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Succinoylation of sago starch in the *N*,*N*-dimethylacetamide/lithium chloride system

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Abstract

The modification reaction of sago starch with succinic anhydride (SA) using pyridine (PY) and/or 4-dimethyaminopyridine (DMAP) as catalyst and *N*,*N*-dimethylacetamide (DMA)/lithium chloride (LiCl) system as solvent was studied. A series of succinylated starch derivatives were prepared with a degree of substitution (DS) ranging from 0.14 to 1.54. The structure of the resulting polymers determined by means of ^{13}C NMR spectroscopy indicated that substitution preferably occurs at the C_2 and C_6 hydroxyl groups. The thermal stability of the material was decreased by chemical modification. Effects of reactant molar ratio, reaction time, and the concentrations of DMAP and LiCl on the reaction efficiency are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Sago starch; Succinoylation; *N*,*N*-dimethylacetamide; Thermal stability

1. Introduction

Sago starch is obtained from the stems of sago palms, and is a useful resource for foodstuffs (Muhammad, Hussin, Man, Ghazali & Kennedy, 2000). Sago starch can be used for the same purpose as any other kind of starch. As a cheap and adequate source of energy, sago starch fulfils a vital need for the local people. Traditionally, it is processed into various products such as sago noodle, sago biscuit, and sago pearl (Cui & Oates, 1997). Although sago starch was used for a long time especially in south east Asia in the food industry, a large portion of it has not yet sufficiently been utilised (Ahmad, Williams, Doublier, Durand & Buleon, 1999). In addition, the starches from corn, waxy maize, tapioca, and potato are widely used by commercial derivatisation for industries such as in food and paper industries. However, the large amounts of sago starch, which has a potential market, have not been commercially derivatised for industrial materials. Thus, the development of effective technologies for derivatisation of sago starch as novel materials for industries is considered to be both important and significant.

One very attractive feature of starch is its chemical composition, with a large amount of relatively easily accessible hydroxyl groups that can be used for the attachment of a variety of functional groups. The preparation of a wide range of starch esters has been performed under variable reaction conditions. Such modifications have a renewed interest for the preparation of modified starches with acetate, hydroxypropyl, alkyl siliconate, and fatty acid ester groups to impart water resistance to the products in order to replace partially or totally the synthetic non-biodegradable plastics. Replacement of petroleum-based plastics with materials from agro-resources, particularly starch, is attractive from the standpoint of providing biodegradation properties to the end product (Aburto, Alric, Thiebaud, Borredon, Bikiaris, & Prinos et al., 1999). Formation of starch succinates and adipates increases the hydrophilicity of modified starches. Furthermore, high densities of starch side-chain carboxylic groups provide useful properties such as metal chelation (Jeon, Viswanathan & Gross, 1999). In addition, starch succinates offer a number of very desirable properties such as high viscosity, low-temperature viscosity stability, high thickening power, low gelatinisation temperature, clarity of cooks, and good filming properties. Thus, succinate derivatives have been recommended as binders and thickening agents in foods, tablet disintegrants in pharmaceuticals, surface sizing agents and coating binders in paper (Wang, Shogren & Willett, 1997). Modifying starch

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with anhydrides such as succinic and maleic or phthalic anhydride represents a potential way of introducing new material properties.

During the past ten years, our research group has been involved in modification reactions from renewable and biodegradable polysaccharides such as hemicelluloses from agricultural straws and starch from sago palm (Fang, Sun, Fowler, Tomkinson & Hill, 1999; Sun, Tomkinson, Liu & Geng, 1999). One challenge in attaining rapid and homogenous reactions with control over the degree of substitution (DS) has been to find a suitable solvent for the hemicelluloses and starch, respectively. Dimethylformamide (DMF)/lithium chloride (LiCl) was found to be served as good solvent for hemicelluloses, whereas dimethylacetamide (DMA)/LiCl was observed to be served as good solvent for starch, allowing a variety of uniform reactions to be conducted under homogeneous conditions, in which the substitutions along the polysaccharide backbone can be attached with satisfactory yields and with little depolymerisation of the polysaccharides chain.

In this study, carboxylic acid functionalities were introduced to sago starch by modification with succinic anhydride (SA) in the *N*,*N*-dimethylacetamide/LiCl systems under various conditions. The modified starches were then characterized by yield of succinoylation, DS, Fourier transform infrared (FT-IR) and ^{13}C nuclear magnetic resonance (NMR) spectroscopies, and thermal analysis.

2. Experimental

2.1. Materials

The meal of sago palm was kindly supplied by the south China University of agriculture, Guangzhou, and was ground to pass a 1.6 mm screen. The ground sago pith was dried in a cabinet oven with air circulation for 16 h at 50°C. DMA solvent was dried prior to use according to conventional methods. Anhydrous LiCl was dried at 130°C for 2 h before use. SA and 4-dimethyaminopyridine (DMAP) were purchased from sigma chemical company (Xian, China).

2.2. Extraction of sago starch

The ground sago palm pith (120 g) was steeped in 1500 ml water for 4 h at 25°C. A ratio of one part soaked grains to three parts distilled water was mixed in a Warring blender at low speed. The resultant slurry was then passed through a 20 μm nylon cloth. The residue was washed five times with distilled water and dried at 55°C in an oven for 16 h. The combined extractions were concentrated by a rotary vacuum evaporator at 40°C. The water-soluble sago starch was obtained by precipitation of the concentrated filtrate with four volumes of ethanol. After being washed with 70% ethanol, the isolated water-soluble sago starch was air-dried with a yield of 56.8%. The starch contained 10.8% moisture (determined from the weight loss after drying in an oven at 105°C for 2 h), 2.8% β-glucan, 1.8% hemicelluloses, 0.1% ash, 0.15% lipids, and 0.10% crude protein.

2.3. Succinoylation of sago starch

The succinic derivatives of starch containing free carboxylic groups were prepared by reaction of the water-soluble sago starch with SA in DMA/LiCl systems, and its procedure was as follows: 0.81 g starch (0.015 mol of hydroxyl functionality) was added in 15 ml water under stirring and heated to 95°C until completely dissolved (approximately 5 min). Then 20 ml DMA was added and the reaction was stirred for 5 min. The water was removed from the swollen gel by repeated distillation under reduced pressure at 50°C. After addition of required amounts of LiCl and DMAP, the swollen starch was succinylated by addition of 30 ml of pyridine (PY) and either 1.5 g (0.015 mol of carboxyl functionality, molar ratio 3:1) or 3.0 g (0.03 mol of carboxyl functionality, molar ratio 6:1) SA, previously dissolved in 10 ml DMA, over a time period of 10 min, respectively. The homogeneous reaction mixture was stirred for a total period of 0.5, 1, 1.5, 2, 2.5, and 3 h at 105°C, respectively. Upon completion of the reaction, the resulting reaction mixture was cooled to room temperature, and the soluble succinylated product was isolated by precipitation with 120 ml of ethanol with stirring. The white product that separated from the solution was filtered off and washed thoroughly with ethanol and acetone to eliminate any colour impurities and by-products. Finally, the product was first air-dried for 24 h and then further dried in an oven at 55°C for another 18 h.

2.4. Characterization of the succinylated sago starch

Yield percentages were calculated based on the assumption that all the starch was converted to tri-succinylated starch. In the case the yield percentage and the degree of substitution (DS) would be 100% and 3.0, respectively. The unreacted SA in the mixture of reactions was separated from the product by dissolving in ethanol and acetone.

The chemical structure of the starch derivatives was evaluated by FT-IR 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. Solution-state ^{13}C-NMR spectra were obtained on a Bruker MSL-300 spectrometer at 300 and 74.5 MHz. They were 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 s delay time between scans were used.

Thermal stability of succinylated starch was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyser (NETZSCH STA-409). The sample weighed between 10 and 15 mg. The scans were run from room

Table 1
The yield (Based on assumption that all of the starch is converted to tri-succinylated starch (yield, 100%; DS, 3.0). If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 35.1% for succinoylation with a DS value of 0.0) of succinylated sago starch and the DS

Succinoylation condition						Succinylated starch		
Molar ratio[a]	T[b]	Time (h)	(DMA/PY[c])	L/S[d]	DMAP[e]	Preparation No.	Yield (%)	DS[f]
3:1	105	2	1/1	1:1	0	1	51.1	0.74
3:1	105	2	1/1	1.5:1	0	2	56.7	1.00
3:1	105	2	1/1	3:1	0	3	58.9	1.10
3:1	105	2	1/1	6:1	0	4	61.5	1.22
3:1	105	2	1/1	9:1	0	5	68.0	1.52
3:1	105	2	1/1	12:1	0	6	57.6	1.04
6:1	105	2	1/1	1:1	0.025	7	64.5	1.36
6:1	105	2	1/1	1:1	0.075	8	67.6	1.50
6:1	105	2	1/1	1:1	0.10	9	67.6	1.50
6:1	105	2	1/1	1:1	0.15	10	68.0	1.52
6:1	105	2	1/1	1:1	0.20	11	68.4	1.54
3:1	105	0.5	1/1	1:1	0	12	38.0	0.14
3:1	105	1	1/1	1:1	0	13	43.3	0.38
3:1	105	1.5	1/1	1:1	0	14	48.5	0.62
3:1	105	2.5	1/1	1:1	0	15	55.4	0.94
3:1	105	3	1/1	1:1	0	16	58.9	1.10

[a] Molar ratio represents the mol of SA/mol of anhydroglucose units in starch.
[b] Abbreviation for reaction temperature (°C).
[c] Abbreviation for *N*,*N*-dimethylacetamide/PY (v/v).
[d] Abbreviation for the mol of lithium chloride/mol of anhydroglucose units in starch.
[e] Abbreviation for 4-dimethylaminopyridine added (g).
[f] Abbreviation for DS.

temperature to 600°C at a rate of 10°C/min under a dry air atmosphere.

3. Results and discussion

3.1. Yield and degree of substitution

The modification of starch in the DMA/LiCl system represents a suitable and effective method for the chemical modification of starch, particularly esterification. The system acts as a solvent for both the starting starch and the final products. By using different amounts of SA, it is possible to prepare esters with different degrees of substitution (DS). In this case, the theoretical maximum DS is 3.0. Table 1 gives the experimental conditions for the succinoylation reaction and the corresponding yield and DS. It is presumed that one attached succinic acid will result in one carboxylic acid. Due to the lack of associated unreacted SA in the isolated products, the DS values of the starch derivatives were calculated from the yield percentage of succinylated starch on the assumption of each anhydroglucose unit in starch containing three free hydroxyl groups, and each SA molecule reacting with one free hydroxyl group in one carboxylic acid.

To determine possible degradation of the starch in the system, a control experiment was carried out in which the starch was exposed to the same reaction condition (105°C, 2 h, DMA/PY = 1:1, L/S = 1:1), but in the absence of SA. The determined weight loss was 1.8%, indicating that no significant degradation occurred under the reaction condition given. Similar phenomenon was observed during the esterification of hemicelluloses in *N*,*N*-dimethylformamide (DMF)/LiCl systems using triethylamine as a catalyst (Fang et al., 1999). Furthermore, based on modification reaction of dextran with SA using PY as catalyst and DMF/LiCl system as solvent, Arranz, Sanchez-Chaves & Ramirez (1992) demonstrated that the acylation reaction is more efficient in the presence of PY and the reaction rate depends on the SA concentration. Further studies found that the reaction without catalyst can be interpreted by using a second-order rate law. In contrast, it is not possible to interpret the equimolecular reaction catalysed by PY by a second order rate law. It is clear that two different mechanisms occurred during the reaction, without catalyst and with catalyst (Arranz et al., 1992). In this study, the succinoylation reactions were, therefore, performed using PY and/or DMAP as catalyst at two different reactant molar ratios and various reaction times. As can be seen from the Table 1, the yield and DS ranged from 38.0 to 68.4% and from 0.14 to 1.54, respectively, and were found to increase with the reaction time, reactant molar ratio, DMAP concentration, and mole of LiCl. Lowest yield (38.0%) and DS (0.14) was obtained with preparation 12 when a short period of reaction time (0.5 h) was used, suggesting that if the succinoylation reaction did not proceed to give a high DS, mostly unreacted

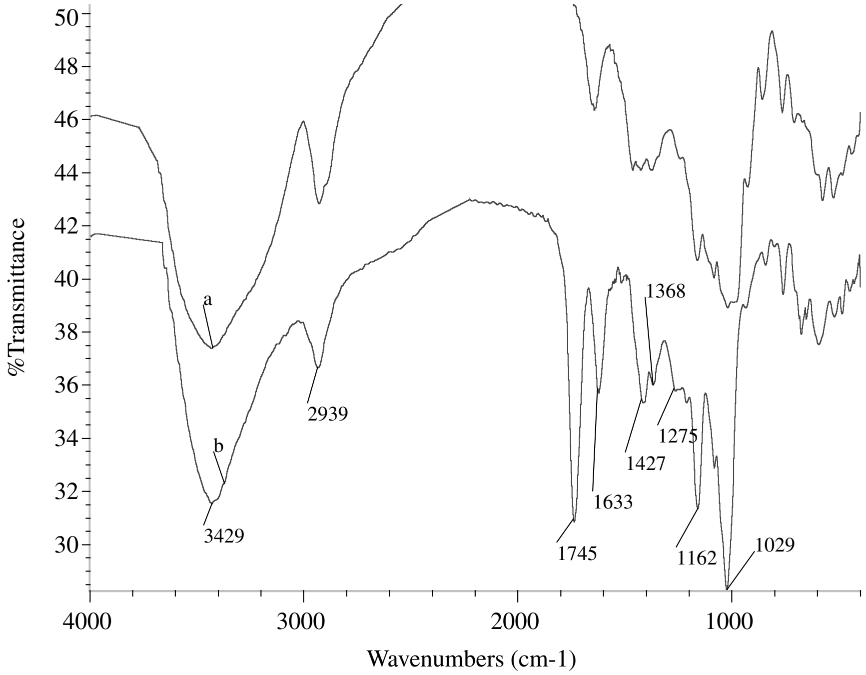

Fig. 1. FT-IR Spectra of native sago starch (spectrum a) and succinylated sago starch preparation 2 (spectrum b).

or lightly succinylated starch was obtained. On the other hand, sample 11 with a reactant molar ratio of 6:1 and an addition of 0.2 g DMAP as a catalyst gave a highest yield of 68.4% with a DS value of 1.54. This increase of reaction efficiency with reactant molar ratio could be interpreted in terms of greater availability of SA molecules in the proximity of the starch molecules at higher concentration of the esterifying agent (Khalil, Hashem & Hebeish, 1995). An increase in DS from 1.36 (sample 7) to 1.54 (sample 11) with an increase in the amount of DMAP used from 0.025 to 0.20 g revealed that DMAP is a useful catalyst for the succinoylation of sago starch, especially at low quantities between 0.025 and 0.075 g. Its use must be limited. Meanwhile, as shown in samples between 12 and 16, an extension of reaction time from 0.5 (sample 12) to 1.0 (sample 13), to 1.5 (sample 14), to 2.5 (sample 15), and to 3.0 h (sample 16) resulted in a significant increment of DS from 0.14 to 0.38, to 0.62, to 0.94, and to 1.10, respectively.

The data in Table 1 (samples 1–6) indicated that the concentration of LiCl also had an important effect on the SA bondings and the reaction efficiency. Increase in molar ratio of LiCl//anhydroglucose units in starch from 1:1 to 9:1 led to an increment in the yield and DS from 51.1 to 68.0% and 0.74 to 1.52, respectively. In contrast to the increasing trend, the succinoylation yield decreased by growth of the molar ratio from 9:1 to 12:1, indicating a highest value was obtained with a moderated molar ratio of LiCl/anhydroglucose units in starch (9:1). In a previous study on homogenous esterification of hemicelluloses (Fang et al., 1999), we found that DMF/LiCl acted as the solvent for the esterified hemicelluloses, which would ensure not only high substitution but also more uniform substitution due to greater accessibility of the reagent. DMA has structural characteristics similar to DMF and, therefore, is expected to allow complete solvation of the succinylated starch in the presence of LiCl. McCormick and Callais (1987) have also reached similar conclusions for the derivatisation of cellulose in DMA/LiCl solutions. The mechanism of complexation of DMA/LiCl with chitin (Terbojevich, Carraro & Cosani, 1988; Vincendon, 1985) has been extensively investigated. It has been suggested that Li^+ complexes with the carbonyl atoms of up to four DMA molecules to produce a macrocation, leaving the Cl^- free to hydrogen bond with the hydroxyl protons. This competitive hydrogen bond formation serves to disrupt the existing intra- and intermolecular hydrogen bonding, therefore enabling solubilisation of the product (McCormick & Dawsey, 1990; Williamson, Armentrout, Porter & McCormick, 1998). In this study, the solution remained clear throughout the reaction by using a 1:1 volume ratio of DMF/PY as both solvent and catalyst, indicating homogeneous reaction of the succinoylation. In addition, we also found that first dispersion of native sago starch in water and then reaction in DMA/LiCl system can lead to a highly swollen gel suspension of the polymer and activate the polymers. All in all, the esterification of sago starch in DMA/LiCl represents a suitable and effective method for the preparation of succinylated starch. The DS can be simply controlled by the molar ratios of SA or LiCl/anhydroglucose units in starch and the concentration of DMAP catalyst. It is very likely that for a complete substitution (DS = 3.0), a higher proportion of SA and a longer reaction time are needed.

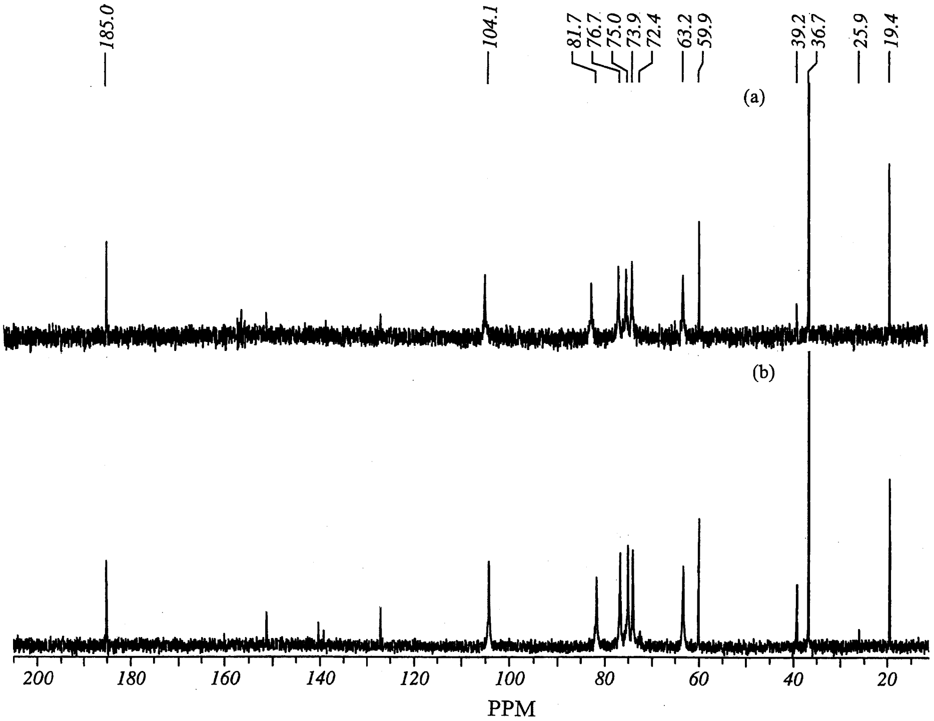

Fig. 2. ^{13}C NMR Spectra of succinylated sago starch preparations 13 (spectrum a) and 12 (spectrum b).

3.2. FT-IR Spectra

FT-IR Spectra of native sago starch (spectrum a) and succinylated sago starch preparation 2 (spectrum b) are depicted in Fig. 1. Obviously, the succinylated starch spectrum b is characterized by the presence of two important ester bands at 1745 and 1162 cm^{-1}. The former band at 1745 cm^{-1} is attributed to absorption by carbonyl bonds in esters. The latter band at 1162 cm^{-1} is assignated to the C–O stretching in the esters (O=C–O–CHCH$_2$–) (Fringant, Desbrieres & Rinaudo, 1996; Marcazzan, Vianello, Scarpa & Rigo, 1999). It is very likely that the carbonyl bonds in free carboxylic acids at 1712 cm^{-1} strongly overlapped with the previous one, and the formation of the monoester in the homogeneous esterification was dominant. On the other hand, it should be noted that, with longer reaction time, starch-attached succinic acid may continue to react with hydroxyl groups in crosslinking reactions. As illustrated in Fig. 1, the presence of the ester band at 1745 cm^{-1} alone also implied that reaction at both carboxylic groups occurred with the formation of diesters. The extent of crosslinking has been reported to be dependent on reaction time, the concentration of reactants and catalyst during the succinoylation of cellulose (Gellerstedt & Gatenholm, 1999; Hirabayashi, 1984). In this study, it is possible that PY can reduce crosslinking since it is capable of forming sats with carboxylic groups. The reason for the minor occurrence of crosslinks in the DMA/LiCl homogenous system is probably due to the extreme distance between hydroxyl groups on adjacent starch chains (Hirabayashi, 1984). The coupling of O–H deformation and C=O stretching in carboxylic acid gives a peak at 1427 cm^{-1} (Bruneel & Schacht, 1994). A shoulder at 1275 cm^{-1} is indicative of carbon single bonded hydroxyl group (O=C–OH) stretching vibration in carboxylic acid. In comparison, the band at 1029 cm^{-1}, which relates to the symmetrical stretching of an ether bond (C–O–C) in both native and succinylated sago starch, was not changed significantly, indicating that the α-glucosidic linkages between the sugar units were not modified by the succinoylation reaction. The absorption at 1633 cm^{-1} is principally associated with the absorbed water (Kacurakova, Belton, Wilson, Hirsch & Ebringerova, 1998; Sun, Tomkinson, Ma & Liang, 2000). The strong band at 3429 cm^{-1} is due to the OH stretching in both native and succinylated sago starch, and its intensity decreased in the esterified derivatives (Aburto, Thiebaud, Alric, Borredon, Bikiaris & Prinos et al., 1997). The methylene group deformation occurs at 2939 cm^{-1}. As expected, the disappearance of peaks at 1850 and 1780 cm^{-1} in spectrum b confirmed that the products are free of the unreacted SA (Gu & Yang, 1998; Yang & Wang, 1996).

3.3. ^{13}C NMR spectra

The chemical changes in the structure of succinoylated starches were also verified by ^{13}C NMR spectroscopy. Fig. 2 gives the ^{13}C NMR spectra of succinylated sago starch preparations 13 with a DS value of 0.38 (spectrum a) and 12 with a DS value of 0.14 (spectrum b). Clearly, the

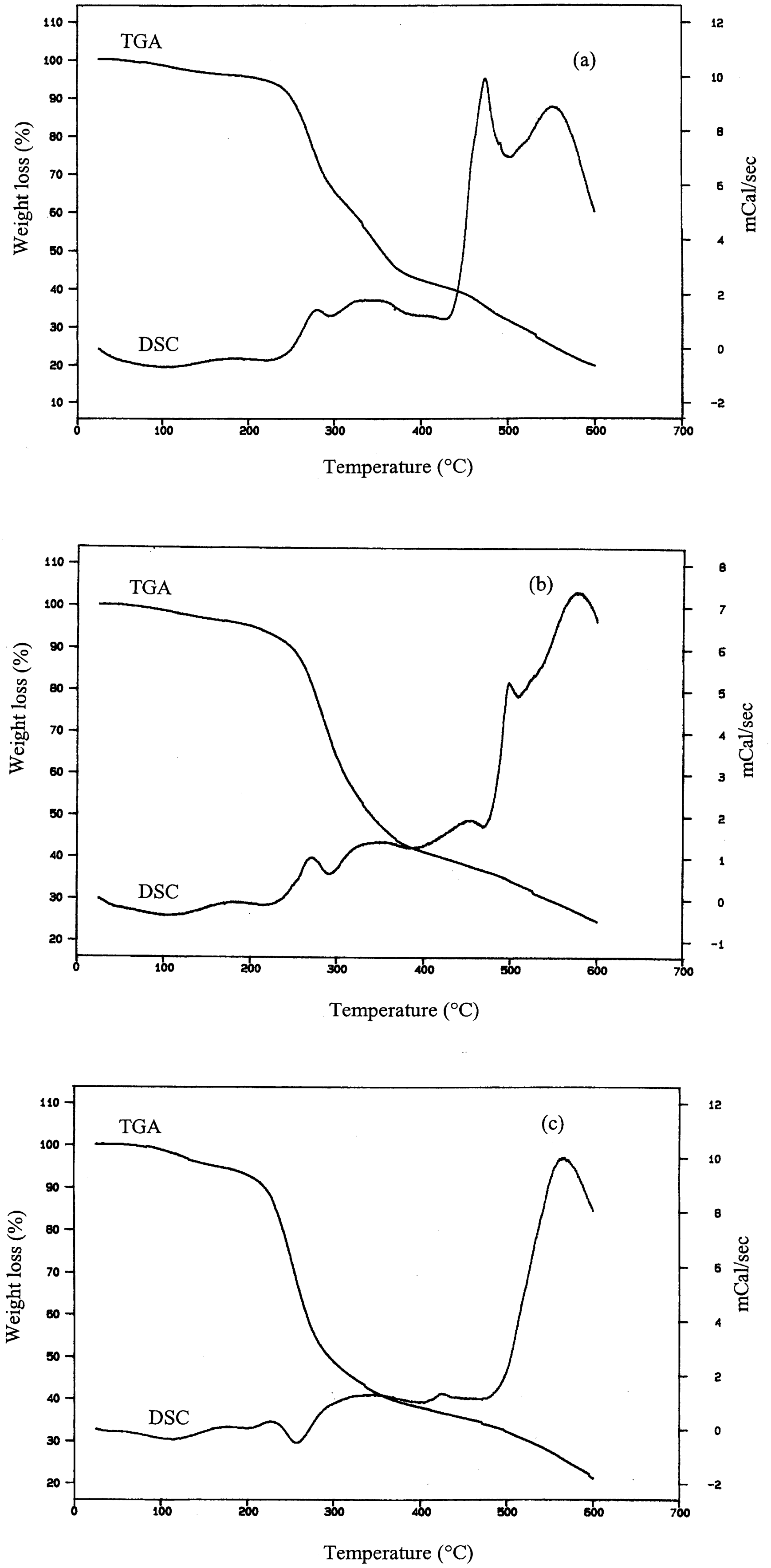

Fig. 3. The thermograms of succinylated sago starch preparations (a) 12, (b) 1, and (c) 7.

occurrence of four signals at 19.4, 25.9, 36.7, and 39.2 ppm indicative of presence of methylene carbon atoms and a group band at 185.0 ppm for characteristic of carboxylic acid groups supported the monoester reaction under the succinoylation conditions given. It is important to note that the C=O signal in carbonyl ester groups does not appear in both of the spectra in Fig. 2 due to the slight succinoylation as shown by the much lower DS values between 0.14 and 0.38, however, the C–O signal in carbonyl ester groups or carboxylic groups occurs at 59.9 ppm.

It is known that, in general, primary hydroxyl groups are more reactive than secondary hydroxyl groups, and for carbohydrates, the secondary hydroxyl groups at C_2 are more reactive than the hydroxyl groups at C_3 and C_4 (Bruneel & Schacht, 1994; Sierakowski, Milas, Desbrieres & Rinaudo, 2000). As can be seen from the Fig. 3, the carbon atoms of C_1, C_4, C_3, C_2, C_5, and C_6, in the anhydroglucose units of sago starch can be unambiguously attributed on both spectra with signals at 104.1, 81.7, 76.7, 75.0, 73.9, 72.4, and 63.2 ppm, respectively. To assign the site of substitution after reaction of starch with SA, a comparison of the two succinylated starch spectra and with the native sago starch spectrum (spectrum not shown) was carried out. In the case of experimental conditions used in the present work, the spin-lattice relaxation times and the nuclear overhauser effect factors of all six carbons of the anhydroglucose units must be very similar in order to evaluate the relative DS values for individual hydroxyl groups attached to C_2, C_3, and C_6-carbons by peak area. The results showed that the intensity of signals at C_6 and C_2 carbons of anhydroglucose unit decreased from native starch to succinylated sago starch sample 12 (spectrum b) and to the sample 13 (spectrum a), indicating that a partial substitution occurred at both C_6-primary hydroxyl group and the C_2-secondary hydroxyl group. A slightly more reduced intensity at C_2 hydroxyl group than that at C_6 hydroxyl group in spectrum a for sample 13 with a DS value of 0.38 revealed that during succinoylation the hydroxyl groups at C_2 reacted preferably. These observations were, in general, consistent with the results obtained from the modification of reaction of dextran with SA using PY as catalyst and DMF/LiCl system as solvent by Arranz et al. (1992). The authors reported that the reactivity of individual hydroxyl groups decreased in the order $C_2 \approx C_3 > C_4$, and for samples with higher DS the order was $C_4 > C_3 > C_2$, which were explained by considering the formation of intramolecular hydrogen bonds as well as by steric considerations.

3.4. Thermal properties

To investigate the thermal stability of the prepared esters, the degradation properties were examined as a function of weight loss and the DS. From a previous study of ours in water-soluble sago starch, it was found that the sago starch was thermally stable up to 276°C. Beyond this temperature, thermal degradation occurred (Morita, 1956; Sun & Tomkinson, 2000). Fig. 3 presents the TGA thermograms of samples (a) 12 with a DS value of 0.14, (b) 1 with a DS value of 0.74, and (c) 7 with a DS value of 1.36. As observed, the succinylated sago starch samples 12, 1, and 7 started decomposition at 226, 215, and 200°C with an increase in DS from 0.14 to 0.74, and to 1.36, respectively. Weight loss was 10.0% when the temperature reached 256°C for sample 12, 254°C for sample 1, and 219°C for sample 7, respectively. Similarly, as the temperature was raised to 300°C, the weight loss accounted for 33% for sample 12, 37% for sample 1, and 50% for sample 7, respectively. These data verified that the succinylated sago starch had lower thermal stability than unmodified sago starch, and the thermal stability decreased with the DS. However, this is still a satisfactory thermal stability of the succinylated sago starch up to 200°C.

In Fig. 3 DSC curves were also performed to examine the transitions as affected by modification with SA. As illustrated in Fig. 3, all three succinylated sago starch samples displayed one noticeable endothermic transition with a peak at 298°C for sample 12, 293°C for sample 1, and 257°C for sample 7, respectively. This observation suggested that succinoylation had a great effect on the temperature of this endothermic transition, which decreased with an increase in DS. This endothermic peak is attributed to the melting of the crystallised part of the polymers since some part of the succinylated starch chains can arrange and crystallise as the temperature increases (Fringant et al., 1996).

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