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The chemical modification of a range of starches under aqueous reaction conditions

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Abstract

A series of starch esters with different side-chain lengths and moderate DS-values was prepared and studied. The esters were prepared by acylation of the gelatinised starch with the appropriate acid chloride in 2.5 M aqueous sodium hydroxide (NaOH) solution, which represents an economical and facile method for the preparation of esterified starches. The alkali solution acted as the medium for the derivatisation and ensured uniform substitution by enhancing solubility of the starch and accessibility of the reagent. Successful esterification was limited to acid chlorides containing between six and 10 carbon atoms. Shorter or longer chain-length acid chlorides did not react under these conditions to form esters, as confirmed by FT-IR spectroscopic and elemental analyses, as well as by intrinsic viscosity analysis.

Keywords: Starch; Modification; Acylation

1. Introduction

The chemical modification of starches continues to attract the attention of researchers for applications as diverse as biodegradable packaging materials to components of oil drilling muds (Albertsson & Karlsson, 1995; Jane, 1995).

The modification of intact starch granules has been known for many years; indeed such modified starches have approval for food use in which they act as thickeners and gelling agents. Similarly, they are used as sizing agents in textiles and as adhesives for paper and paper products. Typically, modifications are made to DS-values of <0.1 (Whistler & BeMiller, 1997).

In recent years, a number of authors (Aburto, Alric, & Borredon, 1999a; Aburto et al., 1999b, 1997; Fang, Fowler, Tomkinson, & Hill, 2002a; Thiebaud et al., 1997) have reported the preparation of modified starches to higher degrees of substitution, relying on the use of organic solvents to provide suitable reaction conditions for modification to, for example, esters. Such procedures rely on the use of sophisticated experimental techniques, solvents, or systems of solvents, to ultimately achieve homogeneous modification of the chosen starch. When starch is homogeneously esterified in such a manner with fatty acid chlorides derived from vegetable oils, then the resulting products are thermoplastic and have potential for use in the manufacture of biodegradable films (Fang, Fowler, Tomkinson, & Hill, 2002b). However, these techniques are expensive, typically use toxic solvents and, we believe, are not viable for the large scale industrial production of modified starches.

The homogeneous modification of starch relies upon the destructurisation of the semi-crystalline starch granules and the effective dispersion of their component amylose and amylopectin polymers. In this way, the reactive sites (hydroxyl groups) of the polymers become accessible to electrophilic reactants. Starch is effectively destructured by gelatinisation in hot water, the precise temperature (which can vary extensively) depending on the source of starch or, more correctly on the branch chain-length of the amylopectin component. High amylose starches (typical amylose:amylopectin ratio 70:30) gelatinise at around 160–170 °C, whilst wheat starch (amylose:amylopectin ratio 28:72) gelatinises in the range 52–65 °C (Whistler & BeMiller, 1997).

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The temperature of gelatinisation can be raised or lowered by addition of various electrolytes to an aqueous dispersion of starch in water. Aqueous NaOH is known to reduce the gelatinisation temperature of starches, and both amylose and amylopectin are readily soluble in 0.1–1.0 M alkali. However, recent papers (Billmers & Tessler, 1994; Wang & Wang, 2002) have described the subsequent depolymerisation of both amylose and amylopectin when treated with aqueous alkali but to the best of our knowledge, there is no definitive account of the extent. Conversely, BeMiller (1965) has reported that under usual laboratory conditions (up to 1N alkaline conditions and less than 100 °C), the alkaline decomposition of polysaccharides is a rather slow reaction, even in the presence of oxygen (O_2) although this reaction is considerably faster than the anaerobic one.

In parallel work (Fang, Fowler, Sayers, & Williams, 2003), we have established that a range of starch granules is optimally solubilised in 2.5 M aqueous NaOH solution with minimal degradation of the polymeric components. Aqueous alkali forms the basis of the Schotten–Baumann (Baumann, 1886; Schotten, 1884) procedure for the preparation of esters from alcohols and acyl chlorides, often carried out in the presence of a catalyst such as pyridine or triethylamine. We were intrigued that the Schotten–Baumann procedure, when applied to starches, could afford a simple procedure for the preparation of homogeneously substituted starch esters as a more economic and environmentally friendly alternative to the organic solvent routes outlined above.

Indeed, recent work by Queneau and colleagues (Descotes et al., 1999; Thevenet, Descotes, Bouchu, & Queneau, 1997; Thevenet et al., 1999) has demonstrated the suitability of the method for the aqueous esterification of sucrose. Thus, the possibility of using aqueous alkali as an alternative solvent for the esterification of starches to moderate degrees of substitution (DS-values <0.5) was studied. The range of demonstration acylation reactions comprised ethanoylation (C_2), butanoylation (C_4), hexanoylation (C_6), heptanoylation (C_7), octanoylation (C_8), nonanoylation (C_9), decanoylation (C_{10}), dodecanoylation (C_{12}), hexadecanoylation (C_{16}) and octadecanoylation (C_{18}). Modified starches were prepared and characterised chemically by FT-IR spectroscopic and elemental analyses. All physical characterisations of the modified starches were performed by intrinsic viscosity measurements.

2. Experimental

2.1. Materials

Four starches were acquired for the study, three of corn (maize) origin and one of wheat. Hylon VII (70% amylose:30% amylopectin); Hylon V (50% amylose:50% amylopectin) and Amioca (99% amylopectin) were from corn and were supplied by National Starch and Chemical. Abrastarch (28% amylose:72% amylopectin) was a commercial wheat starch, provided by ABR Foods Ltd. Ethanoyl, butanoyl, hexanoyl, heptanoyl, octanoyl and nonanoyl chlorides were obtained from Aldrich. Decanoyl chloride was obtained from Lancaster Synthesis Ltd. Dodecanoyl and hexadecanoyl chlorides were purchased from Acros. Octadecanoyl chloride was supplied by Fluka. 4-Dimethylaminopyridine (DMAP), triethylamine (TEA), pyridine and *N,N*-diisopropylethylamine (DIEA) were obtained from Aldrich. All reagents were used without further purification.

2.2. Synthesis of acylated starches

Starch (6.75 g) was added to NaOH solution (50 ml, 2.5 M) at room temperature with mechanical stirring under an atmosphere of N_2, until the starch granules gelatinised fully (30 min). The reaction catalyst (Table 1) was added (or not) and, after 5 min, 0.5 mol equivalents of the required acid chloride was then added dropwise and the reaction mixture was stirred for 1 h. Upon completion of the reaction, the mixture was neutralised to pH 7 with acetic acid, and the acylated starch was isolated by precipitation in methanol (150 ml). The product was collected by filtration, washed with 70% aqueous solution of methanol (150 ml) and re-collected. This process was repeated twice to eliminate impurities, such as fatty acids and their salts. After filtration, residual methanol was removed by evaporation in air, and the starch ester was dried at 50 °C overnight and weighed. The dried samples were kept in

Table 1
The range of reaction conditions investigated to achieve potential starch esterification

Reaction no.	Catalyst	Acyl chloride	Yield (%)	FT-IR (cm^{-1})
1	None	Acetyl	n.r.	n.o.
2	DMAP	Acetyl	n.r.	n.o.
3	TEA	Acetyl	n.r.	n.o.
4	Pyridine	Acetyl	n.r.	n.o.
5	DIEA	Acetyl	n.r.	n.o.
6	None	Butyryl	n.r.	n.o.
7	Pyridine	Butyryl	n.r.	n.o.
8	TEA	Butyryl	n.r.	n.o.
9	None	Octanoyl	75	1743
10	Pyridine	Octanoyl	72	1749
11	TEA	Octanoyl	75	1743
12	DIEA	Octanoyl	84	1743
13	None	Stearoyl	n.r.	n.o.
14	Pyridine	Stearoyl	n.r.	n.o.
15	TEA	Stearoyl	n.r.	n.o.
16	DIEA	Stearoyl	n.r.	n.o.

Hylon VII (6.75 g, on a dry-weight basis) was used in the reactions, Acylating agent/glucosyl unit molar ratio was 0.5. Reaction time was 1 h; [NaOH] was 2.5 M. n.r., No product recovered; n.o., no carbonyl signal observed in the range 1735–1750 cm^{-1}.

a desiccator over phosphorus pentoxide (P_2O_5) for further analysis.

2.3. Characterisation

Elemental analysis was used to establish the DS-values of modified starches. Samples of solid polymer were ground to a powder and dried at 100 °C for 24 h, then analysed on a Carlo Erba EA 1108 CHN S–O instrument to measure the carbon and hydrogen content in the substituted starch samples. The DS-values were calculated from the %carbon contents.

For Fourier transfer infrared (FT-IR) spectroscopic analysis, the modified sample was ground using a Mikro-Dismembrator (2000 rpm for 3 min). The fine powder sample was then mixed with dry potassium bromide (KBr) in a sample to KBr ratio of 1:100, and mixing was performed in a vibratory ball mill capsule for 5 min. The ground mixture was then transferred to a Specadie to produce a 8.5 mm diameter film that was analysed in the beam of the FT-IR spectrophotometer (Nicolet Magna IR 750, series II).

The solubility of the products was measured at 5% (w/v) concentration in different organic solvents with stirring at room temperature.

The intrinsic viscosities of the native and acylated starches were determined in dimethylsulfoxide (DMSO). Starch (0.25 g) was dissolved in DMSO (5 ml) with heating and stirring and flow times measured in triplicate at 25 °C using a Ubbelohde type 75 viscometer at varying concentrations by diluting in situ. The intrinsic viscosities were obtained from the intercept of the plot of reduced viscosity against concentration.

3. Results and discussion

3.1. Initial reaction screening

A series of experiments (Table 1) was carried out to initially assess acyl chloride reactivity and catalytic activity for a range of acyl chlorides and organic bases towards starch.

Example acyl chlorides (ethanoyl, butanoyl, octanoyl and octadecanoyl) were selected to investigate how their reactivities (mediated most significantly by the hydrophobic and steric effects induced by the differing chain lengths) influenced the final products. Furthermore, a range of organic bases including pyridine, triethylamine, and Hünig's base (*N,N*-diisopropylethylamine) were studied to assess their influence (pKa and steric effects) on the reaction outcomes. It was, however, supposed that basicity would not exert a major effect in the overwhelming presence of 2.5 M aqueous NaOH solution. Hylon VII was selected as the candidate starch in the trial experiments.

In a typical reaction trial, the required starch was dissolved and gelatinised in aqueous alkali at ambient temperature and under a streaming atmosphere of nitrogen (N_2). At this point, the required organic base was added if required. Finally, the appropriate acyl chloride was added. After 1 h, the reaction mixture was neutralised and the unreacted starch or derivatised starch product was precipitated and isolated from the solution. FT-IR spectroscopy was used as the primary means to assess whether on not (partial) reaction had occurred (see below for further discussion and spectra). Esterification would result in the presence of a carbonyl signal in the FT-IR spectrum (ca. $1740\ \mathrm{cm}^{-1}$) distinct from the carbonyl signals of both unreacted acyl chloride (ca. $1800\ \mathrm{cm}^{-1}$) or the hydrolysis products, carboxylic acids (ca. $1700\ \mathrm{cm}^{-1}$) and their salts (ca. $1640\ \mathrm{cm}^{-1}$). Reaction yields were calculated on the basis of complete reaction of acyl chloride and isolation of uncontaminated, desired product. The reaction conditions applied and yields obtained are shown in Table 1. It is noteworthy that the only successful esterification occurred in the case of reaction with octanoyl chloride. Only unreacted starch (no reaction products) were isolated when ethanoyl, butanoyl or octadecanoyl chlorides were used as acylating agents. It is clear that a competition between acyl group substitution and acid chloride hydrolysis (or product saponification) occurred, particularly for those acyl chlorides (ethanoyl, butanoyl) that were water-miscible. With increasing chain-length, the poorly soluble octanoyl chloride competed effectively in favour of substitution over hydrolysis. However, the same conditions applied to the higher fatty acid chloride (octadecanoyl) led to no reaction. Presumably, miscibility effects governed the outcome of the reaction in this case and acid chloride hydrolysis occurred at the expense of esterification.

3.2. Esterification study

The first iteration of the work programme described above screened a broad range of reaction conditions and indicated where further attention should be directed to optimise esterification. Thus, reaction with octanoyl chloride gave the most successful results. We have proposed that the competition between acyl chloride reactivity and hydrolysis (mediated by steric effects and reagent solubility) was responsible for this phenomenon. In order to test the hypothesis, a second iteration of reactions with acyl chlorides was investigated with carbon chains of length ±2 from octanoyl (C_8). Thus, the reactivity of hexanoyl, heptanoyl, octanoyl, nonanoyl and decanoyl chlorides was investigated using the reaction parameters described above. Furthermore, in these cases, the entire range of starches with high amylose, high amylopectin and conventional amylose:amylopectin ratios was studied to assess the generality of the reaction conditions. It is noteworthy that product recovery was similar for each starch source reacted with a given acyl chloride. This led to the conclusion that the reaction conditions were equally applicable to high amylose starches as to high amylopectin starches.

3.3. FT-IR spectroscopic study

In all cases, reaction products were isolated all exhibiting characteristic ester band signals (1749 cm^{-1}) in their FT-IR spectra. The FT-IR spectra of the four native starches, Amioca, Abrastarch, Hylon V and Hylon VII are shown in Fig. 1a–d. All four spectra have similar profiles. Distinctive peaks in all spectra are described as follows. In the fingerprint region, there are several discernible absorbancies at 1156, 1083, 1023 and 937 cm^{-1}, which are associated with native starch and attributed to C–O bond stretching (Goheen & Wool, 1991). The peaks at 1083 and 1023 cm^{-1} are characteristic of the anhydroglucose ring O–C stretch. A characteristic peak occurred at 1640 cm^{-1}, which is presumably a feature of tightly bound water present in the starch (Kacurakova, Belton, Wilson, Hirsch, & Ebringerova, 1998; Kacurakova & Wilson, 2001; Kalutskaya, 1988). A strong absorption band at 1023 cm^{-1}, probably due to the stretching of the C–OH bond, was present in the spectra of the starches consistent with the earlier report by Marcazzan, Vianello, Scarpa, and Rigo (1999). An extremely broad band due to hydrogen bonded hydroxyl groups (O–H) appeared at 3400 cm^{-1} which was attributed to the complex vibrational stretches associated with free, inter and intra-molecular bound hydroxyl groups which make up the gross structure of starch (Fang et al., 2002a). The band at 2926 cm^{-1} is characteristic of C–H stretches.

Fig. 2a–d shows the FT-IR spectra of octanoylated Amioca, Abrastarch, Hylon V and Hylon VII starches. All of these spectra have similar profiles. In comparison with the spectra of the unmodified starches, the major change is the presence of a carbonyl C=O absorption frequency at 1749 cm^{-1}. The C–H stretching absorbance centred on 2926 cm^{-1} is increased in intensity upon esterification. The occurrence of a shoulder at 2860 cm^{-1} on the absorbance centred at 2926 cm^{-1} in the spectra was attributed to the methyl and methylene C–H stretching bands associated with the hexanoyl substituents. The strong O–H stretching band at 3400 cm^{-1} in the native starches decreased only slightly in intensity following the esterification reaction, as the relatively low DS-value of hexanoylation meant that a significant quantity of unreacted hydroxyl groups was still present.

FT-IR spectroscopic analysis was similarly applied to the hexanoylated, heptanoylated, nonanoylated and decanoylated starches The intensity of the C–H stretching bands at 2926 and 2860 cm^{-1} increased with increasing carbon-chain length relative to the O–H absorbance (3400 cm^{-1}). In summary, similar spectroscopic profiles to the octanoylated material were obtained in all cases. These revealed the similar structures of the acylated starches, with all presenting an intense ester carbonyl band at 1749 cm^{-1}. The absence of an absorption at ca. 1800 cm^{-1} in all spectra indicated that the products were isolated free of the unreacted acyl chloride. Furthermore, the absence of an absorption at ca. 1710 cm^{-1} in all spectra also confirmed that the products were isolated free of any

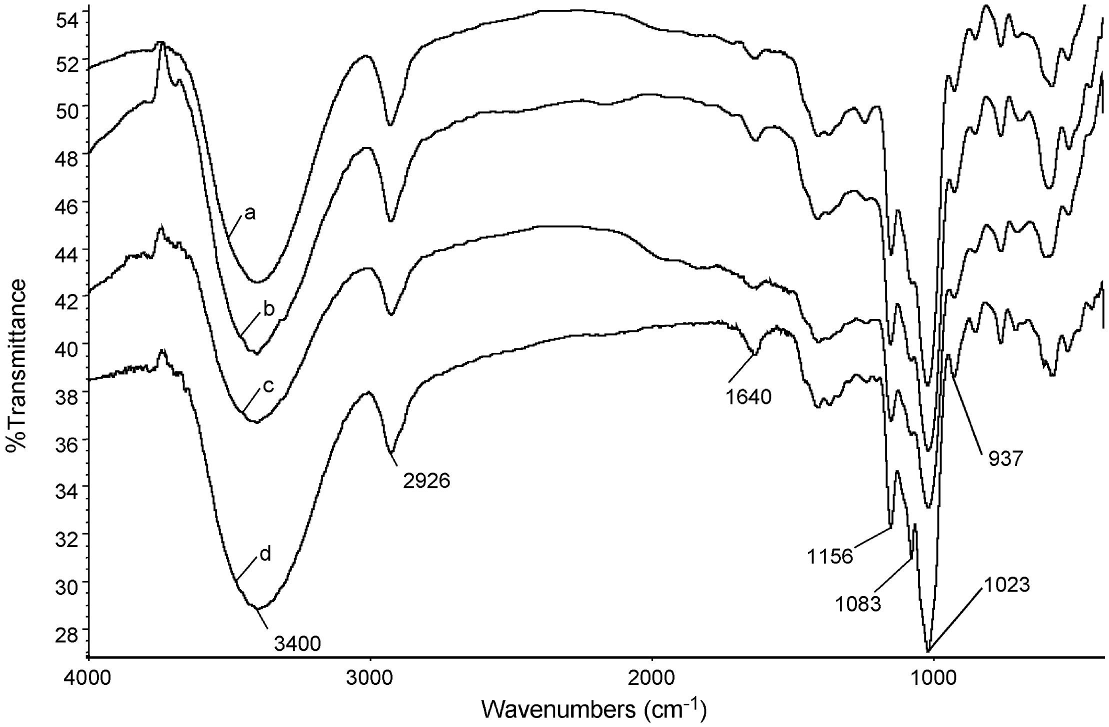

Fig. 1. FT-IR spectra of Amioca (a), Abrastarch (b), Hylon V (c) and Hylon VII (d) starches.

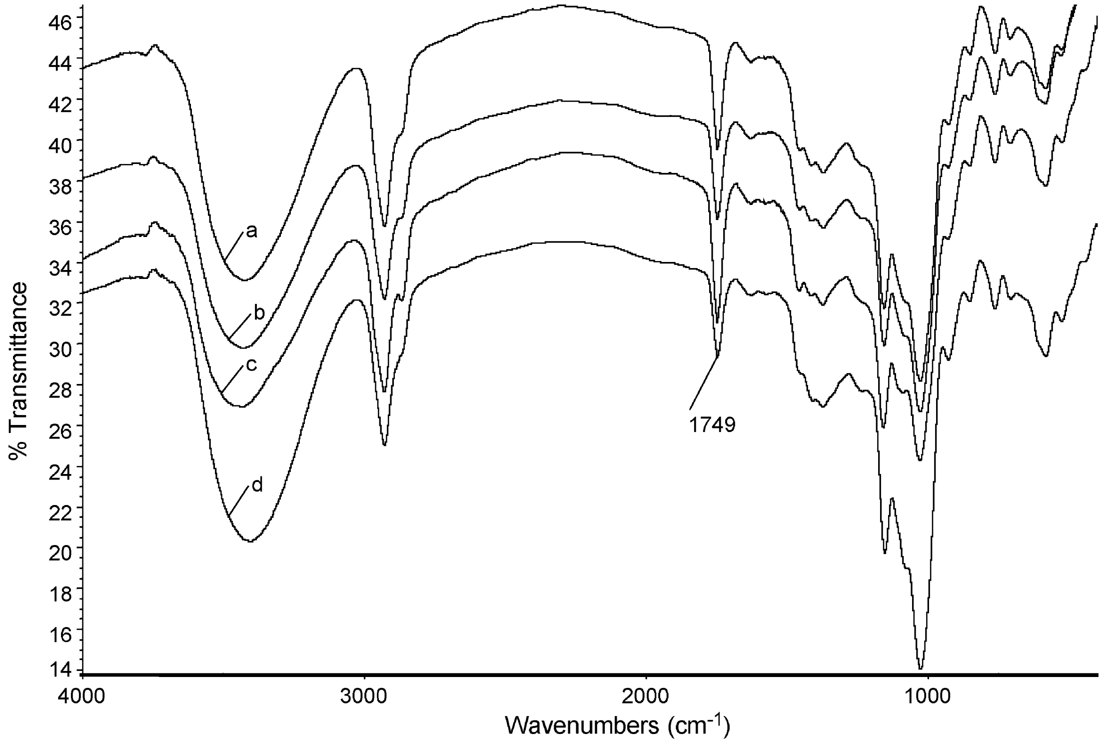

Fig. 2. FT-IR spectra of octanoylated Amioca (a), Abrastarch (b), Hylon V (c) and Hylon VII (d) starches.

fatty acid which was a likely by-product formed by hydrolysis of the corresponding acyl chloride when reacted under aqueous alkaline conditions and subsequently neutralised.

3.4. Yields of products and DS-values

Product yields were determined from the weight of recovered starch product and calculated on the basis of 100% theoretical conversion of acyl chloride to ester. The results are reported in Table 2.

Evidence of the extent of the reaction of the hexanoyl, heptanoyl, octanoyl, nonanoyl and decanoyl chlorides with four types of starches modified in the second iteration in 2.5 M NaOH (Table 2) was obtained by elemental analysis. Increases in the carbon and hydrogen density in the products evidenced introduction of the acyl group. Certain assumptions were necessary to undertake this evaluation: (1) the products were assumed to consist solely of acylated starch; (2) all by-products were removed entirely; (3) the samples under analysis were assumed to contain no residual solvents or moisture absorbed from the atmosphere. Both the theoretical and actual measured carbon and hydrogen proportions of the recovered derivatised starches (expressed as percentages), and the calculated DS-values derived from them, are reported in Table 2.

Native, pure and anhydrous starch contains by weight 44.4% carbon, 6.2% hydrogen and 49.4% oxygen. The results in Table 2 show that the carbon content of all samples was higher than 44.4% indicating an increase in carbon density resulting from successful esterification. On the basis of %carbon, the DS-values obtained in this set of experiments ranged from 0.1 to 0.29. In each series of acyl chlorides, reactions with the four starch types afforded very similar DS-values and yields. The exception was for the octanoylation reaction in which Amioca starch, DS-value 0.16, appeared somewhat lower than expected. All samples had measured DS-values lower than the theoretical (0.5). Product recovery in the range 72–79% for the hexanoylated to nonanoylated starches was acceptable. Lower recovery of the decanoylated starches (63–67%) led to the conclusion that increasing hydrophobic effects were reducing accessibility towards the starch and favouring reagent hydrolysis rather than the desired substitution reaction, as had been observed for octadecanoyl chloride in the first round of experiments.

It was demonstrated that the extent of reaction was related to the carbon-chain length of the acyl chloride reagent: the relationships are illustrated in Fig. 3. Esterification only occurred with acyl chlorides of carbon-chain length 6–10. This further evidenced that activated starch and ‘free’ water or hydroxide compete to react with the acyl chloride. In the range C_6–C_{10}, reaction conditions are appropriate for successful reaction with starch. Outside that range, the acyl chlorides were hydrolysed under the reaction conditions and converted to their salts and no starch substitution occurred. Heptanoylation gave optimum DS-values on the basis of the evidence presented in Fig. 3.

Table 2
Characterisation of modified starches based on Elemental analysis and FT-IR spectroscopy

Acyl chloride	Starch code	Theoretical C%	Measured C%	Theorectical DS-value	Actual DS-value	Yield (%)
Hexanoyl	Hylon VII	51.18	46.562	0.5	0.13	74
	Hylon V	51.18	47.078	0.5	0.17	74
	Abrastarch	51.18	45.931	0.5	0.12	75
	Amioca	51.18	46.785	0.5	0.15	75
Heptanoyl	Hylon VII	52.29	48.964	0.5	0.25	78
	Hylon V	52.29	48.823	0.5	0.24	79
	Abrastarch	52.29	49.566	0.5	0.29	78
	Amioca	52.29	49.586	0.5	0.29	76
Octanoyl	Hylon VII	53.33	49.054	0.5	0.23	78
	Hylon V	53.33	49.547	0.5	0.27	79
	Abrastarch	53.33	49.365	0.5	0.24	76
	Amioca	53.33	47.918	0.5	0.16	72
Nonanoyl	Hylon VII	54.31	50.547	0.5	0.27	74
	Hylon V	54.31	50.404	0.5	0.26	74
	Abrastarch	54.31	49.427	0.5	0.21	74
	Amioca	54.31	49.969	0.5	0.24	72
Decanoyl	Hylon VII	55.23	46.355	0.5	0.10	67
	Hylon V	55.23	46.111	0.5	0.10	66
	Abrastarch	55.23	45.669	0.5	0.10	67
	Amioca	55.23	45.922	0.5	0.10	63

Yields were determined on the basis of recovered starch product.

3.5. Solubility

In general, the introduction of hydrophobic acyl groups into the molecular structure of starch will alter its solubility properties. The solubility of an acylated starch is dependent upon: (1) the extent of acylation; (2) the nature of the acyl substitution; (3) the type of starch; and (4) the solvent and temperature.

The low DS-value starch esters (hexanoyl to decanoyl starches derived from Hylon VII, Hylon V, Abrastarch and Amioca, Table 2) obtained have the appearance of a white powder. A 5% w/v concentration of each starch ester was examined in a range of organic solvents to investigate their solubility. All the esters were found to be soluble in warm DMSO, but insoluble in other common organic solvents at room temperature. However, they were partially soluble in hot pyridine and toluene. Thus, the solubility was not significantly enhanced due to the relatively low extent of substitution and consequently significant hydroxyl group density remaining on the starch esters following reaction.

3.6. Measurement of viscosity

The intrinsic viscosities of the native and acylated Hylon VII starch were determined using DMSO as solvent. Measurements of the other modified starches were hampered because of their insufficient solubility at 25 °C. The results for Hylon VII and its derivatives are reported in Table 3. The intrinsic viscosities of both the modified and unmodified starches are of the same order of magnitude.

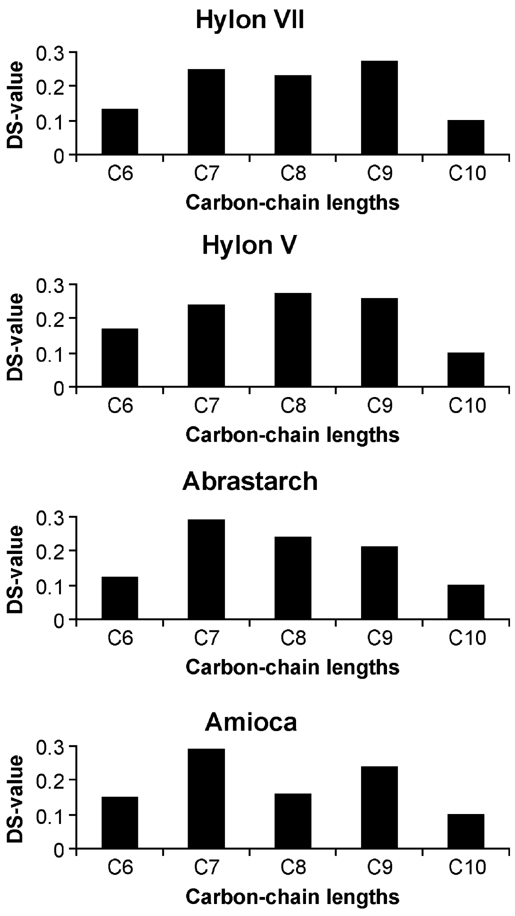

Fig. 3. DS-values of acylated starches versus carbon-chain lengths.

Table 3
The intrinsic viscosities of native and acylated HylonVII

Sample	Intrinsic viscosity (cP)
Hylon VII (native)	40
Hylon VII (hexanoyl)	40
Hylon VII (heptanoyl)	42
Hylon VII (octanoyl)	40
Hylon VII (nonanoyl)	40
Hylon VII (decanoyl)	51

This evidences that the modification procedures applied resulted in only substitution of the starch hydroxyl groups and little depolymerisation of the polymer chains.

4. Conclusions

A series of starch esters with different side-chain lengths and moderate DS-values was prepared by acylation of the polymer with the appropriate acid chlorides in aqueous conditions. The alkali solution acted as the solvent for the derivatives and ensured uniform substitution by enhanced accessibility of the reagent. Successful reaction was limited to acid chlorides containing 6–10 carbon chains. Shorter or longer carbon chain acid chlorides did not react under those conditions to form esters, as confirmed by FT-IR spectroscopic analysis.

It is concluded that, under optimised aqueous alkali conditions, a range of starches can be modified homogeneously to moderate levels of substitution (DS-values ≤ 0.3) with little or no depolymerisation of the starch chain either during the solubilisation or modification processes. The procedure is equally applicable to high amylose, high amylopectin or conventional (typical amylose:amylopectin ratio of 20:80) starches.

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