ELSEVIER

Thermochimica Acta 324 (1998) 1–8

thermochimica acta

The effect of chemical modification on starch studied using thermal analysis

Poonam Aggarwal, David Dollimore*

Department of Chemistry, University of Toledo, Toledo, OH 43606, USA

Abstract

The use of chemically modified corn starch in widely accepted in the pharmaceutical and food industry. There are numerous applications of such modified products. In this investigation, corn starch, amylose and amylopectin from corn starch were cationically modified. The modified products were obtained using a quaternary ammonium salt and these cationic products were compared with their native compounds and characterized. In this study, the thermal analysis behavior of the native and modified products were investigated. The thermal degradation was carried out using a simultaneous TG-DTA unit and a DSC unit. The aim of this work was to modify these materials to render their surface cationic, and then carry out an analytical examination of the modified and the unmodified materials. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Modified starch; Thermogravimetry

1. Introduction

When the properties of native starch have been altered, it is called a modified starch. Native starch was first modified in order to improve its functionality for industrial applications and, thus, expand its usefulness, so it could be cooked at higher concentrations than the native material. These modifications involve treatment of the starch granule by chemical or physical means to cause rupturing of some or all of the starch molecules, thus weakening them and decreasing their capacity to swell on pasting. This results in lowering of the viscosity of the sol produced, thus permitting the resultant sol to be dispersed at higher concentrations. Starch is a polymer of amylopectin and amylose which are, in turn, made up of anhydro glycose units connected to each other by α-(1,4) and α-(1,6) linkages. The molecular scissions that occur during starch conversions, take place at the α-(1,4) D-glucosidic linkage although some scission at the α-(1,6) linkage may also occur [1]. Other properties besides the molecular size and viscosity characteristics may also become altered in the process. The properties of the converted starches vary, depending on the method of conversion. Chemically modified starches have been developed to overcome the shortcomings of native starches (water repellence, insolubility or failure of granules to swell and develop viscosity in cold water, excess or uncontrolled viscosity after cooking, etc.) extending the usefulness of starch for many industrial applications. In the recent past, starch has been modified cationically using cationic ammonium salts to form modified starches that are used as additives in the paper, cosmetic and related industries [2–5]. This modified product has qualities that are essentially different from the original unmodified material, increasing the utility of this material. Corn starch has been modified using 3-chloro-2-hydroxypropyltrimethylammonium chloride, a quaternary ammonium salt [6,7]. It seemed prudent to carry out a similar modification on individual starch compounds,

---

*Corresponding author. Tel.: +1-419-5302109; fax: +1-419-5304033; e-mail: ddollim@uoft02.utoledo.edu

PII: S0040-6031(98)00517-6

amylose and amylopectin, which are similar in structure to starch to see if these materials could also be similarly modified since they resemble one another structurally.

In the present study, starch was modified cationically using the procedure outlined above. The modified products were then examined using various analytical techniques. The structure of the cationic starch formed was determined by solid-state NMR. From the nitrogen content the degree of substitution (DS) was calculated. The amount of nitrogen present was determined and compared with the unmodified material. From this value, the DS was determined. Substitution occurs at the OH-groups, so the average number of substituents per anhydroglucose unit is the DS. The integration of the peaks obtained from NMR data also gave an indication of the DS values. The native and the modified materials were then treated to thermal analysis. The thermal analysis was carried out using a simultaneous thermogravimetry (TG) unit, in an atmosphere of flowing dry nitrogen, where the amount of material lost when subjected to a programmed heating regimen is determined. Derivative thermogravimetry (DTG) was also used to determine the number of stages over which the material degrades.

2. Materials and methods

Corn starch, amylose and amylopectin were from Sigma, 3-chloro-2-hydroxypropyltrimethylammonium chloride in the form of a solid (98%) was from Fluka, sodium sulfate from Fisher Scientific.

3. Preparation of cationic starch

The cationic ether materials were prepared according to the procedure of Carr and Bagby [8]. In a 250-ml closed container, 100 g of starch was slurried with 250 ml of distilled waster, 42 g Na_2SO_4, and 2.0 g NaOH, at 50°C for 5 min. Five grams of 3-chloro-2-hydroxypropyltrimethylammonium chloride was then added and the mixture stirred at 50°C in a water bath for 6 h. After cooling to room temperature, the pH was adjusted to 5.5. The mixture was then centrifuged and the supernatant discarded. The solid residue was then washed with 75% ethanol unit it was free of chlorides. It was then filtered and dried under the hood at room temperature. The same procedure was used for all the materials modified.

Elemental analysis was carried out to determine the nitrogen content in the substituted and native starch samples. From the nitrogen content the DS was determined. The structure of the product formed was analyzed using solid-state NMR. A 50-MHz spectrophotometer, using cross polarization and magic angle spinning was used at 1 ms contact time and a 4 s pulse delay sequence. This data was also used to calculate the DS in each case and was determined by integration of the peaks.

$$\mathrm{DS} = \frac{A_{56}}{A_{100} + A_{70} + A_{82} + A_{62} + A_{56}} \tag{1}$$

where A_x corresponds to the integrated area of peak x.

The thermogravimetry experiments were conducted using a simultaneous TG-DTA unit from TA instruments, model # 2960. The atmosphere around the samples was maintained constant using a gas flow rate of 100 ml min^{-1}. Platinum crucibles were used to hold the samples, with an empty crucible being used as reference. Both, the native and the modified materials were treated in exactly the same way. Thermal characteristics of the native and modified materials obtained were then studied using a DSC. One milligram of the modified and native materials were mixed with 9 mg of distilled water in a DSC sample pan and sealed hermetically. Samples were heated at a heating rate of 10°C min^{-1} using an empty pan as reference. Transition temperatures were recorded from a plot of heat flow vs. temperature. (30° to 140°C). The peak temperature (T_p) for the gelatinization was determined from the curve. X-ray diffraction patterns were obtained using a Scintag XRD 200 X-ray powder diffractometer. This is mounted on an X-ray generator operating at the CuK_α wavelength (1.542 Å). Samples were pressed into a sample holder and scanned for $2<\theta<35$.

4. Results and discussion

Starch contains an abundance of hydroxyl groups. Each anhydro glucose unit contains two secondary hydroxyl and a large majority containing primary hydroxyls. The hydroxyls potentially are able to react with any chemical capable of reacting with alcoholic hydroxyls. Corn starch was modified cationically using 3-chloro-2- hydroxypropyltrimethylammonium chloride, which is a quaternary ammonium salt, following the procedure outlined by using an aqueous starch slurry. Amylopectin and amylose obtained from corn starch were also modified in the same fashion. The degree of substitution for the products obtained in each case was calculated from the amount of nitrogen present. The amount of nitrogen present was determined and compared with the unmodified material. From this value, the DS was determined.

The structural determination using solid-state NMR was carried out using ^{13}C NMR [9]. A DS value of 0.03–0.04 was obtained (Table 1). Both, the modified corn starch as well as the unmodified material have been well characterized using this technique [10–14]. From the plot (Fig. 1), the peak at ≈62 ppm corresponds to the pendant methylene carbon atom present in starch. The peak at 100 ppm is due to the anomeric methine carbon atom. The peaks from 82 to 72 ppm are due to the rest of the carbon atoms present in the anhydroglucose units of starch. As can be seen from the plot (Fig. 2), the cationic material has an additional peak at 56 ppm attributed to the CH_3 group substituted cationic group. Amylose and amylopectin were also similarly modified and examined by NMR; however, no significant differences were observed between the NMR obtained for corn starch and these materials. Earlier reports of NMR obtained from maize, amylomaize and waxy maize showed similar results, indicative of the fact that the amylose-to-amylopectin ratio is not significant in the spectral intensities obtained for the NMR of these materials. The modified and native materials, were then subjected to thermal degradation using TG. As can be seen from the TG plot of amylose in an atmosphere of flowing dry nitrogen (Fig. 3), there is no mass loss until a temperature of 260°C is reached. On further heating there is a sharp weight loss, to give a residue of 26% at 600°C. The DTG curve shows a single peak for this degradation to a carbonaceous residue. In the case of the cationically modified material, decomposition commences at 230°C with a steady loss continuing with an increase in temperature, till 600°C, when

Table 1
Values for the degree of substitution obtained for the different starch materials modified

Material	Degree of substitution(DS) [a]
Modified starch	0.04
Modified amylose	0.03
Modified amylopectin	0.04

[a] 4/100 Units of glocuse or 4/300 hydroxyl groups.

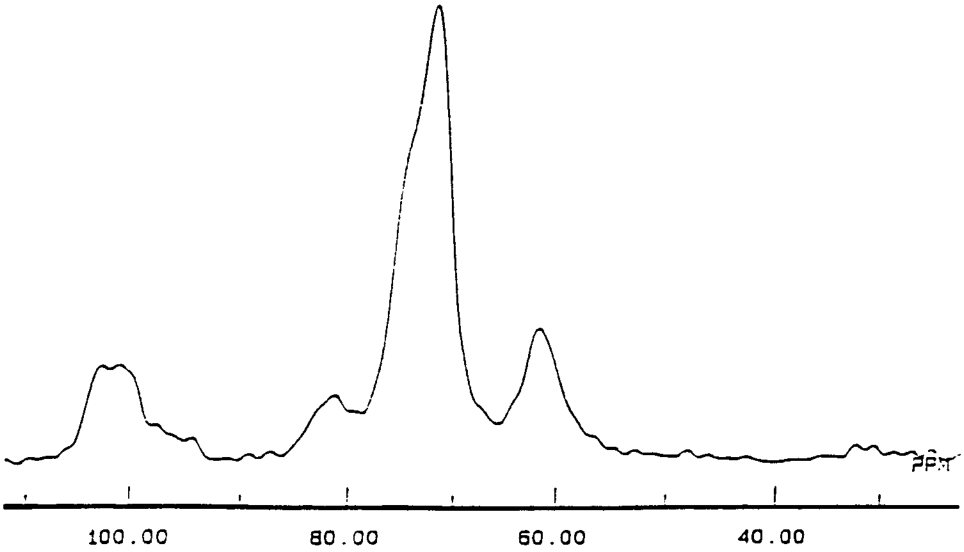

Fig. 1. ^{13}C solid-state NMR plot of corn starch.

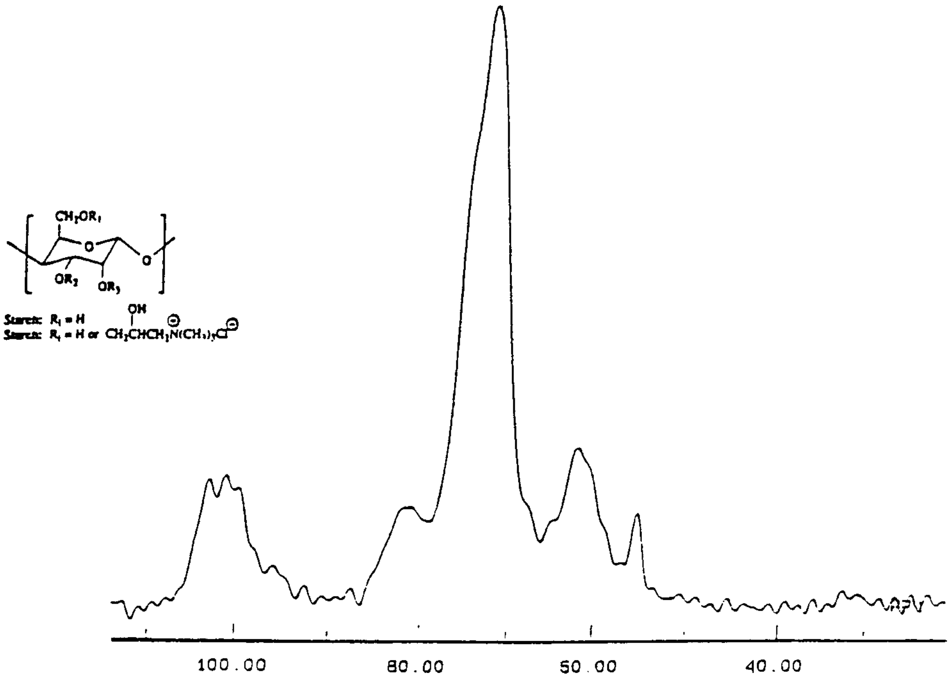

Fig. 2. ^{13}C solid-state NMR plot of modified corn starch.

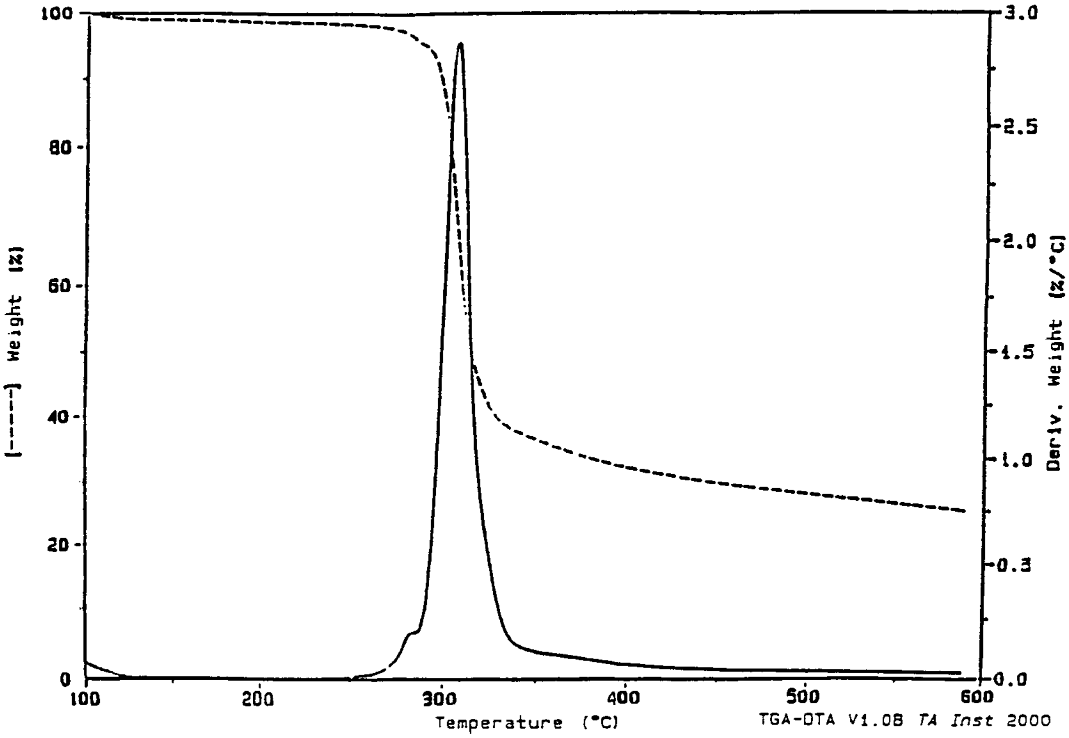

Fig. 3. TG-DTG plot of amylose in an atmosphere of flowing dry nitrogen.

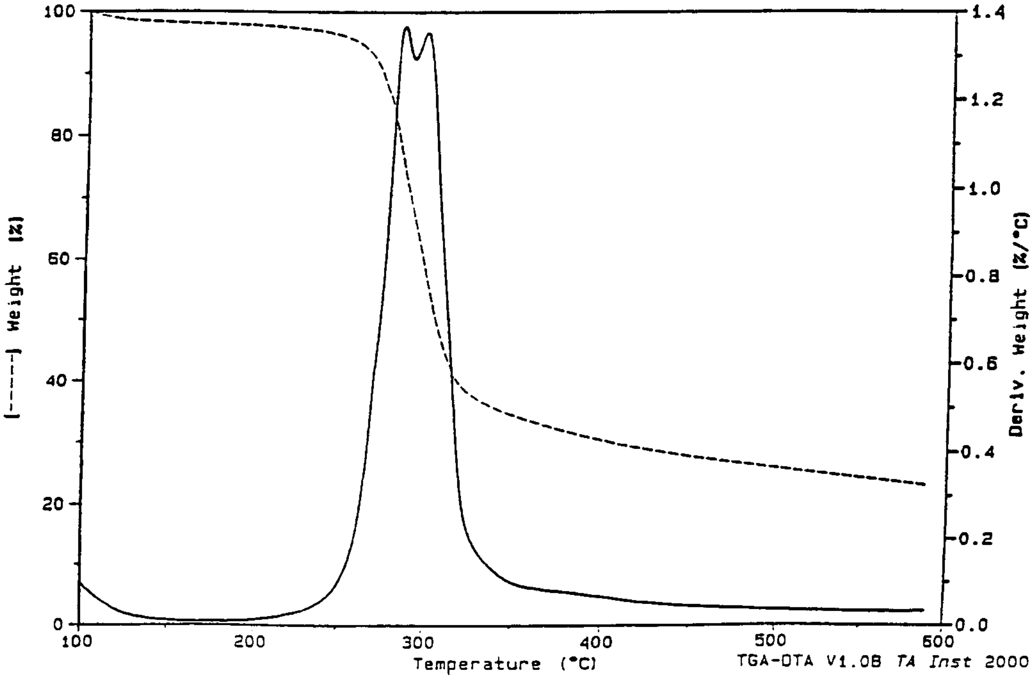

Fig. 4. TG-DTG plot of modified amylose in an atmosphere of flowing dry nitrogen.

almost 80% of the material is lost (Fig. 4). The DTG plot (also Fig. 4) showed an additional peak at 275°C together with the peak at 300°C which corresponded with a single peak in the unmodified material at that temperature. Such behavior might be expected because part of the original material has been converted into a new form. The modified material has to be regarded as part cationic in character and part unmodified. Both parts are of similar composition, so the appearance of the double peak simply represents the overlapping degradation of the two components. Similar results were obtained from all the modified materials. All this data collected in nitrogen can also be correlated with the TG-DTA analysis of experiments in flowing air. A general scheme for thermal degradation has been proposed to show that combustible volatiles are initially produced [15–17]. This is an endothermic process that appears as an exotherm in air because of ignition of the material. This region is termed ‘flaming combustion’. The carbonaceous residue produced can also react with oxygen to produce simple gases, Co, CO_2 and H_2O; this region is termed ‘glowing combustion’. In nitrogen, the degradation terminates with the production of carbon.

Various theories have been used to describe the initial series of changes, all of them leading to depolymerization, when in nitrogen these depolymerized materials degrade to carbon but the originators of the various schemes are not so clear at this point. Briefly, the schemes proposed utilize the formation of 1,6 anhydro rings, transglycosylation and radical mechanisms [18–20]. Rising temperature TG has been performed on pure corn starch (under a nitrogen atmosphere) in order to analyze the breakdown that it undergoes when subjected to higher temperatures. The degradation commences at ca. 250°C. and continues to degrade until 500°C. A two-step degradation process occurs under an air atmosphere. For either atmosphere, the major weight loss, corresponding to the complete breakdown of starch, starts at the temperature (≈250°C) indicating that initiation of the breakdown is a non-oxidative process. In air, after the initial weight loss, the second slower but accelerated process starts. This second process does not occur under inert atmospheres and is, therefore, considered to be the oxidation of the partially decomposed starch. The DTG plot reveals two regions of combustion. This is readily apparent on inspection of the DTA plot for

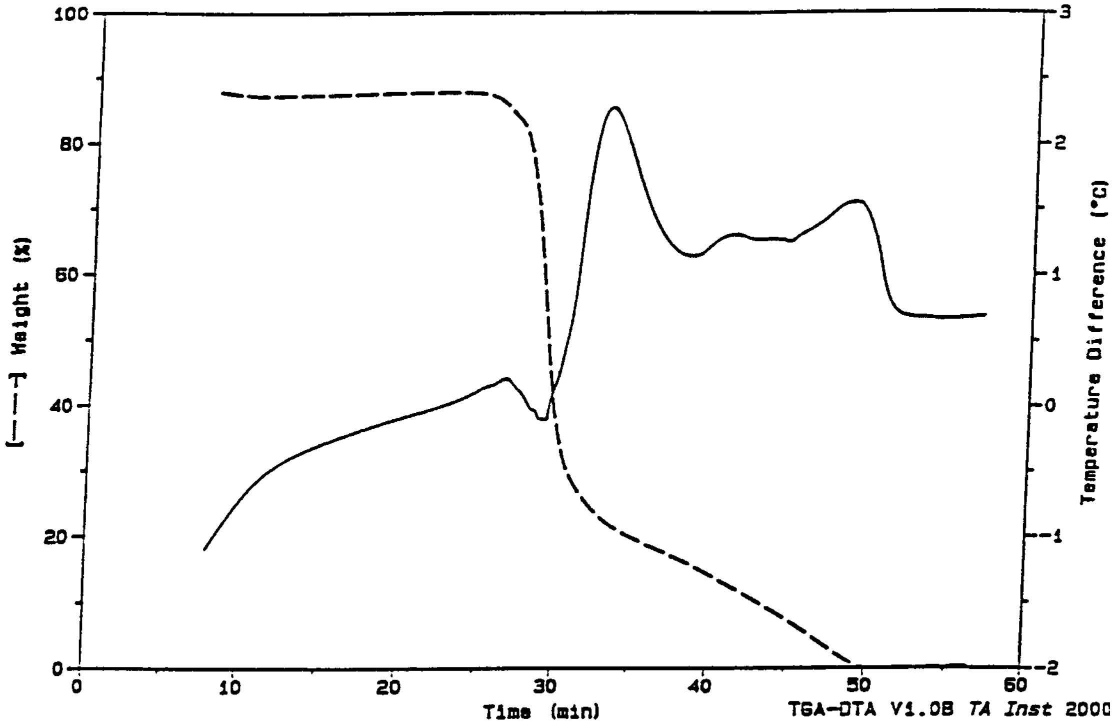

Fig. 5. plot of corn starch in an atmosphere of flowing dry air.

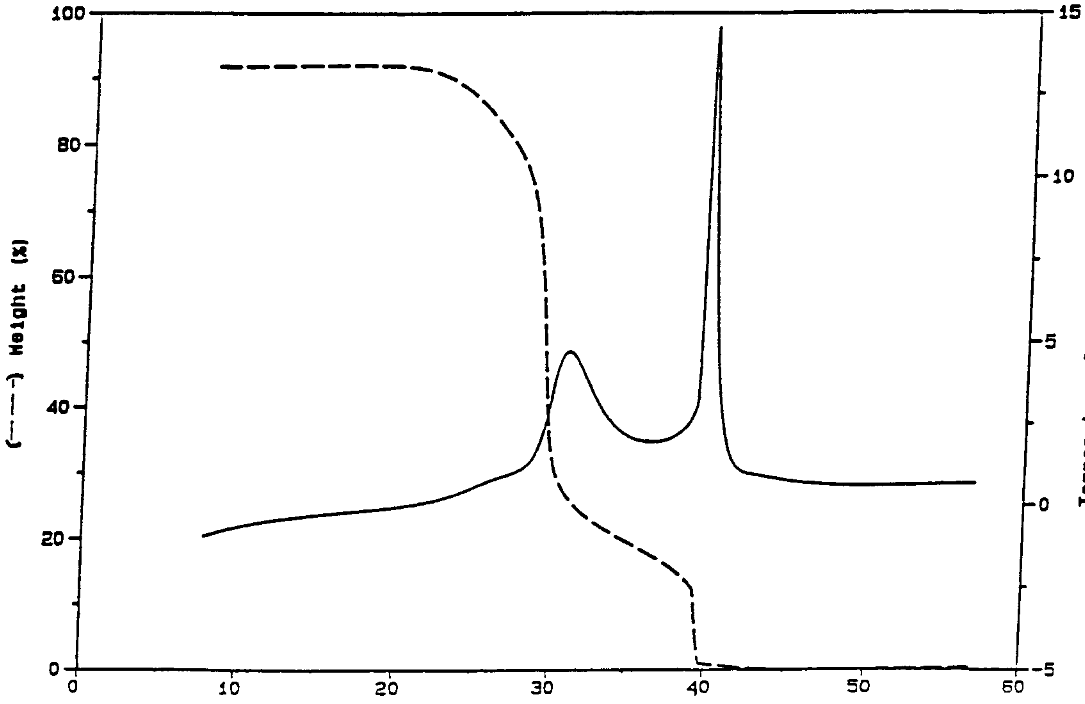

Fig. 6. TG-DTA plot of modified corn starch in an atmosphere of flowing dry air.

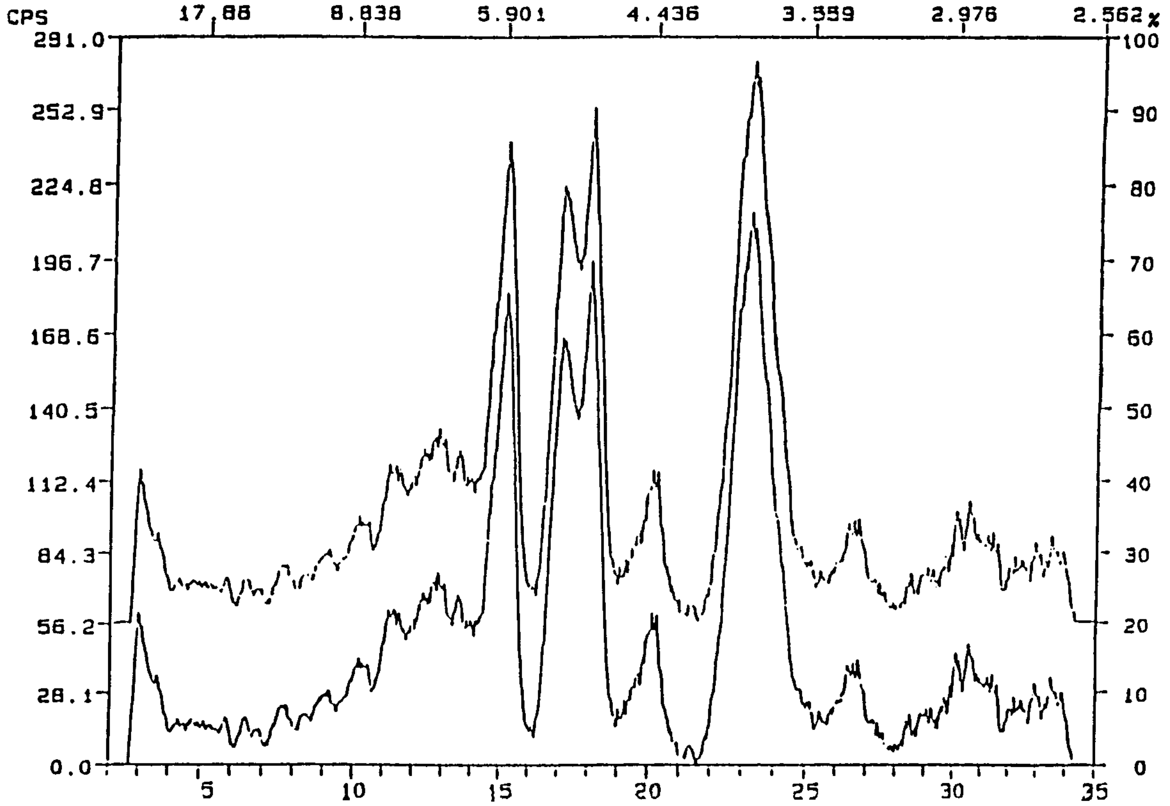

Fig. 7. XRD pattern of native and modified corn starch.

Table 2
DSC results obtained for native and modified starch showing the peak gelation temperatures

Material	T_p [a] for gelation
Native corn starch	68.5°C
Modified corn starch	60°C
Native amylose	71°C
Modified amylose	65°C
Native amylopectin	65°C
Modified amylopectin	55°C

[a] T_p refers to peak gelatin temperature on the DSC plot.

the corn starch and modified corn starch shown in Figs. 5 and 6. It shows the start of an endothermic degradation taking place under the gaseous combustion of the gases being released in a large exothermic event. The second region of mass loss corresponds to the ignition of the solid carbonaceous residue in a self-sustained exothermic process leading to a second exothermic event or as a shoulder to the first peak in the region usually termed as a region of 'glowing combustion'.

In order to investigate whether substitution had an effect on gelatinization temperatures of starch, the modified and native material were gelatinized on a DSC unit. The DSC thermograms for all the samples recorded at a concentration of 1 : 10 w/w, gave a single narrow gelatinization endotherm. This phenomenon has been ascribed to the water-mediated melting of starch crystallites initiated by the stripping of starch chains in the swollen amorphous regions of the granule. Corn starch gel showed a peak temperature of 68.5°C. Cationic corn starch, on the other hand, showed a T_p of 60°C. A similar pattern was obtained with all the samples examined (Table 2). Several investigators had established the principle that cross-linked and substituted starch granules exhibit lower gelatinization temperatures. Kartha and Srivastava [21] considered that highly cross-linked starches had a lower proportion of starch granules that were capable of gelatinization by heat. This would decrease the energy required for starch gelatinization. The same general trend was observed in all the modified materials examined in this study.

The native and cationic starch granules exhibited the characteristic A-type X-ray diffraction pattern with strong intensity lines at mean inter-planar spacing (Fig. 7). The substitution of the cationic group did not affect the intensity of the diffracted beams in all the cases examined. This supports the hypothesis earlier that substitution groups are concentrated in the amorphous regions of the granule.

5. Conclusions

The materials studied were successfully modified using a cationic salt. Characterization of the materials using NMR gave the degree of substitution of the modified starch products and this was comparable with results obtained from elemental analysis. The TG plots clearly show the presence of the modified material distinct from the native one by the occurrence of the double peaks. In all cases, the TG-DTG in nitrogen shows an endothermic degradation to carbon but, generally, the carbon residue is enhanced by the cationic treatment. In air, quite clearly gaseous combustion is followed by glowing combustion, both being sufficiently exothermic to cause appreciable distortion in the imposed temperature program. The DSC data demonstrate marked decrease in gelation temperature because of cationization. The X-ray data suggest that the modification occurs in the amorphous region of the starch granules.

References

[1] K. Phillips, W. Williams, in Cellulose and its Derivatives, Chichester, 1985, p. 100.

[2] G.E. Hamerstand, B.T. Hofreiter, C.L. Mehltretter, W.E. Schulze, D.J. Kay, Tappi 44 (1961) 430.

[3] D. Glittenberg, Tappi 77 (1993) 215.

[4] W. Nachtergaele, Starch/Stärke 41 (1989) 310.

[5] W.J. Lim, Y.T. Liang, P.A. Seib, Cereal Chem. 69 (1992) 237.

[6] M.E. Carr, J. Appl. Polym. Sci. 54 (1994) 1855.

[7] G.D. Valle, P. Colonna, J.T. Nantes, Starch/Stärke 43 (1991) 300.

[8] M.E. Carr, M.O. Bagby, Starch/Stärke 33 (1981) 310.

[9] R.K. Harris, in Nuclear Resonance Spectroscopy, Pittman Publishing, London, 1983, p. 100.

[10] W.E. Killinger, D. Murray, G.R. Hatfied, Starch/Stärke 47 (1994) 311.

[11] M. Yalpani, in Industrial Polysaccharides: Genetic Engineering: Structure, Property Relations and Applications, Elsevier Science Publishers, B.V., Amsterdam, 1987, p. 112.

[12] M. Kainosho, K. Ajisaka, Tetrahedron Lett. 18 (1978) 1563.

[13] M.J. Gidley, M.B. Stephen, J. Am. Chem. Soc. 110 (1988) 3820.

[14] M. Gurruchaga, I. Goni, B. Vazquez, M. Valero, G.M. Guzman, Macromol. 25 (1992) 3009.

[15] Y. Tsuchija, K. Sumi, J. Appl. Polym. Sci. 14 (1970) 2003.

[16] S.L. Madorsky, V.E. Hart, S.J. Straus, Res. Nat. Bur. Stand. 56 (1956) 343.

[17] F.A. Wodley, J. Appl. Polym. Sci. 15 (1971) 835.

[18] O.P. Golova, Usp. Khim. 44 (1975) 1454.

[19] F. Shafizadeh, R.A. Susott, G.D. McGinnis, Carbohydr. Res. 22 (1972) 63.

[20] D. Dollimore, P. Spooner, A. Turner, Surface Tech. 4 (1976) 121.

[21] K.P.R. Kartha, H.C. Srivastava, Starch/Stärke 37 (1985) 297.