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PROPERTIES AND APPLICATIONS OF DIALDEHYDE STARCH

Abstract

The term dialdehyde starch is commonly used to describe the polyaldehyde material derived after periodate oxidative cleavage of the C2-C3 bond in starch. Upon oxidation of starch with periodate many inherent product characteristics are altered. The few things common between native potato starch and its dialdehyde form are the granular shape and the biopolymeric character. The newly introduced aldehydes strongly affect the inter and intramolecular interactions: helix formation becomes disrupted and crystallinity disappears. In particular, beyond a degree of oxidation of 40 %, dialdehyde starch granules were observed to be amorphous. Iodine staining and complexing with lysolecithine was also reduced pointing at a loss of helical shaped chains.

The aldehydes in dialdehyde starch are not present as such, but appear to be hydrated or to be involved in hemiacetal or eventually acetal linkages with neighbouring alcohol functions. These hemiacetal bridges can be formed intra or intermolecular resulting in the formation of an intragranular network. The knowledge of fundamental physico-chemical properties is the bases to explain many aspects of the behaviour of dialdehyde starch during production and applications. In particular the swelling capacity in water has been subject of interest, both at room temperature and during gelatinization. Throughout this research dialdehyde starches with different degrees of oxidation have been studied to screen deviating product properties.

Introduction

Dialdehyde starch is a promising starch derivative with the potential for many industrial applications, e.g. in paper, textiles, glues, coatings, etc. [1-7]. Especially in the paper industry, dialdehyde starch has been proven to work very efficiently as a wet-strength agent [8-15]. Dialdehyde starch is the product of the oxidative cleavage of the glycol groups present in the glucopyranose rings. The synthesis can be performed selectively with periodate as an oxidant [16-19]. Starch can be oxidized to predetermined dialdehyde content depending on the requirements with respect to chemical and physical properties. Dialdehyde starch is a cold water insoluble and biodegradable polymer. The rate of biodegradation depends on the degree of oxidation

[20]. In spite of the wide scope of applications, the use of dialdehyde starch has been limited up to now owing to its high price. In order to reduce the production costs, processes have been designed to combine the oxidation of starch with the regeneration of periodate [1-5, 21-34].

The preparation, properties and uses of dialdehyde starch have frequently been reviewed [1-7]. Several chemical reactions have been reported with, e.g. sodium borohydride, bisulphite and a variety of amines (ammonia, urea, hydroxylamine, melamine). Although numerous derivatives are known, most of the industrial applications of dialdehyde starch are based on its cross-linking capacity. Various natural and synthetic polymers containing hydroxyl or amino groups have been treated with dialdehyde starch to improve the strength or to alter the solubility in water.

The application of dialdehyde starch to improve the wet-strength of paper products, such as wrappings, sanitary tissues, towelling maps, etc. is well documented [8-12]. During the paper making process, dialdehyde starch is mostly applied by wet-end addition: after being dispersed in water it is added to the suspension of paper pulp before sheet formation. Upon mixing and removal of water, hemiacetals are formed between the hydrated aldehyde groups of dialdehyde starch and the hydroxy groups of cellulose. These hemiacetals act like intermolecular cross-links, thus creating a reinforcement of the paper.

The general aim of this research at our institute is to revalue the use of dialdehyde starch for industrial purposes. Present scepticism about the industrial application of dialdehyde starch is mainly based on the unattractive price and the limited knowledge of fundamental product properties and efficient processing conditions. Certainly, a reduction of the actual price of dialdehyde starch is essential to compete with synthetic alternatives, e.g. in the paper industry. Moreover, it is important to achieve more experience with the characteristic product properties; especially the product stability and reactivity are important parameters that determine the efficiency of further use.

Materials and methods

A series of dialdehyde starches with a degree of oxidation (DO) varying from 1 to 99 % have been synthesized by periodate oxidation of potato starch as described earlier [35]. The oxidation has been performed in a 10 wt % aqueous solution at pH 3.5 and 25°C in the dark. After filtration and washing 5 times with the same volume of water, the products have been freeze-dried.

Chemical and structural analyses of the dialdehyde starches have been performed as described in a previous paper [35].

The swelling capacity of the products was determined by measurement of the increase in weight after suspending in water for 30 minutes, followed by isolation of the suspended granules by centrifuging [35].

The water absorption was calculated as the mass of water absorbed over the initial mass of dry material [35].

Viscosity changes during gelatinization have been measured in a Brabender Viskograph-E following a conventional gelatinization program [36]. Viscoelastic measurements during gelation were recorded with a Bohlin VOR Rheometer [36].

Abbreviations

DAS-X dialdehyde starch with a degree of oxidation equal to X, the number X referring to the percentage of oxidized anhydroglucose units (e.g. DAS-50 and DAS-100).

PS native potato starch.

Results and discussion

Product properties

With wide-angle X-ray scattering (XRD), differential scanning calorimetry and optical microscopy, all crystallinity and structural ordering has been proven to be lost

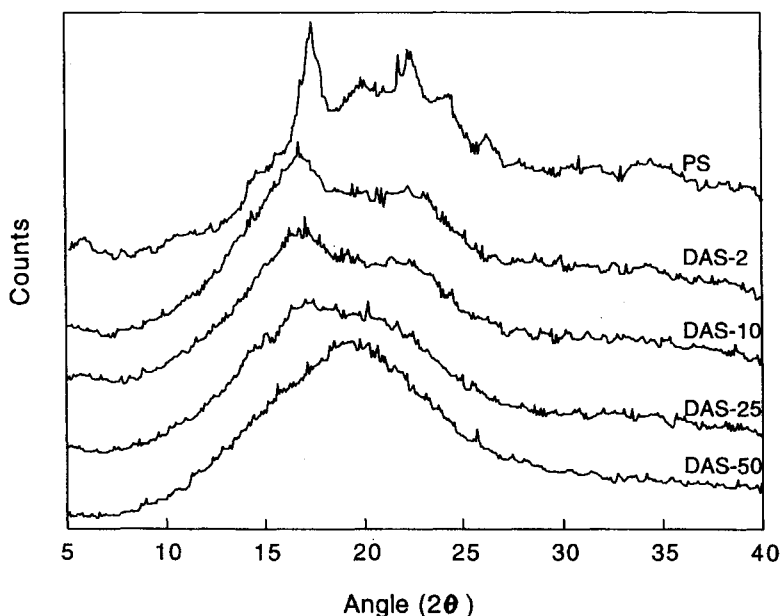


Fig. 1. X-Ray diffractograms of different dialdehyde starches and native potato starch.

beyond degrees of oxidation of $\pm 40\%$ [35]. Nevertheless the granular shape of the material was retained. The loss of B-type crystallinity in native potato starch, measured with XRD is illustrated in Fig. 1. The material was according to all applied analysis procedures amorphous at degrees of oxidation beyond 40%. Also complexing with iodine or lysolecithine has been observed to be very low for higher degrees of oxidation [35]. The presence of aldehyde groups at C2 and C3 are expected to disturb helix formation. The effective helical chain length for complexing reactions diminishes gradually upon oxidation.

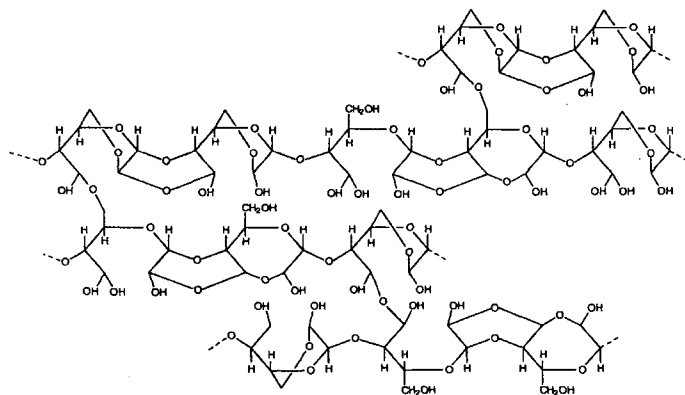


Fig. 2. Cross-linked dialdehyde starch fragment.

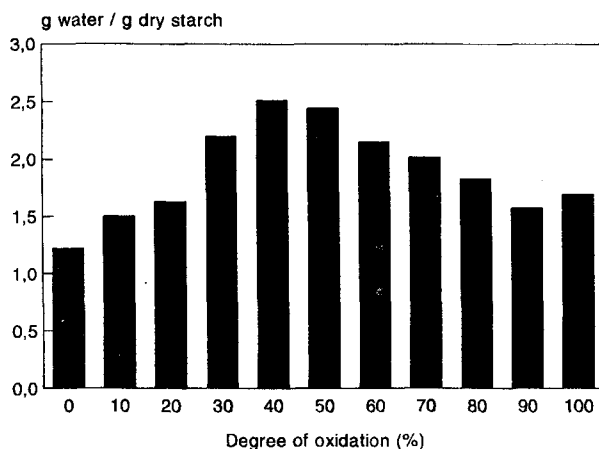


Fig. 3. Swelling capacity as function of the degree of oxidation.

The aldehydes in dialdehyde starch are not present as such but appear to be hydrated or to be involved in hemiacetal or eventually acetal linkages with neighbouring alcohol functions [37]. These hemiacetal bridges can be formed inter or intramolecularly resulting in the formation of an intergranular network.

The molecular fragment presented in Fig. 2 illustrates the type of interactions that might occur and result in cross-linking.

Behaviour of dialdehyde starch in water

Loss of crystallinity enhances swelling whereas hemiacetalization (and cross-linking) of the aldehyde groups inhibit swelling. Swelling at ambient temperature is due to this counteracting effect maximal at intermediate degrees of oxidation (Fig. 3) [35].

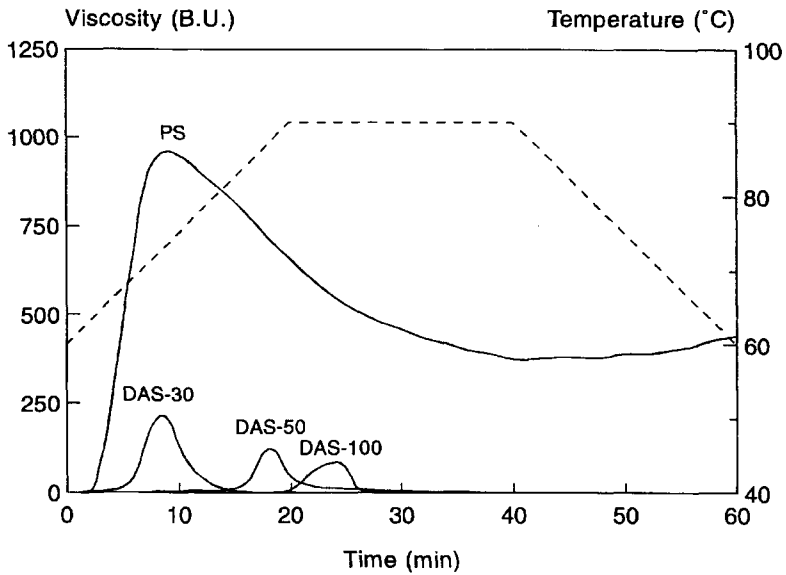


Fig. 4. Viscosity changes during gelatinization in a Brabender Viskograph.

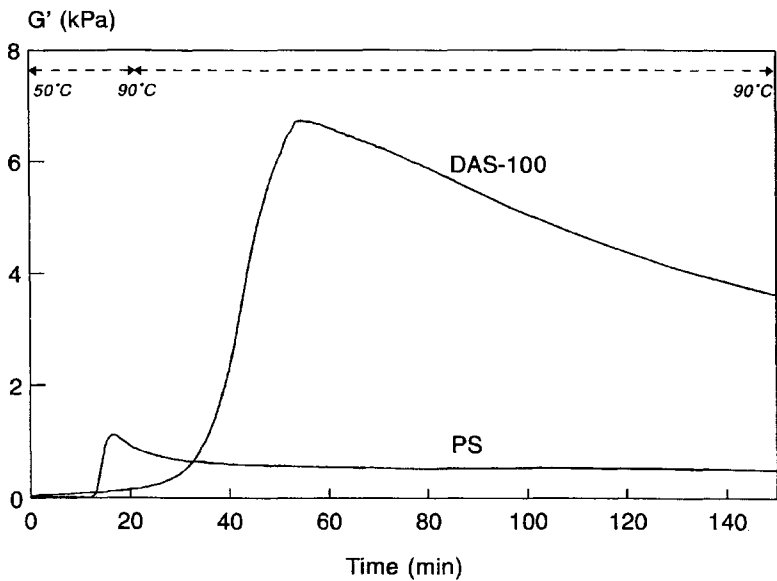


Fig. 5. The elastic response of DAS-100 and native potato starch at 20 wt % concentration during heating in a Bohlin Rheometer.

Swelling capacity upon heating was observed to be very low compared with native potato starch [36]. Above the melting temperature of crystallites, the swelling capacity of the starches diminishes with rising degree of oxidation (Fig. 4). The underlying effect is hemiacetal induced cross-linking in combination with an increased hydrophobic character. Above a critical concentration, highly visco-elastic particle gels were obtained, as soon as the particles were swollen into a close-packing stage [36]. The granules retained their rigid structure and were slightly deformable, in contrast with native starch granules, which swell considerably and therefore lose rigidity. This explains the high elastic response of the DAS gels relative to the native potato starch gels (Fig. 5). The critical concentration for gel formation (14 wt %), deviating from that of native starch, is attributed to a different conformation and functionality and a higher temperature lability of DAS.

Thanks to aldehyde induced hemiacetalization, the granules are reinforced, but the respective cross-links are pH sensitive. Granular swelling increases upon working at higher pH values. This effect can be advantageous for the removal of iodate from the reaction mixture during washing. But degradation, and the concurrent release of low molecular weight material, might cause problems during the separation of iodate from organic material.

The most important differences in properties between dialdehyde starch and native potato starch are compared in Table 1.

Table 1

The most important differences in properties between dialdehyde starch and native potato starch

	Dialdehyde starch	Native potato starch
Crystallinity	DO > 30: amorphous	semi-crystalline
Iodine staining	DO < 30: brown – yellow	amylose: blue; amylopectin: brown
Swelling at room temperature	low (high for intermediate DO)	low
Swelling upon heating	low at 70 – 90°C	high at ± 60°C
Viscosity 5 wt %	low	high
Visco-elasticity 15 wt %	high	low
Paste stability	no retrogradation	retrogradation
Molecular stability	> pH 5: low	higher

In the past only DAS-100 has been subject of interest with regards to applications. The use of DAS-50, however, might occasionally be advantageous. Table 2 gives an overview of the fundamental differences between DAS-50 and DAS-100.

Besides for a lower periodate consumption, the production of DAS-50 is advantageous with respect to the required reaction time to obtain the desired degree of oxi-

dition. The periodate oxidation of starch initially follows second order kinetics. A clear deviation from this second order model, however, was observed halfway the reaction. The involved reaction inhibition was attributed to the formation of hemiacetals between newly formed aldehyde groups and adjacent alcohol functions [37]. Un-oxidized diol units are thus protected for further reaction. Upon continued oxidation, the availability of diol units gradually decreases and the reaction rate slows down. Consequently, complete oxidation of starch to dialdehyde starch becomes a time-consuming process (> 24 h), unless a surplus of periodate is applied. The reaction time needed to prepare DAS-50 is considerably lower (± 1 h).

Table 2

Fundamental differences between DAS-50 and DAS-100

	DAS-50	DAS-100
Reaction time*	± 2 h	> 24 h
Periodate consumption per mol*	2 mol	1 mol
Washing efficiency after two washing cycles*	± 99 %	± 95 %
Swelling	high	low
Dispersibility	80°C	90°C
Particle rigidity	low	high

*The batch process.

Washing of the products is very important not only for purification but also for recovery of the periodate. The price of the process strongly depends on the recovery of iodate or periodate out of the reaction mixture. The periodate dissipation therefore has to be minimized. The washing efficiency of batch-wise prepared products has been investigated as function of the respective degree of oxidation. It was found that washing efficiency is maximal for intermediate degrees of oxidation (DAS-40 till DAS-60) [35]. This phenomenon was related to the swelling of the material, which was also observed to be maximal for the same products. Obviously, swelling has a positive effect on the accessibility of the granules: an increased water flow through the granules enhances the removal of iodate.

DAS-50 is dispersed more easily than DAS-100, due to the lower extent of hemiacetal induced cross-linking [35]. DAS-100, on the other hand is less alkali sensitive, at least with respect to the granular integrity [39]. Both DAS-50 and DAS-100, exhibit extensive molecular degradation when heated at pH 7. The stability of the viscoelastic particle gels was higher for DAS-100, as particle rigidity increased with increasing aldehyde content [35].

Conclusions

The broad based research described in this paper has led to interesting knowledge on the fundamental product properties of dialdehyde starches. Physical properties have been observed to be highly dependent on the degree of oxidation of the dialdehyde starch. A relation has been established between the chemical and physical structure and the behaviour of dialdehyde starch in aqueous suspensions under various conditions.

The preferential degree of oxidation depends on the desired performances of the dialdehyde starch. The production costs of DAS-50 are without any doubt lower than for DAS-100, not only for a reduced periodate consumption but also for a shorter reaction time and a higher washing efficiency. The surplus value of the higher aldehyde content in DAS-100 has to be weighed over the increased production costs.

REFERENCES

- [1] Tegge G.: *Starch*, **12**, 1960, 321.
- [2] Mehlretter C.L.: *Starch Chemistry and Technology 2*, Acad. Press, New York, 1967, pp. 433.
- [3] Beduneau H.: *Rev. Prod. Chim.*, 1961, 598.
- [4] Mehlretter C.L.: *Starch*, **18**, 1966, 208.
- [5] Radley J.A.: *Starch Production Technology*, Appl. Science Publ., London, Ch. 19, 1976, 423.
- [6] Babor K., Kalac V., Tihlarik K.: *Listy Cukrovar*, **80**, 1964, 265.
- [7] McGuire T.A., Mehlretter C.L.: *Starch/Stärke*, **23**, 1971, 42.
- [8] Hofreiter B.T., Hammerstrand G.E., Mehlretter C.L., Schulze W.E., Ernst A.J.: *Tappi*, **43**, 1960, 639.
- [9] Hammerstrand G.E., Hofreiter B.T., Mehlretter C.L., Schulze W.E., Kay D.J.: *Tappi*, **44**, 1961, 430.
- [10] Hofreiter B.T., Hammerstrand G.E., Kay D.J., Rist C.E.: *Tappi*, **45**, 1962, 177.
- [11] Mehlretter C.L., Yeates T.E., Hammerstrand G.E., Hofreiter B.T., Rist, C.E.: *Tappi*, **45**, 1962, 750.
- [12] Hammerstrand G.E., Hofreiter B.T., Kay D.J., Rist C.E.: *Tappi*, **46**, 1963, 400.
- [13] Laleg M., Pikulik I.I.: *J. Pulp Paper Sci.*, **19**, 1993, J248.
- [14] Hofreiter B.T., Heath H.D., Ernst A.J., Russel C.R.: *Tappi*, **57**, 1974, 81.
- [15] Jones E.J., Weber B., Swanson J.W., Mehlretter C.L., Senti F.R.: *Tappi*, **42**, 1959, 862.
- [16] Malaprade L.: *Bull. Soc. Chem.*, **43**, 1928, 683.
- [17] Jackson E.L.: *Org. Reactions*, **2**, 1944, 341.
- [18] Bobbett J.M.: *Adv. in Carbohyd. Chem.*, **11**, 1956, 1.
- [19] Guthrie R.D.: *Adv. in Carbohydr. Chem.*, **16**, 1961, 105.
- [20] van der Zee M., Stoutjesdijk J.H., van der Heijden P.A.A.W., de Wit, D.: *J. Env. Pol. Degr.*, **3**, 1995, 235.
- [21] Heit A.H., Williamson, J.N.: U.S. Pat. 3703508, 1972.
- [22] Mehlretter C.L.: U.S. Pat. 2830941, 1958.
- [23] Langhammer G., Gabert A., Gerhard L., Wand H., D.D.: Pat. 87778, 1972.
- [24] Pfeifer V.F., Sohns V.E., Conway H.F., Lancaster E.B., Dabic S., Griffin E.L.: *Ind. Eng. Chem.*, **52**, 1960, 201.
- [25] Conway H.F., Sohns V.E.: *Ind. Eng. Chem.*, **51**, 1959, 637.
- [26] Mehlretter C.L.: U.S. Pat. 2713553, 1955.
- [27] Dvonch W., Mehlretter C.L.: U.S. Pat. 2648629, 1953.

- [28] Mehlretter C.L., Rankin J.C., Watson P.R.: *Ind. Eng. Chem.*, **49**, 1975, 350.
- [29] Ramaswamy R., Venkatachalapathy M.S., Udupa H.V.K.: *Indian J. Technol.*, **1**, 1963, 115.
- [30] Mantell C.L.: *I&EC Proc. Des. Dev.*, **1**, 1962, 144.
- [31] Varma J.P., Khisti R.S.: *Chem. Eng. World*, **10**, 1975, 117.
- [32] Mezynski L., Grzeskowiak M.: *Przem. Chem.*, **50**, 1971, 73.
- [33] Conway H.F., Lancaster E.B., Sohns V.E.: *Electrochem. Tech.*, **2**, 1964, 43.
- [34] Borchert P.J.: *Kunststoffe*, **51**, 1961, 137.
- [35] Veelaert S., Polling M., de Wit D.: *Starch/Stärke*, **47**, 1995, 263.
- [36] Veelaert S., de Wit D., Gotlieb K.F., Verh, R., Submitted for publication in *Carbohydrate Polymers*, 1996.
- [37] Veelaert S., de Wit D., Tournois H.: *Polymer*, **35**, 1994, 5091.
- [38] Veelaert S., de Wit D., Gotlieb K.F., Verh R., Submitted for publication in *Carbohydrate Polymers*, 1996.

WŁAŚCIWOŚCI I ZASTOSOWANIE SKROBI DIALDEHYDOWEJ

Streszczenie

Pod pojęciem skrobi dialdehydowej zazwyczaj rozumie się polialdehyd otrzymywany przez spowodowane jodem (V) utleniające rozszczepienie wiązań C2–C3 w skrobi. Pod wpływem utleniania zmienia się szereg właściwości produktu. Należy do nich, między innymi, kształt gałeczek, polimeryczny charakter.

Wprowadzane grupy aldehydowe wyraźnie zaburzają oddziaływania wewnątrz- i międzycząsteczkowe. Nie może powstawać helisa skrobiowa i zanika krystaliczność. Szczególnie, w skrobi dialdehydowej o stopniu utlenienia 40 %, gałeczki są bezpostaciowe. Zanika ich zdolność barwienia się jodem i tworzenia kompleksu z lisolectyną, co wskazuje na brak łańcuchów mogących się związać w helisę.

Aldehydy w skrobi dialdehydowej nie istnieją w stanie wolnym, lecz są albo hydratowane albo istnieją jako hemiacetale, a nawet acetale przy współdziałaniu sąsiadujących z nimi grup hydroksylowych. Powstające mostki hemiacetalowe mogą mieć charakter wiązań wewnątrz i międzycząsteczkowych. W tym drugim przypadku sieciują się gałeczki. Szereg przejawów zachowania się skrobi dialdehydowej w czasie jej produkcji i zastosowania można wyjaśnić na podstawie podstawowych właściwości fizykochemicznych tego produktu. Ze szczególnym zainteresowaniem spotkała się w tym względzie zdolność do pęcznienia w wodzie zarówno w temperaturze pokojowej jak i w czasie kleikowania. W niniejszej pracy przebadano skrobie dialdehydowe o różnym stopniu utlenienia w celu ustalenia właściwości odróżniających te produkty od siebie. 