RETROGRADATION OF STARCHES AND MALTODEXTRINS OF ORIGIN VARIOUS

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Background. The retrogradation which occurs during the processes food storage is an essential problem in food industry. In this study, the ability to retrograde of native starches and maltodextrins of different botanical origin was analysed.

Material and methods. The materials were starches of various botanical origin, including commercial samples: potato, tapioca, wheat, corn, waxy corn starches, and laboratory isolated samples: triticale and rice starches. The above starches were used as material for laboratory production of maltodextrins of medium dextrose equivalents (DE in the range from 8.27 to 12.75). Starches were analysed for amylose content, while the ratio of non-branched/long-chain-branched to short-chain-branched fractions of maltodextrins was calculated from gel permeation chromatography data. The susceptibility to retrogradation of 2% starch pastes and 2% maltodextrin solutions was evaluated according to turbidimetric method of Jacobson.

Results. The greatest starch in turbidance of starch gels was observed within initial of the test. days. Initial retrogradation degree of cereal starches was higher than that of tuber and root starches. The waxy corn starch was the least prone to retrograde. The increase in turbidance of maltodextrin solutions were minimal. Waxy corn maltodextrin was not susceptible to retrogradation. Among other samples, the lowest susceptibility to retrogradation after 14 days was found for rice maltodextrin, while the highest for wheat and triticale maltodextrin.

Conclusions. On the basis of this study, the retrogradation dependence on the kind of starches and the maltodextrins was established and the author stated that all the maltodextrins have a much less ability to retrogradation than the native starches.

Key words: starches of various origin, maltodextrin, retrogradation
INTRODUCTION

Retrogradation plays an important role in forming consumers’ utility of food products. It is usually described as recrystallization during storage after starch pasting. The change in crystalline structure after pasting involves the formation of ordered double-helical structure from amorphous glucans [Kulik and Haverkamp 1997].

Retrogradation is induced by low temperature, high amylose content and the presence of polar substances, such as salts [Nebesny 1991]. On the other hand, the surfactants hinder retrogradation. Overall starch susceptibility to retrogradation is also controlled by its molecular weight, concentration, temperature, and presence of non-starch components (salts, saccharides, lipids, acids, hydrocolloids, surfactants) [Durán et al. 2001, Jacobson et al. 1997, Sandhu and Singh 2007, Smits et al. 2003]. In consequence of retrogradation the intermolecular distances between starch molecules diminish. This leads to the removal of water from gel, and in consequence dehydration of the material. The phenomenon could be observed as occurrence of water on gel surface, known as synaeresis [Karim et al. 2000, Napierala 1998].

During storage of starch gel, especially at low temperature, insoluble starch – especially amylose – precipitates [Karim et al. 2000, Napierala 1998]. Retrogradation occurs not only in amylose fraction but also amylpectin from gelatinized granules. Association of linear amylose molecules takes place quickly at the first stage of retrogradation, while slow increase in starch gel rigidity is attributed to amylpectin crystallization [Zobel 1988]. This process is also faster at low temperature. Significant acceleration may be obtained by repeated cycles of freezing and thawing of starch gel [Colwell et al. 1969, Fortuna and Juszczak 1998, Jankowski 1990]. It was found that cereal starches are more prone to retrogradation than potato, and in the cases of bimodal distribution small granules are less susceptible to this process than large granules and non-fractionated starch [Fortuna and Juszczak 1998].

The aim of the study was to evaluate the susceptibility to retrogradation of starches of various botanical origin and the corresponding maltodextrins produced on laboratory scale. Before the actual evaluation basic characteristics of the studied material were examined.

MATERIAL AND METHODS

The material consisted of starches of various botanical origin, consisting of commercial samples:

– potato starch “Superior” (Przedsiębiorstwo Przemysłu Ziemniaczanego S.A. in Niechlów)
– wheat starch (Przedsiębiorstwo Przemysłu Ziemniaczanego S.A. in Niechlów)
– corn starch (National Starch & Chemical)
– waxy corn starch (National Starch & Chemical)
– tapioca starch (National Starch & Chemical)

and laboratory isolated samples:

– triticale starch (variety Pronto s-elita, cultivated at Danko-Horyń)
– rice starch from rice flour originated from Thailand.
The starches were used to produce maltodextrins on laboratory scale, by enzymatic hydrolysis with commercial preparation BAN 240 L produced by Novozymes (Denmark). The suspension at 25°C was treated with 0.025 cm³ of enzymatic preparation BAN 240L and heated in 40 minutes to reach 84°C. The temperature was controlled all the time, and the mixing rate was 550 rpm. By modifying reaction time (under optimal conditions – 84°C) depending on susceptibility of starch to enzymatic hydrolysis, the maltodextrins with medium dextrose equivalents were obtained (DE in the range from 8.27 to 12.75). The value of dextrose equivalent was evaluated by Schoorla-Regenbogen method [PN-78/A-74701 1978].

Initial starches were analysed for amylose content according to Morrison and Laignelet [1983]. In the maltodextrins the ratio of non-branched/long-chain-branched to short-chain-branched fraction was calculated from gel permeation chromatography data. GPC analysis was performed by using four columns with following sizes and gels [Sephacryl/Pharmacia]:
- diameter 16 mm, length 35 cm, filled with S-200
- diameter 16 mm, length 88 cm, filled with S-200
- diameter 16 mm, length 88 cm, filled with S-500
- diameter 16 mm, length 88 cm, filled with S-1000.

For calculation of molecular weight, pullulan standards P-10, 50, 200, 800 (Shodex Standard, Macherey-Nagel) were applied, which were corresponding to molecular weights: 12.200, 48.000, 186.000 and 853.000 Da. The standards at quantity 5 mg were dissolved in 2.5 cm³ distilled water and put on the columns [Praznik et al. 1983, 1987]. GPC analysis was performed at ambient temperature by using 0.003 M sodium carbonate as an eluent (flow rate 16.5 cm³/h). The eluate was divided in fraction collector in 130 fraction with volume 5 cm³ each. Fraction analysis included:
- determination of total carbohydrates by anthrone method, measuring the absorbance at λ = 540 nm [Morris 1948] by using Specord M 42 (Carl Zeiss, Germany) spectrophotometer
- determination of iodine-starch complex, at wavelengths λ = 525 nm and 640 nm [Praznik et al. 1983]
- determination of apparent amylose in each of the fractions. Blue value was used as an indicator of amylose content (BV), which is defined as the absorbance of iodine diluted in 100 cm³ of water by 10 mg of starch (d.m.). It is calculated as follows:

\[ BV = A \cdot 10 \text{ mg/d.m.} \]

where:
- A – absorbance at λ = 640 nm,
- d.m. – dry mass in 100 cm³ of measuring solution [mg].

Total carbohydrate content was used as dry mass for each of the analysed fractions [Morris 1948], and the formula was adjusted to the volume 5 cm³.

By means of turbidimetric method, according to Jacobson et al. [1997], the susceptibility to retrogradation of 2% starch pastes and 2% maltodextrin solutions was evaluated. The studies were performed at 8°C.
RESULTS AND DISCUSSION

Table 1 contains the results of amylose content. It was measured because of many reports which demonstrate that the retrogradation susceptibility depends on the amylose level [Fredriksson et al. 1998, Hoover 2001]. The highest content of linear glucans was observed in potato starch, while the lowest in waxy corn. The level of amylose reported here for potato starch is slightly higher than in the studies of Fortuna and Juszczak [1998], and even more as compared to results of Swinkels [1985]. The content of amylose in triticale starch is slightly lower than in the reports of Gambuś et al. [1992] and Fortuna and Juszczak [2000]. It could be caused by the varietal differences between analysed samples. Gambuś et al. [1992] examined starch from triticale variety Ugo, Fortuna and Juszczak [2000] – variety Bolero, and the presented results refer to the variety Pronto s-elita. Amylose content in tapioca starch is higher than reported by Swinkels [1985] and Fortuna and Juszczak [2000]. In case of corn starch slightly lower values are given by Fortuna and Juszczak [2000], while Swinkels [1985] and Rahman et al. [2000] report higher amylose levels. Examined rice starch is less abundant in amylose than samples from the studies of Jane et al. [1996] and Schierbaum et al. [1991], and its values are only a half of those reported by Fortuna and Juszczak [2000] and Rahman et al. [2000]. In case of wheat starch the data correspond well to those observed by Fortuna and Juszczak [2000]. The level of amylose in waxy corn starch is also in the limits reported by these authors. According to Jane et al. [1996] such starch contain amyloze at levels from 0 to 2%.

Table 1. Amyloses content of native starches

<table>
<thead>
<tr>
<th>Kind of starch</th>
<th>Amylose content, g/100 g d.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato</td>
<td>29.6</td>
</tr>
<tr>
<td>Tapioca</td>
<td>21.5</td>
</tr>
<tr>
<td>Wheat</td>
<td>20.0</td>
</tr>
<tr>
<td>Triticale</td>
<td>21.8</td>
</tr>
<tr>
<td>Corn</td>
<td>19.8</td>
</tr>
<tr>
<td>Waxy corn</td>
<td>1.0</td>
</tr>
<tr>
<td>Rice</td>
<td>7.2</td>
</tr>
</tbody>
</table>

It is worth of noting that various methods were used to measure amylose content in starch. The reported data are based on the method of Morrison and Laignelet [1983], which allow to measure so called apparent amylose. During the measurement some interference of lipids present in the sample could be found [Knuston 1999].

After examination of native samples, the maltodextrins were obtained on laboratory scale, and DE corresponding to those hydrolysates were given in Table 2.

In order to obtain maltodextrins with medium DE, in the range between 8.27 to 12.75 the time and dosage of the enzymes were adjusted (Table 2). In the case of potato starch, which is least prone to the action of α-amylase, the time was extended. The resistance of this starch to the action of enzymes is reported by many authors [Fuwa et al. 1977, Sawicka-Żukowska et al. 1999]. The shortest times of enzymatic action were
Table 2. Selected physico-chemical properties of maltodextrins

<table>
<thead>
<tr>
<th>Kind of maltodextrin</th>
<th>DE value</th>
<th>Time of hydrolyse (min)</th>
<th>Amount of fraction nb/lcb (%)</th>
<th>Amount of fraction scb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato</td>
<td>8.73</td>
<td>15*</td>
<td>1.1a</td>
<td>98.9a</td>
</tr>
<tr>
<td>Tapioca</td>
<td>11.64</td>
<td>10</td>
<td>1.6a</td>
<td>98.4a</td>
</tr>
<tr>
<td>Wheat</td>
<td>12.75</td>
<td>5</td>
<td>1.0a</td>
<td>99a</td>
</tr>
<tr>
<td>Triticale</td>
<td>9.13</td>
<td>15</td>
<td>3.4</td>
<td>96.6</td>
</tr>
<tr>
<td>Corn</td>
<td>8.27</td>
<td>15</td>
<td>5.1</td>
<td>94.9</td>
</tr>
<tr>
<td>Waxy corn</td>
<td>8.84</td>
<td>10</td>
<td>0.2</td>
<td>99.8</td>
</tr>
<tr>
<td>Rice</td>
<td>9.06</td>
<td>15</td>
<td>1.2a</td>
<td>98.8a</td>
</tr>
</tbody>
</table>

*Double dosis of enzymatic preparation was applied.

Values in the table marked with the same letters do not differ statistically at the level of significance $\alpha = 0.05$.

applied in the case of wheat maltodextrin. According to Wjibenga [1991] wheat starch is hydrolysed fastest, among various starchy materials. This view is also supported by other sources [Fortuna et al. 2001, Gallant et al. 1972, Rojas et al. 2001, Sawicka-Żukowska et al. 1999].

Maltodextrins are starch hydrolysates, so the determination of amylose would be in this case misleading. However, in case of hydrolysates the iodine affinity could still be applied in order to classify non-branched/long-chain-branched glucans, that have higher absorbance at $\lambda = 640$ nm or bigger ratio $A_{640}/A_{525}$ and short-chain-branched fraction with higher absorbance at $\lambda = 525$ nm and lower ratio $A_{640}/A_{525}$ [Huber and Praznik 1984]. In Table 2 the results of GPC data are give, and the amounts of nb/lcb and scb fractions are reported. The lowest content of nb/lcb, and the highest scb glucans was found for maltodextrin derived from waxy corn starch. Figure 1 demonstrates the molecular weight distribution of the maltodextrins with the numbers of collected fractions. Chromatography data clearly indicate, that in analysed samples there are no glucans with molecular weights in the range between $10^7$-$10^8$. Oligosaccharides are apparent only at approximately 60 analysed fraction. In the case of waxy corn maltodextrin the small shift towards higher average molecular weights could be observed.

Figures 2 and 3 represent the retrogradation ability of 2% starch pastes stored for 21 and 2% maltodextrin solutions stored for 14 days. Turbidimetric analysis of retrogradation allows to obtain the qualitative description of this process. The effect of storage was represented on graphs as turbidance changes. Turbidimetric assessment of retrogradation [Jacobson et al. 1997] allows to distinguish between starches and maltodextrins. Initial turbidity measurement, as in the work of Jacobson et al. [1997], allowed to divide the native starches into three groups (Fig. 2). First included potato and tapioca starches, which displayed low turbidity, the second waxy corn starch, and the third wheat, triticale, corn and rice starches. Similar results were obtained by Craig et al. [1989]. Initial retrogradation degree of cereal starches was then higher than tuber and root starches. Such a dependence was already mentioned by Błaszczyk et al. [2001]. The highest change in turbidity was observed in two first days for majority of starches, with the exception of tapioca starch, where it increased mainly between 3rd and 7th day. According
Fig. 1. Gel permeation chromatography of maltodextrins. From the bottom in the order: waxy corn, corn, wheat, triticale, rice, tapioca, potato. On the y-axis total content of carbohydrates in the fractions.

Fig. 2. The susceptibility of 2% starch gels to retrogradation in temperature 8°C
Retrogradation of starches and maltodextrins of origin various

to Milles et al. [1985] and Zhang and Jackson [1992] the association of linear amylose molecules occurs rapidly in the first stage of retrogradation, while slow increase in rigidity of ageing gel, should be ascribed to amylopectin crystallisation. In this study the highest increase in turbidity over the whole time of analysis was observed for potato starch, which was most transparent on the first day, and most opalescent on the last day. Wheat, triticale and rice starches revealed turbidity on the same level for the whole time of experiment, so their susceptibility to retrogradation was similar. The analysed waxy corn starch was least prone to retrogradation, which confirms earlier reports of Jacobson et al. [1997], Raulet et al. [1990] and Swinkels [1985]

Figure 3 represents the results of retrogradation susceptibility of 2% maltodextrin solutions stored at 8°C. It could be observed that the degree of retrogradation was only slightly changed during following days, and that the highest increase of turbidity was found for potato maltodextrins (which corresponds to native potato starch). In case of waxy corn maltodextrin no increase in turbidance was noted for the whole period of analysis.

Retrogradation depends on molecular changes in the examined starch hydrolysates. Its rate is mainly determined by the chain length of biopolymer [Pfannemüller 1992]. In case of potato, tapioca, wheat and triticale maltodextrins it could be found, that the change in turbidity at the initial stage of analysis was higher than for native starches. This increase in the initial rate of retrogradation could be caused by greater mobility of short amylopectin fragments, and smaller changes in the dimension of linear glucans present in solution. Due to the hydrolysis amylopectin fragments were reduced to the size of amylose, but they have still unhydrolysed side-chains. Shorter amylopectin
fragments could faster form centers of crystallization and increase volume of the crystals [Zhang and Jackson 1992]. Figure 3 suggests that waxy corn maltodextrin was not susceptible to retrogradation. GPC analysis of this sample revealed the lowest percentage of linear oligosaccharides, and long chains of amylopectin with the affinity to iodine. Among other samples, the lowest susceptibility to retrogradation was found for rice maltodextrin, and the highest for wheat and triticale.

The existing literature contains only data on the influence of maltodextrin on retrogradation of starch. Wang and Jane [1994] examined the impact of glucose, fructose, maltose, sucrose and maltodextrins on retrogradation of starch. Addition of fructose caused the major increase in retrogradation as compared to glucose, maltose, sucrose and maltodextrins during storage at temperature 2° and –20°C. The retrogradation of maltodextrin solutions of different concentration was also studied, and it was shown, that at concentration 40% the retrogradation at 2°C may be observed after 7 days of storage, while at low concentrations (6, 9, 26 i 29%) it doesn’t occur even after 21 days. Rojas et al. [2001] state, that maltodextrins of low dextrose equivalent (DP 3-7) could be responsible for retardation of bread staling. The same observation could be supported by a fact, that oligosaccharides with a DP 3-5, according to Durán et al. [2001], decrease retrogradation enthalpy. Studies of other authors indicate, that sugars (glucose, fructose, maltose) inhibit retrogradation of rice and potato starch [Chang and Liu 1991, Katsuta et al. 1992, Kohyama and Nishinari 1991]. Hydrogen bonds between starch chains lead to crystallization, which could be modified by saccharides, that cause a decrease of retrogradation rate.

Summarising it could be stated that maltodextrins used at low concentrations may be used as additive to food products, that could retard retrogradation of starch.

CONCLUSIONS

1. All the applied maltodextrins revealed much lower susceptibility to retrogradation as compared to corresponding native starches.
2. Basing on the turbidity data it was observed that the susceptibility of starch to retrogradation after 21 days was as follows potato > wheat, triticale, rice, corn > tapioca > waxy corn.
3. Turbidimetric method allowed to rank the retrogradation susceptibility of maltodextrins after 14 days in the following order: triticale > wheat > tapioca > corn > rice, potato > waxy corn.
4. The addition of low levels of maltodextrins to food products may prevent to some extent the retrogradation of starch.

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RETOGRADACJA SKROBI I MALTODEKSTRYN
RÓŻNEGO POCHODZENIA

Wstęp. Retrogradacja zachodząca w czasie przechowywania produktów spożywczych jest istotnym problemem. Dlatego też w pracy przebadano zdolność do retrogradacji skrobi różnego pochodzenia botanicznego oraz otrzymanych laboratoryjnie maltodekstryn.
**Material i metody.** Materiałem badawczym były skrobie handlowe i naturalne różnego pochodzenia: ziemniaczana, tapiokowa, pszenenna, pszenżytna, ryżowa, kukurydziana i kukurydziana woskowa. Ze skrobi otrzymano na skalę laboratoryjną maltodekstryny średnioscukrzone o DE w zakresie 8,27-12,75. Skrobie wyjściowe przebadano pod względem amylozy metodą Morrisona, a dla otrzymanych maltodekstryn wyznaczono stosunek frakcji nb/leb do scb z użyciem GPC. Stosując metodę Jacobsona, wyznaczono skłonność do retrogradacji 2-procentowych kleików skrobiowych i 2-procentowych roztworów otrzymanych maltodekstryn.


**Wnioski.** Na podstawie badań stwierdzono, że wszystkie maltodekstryny odznaczają się dużo mniejszą zdolnością do retrogradacji w porównaniu ze skrobiami wyjściowymi oraz ustalono jak kształtuję się skłonność do retrogradacji badanych skrobi i maltodekstryn.

**Słowa kluczowe:** skrobie różnego pochodzenia, retrogradacja, maltodekstryny

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