ELSEVIER

Carbohydrate Polymers 47 (2002) 245–252

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

The preparation and characterisation of a series of chemically modified potato starches

J.M. Fang[a], P.A. Fowler[a,*], J. Tomkinson[a], C.A.S. Hill[b]

[a]*The BioComposites Centre, University of Wales, Bangor, Gwynedd LL57 2UW, UK*
[b]*The School of Agricultural and Forest Sciences, University of Wales, Bangor, Gwynedd LL57 2UW, UK*

Received 1 December 2000; accepted 11 January 2001

Abstract

A range of substituted starches has been prepared at moderate temperature (≤90°C) from gelatinised potato starch by treatment in lithium chloride/*N*,*N*-dimethylacetamide (DMAC) solution with acyl chlorides. Oleoyl, palmitoyl, lauroyl, capryloyl and butyryl modified starches have been synthesised with degrees of substitution (DS-values) ranging from 0.3 to 3. Characterisation by FT-IR spectroscopy and elemental analysis has confirmed reaction and degree of substitution obtained. DS-Values were controlled by metered addition of stoichiometric quantities of the required acyl chloride. Such structural modification of starch resulted in a significant change of physicochemical properties, and increased hydrophobicity with increasing acylation extent. It was found that the modified starches had improved thermal stabilities and enhanced solubilities in organic solvents.

Keywords: Starch; Esterification; Modification

1. Introduction

Starch is a naturally occurring polysaccharide that has been widely studied for many years in the field of materials (Ellis, Cochrane, Dale, Duffus, Lynn, Morrison et al., 1998; Houghton, 1938). However, the hydrophilic nature of starch is a major constraint that seriously limits the development of starch-based materials. Chemical derivatisation has been studied as a way to solve this problem and to produce water resistant materials (Peltonen & Harju, 1996). Depending on the nature of the substituents and on the degree of substitution (DS), the properties of the modified starch can be varied extensively (Röper, 1996). Esterification with organic acids is known to result in thermoplastic and hydrophobic materials when the DS is high enough (Peltonen & Harju, 1996).

A number of groups have recently reported the use of organic solvents and mixtures thereof to achieve firstly starch solubilisation and then modification (Aburto, Alric, Thiebaud, Borredon, Bikiaris, Prinos et al., 1999; Fringant, Rinaudo & Bardet, 1998; Heinze, Talaba & Heinze, 2000; Peltonen & Harju, 1996). Indeed this centre has developed one such route (Hylnianski, 1997). We report now on the versatility of this method for the modification of potato starch to defined levels of substitution, by metered addition of acylating agent to a presolubilised starch.

2. Experimental procedures

2.1. Materials

Potato starch was obtained from Fluka AG. Butyryl, capryloyl, lauroyl, palmitoyl, and oleoyl chlorides were purchased from Fisher Scientific. Lithium chloride (anhydrous) and pyridine were obtained from Lancaster Synthesis Ltd. *N*,*N*-Dimethylacetamide (DMAC) was purchased from Aldrich Chemical Company. All reagent grade chemicals were used without further purification.

2.2. Preparation of acylated starch

A mixture of H_2O (500 ml) and potato starch (60 g, 0.37 mol) was heated to 80°C, with stirring, and the mixture was maintained at that temperature for ca. 1 h. DMAC (500 ml) was added and the temperature was re-adjusted to 80°C. A mixture of DMAC and H_2O (ca. 1500 ml) was removed by distillation under reduced pressure at 90°C whilst, at the same time, aliquots of DMAC (250 ml) were added to maintain a reaction volume minimum of 500 ml. This process was repeated until the mixture was deemed anhydrous by obtaining a DMAC distillate of constant

* Corresponding author. Fax: +44-1248-370-594.
E-mail address: p.a.fowler@bangor.ac.uk (P.A. Fowler).

0144-8617/02/$ - see front matter
PII: S0144-8617(01)00187-4

boiling temperature. LiCl (3 g, 0.07 mol) was then added, with stirring. After 10 min, the reaction temperature was adjusted (Table 1) according to the modification to be made, appropriate quantities of pyridine and acyl chloride were added (Table 1) and the solution was stirred for 30 min. With the exception of Reaction No. 3 (see below), the mixture was poured into vigorously stirred aqueous MeOH (70% v/v) (1500 ml) whereupon the product precipitated. It was washed with further aqueous methanol (2×1500 ml) and dried at 40°C. The crude product was re-dissolved in hot toluene (3000 ml) and then precipitated by addition to acetone (2×1000 ml). The product was filtered and dried overnight (50°C) before weighing. The dried samples were stored in a vacuum desiccator over P_2O_5 for further analysis.

In the case of Reaction No. 3, the reaction mixture was subjected to exhaustive dialysis by treatment in visking tubing (MWCO 12–14,000 daltons) with H_2O to obtain salt- and solvent-free material after isolation by evaporation from H_2O. The glassy sample was stored in a vacuum desiccator over P_2O_5 for further analysis.

2.3. General methods and analysis

Elemental analysis was performed on dry, finely ground samples using a Carlo Erba EA 1108 CHN S-O instrument. DS-Values for acylated starch were calculated on the basis of measured % C.

Fourier transform infrared (FT-IR) spectra were acquired on a Nicolet 750, series II FT-IR instrument using potassium bromide (KBr) discs prepared from powdered samples mixed with dry KBr in the ratio 1:100.

The solubility of the product was measured at 5% w/v concentration in different organic solvents.

Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) measurements of vacuum dried (50°C for 24 h) samples were performed in a Simultaneous Thermal Analyser (STA 625). Samples (ca. 10 mg) were heated at a rate of 10°C min^{-1}, in the range ambient to 600°C. Static air was used as the purge gas.

3. Results and discussion

The potential of the previously reported starch solubilisation technique was explored in this work. The challenge addressed was the consistent and reproducible delivery of modified potato starch with short, medium and long chain acid chlorides to controlled DS-levels. Use of the lithium chloride/DMAC system is well known for the solubilisation of polysaccharides (Dawsey & McCormick, 1990; Marson & El Seoud, 1999; McCormick & Callais, 1987; Striegel, 1997; Tosh, Saikia & Dass, 2000). Key to this variation on that system was the prior gelatinisation and disruption of the starch granules by swelling in hot water. Subsequent transferral to lithium chloride and DMAC occurred without the reaction temperature ever exceeding 90°C. It is believed that the maintenance of a low reaction temperature minimises starch depolymerisation whilst solubilisation of the swollen starch in anhydrous solvent activates the exposed hydroxyl groups to attack by electrophilic reagents.

3.1. Starch solubilisation

A 12% w/v mixture of potato starch in water was stirred vigorously and heated beyond its gelatinisation temperature to entirely disrupt the granular structure. Examination of aliquots under a light microscope detected no presence of granule ghosts in the viscous solution. Portionwise addition of DMAC to, and preferential distillation of water from, the reaction mixture followed, until three times the volume of added water was collected. At this stage the reaction system was deemed to be anhydrous and the water swelling/solvent exchange was complete. The suspension temperature was adjusted to 80°C and lithium chloride was added to the

Table 1
Reaction conditions for potato starch acylation (reactions 1 and 2: reaction time 20 min at 40°C; remaining samples: reaction time 30 min at 80°C)

Reaction No.	Alkyl chain	Potato starch (mol)	Acid chloride (mol)	Pyridine (mol)	Theoretical DS-value
1	C_4	0.37	1.11	1.11	3.0
2	C_4	0.37	0.56	0.56	1.5
3	C_4	0.37	0.19	0.19	0.5
4	C_8	0.37	1.11	1.11	3.0
5	C_8	0.37	0.56	0.56	1.5
6	C_8	0.37	0.19	0.19	0.5
7	C_{12}	0.37	1.11	1.11	3.0
8	C_{12}	0.37	0.56	0.56	1.5
9	C_{12}	0.37	0.19	0.19	0.5
10	C_{16}	0.37	1.11	1.11	3.0
11	C_{16}	0.37	0.56	0.56	1.5
12	C_{16}	0.37	0.19	0.19	0.5
13	C_{18}	0.37	1.11	1.11	3.0
14	C_{18}	0.37	0.56	0.56	1.5
15	C_{18}	0.37	0.19	0.19	0.5

Table 2
Calculated DS-values based on elemental analyses, and yields of modified starches (note: accepted experimental error of ±0.3% in the measurement of elemental analyses results in an error range of ±DS value units as indicated in column 7)

Reagent	Starch/reagent molar ratio	Elemental analysis				Actual DS-value	Yield (%)
		Carbon (%)		Hydrogen (%)			
		Theoretical	Found	Theoretical	Found		
Butyryl chloride	1:3.0	58.05	57.6	7.58	7.5	2.79 ± 0.14	98
	1:1.5	53.93	54.0	7.16	7.1	1.52 ± 0.08	98
	1:0.5	48.73	47.2	6.64	6.5	0.30 ± 0.02	98
Octanoyl chloride	1:3.0	66.64	66.4	9.69	9.7	2.89 ± 0.13	95
	1:1.5	61.52	61.4	8.89	9.2	1.48 ± 0.05	97
	1:0.5	53.33	53.1	7.61	7.6	0.48 ± 0.02	96
Lauroyl chloride	1:3.0	71.15	70.8	10.80	10.8	2.86 ± 0.14	90
	1:1.5	66.18	66.3	9.95	10.7	1.53 ± 0.08	93
	1:0.5	56.90	57.15	8.36	8.5	0.52 ± 0.02	96
Palmitoyl chloride	1:3.0	73.92	74.0	11.49	11.35	3.00 ± 0.15	90
	1:1.5	69.33	69.4	10.67	10.8	1.51 ± 0.06	93
	1:0.5	59.77	59.8	8.95	9.1	0.50 ± 0.02	95
Oleoyl chloride	1:3.0	75.42	75.3	11.18	11.1	2.92 ± 0.17	94
	1:1.5	70.93	80.0	10.46	10.2	1.51 ± 0.06	96
	1:0.5	61.20	61.65	8.90	9.0	0.52 ± 0.02	95

reaction flask. Solubilisation was complete within five minutes and the grey/opaque suspension became a transparent, colourless solution.

Formation of the homogeneous solution is mediated by lithium chloride in DMAC. The lithium chloride, DMAC and starch are believed to form a ternary complex, as is the case for cellulose, which, to some extent (El-Kafrawy, 1982; McCormick, Callais & Hutchinson, 1985; Morgenstern & Kammer, 1996), modifies the original pattern of inter- and intra-molecular hydrogen bonds within and between the cellulose chains. At the same time, the hydrogen bond acceptor properties of DMAC are expected to enhance the nucleophilicity of the exposed hydroxyl groups to attack by various electrophilic reagents. The formation of a homogeneous solution formed the basis of the ensuing work.

Thus, potato starch was modified using various acyl chlorides (butyryl → oleoyl) under homogeneous reaction conditions. The inclusion of pyridine acts not only as a nucleophilic acylation catalyst, but also as a base. During the reaction, hydrochloric acid is formed as a by-product, which reacts with excess pyridine to form its pyridinium salt; this salt is easily separated from the reaction product by dissolution in 70% w/v aqueous MeOH, the solvent mixture used to precipitate the desired product.

The DS-value of the resultant modified starch can be controlled simply by varying the mole ratio of reagent. The shorter chain length acyl chlorides (e.g. butyryl chloride) have higher reactivities and faster reaction rates, typically requiring that the reaction be carried out at a lower temperature (40°C) and for a shorter reaction time (20 min) than for the longer carbon chain acyl chlorides (e.g. palmitoyl chloride, oleoyl chloride) which require that the reaction be performed at a higher temperature (80°C) and for a slightly longer reaction time (30 min).

3.2. Yield and DS-value of acylated starch

The DS for a starch derivative is defined as the number of hydroxyl (OH) groups substituted per D-glucopyranosyl structural unit of the starch polymer. Since each D-glucose unit possesses three reactive hydroxyl groups, so the maximum possible DS-value is 3.

The DS-values of acylated starch were calculated on the basis of measured % C from elemental analysis results and ranged from 0.30 to 3.00. The yield of recovered material in all cases was 90% or better (Table 2). As can be seen from Table 2, it is clear that the measured DS-values are close to their theoretical values. Therefore, the reactions to form acylated starches can be controlled with high accuracy by adjusting the molar ratio of reagent and catalyst in the reaction mixture, in order to obtain the desired DS-value.

3.3. FT-IR spectra

The FT-IR spectra of unmodified and certain modified potato starches are shown in Figs. 1–3. In the fingerprint region of the spectrum of unmodified starch (Fig. 1), three characteristic peaks appear between 937 and 1156 cm^{-1}; these peaks are attributed to C–O bond stretching. The peaks at 1083 and 1023 cm^{-1} are characteristic of the anhydroglucose ring O–C stretch. Another characteristic peak occurs at 1640 cm^{-1}, which we believe to be a feature of tightly bound water present in the starch. An extremely broad band due to hydrogen bonded hydroxyl groups (O–H) appears at its most intense at 3403 cm^{-1} that is attributed to the complex vibrational stretches associated with free,

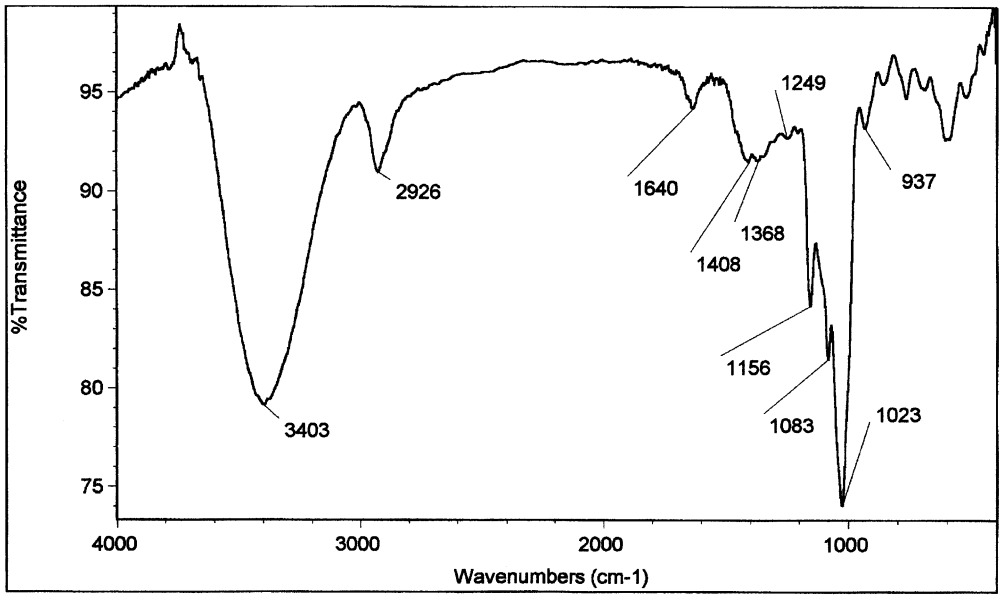

Fig. 1. FT-IR spectrum of unmodified potato starch.

inter- and intra-molecular bound hydroxyl groups which make up the gross structure of starch. The sharp band at 2926 cm^{-1} is characteristic of C–H stretches associated with the ring methine hydrogen atoms.

The FT-IR spectra of lauroylated potato starches were recorded for decreasing DS-values and are shown in Fig. 2. Fig. 2a represents a high DS-value lauroylated starch (DS ca. 3), Fig. 2b represents a medium DS-value lauroylated starch (DS ca. 1.5), Fig. 2c shows the spectrum of the low DS-value (ca. 0.5) lauroylated starch. These spectra provide evidence of lauroylation by the presence of the ester carbonyl group stretch at 1739 cm^{-1} (C=O). The occurrence of two peaks of strong intensities at 2926 and 2860 cm^{-1} in the spectra is attributed to the methyl and methylene C–H stretching associated with the lauroyl substituents. The strong band at 3403 cm^{-1} (hydroxyl groups) of native starch (Fig. 1) decreases in intensity after the acylation reaction as the number of hydroxyl groups present diminishes. All three spectra have similar profiles. However, a few differences can be observed. Fig. 2a shows the most intense carbonyl peak at 1739 cm^{-1}, and correspondingly weakest hydroxyl stretching band at 3403 cm^{-1}, as expected for a high degree of lauroylation. Conversely, Fig. 2c shows the weakest ester peak and only slight reduction in the intensity of the O–H stretch because of the low DS-value of lauroylation. It is clearly seen that as DS-value rises, the ester band becomes more intense. As the DS-value tends towards 3, the hydroxyl stretch almost disappears. The bands in the fingerprint region associated with C–O stretching (1083, 1030 cm^{-1}) decrease in relative intensity to those associated with the C–H stretch when the influence of the lauroyl groups becomes more pronounced as the DS-values increase.

Fig. 3 shows the FT-IR spectra of butyrylated starch (Fig. 3a), octanoylated starch (Fig. 3b), and palmitoylated starch (Fig. 3c) of theoretical DS-value 3. These similar spectroscopic profiles reveal the similar structures of the acylated starches, all of them containing an intense ester carbonyl band at 1746 cm^{-1}. However, among them are some differences. As the carbon chain length of the acyl group increases from a four-carbon chain (Fig. 3a) to a sixteen-carbon chain (Fig. 3c), the signals of the symmetrical methyl and methylene C–H bands at 2853 and 2926 cm^{-1} become more intense with increasing carbon chain length.

3.4. Thermal properties

Thermal stabilities of the starch esters were studied by TG and DSC. Fig. 4 shows the results of TG analyses for native (Fig. 4a) and lauroylated potato starch (DS-value, 1.5) (Fig. 4b). The TG spectra were used to determine the weight loss of the material as it was heated, cooled, or held isothermally. Differential scanning calorimetry was used to measure the presence of exothermal or endothermal changes as the temperature was increased. The DSC spectra (Fig. 4) reveal that the unmodified starch has one distinct reaction zone, whilst the lauroylated starch derivative has three reaction zones. This indicates different thermal degradation characteristics between the modified and unmodified starch. The trace of unmodified potato starch (Fig. 4a) shows a prominent effect at 380°C with about 60% of the total weight lost. In comparison, the DSC curve of the lauroylated potato starch (Fig. 4b) exhibited about 80% of the weight lost at 380°C. As can be seen from Fig. 4, the TG traces reveal that unmodified potato starch is stable up to 200°C, with maximum rate of decomposition occurring at 250°C. The lauroylated potato starch appears to be more stable since onset of decomposition is at higher temperature (300°C). This observation is in agreement with the earlier

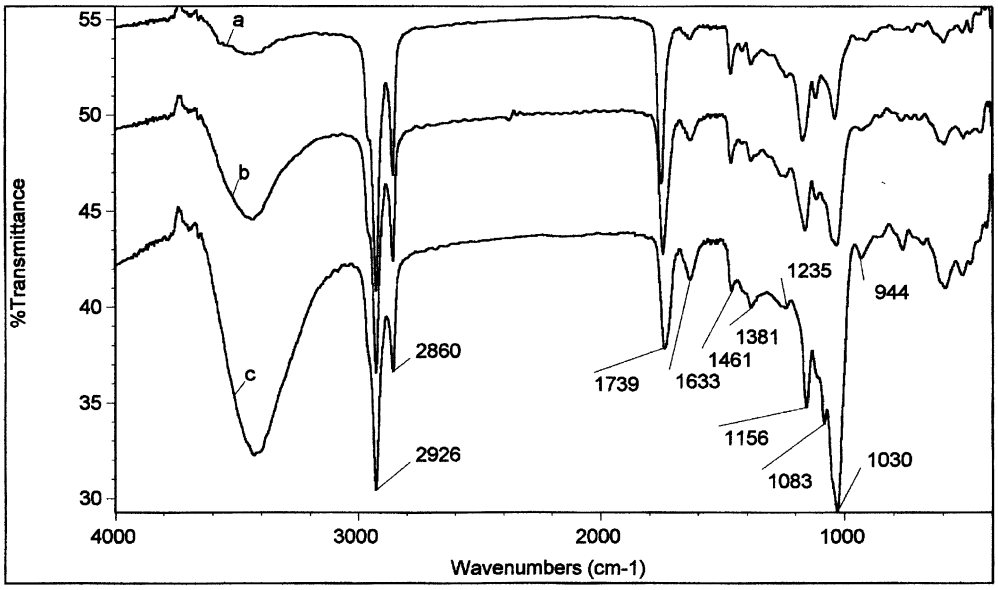

Fig. 2. FT-IR spectra of lauroylated starch with different DS-values, spectrum **a** (DS 2.9); spectrum **b** (DS 1.5); and spectrum **c** (DS 0.5).

report from Thiebaud, Aburto, Alric, Borredon, Bikiaris, Prinos et al. (1997) in which octanoated and dodecanoated starch esters were found to have greater thermal stability than unmodified starch. This greater thermal stability of the esters is probably due to the lower amount of remaining hydroxyl groups after acylation. It has long been reported (Morita, 1956) that the main decomposition mechanism of starch is the dehydration reaction between starch molecules. Thus, thermal stability increases with the degree of substitution since a large proportion of acyl functionality prevails.

3.5. Solubility

Undamaged starch granules are not soluble in cold water but can absorb water reversibly; that is, they can swell slightly and then return to their original size on drying (Whistler & BeMiller, 1997). Introduction of hydrophobic acyl groups into the molecular structure of starch was expected to alter its solubility properties. Such alteration relied essentially on the degree of substitution and the nature of the starch. The solubility of an acylated starch is

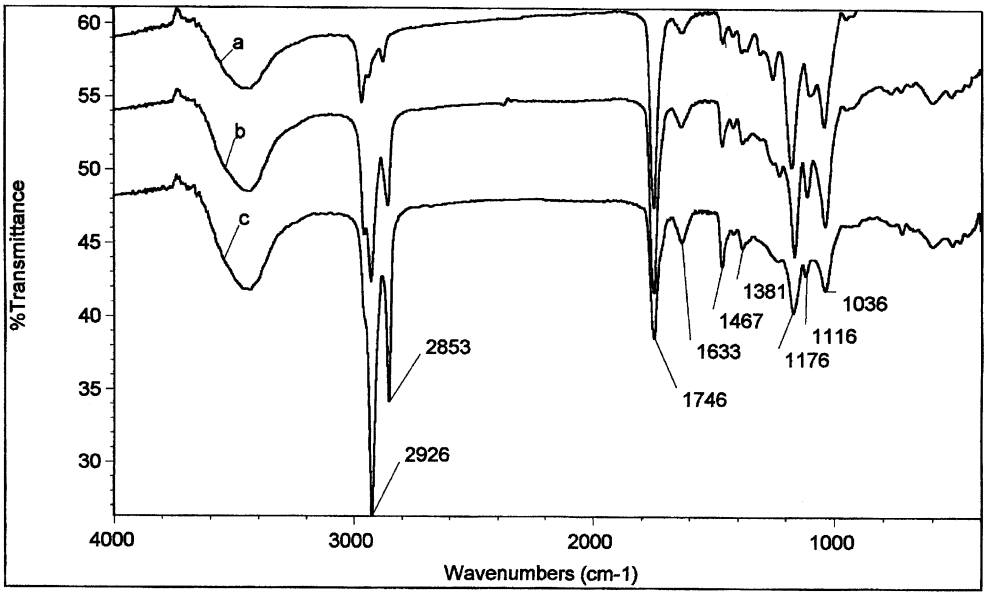

Fig. 3. FT-IR spectra of butyrylated starch (a), octanoylated starch (b), and palmitoylated starch (c) with theoretical DS-value 3.

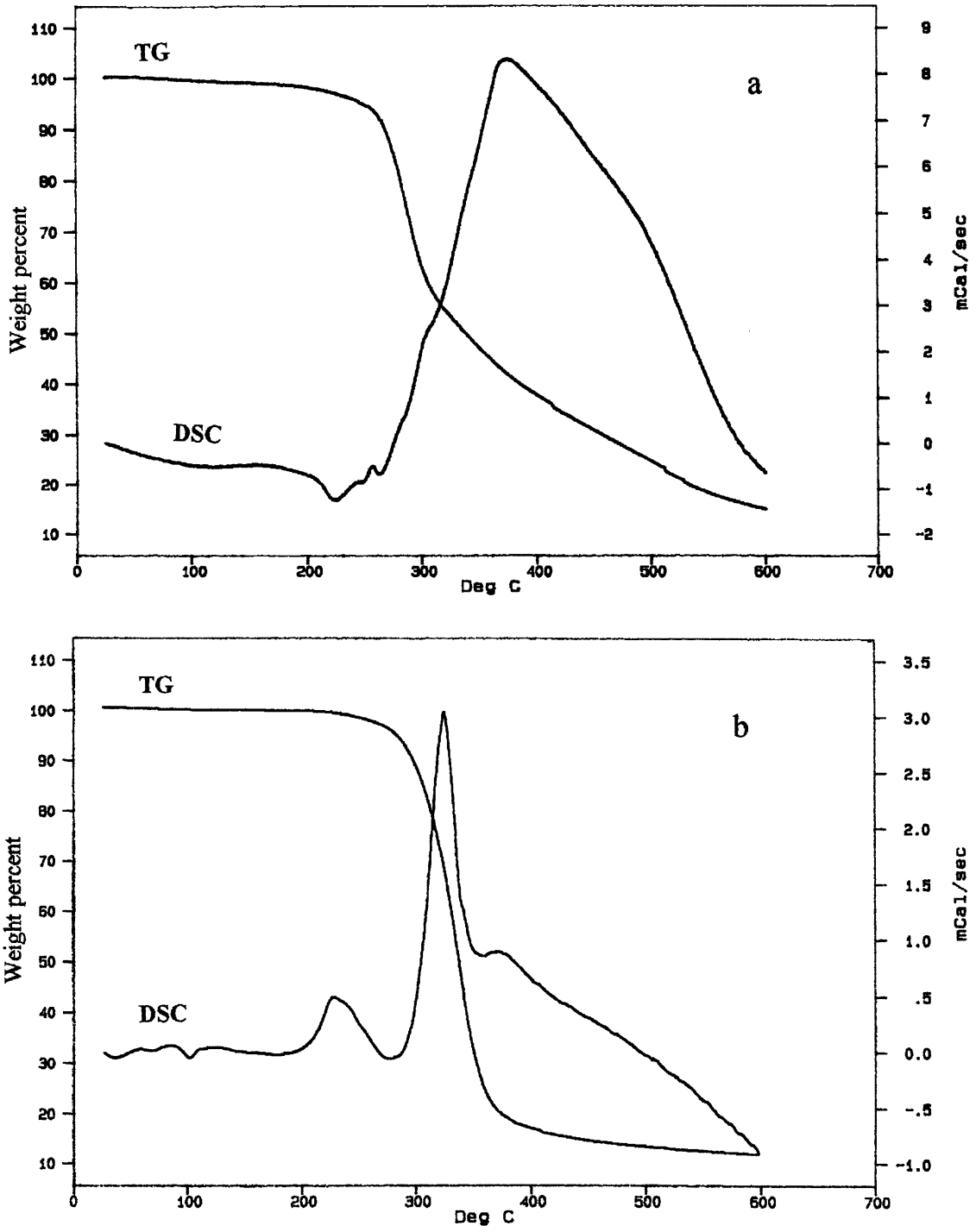

Fig. 4. Thermogram of potato starch (a) and lauroylated starch (b, DS-value 1.5).

dependent upon: (1) the extent of acylation; (2) the degree of degradation of the acylated molecule; (3) the degree of polymerisation of the ester; (4) the fractionation of the starch or the derivative; (5) the nature of the acyl substituent; (6) the type of starch, and (7) the solvent and temperature (Degering, 1953).

Butyrylated starch of low butyryl value (ca. 0.3) is water soluble. When the derivative is not degraded, however, we have shown that butyrylated potato starches of DS-values ca. 1.5 and 3 are not water soluble. Our butyryl derivatives (DS-values 1.5, 3) of potato starch are soluble in benzene, acetone, ethanol, chloroform, and ethyl acetate.

The high DS-values (1.5, 3) octanoylated potato starches are soluble in dimethysulfoxide, tetrahydrofuran, pyridine, chloroform, dichloromethane, acetone and toluene, but the low DS octanoylated starch (ca. 0.5) is insoluble in toluene

and chloroform at room temperature and under boiling conditions.

Table 3 shows that different DS-values affect the solubility of modified starches. From the results it is seen that high DS palmitoylated starch has good general solubility in organic solvents, whereas low DS palmitoylated potato starch has poor solubility. The low DS-value lauroylated and oleoylated starches (DS ca. 0.5), also showed good solubility in dimethysulfoxide, tetrahydrofuran, pyridine, and were partially soluble in chloroform, dichloromethane and hot toluene.

4. Conclusions

A series of starch esters with different degrees of substitution and side-chain lengths has been prepared and studied. The esters were prepared by acylation of the polysaccharide with the appropriate acid chlorides in homogeneous DMAC/LiCl solution, which represents a suitable, effective, and rapid method for the preparation of acylated starch with controllable substitution of the free hydroxyl groups in native starch. The DMAC/LiCl acted as the solvent for the derivatives and ensured uniform substitution by ensuring accessibility of the reagent. Preparation of acylated starch was readily controlled with high accuracy by adjusting the amount of pyridine and the molar ratio of reagent and hydroxyl functionality. The reaction conditions were optimised to give controlled DS-values under mild reaction conditions with a short reaction time. Under optimum reaction conditions (molar ratio 1:0.5, 80°C, 30 min), a low DS-value of 0.5 was obtained, whereas, when the molar ratio was 1:3, at the same temperature and reaction time, a high DS-value of 3 was achieved. DS-Values were confirmed by elemental analysis. Such modified polysaccharides have significantly altered solubility properties compared to native starch. Notably, the solubility in organic solvents and hydrophobicity increases with the degree of substitution and side-chain length. The thermal properties of the esters also depend on the degree of substitution. By changing the fatty chain and the degree of substitution, materials with a wide range of properties may be prepared.

Table 3
Solubility of various substituted palmitoylated potato starch

Solvent	Solubility		
	DS-value 3	DS-value 1.5	DS-value 0.5
Acetone	Insoluble	Insoluble	Insoluble
Chloroform	Soluble	Soluble	Mostly soluble
Dichloromethane	Soluble	Soluble	Partly soluble
Dimethylsulfoxide	Swells	Viscous suspension	Insoluble
Ethyl acetate	Insoluble	Insoluble	Insoluble
Pyridine	Soluble	Soluble	Soluble
Tetrahydrofuran	Soluble	Soluble	Soluble
Toluene	Soluble	Soluble	Insoluble

Acknowledgements

This work was supported by the Ministry of Agriculture, Fisheries and Food and Aquasol Limited, British Potato Council, British Sugar Technical Centre and CPL Laboratories under the LINK Crops for Industrial Use programme, contract reference number CSA 3006.

References

Aburto, J., Alric, I., Thiebaud, S., Borredon, E., Bikiaris, D., Prinos, J., & Panayiotou, C. (1999). Synthesis, characterisation and biodegradability of fatty acid esters of amylose and starch. *Journal of Applied Polymer Science*, *74*, 1440–1451.

Dawsey, T. R., & McCormick, C. L. (1990). The lithium chloride/dimethylacetamide solvent for cellulose — a literature review. *Journal of Macromolecular Science — Reviews in Macromolecular Chemistry and Physics*, *C30*, 405–440.

Degering, E. F. (1953). The esters of starch. In J. A. Radley, *Starch and its derivatives* (pp. 298–325). , Vol. 1. London: Chapman & Hall.

El-Kafrawy, A. (1982). Investigation of the cellulose LiCl dimethylacetamide and cellulose LiCl *N*-methyl-2-pyrrolidinone solutions by C-13 NMR-spectroscopy. *Journal of Applied Polymer Science*, *27*, 2435–2443.

Ellis, R. P., Cochrane, M. P., Dale, M. F. B., Duffus, C. M., Lynn, A., Morrison, I. M., Prentice, R. D. M., Swanston, J. S., & Tiller, S. A. (1998). Starch production and industrial use. *Journal of the Science of Food and Agriculture*, *77*, 289–311.

Fringant, C., Rinaudo, M., & Bardet, M. (1998). Preparation of mixed esters of starch or use of an external plasticiser: two different ways to change the properties of starch acetate films. *Carbohydrate Polymers*, *35*, 97–106.

Heinze, T., Talaba, P., & Heinze, U. (2000). Starch derivatives of high degree of functionalization. 1. Effective, homogeneous synthesis of *p*-toluenesulfonyl (tosyl) starch with a new functionalization pattern. *Carbohydrate Polymers*, *42*, 411–420.

Houghton, A. A. (1938). Starch derivatives. *British Patent*, 493,513.

Hylnianski, D. (1997). Preparation of chemically reactive polysaccharides. *PCT application*, WO9817692.

Marson, G. A., & El Seoud, O. A. (1999). A novel, efficient procedure for acylation of cellulose under homogeneous solution conditions. *Journal of Applied Polymer Science*, *74*, 1361–1365.

McCormick, C. L., & Callais, P. A. (1987). Derivatization of cellulose in lithium chloride and *N,N*-dimethylacetamide solutions. *Polymer*, *28*, 2317–2323.

McCormick, C. L., Callais, P. A., & Hutchinson, B. H. (1985). Solution studies of cellulose in lithium chloride and *N,N*-dimethylacetamide. *Macromolecules*, *18*, 2394–2401.

Morgenstern, B., & Kammer, H. W. (1996). Solvation in cellulose–LiCl–DMAC solutions. *Trends in Polymer Science*, *4*, 87–92.

Morita, H. (1956). Characterization of starch and related polysaccharides by differential thermal analysis. *Analytical Chemistry*, *28*, 64.

Peltonen, S., & Harju, K. (1996). Application and methods of preparation of fatty acid esters of polysaccharides. *US Patent* 5,589,577.

Röper, H. (1996). Non-food applications of starch and its derivatives. *Carbohydrates in Europe*, *15*, 22–30.

Striegel, A. M. (1997). Theory and applications of DMAC/LiCl in the analysis of polysaccharides. *Carbohydrate Polymers*, *34*, 267–274.

Thiebaud, S., Aburto, J., Alric, I., Borredon, E., Bikiaris, D., Prinos,

J., & Panayiotou, C. J. (1997). Properties of fatty-acid esters of starch and their blends with LDPE. *Journal of Applied Polymer Science*, *65*, 705–721.

Tosh, B., Saikia, C. N., & Dass, N. N. (2000). Homogeneous esterification of cellulose in the lithium chloride–*N*,*N*-dimethylacetamide solvent system: effect of temperature and catalyst. *Carbohydrate Research*, *327*, 345–352.

Whistler, R. L., & BeMiller, J. N. (1997). *Carbohydrate chemistry for food scientists* (p. 117). St. Paul, MN: Eagan Press.