ELSEVIER

PII: S0144-8617(97)00046-5

Carbohydrate Polymers 33 (1997) 153–162

0144-8617/97/$17.00 + .00

Chemical and physical transitions of periodate oxidized potato starch in water

S. Veelaert[a]*, D. de Wit[a], K. F. Gotlieb[b] and R. Verhé[c]

[a]*TO-DLO, Agrotechnological Research Institute, PO Box 17, 6700 AA Wageningen, The Netherlands*
[b]*Wildervankstraat 12, 9648 LC Wildervank, The Netherlands*
[c]*University of Ghent, Faculty of Agricultural and Applied Biological Sciences, Coupure links 653, 9000 Ghent, Belgium*

(Received 30 March 1996; accepted 9 October 1996)

Physical and chemical transitions of dialdehyde starch in aqueous suspensions have been determined as a function of temperature and pH. The pH conditions were restricted to neutral or lower, since alkaline degradation is commonly recognized. Physical alterations were determined by measuring viscosity transitions at room temperature and upon heating. Chemical degradation was surveyed by controlling the amount of aldehydes, the production of carboxylic acids and the decrease in molecular weight. At neutral conditions and upon heating at 90°C extensive chemical degradation occurred. This was manifested by a gradual conversion of aldehydes into carboxylic acids and alcohols, accompanied by a decrease in molecular weight. Degradation upon heating was minimized by reducing the pH to 3. At ambient temperature, the granular integrity was lost beyond pH 5 or 6 depending on the degree of oxidation of the material. © 1997 Elsevier Science Ltd

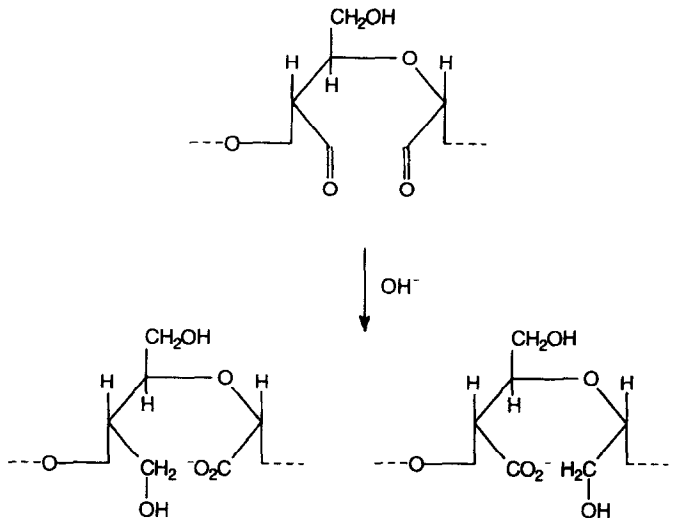
INTRODUCTION

Dialdehyde starch is produced by glycol cleavage oxidation of starch with periodate. Consequent to oxidation, the chemical stability of starch is altered. Degradation in alkaline (BeMiller, 1965; Wise and Mehltretter, 1973; Whistler *et al.*, 1959; Fry *et al.*, 1942) or acid media (Wilham *et al.*, 1971) has been reported in the past. Data on chemical degradation at pH values between 3 and 7, however, are limited. Present investigations have, therefore, been focusing on the behaviour of dialdehyde starch in water at ambient temperature and during heating to 90°C in a pH range from 3 to 7, this being the actual pH range for production, isolation and application of dialdehyde starch in most cases.

The observed transitions in this research will be compared with earlier proposed degradation mechanisms in alkaline media. As alkaline degradation is accompanied by the production of acids, a Cannizzaro reaction has frequently been implicated. Via this reaction two aldehydes are converted into a carboxylic acid and an alcohol (Scheme 1). Alternatively, acid production has been explained by a sequence of reactions, initiated by β-elimination and followed by hemiacetal hydrolysis and a benzil-benzilic acid type of rearrangement (Scheme 2). Indications have been found that both proposed mechanisms are viable during alkaline degradation. Complete identification of all degradation products, however, has not been realized owing to the complexity of the reaction mixtures (Whistler *et al.*, 1959).

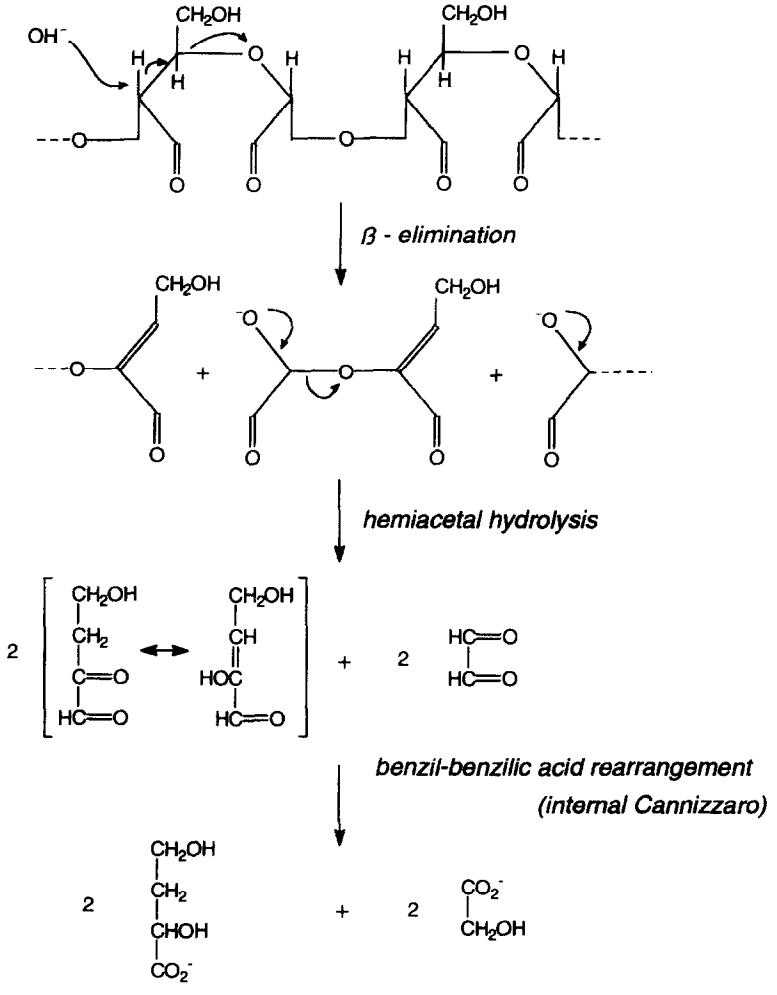
The viscosity behaviour of diluted dialdehyde starch suspensions upon heating has been reported in several papers (Sloan *et al.*, 1956; Levine *et al.*, 1959; Mellies *et al.*, 1958; Veelaert *et al.*, 1996). The delayed and limited swelling of dialdehyde starch granules has been attributed to the formation of internal crosslinks by hemiacetalization (Scheme 3). Light-scattering, sedimentation and viscosity measurements have shown that the average particle weight in solution generally decreases with increased level of oxidation and time of heating (Levine *et al.*, 1959). Upon continued heating, dialdehyde starch becomes completely dispersed, resulting in a low viscosity solution. The fact, however, that the material gelled upon ageing indicated that it still had a relatively high molecular weight (Veelaert *et al.*, 1996). The exact composition of dispersed systems and the molecular weight distribution have not been reported.

*To whom correspondence should be addressed.

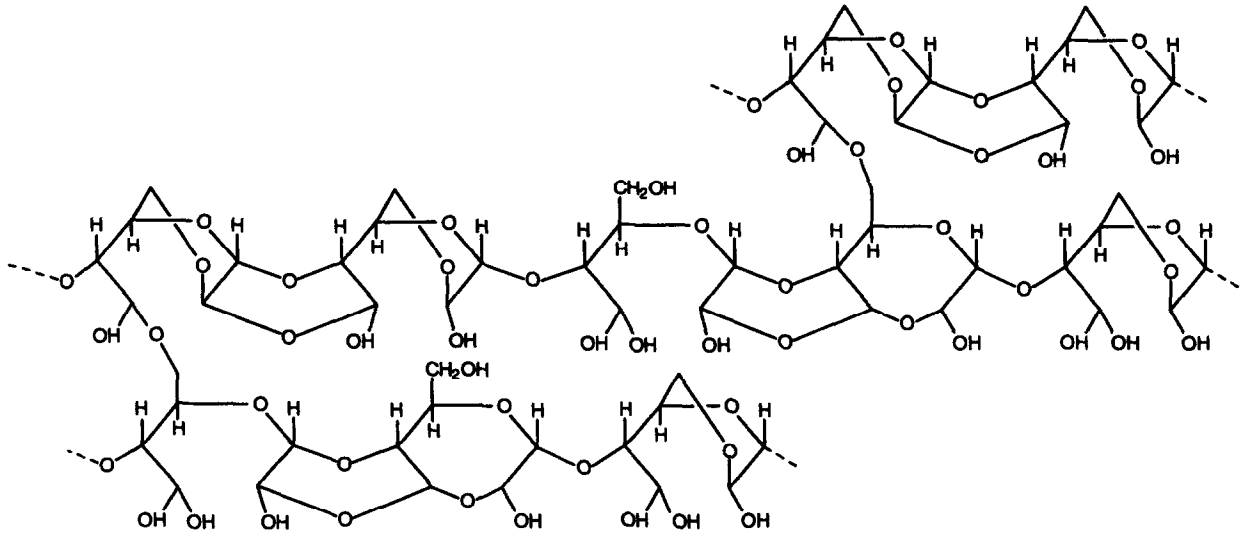


Scheme 1. The Cannizzaro reaction of dialdehyde starch in alkaline medium.

With regard to applications, however, it is necessary to have an idea of the actual composition of dispersed dialdehyde starch systems. This study reports on the physicochemical effects of degradation by measuring the changes in rheological behaviour, the increase in acidity, the decrease in aldehydic reactivity and the decrease in molecular weight. Intermediate and completely oxidized starches have been compared to



Scheme 2. β-climination, hemiacetal hydrolysis and benzil-benzilic acid rearrangement of dialdehyde starch in alkaline medium.



Scheme 3. Possibilities for hemicetal and acetal formation in dialdehyde starch resulting in crosslinking.

characterize the effect of degree of oxidation on stability and reactivity.

The measured data give insight into the effectiveness of dialdehyde starch in further use as e.g. a cross-linker after a heat–pH treatment to obtain a dispersed material. Depolymerization and a decrease of the aldehyde content might be detrimental or at least change the expected effect of dialdehyde starch.

EXPERIMENTAL

Frequently used notation

DAS-50	starch with 50% of the glucose units oxidized
DAS-100	starch with 100% of the glucose units oxidized
(CHO)	amount of aldehyde groups in dialdehyde starch, equal to twice the amount of oxidized glucose units
(COOH)	amount of carboxylic acid groups
(CH_2OH)	amount of alcohol groups
subscript 0	originally present
subscript T	after heating
superscript oxime	converted into oximes (available)
superscript protected	not converted into oximes (protected)
superscript h.p.l.c.	determined by h.p.l.c. analysis (total)

General approach

Dialdehyde starches of known aldehyde content were subjected to various heat treatments in aqueous suspensions at different pH values (it should be noted that the actual pH inside the granules might deviate from the measured pH of the suspension). Acid production ($(COOH)_T$) was determined by continuous titration with sodium hydroxide. The amount of reactive aldehydes ($(CHO)_T^{oxime}$) was subsequently calculated by measuring the oxime formation upon addition of hydroxylamine. The molecular weight distribution was measured by gel permeation chromatography.

The initial degree of oxidation, which corresponds with the aldehyde content ($(CHO)_0$), was determined by h.p.l.c. analysis (Veelaert *et al.*, 1994). The same method was not appropriate to determine the aldehyde content after heating owing to degradation into a complex mixture of products. The aldehyde content was therefore approximated by measuring the amount of aldehydes available for oxime formation ($(CHO)^{oxime}$). The situation where the amount of reactive aldehydes is lower than the actual amount of aldehydes is likely to be encountered in any kind of subsequent reaction of the aldehydes. Table 1 gives a schematic overview of the performed analyses.

Preparation of DAS-50 and DAS-100

Potato starch (18 wt% moisture, purchased from Avebe NV, Foxhol, The Netherlands) was suspended in demineralized water (100 g litre^{-1}, corresponding with 8.2 wt% dry potato starch) and the vessel was subsequently cooled in an ice bath. While stirring with a magnetic stirrer, the required amount of sodium periodate was added (54 g for DAS-50 and 120 g for DAS-100). The pH was controlled during the reaction by continuously adding a solution of NaOH (1 M) with an automatically driven burette. The reaction was performed in the dark at room temperature and

Table 1. Performed analyses of dialdehyde starch before and after heating

	Composition	Analysis
DAS	$(CHO)_0$	h.p.l.c.
		Oxime reaction→$(CHO)_0^{oxime}$
	$(CHO)_T$	Oxime reaction→$(CHO)_T^{oxime}$
Heated DAS	$(COOH)_T$	Alkali consumption
	M_w	Gel permeation chromatography

stopped after 3 h to obtain DAS-50 and after 18 h to obtain DAS-100.

Washing of the material was performed by filtration over a Büchner filter (S and S 589 filter paper) and immediate resuspension of the solids in the same volume of demineralized water. This filtration cycle was repeated several times (mostly five) until all iodic compounds were removed. The pH was controlled during washing and if necessary adjusted to 4 by addition of dilute hydrochloric acid (0.1 M). Some samples were freeze dried after washing. The total moisture content of the resulting samples was determined in a Sartorius moisture analyser by measuring the decrease in weight upon heating at 95°C. The degree of oxidation of the dialdehyde starch was checked as described by Veelaert *et al.* (1994).

Preparation of suspensions and rheological measurements

DAS-50 or DAS-100 samples (250 ml) were taken from the reaction mixtures (see previous paragraph), before or after washing (8.2 wt% in 250 ml water). Several series of suspensions have been measured in order to determine the influence of iodate and pH. The samples, which had not been isolated by freeze drying, were gently stirred for several hours (16 h) prior to measurement. This pretreatment was necessary to obtain homogeneously dispersed systems. The pH was adjusted with either NaOH (1 M) or HCl (1 M).

The suspensions were subjected to heat treatment in the Contraves Rheomat 115, a rotational viscometer equipped with an MS DIN 145 measuring unit and a stirring device to prevent sedimentation of the granules. The apparatus was calibrated by measuring solutions of known viscosity at a shear rate of 120 s^{-1} (100 rpm). The temperature was increased from 20 to 90°C in 2 h, while stirring at 100 rpm and recording the viscosity.

Acid production during heating

A suspension of 2 g dialdehyde starch in 150 ml water was adjusted to pH 7 with NaOH (1 M) for titration of trace formic acid produced during oxidation. From this point all further acid and base consumptions are summed to enable correct calculation of acid production during heating. Under controlled addition of HCl (0.1 M), the pH was readjusted to 3, 5 or 7. The suspensions were subsequently heated in an oil bath to 90°C. Meanwhile, acid production was measured by recording the consumption of NaOH (1 M) to maintain constant pH conditions during heating. After cooling, the suspensions (or solutions) were readjusted to pH 7 with controlled amounts of NaOH in order to allow all acids to dissociate. Additional increase of the pH did not change the extent of dissociation.

Oxime reaction

A series of suspensions of 2 g dialdehyde starch in 150 ml water were pretreated by heating. The pH, the maximum temperature and the time of heating were varied. The pH was adjusted to 5 after cooling. A surplus of hydroxylamine hydrochloride (50 ml of a 1 M solution of $NH_2OH.HCl$) was adjusted to pH 5 with NaOH and subsequently added to the dialdehyde starch dispersion. The conversion of aldehydes into oximes was determined by recording the consumption of NaOH (1 M), performing the reaction at a constant pH of 5.

Nuclear magnetic resonance (NMR)

A dialdehyde starch sample was completely dissolved and degraded by heating for several hours at 90°C in deuterated water. Aceton was added as an internal standard. The ^{13}C spectrum (50 MHz) was recorded with a Bruker AC 200 spectrometer.

Molecular weight determination

The molecular weight distribution was determined with a HPSEC-MALLS-RI, which is a high-performance size-exclusion chromatography unit with a multi-angle laser-light-scattering detector and a differential refractometer (van Soest *et al.*, 1995). Samples (10 $\mu g\,ml^{-1}$) were pretreated by heating dialdehyde starch in water at varying pH and for varying durations. The samples were filtered through a PTFE filter (1 μm) and injected into a sample loop (200 μl). Together with the eluent (a potassium phosphate buffer at pH 3), the sample was pumped into a guard column (TSK PWH-PE prep-guard, 7.5×7.5 mm, Beckman) followed by six main columns (Spherogel-TSK 1000 PW, 2000 PW, 3000 PW, 5000 PWHR and 6000 PW, 30×7.5 mm). Analysis of the eluate was first performed with a Dawn-F multi-angle laser photometer (Wyatt technology), equipped with an

Argon Ion Laser operating at 488 nm and with 15 detectors in the angular range of 15 to 151°. The eluate was subsequently examined with an RI detector (Waters 410 differential refractometer). The total system was held at a constant temperature of 50°C. A dn/dc value of 0.153 ml g^{-1} (Levine *et al.*, 1959) was applied to calculate the molecular weights as described elsewhere (van Soest *et al.*, 1995).

RESULTS AND DISCUSSION

Molecular aspects

This discussion of the results is based on the assumption that aldehydes are converted into carboxylic acids during degradation. The acid and reactive aldehyde content after heating are compared with the aldehyde groups initially present in dialdehyde starch. The purpose of these experiments was to analyse the extent of degradation as function of heating conditions and to characterize the type of degradation and the direct consequences thereof on reactivity and applicability.

Determination of acid production, $(COOH)_T$

Dialdehyde starch suspensions at pH 3, 5 or 7, were heated under controlled feeding of sodium hydroxide (1 M) for pH correction. The hydroxide consumption is depicted as function of time in Fig. 1. For the suspension at pH 7, the acid production started after 10 min, as a temperature of 75°C was reached, whereas at pH 5 it started only at 90°C and at a much lower rate. At pH 3, acid production was very low.

The amount of base added in several experimental series was related to the amount of carboxylic acids produced and was expressed relative to the amount of aldehydes present in the starting product (Table 2). Obviously, the acid release increased with rising pH and temperature of the suspensions. After heating for 5 h at 90°C and pH 7, the acid production corresponded with a conversion of 41% of the aldehydes to carboxylic acid groups. At pH 5 this amount was only 25% and at pH 3 it was 6%. No significant differences were observed between DAS-100 and DAS-50.

Short heating at lower temperatures, 75 and 50°C, appeared to be much less detrimental. Acid production

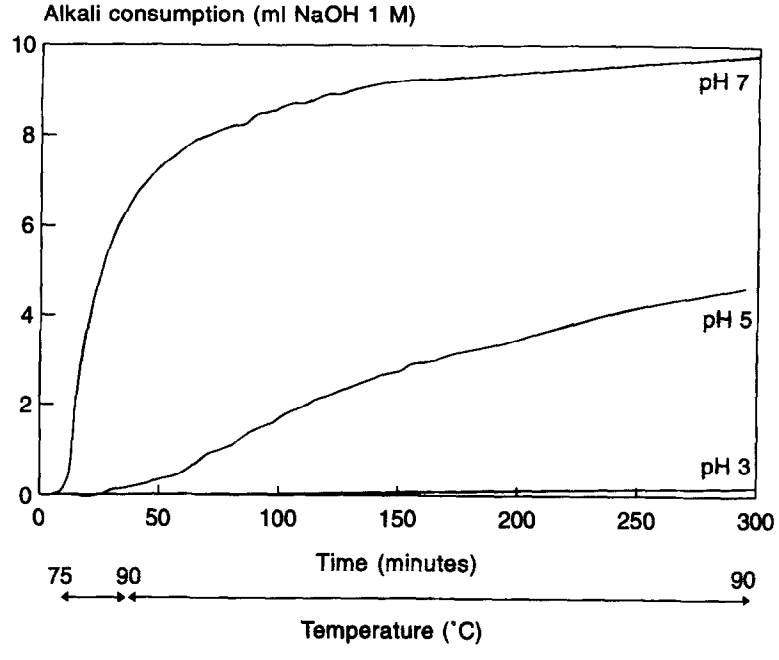


Fig. 1. The alkali consumption during heating of DAS-100 suspensions at different pH values.

Table 2. Acid production upon heating expressed as a percentage of total aldehydes in the starting product (average of three replicas)

	DAS-100			DAS-50
pH	1 h 50°C	1 h 75°C	5 h 90°C	5 h 90°C
3	< 0.05	< 0.05	6.2±2.5	6.4±3.1
5	0.10±0.07	0.10±0.09	25.3±1.2	23.2±2.1
7	0.40±0.09	3.20±0.63	40.7±0.9	40.9±1.9

could be minimized to less than 0.05% on aldehyde bases upon mild heating at pH 3.

Determination of reactive aldehyde content, $(CHO)_T^{oxime}$

Dialdehyde starch suspensions were heated and subsequently cooled to room temperature prior to the addition of a solution of hydroxylamine hydrochloride. The conversion of aldehydes into oximes was followed by titration of the released hydrochloric acid with sodium hydroxide. In general, for untreated dialdehyde starch suspensions, about 50 to 60% of the aldehyde groups are readily available for reaction (Veelaert *et al.*, 1994). Once this degree of conversion is reached, the oxime formation slows down, but still continues to a maximum value of about 80% (see Fig. 2). The very slow reaction of a major portion of the aldehyde groups (≃40%) is attributed to the formation of hemiacetal and acetal groups that protect the aldehydes from further reactions (Veelaert *et al.*, 1994). The actual amount of aldehydes, which is derived from h.p.l.c. analysis, thus consists of the readily available aldehydes, which are determined by oxime formation, plus the unavailable aldehydes:

$$(CHO)_0^{h.p.l.c.} = (CHO)_0^{oxime} + (CHO)_0^{protected}$$

$$\text{with} (CHO)_0^{oxime} \simeq 0.8 (CHO)_0^{h.p.l.c.}.$$

Conversion into oximes of about 80% of the total aldehydes was also observed for DAS-100 samples that were being heated under mild conditions. The respective results are listed in Table 3. Heating at 90°C appeared to have caused a considerable reduction of the available aldehyde groups in DAS-100 and DAS-50: after 5 h no more reactive aldehydes were left at pH 7; at pH 5 the relative free aldehyde content in DAS-100 was reduced to 29% and at pH 3 to 68%.

Both a physical and a chemical effect have to be considered to explain the effect of pH on the reactivity or availability of aldehyde groups. Increase of pH and heating might improve diffusion (of reactant) into the granule, which is in accordance with the noticeable granular swelling. The increase in reactive aldehyde content upon mild heating can be explained by such a physical effect. On the other hand, dialdehyde starch has been shown to be alkali labile during treatment with sodium hydroxide solution and with lime water (Whistler *et al.*, 1959); alkaline degradation at room temperature was accompanied by the conversion of

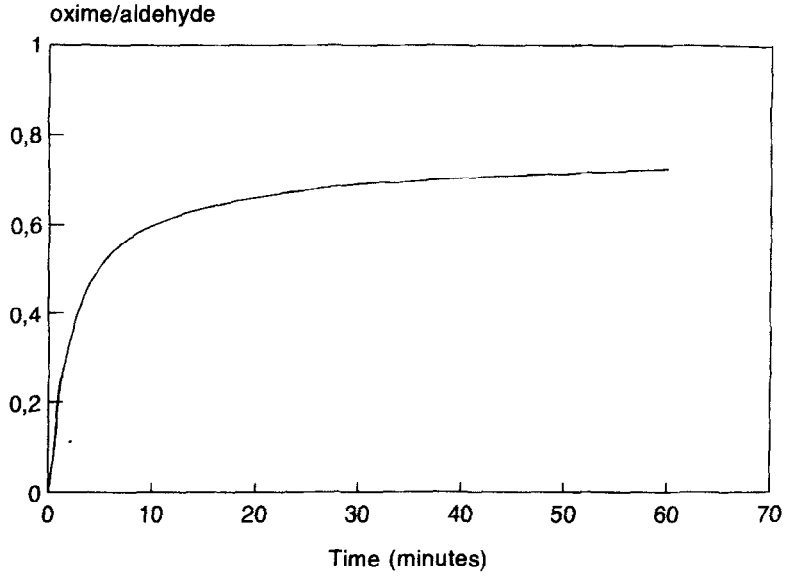


Fig. 2. The conversion of DAS-100 aldehydes into oximes as a function of time after addition of hydroxylamine hydrochloride.

Table 3. The conversion of available aldehydes into oximes expressed as a percentage of total aldehydes in the starting product (average of three replicas)

	DAS-100				DAS-50
pH	25°C [a]	1 h 50°C	1 h 75°C	5 h 90°C	5 h 90°C
3	79.3±1.6	78.8±3.2	80.5±2.5	68.1±1.4	68.3±1.0
5	79.6±2.3	80.9±2.1	80.3±1.8	28.8±2.8	33.2±1.9
7	80.2±2.5	79.9±1.9	77.4±1.6	0.22±2.0	0.15±1.7

[a] The values measured at 25°C correspond with $(CHO_0)^{oxime}$.

aldehydes into carboxylic acids, e.g. by a Cannizzaro rearrangement or by a benzil-benzilic acid type of rearrangement of the β-elimination products. Although present experiments were performed under slightly acidic or neutral conditions, the same type of rearrangements are yet supposed to occur. This assumption is based on the measured increase in acidity and the decrease in aldehyde content as listed in Tables 2 and 3 respectively. The initial amount of aldehydes is supposed to be partly converted into carboxylic acids at a rate depending on heating conditions.

Conversion of aldehydes into carboxylic acids and alcohols, $(CHO)_0 \rightarrow (COOH)_T + (CH_2OH)_T$

The conversion of aldehydes into carboxylic acids following the earlier proposed rearrangements, i.e. Cannizzaro and benzil-benzilic acid rearrangement, is also accompanied by the production of alcohols. In the case of degradation according to the Cannizzaro reaction, the total sum of aldehydes, carboxylic acids and alcohols would be equal to the initial amount of aldehydes. The following equations would then apply:

$$(CHO)_0 = (CHO)_T + (COOH)_T + (CH_2OH)_T;$$
$$(COOH)_T = (CH_2OH)_T.$$

If the Cannizzaro equation is applied for the results of the $(CHO)_T^{oxime}$ and $(COOH)_T$ measurements, it appears that the sum $[(CHO)_T^{oxime} + 2(COOH)_T]$ is about equal to the initial percentage of reactive aldehydes (Table 4):

$$(CHO)_0^{oxime} \approx (CHO)_T^{oxime} + 2(COOH)_T.$$

The sum, after heating DAS-100 at 90°C and at pH 3, 5 and 7 respectively, corresponds with about 81, 79 and 82% of the initial amount of aldehydes. However, the fact that the experimental data correspond fairly well with the Cannizzaro equation, i.e. when $(CH_2OH)_T$ is assumed to be equal to $(COOH)_T$, does not unequivocally imply that mostly Cannizzaro rearrangement takes place. In fact, a Cannizzaro reaction is generally not observed when an α-hydrogen is present, such as for the C4 hydrogen in dialdehyde starch. Several other degradation mechanisms are liable to interfere:

(1) Unlike the Cannizzaro reaction occurring without depolymerization, β-elimination at C4-C5 might result in chain scission. Consequently, since the amount of groups susceptible for degradation rises upon chain scission, additional aldehydes, carboxylic acids and alcohols might result upon a Cannizzaro or a benzil-benzilic acid rearrangement.
(2) Similarly, acid hydrolysis, e.g. at pH 3, might result in chain scission.
(3) The decrease in aldehyde content could also be explained by aldol condensation of a C4 carbon to a carbonyl carbon. Aldol condensation implies that one out of two aldehydes in a unit is lost, while the remaining aldehyde might be converted into a carboxylic acid or an alcohol by a rearrangement.

As a consequence, precise determination of the relative conversion of aldehydes into carboxylic acids and alcohols is rather difficult, since degradation cannot be assigned to one type of reaction mechanism.

Nuclear magnetic resonance

A dissolved dialdehyde starch sample, which was supposed to be partly degraded, was analysed by ^{13}C nuclear magnetic resonance spectroscopy. Besides the peaks appearing between 55 and 110 ppm as expected for carbohydrates, two small multiplets appeared at 142 and 133 ppm representing a double bond conjugated with a carbonyl function. Moreover, some aldehyde peaks were observed around 192 ppm. This spectrum possibly points to the formation of β-elimination products.

Molecular weight

The molecular weight distribution of dialdehyde starch was determined by high-performance size-exclusion chromatography. The decay of the weight average molecular weight M_w was followed as function of pH and time of heating as depicted in Fig. 3.

At pH 7 the average molecular weight was observed to drop considerably upon short heating such that accurate measurements were very difficult. Only if samples were measured immediately after dissolution at pH 7 was it possible to detect some relatively high molecular weight material ($M_w = 1600$). At pH 5 the molecular weight decreased as well but at a much lower rate: M_w was reduced by a factor 16 after heating for

Table 4. $(CHO)_T^{oxime} + 2(COOH)_T$ as a percentage on total aldehydes in the starting product

	DAS-100				DAS-50
pH	25°C [a]	1 h 50°C	1 h 75°C	5 h 90°C	5 h 90°C
3	79.3	78.9	80.6	80.5	81.1
5	79.6	81.1	80.5	79.4	79.6
7	80.2	80.7	83.8	81.6	82.0

[a] The value at 25°C corresponds with $(CHO_0)^{oxime}$.

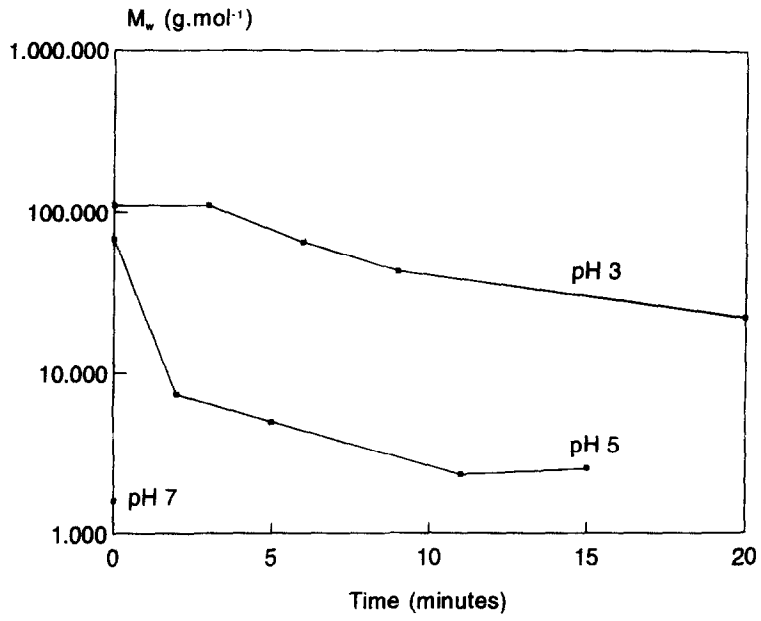


Fig. 3. The decrease in the weight average molecular weight of DAS-100 as a function of heating time at 90°C and at different pH values.

15 min at 90°C; at pH 3 it was reduced by a factor 5. The relatively low M_w values are attributed to some limitations of the apparatus and to incomplete dissolution of the particles. Since the relative portion of the total material that was detected was constant, the M_w values could be compared on a relative scale.

Even though dialdehyde starch shows minor conversion of aldehydes into carboxylic acids and alcohols as long as temperature and pH is controlled (< 0.1% below pH 5 and 90°C), the molecular weight gradually decreases upon heating. The occurrence of acid hydrolysis or eventually β-elimination, resulting in chain scission, is therefore plausible. With increasing pH values, the extent of depolymerization rises and the loss of aldehyde functions becomes significant, in particular at pH 7.

Physical aspects

The stability of dilute dialdehyde starch suspensions was examined by rheological measurements. Any loss of granular stability, reflected by swelling, was evaluated by measuring the viscosity increase upon stirring at the ambient temperature. Also the onset and peak temperature of gelatinization were considered to be valuable parameters; upon loss of granular rigidity, gelatinization will occur at lower temperatures. Molecular degradation, on the other hand, is expected to effect a decrease of the paste viscosity during heating.

In a first series of experiments, DAS-50 and DAS-100 were suspended in water after being isolated in five washing cycles. The curves in Figs 4 and 5 show the short-term effect of pH on the respective viscosity transitions; the pH of each suspension was adjusted immediately before measurement. Inevitable differences between the intragranular pH and the overall pH in suspension should not be ignored. Data on native starch are not presented since the experimental design was not appropriate for native starch due to the high viscosity.

The viscosity response, onset and peak temperature decreased gradually with rising pH in the suspensions, implying that alkali induced granular disruption and probably molecular degradation. The curves for DAS-100 differed in these characteristics from those for DAS-50, in that each viscosity transition was shifted to a higher temperature; the peak viscosity, however, was five times lower.

The effect of pH increase was more pronounced if the suspensions had been stirred for a longer period at ambient temperature; depending on the pH, the oxidized starch granules swelled to a relatively large extent and even dissolved. Moreover, sodium iodate, abundantly present in the crude reaction mixtures, has been shown to intensify the effect of pH. For instance, it was observed that DAS-50 dissolved upon stirring the reaction mixture for 16 h at pH 6.5, while formation of a viscous mass was observed at pH 5.5. The curves in Fig. 6 illustrate the viscosity responses for DAS-50 at pH 4 and 5.5 in the crude reaction mixtures. The initial viscosity plateau measured at pH 5.5 points to swelling at room temperature before measurement. For DAS-100 similar responses were obtained at pH 6 and 7.5.

Obviously, the rate of swelling is influenced by both the pH and the iodate concentration in the respective suspensions. Overall, DAS-100 granules are less susceptible to swelling: the absolute viscosity values are

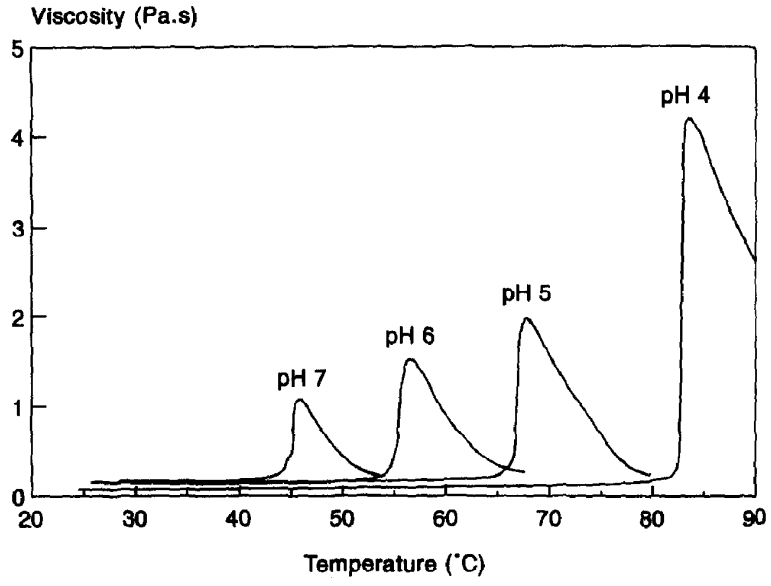


Fig. 4. The gelatinization curves of DAS-50 (8.2 wt%) immediately after isolation from the reaction mixture and pH adjustment.

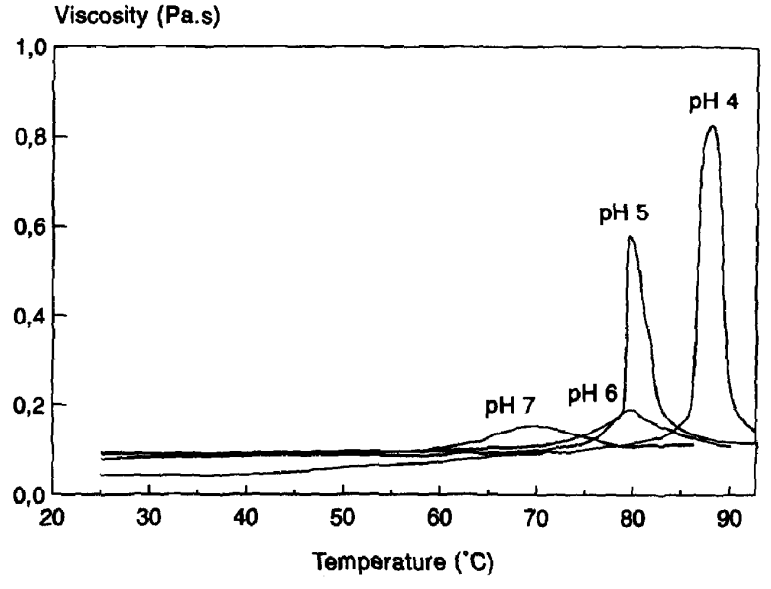


Fig. 5. The gelatinization curves of DAS-50 (8.2 wt%) immediately after isolation from the reaction mixture and pH adjustment.

lower and both peak and onset temperatures are higher than those of DAS-50. So, DAS-100 withstands a higher temperature at a given pH than DAS-50, at least when stable suspensions of unswollen granules are required. Nevertheless, both materials show chemical degradation to a comparable extent when heated at 90°C.

Compared with native starches, dialdehyde starches are characterized by a considerably lower viscosity response. The low swelling of dialdehyde starch granules is attributed to hemiacetal and eventually acetal induced intragranular crosslinking. Granular strength is supposed to be determined by the amount of crosslinks, being proportional to the degree of oxidation; DAS-50 is less reinforced and exhibits more swelling than DAS-100. The significant effect of pH on granular integrity can be ascribed to a loss of crosslinks consequent to degradation of the aldehyde groups and hydrolysis of the hemiacetals or to depolymerization. Based on these observations, the physical properties of dialdehyde starch granules are expected to be highly dependent on the conditions applied during oxidation.

CONCLUSIONS

To avoid chemical and physical degradation of dialdehyde starch in aqueous suspensions, special attention should be paid to the pH. Physical

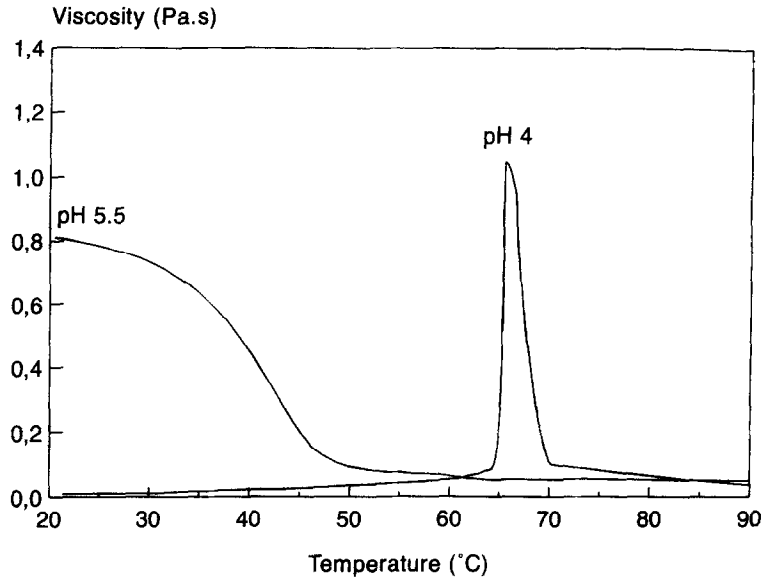


Fig. 6. The gelatinization curves of DAS-100 (8.2 wt%) in the crude reaction mixture, measured after stirring for 16 h at pH 4 and 5.5.

degradation was manifested either during heating by a decrease in viscosity and in gelatinization temperature, or at ambient temperature by swelling into a viscous mass or even dissolution. Granular degradation started once the pH exceeded 4.5 for DAS-50 and 5.5 for DAS-100.

At pH 7 extensive chemical degradation was manifested by a decrease of the aldehyde content, accompanied by acid release and a decrease of the average molecular weight. At pH 5 degradation still occurred but to a much lower extent. Less than 0.05% of the aldehydes were converted into acids at pH 3.

Although by chemical analysis no significant difference in stability was observed between DAS-50 and DAS-100, physical stability appeared to be higher for DAS-100. DAS-50 shows a higher pH sensitivity with respect to its granular integrity than does DAS-100. Differences between DAS-50 and DAS-100 are attributed to different amounts of hemiacetal crosslinks.

The conditions during reaction have to be adapted to the lability of the granules at intermediate degree of oxidation. For DAS-50, the pH should not surpass 4 in the reaction medium. Once DAS-100 is obtained, the pH could eventually rise to 5 during further processing. Suspensions should not be stored when the concentration of iodate is higher than a few per cent (±3 wt% in water). In order to ensure preservation of the chemical structure, dialdehyde starch should be heated at either low pH values (±3–4) and 90°C or at lower temperatures (< 70°C).

ACKNOWLEDGEMENTS

This research was financed by the Dutch Ministry of Agriculture, Nature Management and Fisheries.

REFERENCES

BeMiller, J. N., (1965) *Starch Chemistry and Technology 1*, ed. R. L. Whistler and E. F. Paschall, pp. 521–531. Academic Press, New York.

Fry, E. M., Wilson, E. J. and Hudson, C. S. (1942) *J. Am. Chem. Soc.* **64**, 872–873.

Levine, S., Griffin, H. L. and Senti, F. R. (1959) *J. Polym. Sci.* **35**, 31–42.

Mellies, R. L., Mehltretter, C. L. and Wolff, I. A. (1958) *Ind. Eng. Chem.* **50**, 1311–1314.

Sloan, L. W., Hofreiter, B. T., Mellies, R. L. and Wolff, I. A. (1956) *Ind. Eng. Chem.* **48**, 1165–1172.

van Soest, J. J. G., Benes, K. and de Wit, D. (1995) *Starch* **47**, 429–434.

Veelaert, S., de Wit, D., Gotlieb, K.F. and Verhé, R. (1997) *Carbohydr. Polym.*, **32**, 131–139.

Veelaert, S., Polling, M. and de Wit, D. (1994) *Polymer* **35**, 5091–5098.

Whistler, R. L., Chang, P. K. and Richards, G. N. (1959) *J. Am. Chem. Soc.* **81**, 3133–3136.

Wilham, C. A., McGuire, T. A. and Mehltretter, C. L. (1971) *Starch* **23**, 201–203.

Wise, C. S. and Mehltretter, C. L. (1973) *Starch* **25**, 51–56.