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OBSERVATIONS ON THE AGEING OF POTATO STARCH PASTES MODIFIED WITH COMPLEXING AGENT

Abstract

The effects of gelatinisation and complexing conditions on stability of the potato starch solution were observed in a period of two weeks. Different methods of preparing 2% (w/v) starch aqueous solution with 0.25 μM Rose Bengal were tested. The differences in behaviour of all samples during storage were significant, which proves that the way in which starch pastes with dye have been prepared is of crucial importance. The most effective retrogradation delay and the least significant structural changes during storage were observed in starch – Rose Bengal solution prepared by immediate high temperature treatment above the gelatinisation temperature with preliminary swelling the starch with dye. This treatment facilities more effective intermolecular association with dye molecules resulting in polymer ordering and spatial network stability.

Introduction

Starch solution obtained as a result of boiling an aqueous polymer suspension for a long time under normal pressure conditions exhibits a tendency to aggregate its components during cooling down and long time storing. In an appropriate high concentration such a polymer solution reveals the ability to form a spatial gel network [16]. All these time-varying association – aggregation processes, known as starch retrogradation, have been the subject of many investigations [1-8, 12, 13]. Retrogradation of starch solutions results in many physical changes such as an increase in viscosity, development of opacity and turbidity, precipitation of insoluble crystalline starch and syneresis of water. These physical changes are related to qualitative parameters of starch convention products. Therefore it is very important to design all the factors which may control starch changes during long time storing. One of them are starch paste processing conditions and complexing with low-molecular compound. The ability of amylose to form inclusion complexes with different compounds can be used as

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considerable in influencing the structural changes during storage [14]. Hizukuri *et al.* [4] observed that retrogradation in sufficiently gelatinised starch can be inhibited. The relationship between method of starch gelatinisation and the crystallinity of storaged starch and degree of retrogradation during storage was studied by Mizuno [8].

The purpose of this work was to study the influence of hydrothermal processing conditions and complexing on the stability and physical properties of potato starch aqueous solutions during long time storing in the presence of Rose Bengal, used as complexing agent required for stabilisation of starch solution.

Materials and methods

A soluble potato starch obtained from Polish Chemical Reagent – Gliwice was used in the experiment without further purification. Rose Bengal (RB) sodium salt was obtained from Sigma Co. The starch concentration was 0.02 g/cm^3, whereas dye concentration was 0.25 μM. The methods of hydrothermal processing of starch with Rose Bengal are need to be indicated in detail, because they were modified. All aqueous starch suspensions were heated at boiling temperature in the same time period of 30 minutes. The first modification depended upon heat treatment: for some probes (from no 1 to 5) the contact of starch with water occurred at room temperature and for the others (probes no 6 and 7) – the contact with water occurred immediately at boiling temperature. The next modification concerned the moment of Rose Bengal addition: it was added to starch before heat treatment for probes no 1, 5 and 6; at the end of starch solution boiling – in probes 3 and 7; during starch paste cooling down, at 50°C – in probe no 2 and in probe no 4 – after 1 h of starch paste storing at room temperature. The third processing modification was related with preliminary 1 hour starch swelling in water, without a complexing agent – in probe no 4, and in the presence of Rose Bengal – in probe no 5. All starch solutions, prepared in such a way, were exposed for long time storage at a stable temperature of 27°C.

Measurements of proton spin-lattice relaxation rate, R_1 were carried out using a 30-MHz pulse NMR spectrometer. Signal of free induction decay was recorded after a two-pulse sequence π - τ - $\pi/2$. The data set obtained were analysed using the two-dimensional NMR signal – analysing program CracSpin [15].

Optical rotation (OR) measurements were performed using POLAMAT A produced by Carl Zeiss Jena, in 1dm cell, at three wavelengths: λ = 366 nm, 406 nm and 436 nm.

Results and discussion

Potato starch pastes of 2% (w/v), prepared according to the above description, were observed during long-time storing at a constant temperature. Some main changes observed in starch paste probes during ageing are presented in Table 1.

Table 1

The effect of ageing on some properties of starch pastes (0.02 g/cm^3) with Rose Bengal (25 μM), stored at 27°C

No of probe	Ageing time, days	Turbidity	Precipitation	Microbialogical spoilage	Discolouration
1	1	–	–	–	–
	4	–	–	+	–
	7	–	+	+	–
	10	–	+	++	–
	14	–	++	++	–
2	1	–	–	–	–
	4	–	+	+	–
	7	–	++	+	–
	10	++	+++	++	++
	14	+	+++	++	+++
3	1	–	–	–	–
	4	–	+	+	–
	7	+	+	+	–
	10	++	++	++	+
	14	++	+++	+++	++
4	1	–	–	–	–
	4	+	++	+	–
	7	+	++	++	+
	10	+	++	++	++
	14	+	+++	++	+++
5	1	–	–	–	–
	4	–	–	–	–
	7	–	+	–	–
	10	–	+	–	–
	14	+	+	–	–
6	1	–	–	–	–
	4	–	+	–	–
	7	–	+	+	–
	10	–	+	++	+
	14	–	++	++	++
7	1	–	–	–	–
	4	–	–	–	–
	7	–	–	–	–
	10	–	–	–	–
	14	+	–	–	–

– no effect; + low effect; ++ medium effect; +++ high effect

The comparison of ageing changes in starch pastes with the same ratio of polymer amount and amount of complexing agent, modified during hydrothermal processing, suggests that the molecular structure of polymer with complexing dye in the studied systems is very different. The stability of starch polymer network in water solution is conditioned by efficiency of intermolecular polymer – dye interaction, which can stable amylose helical form and supermolecular ordering.

All starch dispersions were tested after 20 days of storing by optical rotation measurements in spectral range beyond the dye absorption bands. The values of $[\alpha]_\lambda$ for three wavelengths, 366 nm, 406 nm and 436 nm are presented in Table 2.

Table 2

The optical rotation (OR) data at three wavelengths: λ = 366 nm, 406 nm and 436 nm, obtained in potato starch pastes after 20 days of storage at 27°C

Number of probe	$[\alpha]_{366\ nm}$, deg	$[\alpha]_{366\ nm}$, deg	$[\alpha]_{436\ nm}$, deg
Freshly prepared 2% starch paste	20.33		13.50
Freshly prepared 2% starch paste with 0.25μM RB	19.47		13.00
1	19.57	15.32	12.98
2	9.90	7.75	6.55
3	19.24	14.98	12.74
4	16.80	10.90	11.64
5	19.66	14.46	13.30
6	14.44	11.30	9.55
7	18.80	14.20	12.96

Although the changes in starch pastes storing for 20 days at 27°C are considerable, especially the amount of precipitated amylose, discolouration, the differences in optical rotation between freshly prepared starch paste and after long time storing are surprisingly small (Table 2). In probe no 3, for example, in which high amount of precipitate was observed, the optical rotation is comparable with that for probe no 7, the most stable of the starch paste studied. Optical rotation offers one of the simplest and most reliable methods for determining the concentration of polysaccharide in solution [9]. Due to precipitation, starch concentration in long- time storage solution is not the same as before ageing, in freshly prepared starch solution. Nevertheless, the values of OR were not changed in starch pastes with Rose Bengal after long time storing for some probes (Table 2).

It was observed, after 15 days of storing starch pastes with no preservative, two of all starch probes were untouched by micro-organisms. These were probes 5 and 7. The other solutions were significantly destroyed and discoloured, especially starch pastes no 2, 4 and 6. High turbidity has occurred in starch solution samples 2 and 3. It could be noticed, amylose precipitation, coloured by presence of Rose Bengal molecules, formed radically arranged pattern at the bottom of vessel in starch probes no 2 and 3. No comparable effect was observed in other solutions. In all these, much or less changed starch pastes after 20 days of storing, the measurements of proton relaxation rate were performed from upper layer. Spin-lattice proton relaxation rate, R_1, like to spin-spin relaxation rate analysed in [10], was characterised by multiexponential free induction decay, revealing under measurement conditions at least two water proton subsystems with different molecular mobility. The data obtained by fitting procedure with Crac-Spin program for all probes are presented in Table 3.

Table 3

Spin-lattice proton relaxation rate, R_1 and percent contribution of two proton fractions in potato starch pastes after 15 days of ageing at 27°C

No of probe	R_{11}, s^{-1}	A_{11} ,%	R_{12}, s^{-1}	A_{12},%	R_{13},s^{-1}	A_{13} ,%
1	0.454	97.0	18.5	3.0		
2	0.431	96.6	15.6	3.4		
3	0.445	98.2	22.3	1.8		
4	0.441	94.0	39.1	1.9	1.3	4.1
5	0.456	96.5	29.7	3.5		
6	0.412	94.5	26.1	5.5		
7	0.450	97.5	27.1	2.5		

It is evidence, that proton relaxation rate, R_1 in such heterogeneous systems, related to water state and biopolymer matrix should be very complicated. NMR analysis has shown two proton subsystems with different molecular mobility in nearly all starch probes and three proton fractions in starch paste no 4. It should be noticed that in the case of starch paste no 4, complexing agent was incorporated to the starch solution just after 1 hour of cooling down the solution to the room temperature. During this time a spatial network of polymer could be formed as well as high temperature conformational transitions occurred. Rose Bengal molecules were incorporated „too late" for amylose conformation changes input. The effectiveness of complexing process in starch solution highly depends on temperature. In starch paste, cooled down to the room temperature amylose – RB interactions were significantly restricted. In this starch paste (no 4) three protons fractions were observed in NMR measurements, which proved polydispersity of the system.

Three used hydrothermal processing of potato starch paste with a complexing agent are schematically presented in Fig. 1.

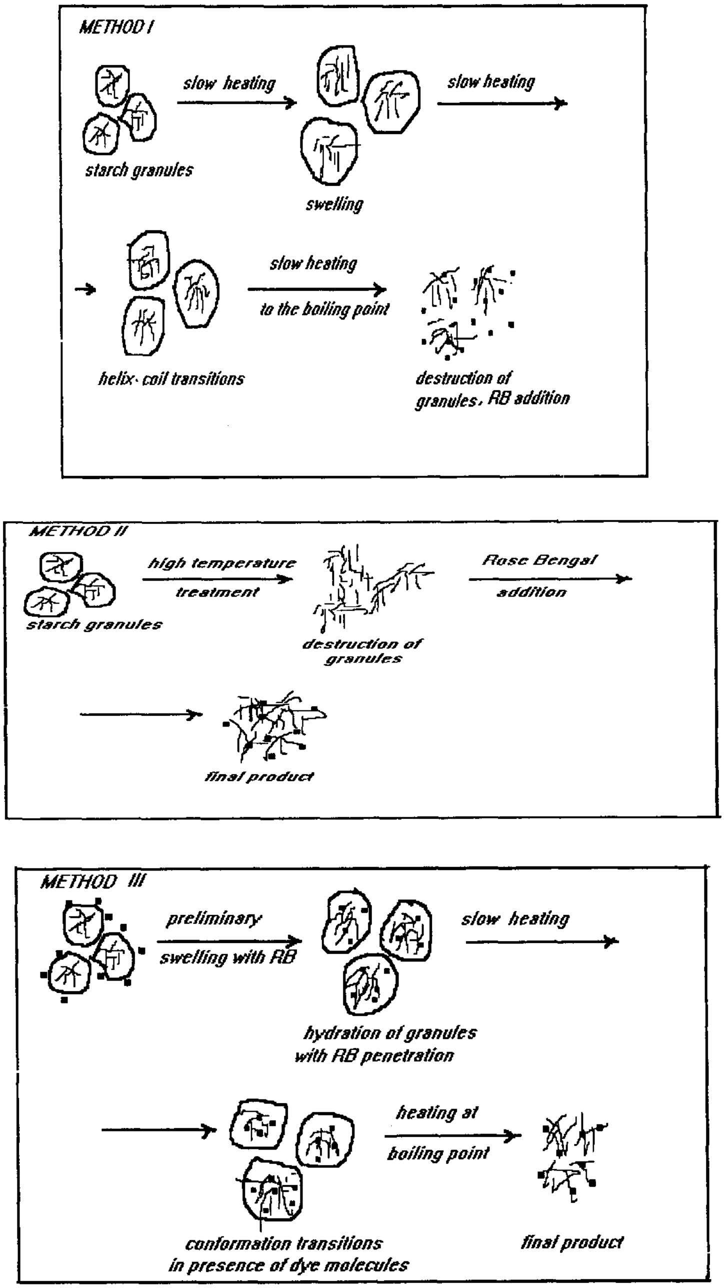

Fig. 1. Diagrams illustrating three hydro-thermal processing used in potato starch paste with complexing agent, Rose Bengal (•).

During slow heating of a starch suspension (Fig. 1 – Method I), a gradual disruption of starch granules takes place, accompanying with swelling, conformational transitions of amylose and amylopectin chains within. It is known, that the total granule disruption arises at temperature above 90°C [11]. Therefore, in starch paste obtained according to method I, some "trace" of granule disordering remains, which unfavourable effects on polymer chains entaglement in the whole system (probes 1, 2, 3, 4).

Quite different molecular conditions for starch pasting are in a starch suspension treated immediately with high temperature, above 90°C (Fig. 1 – Method II). Instantaneous starch granule disruption facilitates mutual polymer chains penetrating. It should influence structural homogeneity of starch paste at a molecular level. The interaction of Rose Bengal with starch may result in a more stable network (probe 7).

Preliminary starch swelling in presence of complexing agent (Fig. 1 – Method III) causing Rose Bengal penetration into starch granules, leads to better "prepare" of granules to form polymer spatial network with Rose Bengal. After high temperature treatment of such prepare starch with complexing agent within granules, starch paste obtained exhibit more resistance on ageing changes (probe no 5).

Conclusions

The study of the effect of dye – polymer interaction on the stability of starch colloidal solutions revealed that:

- the stability of potato starch spatial network modified with a complexing agent, Rose Bengal, is related with the method of hydrothermal processing of starch solutions,
- two agents may play a main role in forming a starch spatial network stable: preliminary swelling of the starch granules with a complexing agent, and – starting the process at high temperature, above gelatinisation temperature, in which random coil – helix conformation transition is observed.
- the interaction between amylose chains and RB molecules is not affected by temperature below the helix-coil transition temperature. When a complexing agent is added to starch solution at lower temperatures, intermolecular interaction is highly restricted, due to unfavourable amylose chain conformation.

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BADANIE STARZENIA PAST ZE SKROBI ZIEMNIACZANEJ MODYFIKOWANYCH CZYNNIKAMI KOMPLEKSUJĄCYMI

Streszczenie

W pracy badano wpływ warunków kleikowania i sposobu wprowadzania czynnika kompleksującego na trwałość kleików skrobi ziemniaka. Próby skrobi o tej samej koncentracji 0.02g/cm^3 i tej samej ilości Rose Bengal, 0.25μM, zastosowanego jako barwnikowy czynnik kompleksujący, obserwowano przez okres ponad dwóch tygodni. Kleiki przechowywano w stałej temperaturze i stałej wilgotności. Znaczne różnicowanie w zachowaniu kleików w czasie starzenia, spowodowane jedynie modyfikowaniem sposobu kleikowania, wskazuje na istotny wpływ tego czynnika na trwałość skompleksowanej skrobi w roztworze. Najbardziej efektywnym na zahamowanie zmian w procesie starzenia, sposobem kleikowania skrobi w obecności RB jest natychmiastowe potraktowanie zawiesiny skrobi w wodzie wysoką temperaturą, przewyższającą charakterystyczną dla skrobi temperaturą przejść konformacyjnych łańcucha polimerowego. Wstepne pęcznienie skrobi wraz z czynnikiem kompleksującym przed kleikowaniem wpływa korzystnie na sieciowanie przestrzenne kleiku i jego trwałość w czasie przechowywania.