR), respectively[9]. The chemical shifts of 4.0–4.9 and 3.4–3.8 ppm are assigned to the equatorial proton and other protons of the anhydroxylose units of hemicelluloses, respectively. Additionally, the methyl protons of the 4-O-methyl-D-glucuronic acid give peaks as a triplet at 0.8–1.1 ppm that are found in the ^{1}H NMR spectrum of the native hemicelluloses as well[21].

The ^{13}C NMR spectrum obtained for sample 1 having a lower degree of substitution is shown in Figure 6. From comparison with the
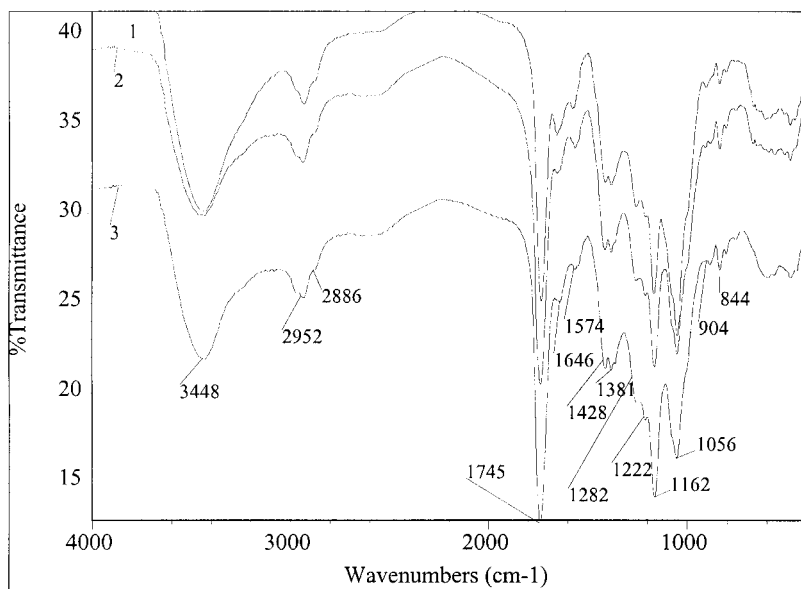
FIGURE 3 FT-IR spectra of succinylated hemicellulosic preparations 1 (spectrum 1), 3 (spectrum 2) and 6 (spectrum 3).

spectrum obtained from the native hemicelluloses (spectrum not shown), it is clear that the presence of signal between 18.8 and 30.9 ppm and two groups of bands centered at 167.0 (data not shown) and 182.5 ppm is indicative of the occurrence of methylene carbon atoms and carbonyl ester and carboxylic acid groups, respectively, corresponding to the formed monosuccinate groups. The signals at 50.8, 51.4, 62.4 and 82.3 ppm arise from the –C–O group in esters. The presence of five peaks at 98.9, 77.2, 76.7, 76.5 and 67.8 ppm corresponds to carbon atoms of C_1, C_4, C_3, C_2, and C_5 in the β-D-Xyl$p$ units of hemicelluloses. The signals at 86.6, 78.5, 77.7 and 66.0 ppm relate to C_4, C_2, C_3, and C_5 of α-L–Ara$f$ residues, respectively. The peak at 73.8 ppm represents C_2 in 1,2,4-linked β–D–Xyl$p$ units. The methyl group in 4-O-methyl-D-glucuronic acid of hemicelluloses exhibits a small signal at 15.3 ppm[22]. The presence of these signals was in agreement with the fact that the succinoylation reaction of a hydroxyl group of hemicelluloses causes an upfield shift of the resonance of the adjacent carbons, and that the resonance of the carbon directly linked to a modified hydroxyl group is shifted downfield with respect to the chemical shift of the carbon bearing an unsubstituted hydroxyl group.
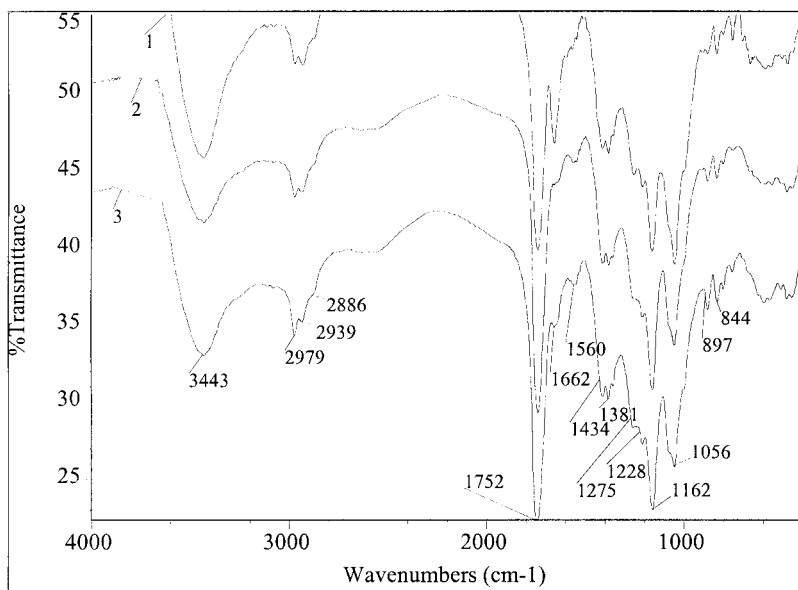
FIGURE 4 FT-IR spectra of succinylated hemicellulosic preparations 9 (spectrum 1), 12 (spectrum 2) and 15 (spectrum 3).
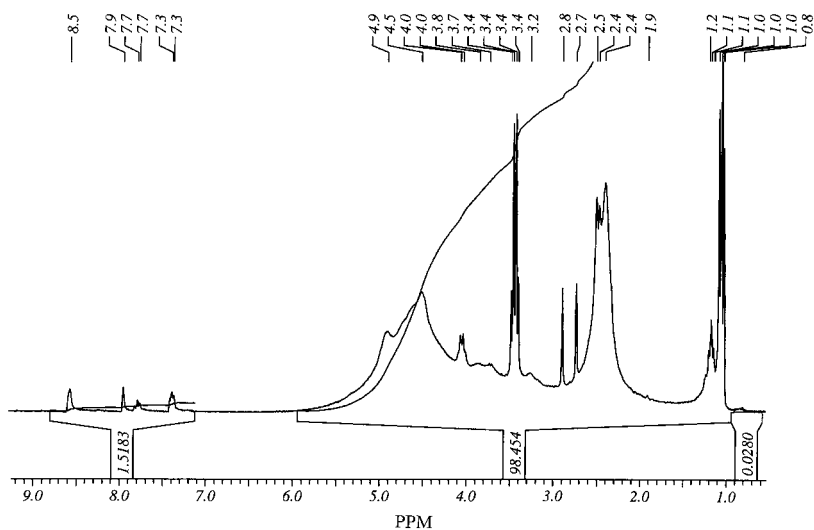

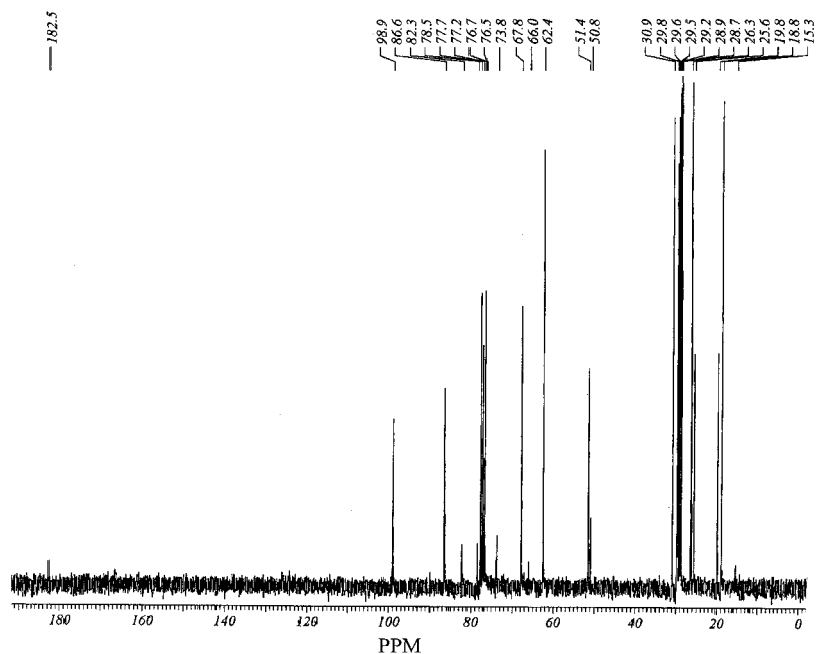**FIGURE 5** ^{1}H NMR spectrum of succinylated hemicellulosic preparation 11.

FIGURE 6 ^{13}C NMR spectrum of succinylated hemicellulosic preparation 1.

Arranz[6] reached similar conclusions in the study of succinoylation of dextran by quite different methods.

Thermal Analysis

The thermal stability of the succinylated polymers was studied by TGA. From a previous study of ours in oleoylated hemicelluloses, it was found that they have higher thermal stability than native hemi-celluloses[4]. In this study, the thermal stability of both unmodified and succinylated hemicellulosic samples was comparatively examined in the temperature range from 25 to 600°C. Figure 7 presents the TGA and DSC thermograms of native hemicelluloses (a) and succinylated poly-mer samples 2 (b) and 10 (c). As observed, the unmodified hemi-celluloses and succinylated polymer samples 2 and 10 are stable up to 207°, 201° and 201°C, respectively. Beyond these temperatures, ther-mal degradation takes place, depending mainly on the degree of sub-stitution of the hemicelluloses. For example, at 50.0% weight loss the decomposition temperatures of native and succinylated polymer
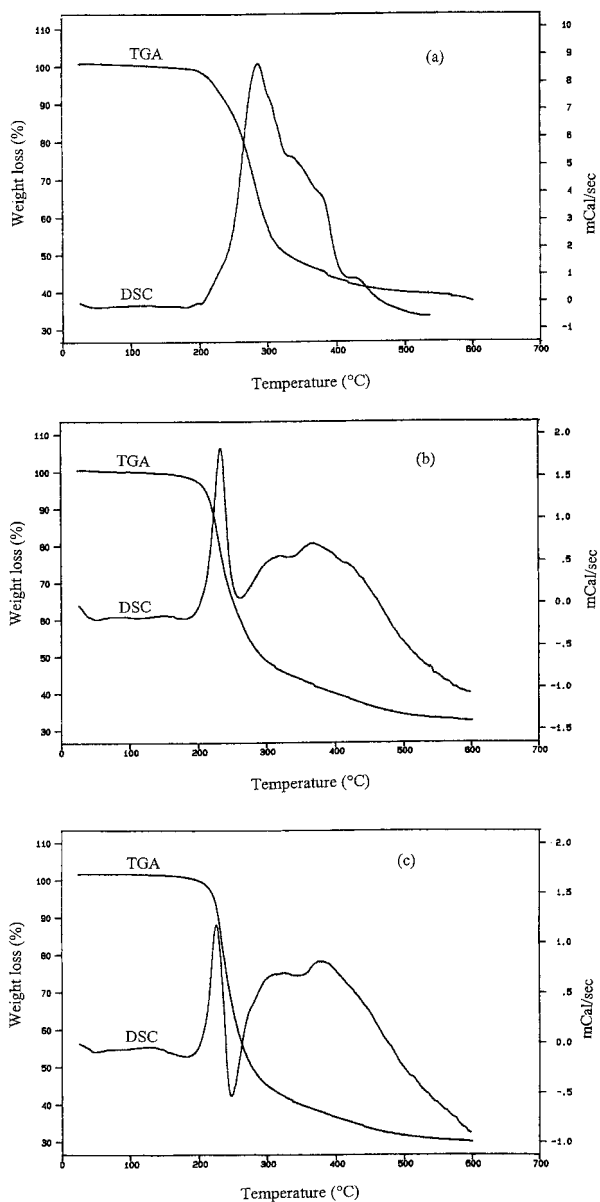
FIGURE 7 Thermograms of native hemicelluloses (a) and succinylated hemi-cellulosic samples 2 (b) and 10 (c).

samples 2 and 10 were observed at 335°C, 295°C and 278°C, respectively. These results revealed that the unmodified hemicelluloses appeared to be more stable than succinylated polymers since their decomposition started at higher temperature. Comparing the thermal stability of the esterified hemicelluloses, no significant differences occurred between the samples, although their thermal degradation relied on the degree of substitution. This lower thermal stability of the succinylated polymers was probably due to the higher amounts of carboxylic acid groups after esterification. However, this thermal stability of the succinylated hemicelluloses to over 200°C is rather satisfactory.

DSC was used to investigate the possibility of interaction between both components[19]. From Figure 7 it is evident that the thermogram of unmodified hemicelluloses exhibited only an exothermic peak, indicating only one component, whereas the succinylated polymer samples 2 and 10 produced both exothermic and endothermic peaks on their thermograms, implying a reaction between native hemicelluloses and succinic anhydride. The endothermic peak was attributed to the melting of the crystallized part of the product. As illustrated in Figure 7, the succinylated polymer samples 2 and 10 gave endothermic peaks at 262° and 248°C, respectively, and their peak intensity increased with the degree of substitution. In other words, the curve of the higher substituted hemicelluloses exhibited a larger endothermic peak and shifted towards lower temperatures. This indicated that some interactions developed between the components of succinylated polymers. This fact reinforced our assumption of mono-esterification between hemicelluloses and succinic anhydride in DMF/LiCl system.

CONCLUSIONS

From the above studies, it can be concluded that succinoylation of hemicelluloses in DMF/LiCl system was an efficient chemical modification for obtaining polymers with carboxylic groups. The preferred reaction conditions that led to the highest degree of substitution were as follows: 6:1 reactant molar ratio, 80°C, 12 h, 2:1 DMF/PY, in which over 90% of the free hydroxyl groups in native hemicelluloses were succinylated. Increasing the molar ratio of succinic anhydride/anhydroxylose unit in native hemicelluloses from 1:1 to 6:1 and reaction time from 1 to 12 h resulted in an increment of product yield by 22.8 and 24.1%, respectively. The thermal stability of the products decreased by chemical modification, but this thermal stability of the succinylated hemicelluloses to over 200°C is rather satisfactory.

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