

RETROGRADATION OF RYE STARCH PASTES

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Abstract. The retrogradation susceptibility of starch determines consumer suitability of food products rich in this polymer. Starch isolated from flour obtained from rye variety 'Amilo', which displays very low amylolytic activity, contains highest amounts of amylose and exhibits strong retrogradation susceptibility. Flour from rye 'Dańkowskie Złote' and commercial rye flour type 720, that have higher amylolytic activity in comparison to 'Amilo', contain starch with lower amounts of amylose and reduced retrogradation susceptibility. Wheat starch displays lower degree of retrogradation in comparison to rye, because of larger amounts of phosphorus (phospholipids).

Key words: rye varieties, rye starch, pentosans, phosphorus, degree of retrogradation

INTRODUCTION

High amylolytic activity of rye is considered to be the main drawbacks of this cereal. The breeding programs that were directed to reduce it resulted in introduction of new varieties, such as 'Amilo', which was obtained, by crossing 'Otello' and 'Dańkowskie Złote' [Żyto... 1994].

The reduced enzymatic activity of 'Amilo' in comparison to other registered Polish varieties, such as 'Dańkowskie Złote' (oldest registered Polish variety), should result in the change of technological properties of the isolated starch such as the tendency to retrograde.

One of the important features of starch, that determines its behaviour in food products, is retrogradation susceptibility. The process depends on the type of starch i.e. amylose to amylopectin ratio, length of starch chains, crystallinity, non-starch components of starch granule, as well as the temperature, concentration of starch paste, pasting method and availability of water during gelatinisation [Jacobson et al. 1997, Fredriksson et al. 1998, Parker and Ring 2001].

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Short-term development of crystallinity in starch gels is related to the formation of amylose aggregates, which increases with the length of its chains. Long-term changes observed in starch gels depend on amylopectin branching, mainly the length of external short branches [Jacobson et al. 1997, Parker and Ring 2001]. According to Shi and Seib [1992] and Parker and Ring [2001] the presence of short amylopectin branches with DP = 6 – 11 may significantly reduce retrogradation.

Gudmundsson and Eliasson [1991] demonstrated in DSC experiments, that among cereal starches, rye retrogrades slower than wheat. They interpreted the results as the effect of various structure of amylopectin. Altered structure of amylopectin, i.e. lower crystallinity of rye starch in comparison to wheat [Schierbaum et al. 1991] was measured.

Also the initial studies based upon determination of free amylose in supernatant [Whistler and Wolfrom 1962], performed by Gambuś et al. [1995] proved lower susceptibility to retrogradation of rye starch pastes. However in further experiments on rye starches [Gambuś and Gumul 2003], that contained higher amounts of amylose in comparison to wheat, displayed higher degree of retrogradation. The presence of lipids reduces degree of pasting and therefore diminishes changes observed afterwards, as retrogradation [Gudmundsson and Eliasson 1991]. Lin and Czuchajowska [1998] found retarded retrogradation in starch in the presence of phospholipids. The role of pentosanes is controversial. Jankiewicz and Michniewicz [1987] suggest, that they play an important role in delaying retrogradation, while Longton and LeGrys [1981] do not share this view. Gudmundsson and Eliasson [1991] state, that the important feature of pentosans is their binding of water. The access of water significantly impacts retrogradation. Its rate is highest at 40-50%, and significantly decreases under 20% or above 90% [Longton and LeGrys 1981, Zeleznak and Hoseney 1986, Gudmundsson and Eliasson 1991].

Although retrogradation determines consumer suitability of starch containing products, there is no available information about this characteristic of starch isolated from polish rye varieties. This is why the aim of the study was to measure the degree of retrogradation of starches isolated from local rye varieties: 'Amilo' (very low enzymatic activity) and 'Dańkowskie Złote' (high enzymatic activity), in comparison to wheat starch 'Sakwa' and starches isolated from commercial rye (type 720) and wheat (type 750) flours.

MATERIAL AND METHODS

Flours were obtained by laboratory milling of rye 'Amilo' and 'Dańkowskie Złote' and wheat 'Sakwa' in a laboratory mill equipped with two pairs of rollers type QG-109, equivalent to Quadrumat Junior. Commercial flours (rye type 720, and wheat type 750) were obtained from Polskie Zakłady Zbożowe w Krakowie (Polish Cereal Company in Cracow). The starches were isolated from the above mentioned flours by laboratory method Richter et al. [1968]. DMSO (Sigma) and orcinol (Merck) were used.

Falling number (FN) was measured by an automated apparatus (Zakład Badawczy Przemysłu Piekarskiego (Research Institution of Baking Industry), Bydgoszcz, Poland). The analysis was performed twice.

Apparent amylose was assessed in two replicates according to Morrison and Laignelet [1983]. Total phosphorus was estimated in duplicate according to Marsh [1959]. Total pentosans were measured in triplicate by the method of Hashimoto et al. [1987]. Degree of retrogradation was evaluated according to Whistler and Wolfrom [1962] with the modification of Gambuś [Gambuś and Gumul 2003]. The analyses were done in duplicate. Size exclusion chromatography was performed on a set of 4 SEC columns filled with Sephacryl gels: 50 × 1.6 cm – S-200, 82 × 1.6 cm – S-200, 90 × 1.6 cm – S-500, 88 × 1.6 cm – S-1000. The eluent – 0.003 M Na₂CO₃ was pumped by a peristaltic pump P-1 (Pharmacia) at a flow rate 30 cm/h. Pullulans (Shodex Standard, Macherey-Nagel) were used as a standard for molecular weight calibration [Praznik et al. 1986]. Concentrations 1.25% of all starches were used. Each analysis was performed 2-times.

All the obtained results were used for calculation of least significant difference (LSD) at the 0.05 level.

RESULTS AND DISCUSSION

In the flours used for starch isolation, enzymatic activity was measured as falling number (Table 1). As expected, the flour from 'Amilo' variety displayed very low enzymatic activity (FN = 420 s), similar to flour from wheat variety 'Sakwa'.

Table. 1. Falling number of flours of rye and wheat varieties and commercial flours
Tabela 1. Liczba opadania mąk z odmian żyta i pszenicy oraz mąk handlowych

Sample of flour – Próbkę mąki	Falling number – Liczba opadania s
Rye – 'Amilo' Żyto 'Amilo'	420.5
Rye – 'Dańkowskie Złote' Żyto 'Dańkowskie Złote'	192.5
Commercial rye (type 720) Handlowa żytnia (typ 720)	156.0
Wheat – 'Sakwa' Pszenica 'Sakwa'	400.5
Commercial wheat (type 750) Handlowa pszenna (typ 750)	367.5
LSD – NIR	22.5

Isolated rye starches varied in respect to amylose content (Table 2 and Table 3) and starch from 'Amilo' contained largest amounts of it. Other rye starches were comparable to wheat ones in this regard.

The level of phosphorus amount (which is measure of phospholipids [Morrison 1981]) was highest in rye starch isolated from variety 'Amilo' (Table 2). It was however almost two times lower than in wheat starches (Table 2) as it was also earlier reported [Gambuś et al. 1995, Gambuś 1997, Nowotna et al. 2006].

Table 2. Content of amylose, phosphorus and total pentosans in starch isolated from rye and wheat flours, %

Tabela 2. Zawartość amylozy, fosforu i pentozańców w skrobi wyizolowanej z mąk żytnich i pszenicznych, %

Source of starch Źródło skrobi	Amylose Amyloza	Phosphorus Fosfor	Total pentosans Pentozany
Flour from rye – ‘Amilo’ Mąka z żyta ‘Amilo’	23.03	0.025	0.58
Flour from rye – ‘Dańkowskie Złote’ Mąka z żyta ‘Dańkowskie Złote’	20.39	0.023	0.55
Commercial rye flour (type 720) Handlowa mąka żytnia (type 720)	19.08	0.018	0.59
Flour from wheat – ‘Sakwa’ Mąka z pszenicy ‘Sakwa’	20.95	0.042	0.45
Commercial wheat flour (type 750) Handlowa mąka pszenna (typ 750)	19.54	0.039	0.34
LSD – NIR	0.57	0.001	0.11

Table 3. Content of amylose and amylopectin and weight average molecular mass (M_w) of the components of starch, isolated from rye and wheat floursTabela 3. Zawartość amylozy i amylopektyny oraz średniej wagowo masy cząsteczkowej (M_w) składowych skrobi, wyizolowanej z mąk żytnich i pszenicznych

Source of starch Pochodzenie skrobi	Amylose Amyloza		Amylopectin Amylopektyna	
	content zawartość %	$M_w \cdot 10^6$	content zawartość %	$M_w \cdot 10^6$
Flour from rye – ‘Amilo’ Mąka z żyta ‘Amilo’	24	4.6	76	9.5
Flour from rye – ‘Dańkowskie Złote’ Mąka z żyta ‘Dańkowskie Złote’	22	2.5	78	15
Commercial rye flour (type 720) Handlowa mąka żytnia (type 720)	20	4.8	80	12
Flour from wheat – ‘Sakwa’ Mąka z pszenicy ‘Sakwa’	22	4.2	78	13
Commercial wheat flour (type 750) Handlowa mąka pszenna (typ 750)	21.5	3.8	78.5	10

Rye starches contained more pentosans (Table 2) than wheat ones, which is a consequence of large amounts of these compounds in whole grains of rye [Żyto... 1994]. Investigated rye starches did not vary in the content of those compounds.

Because retrogradation rate is determined mainly by the length of starch chains, besides analysis of amylose content (Table 2 and 3), the weighted average molecular weights of amylose (M_w AM) and amylopectin (M_w AP) were evaluated in starch samples (Table 3). Comparison of the results presented in Table 3 allows concluding, that

the differences were small, although Mw of amylose in rye starch isolated from 'Amilo' variety and commercial flour are higher than in case of 'Dańkowskie Złote'. Wheat starches have comparable values of Mw AM.

In order to study the retrogradation, the pastes were stored at +20, +8 and -20°C for three days (Fig. 1-3). The process was the highest at -20°C, as it was earlier observed Gambuś et al. [1995] and Gambuś and Gumul [2003]. The differences between samples were most visible at +8°C. Rye starch from 'Amilo' variety displayed highest values of degree of retrogradation (Fig. 2), during three days of storage of its paste. The value decreased consequently for starch from 'Dańkowskie Złote' and commercial rye flour type 720 and the lowest from wheat starches.

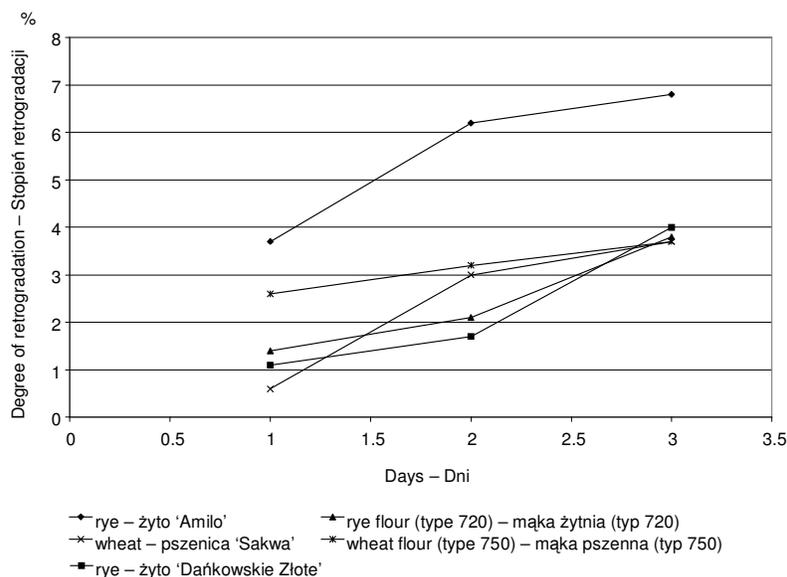


Fig. 1. Degree of retrogradation of starch paste stored for three days at temp. +20°C (LSD; after 1 day = 1.1, 2 day = 1.4, 3 day = 0.7)

Rys. 1. Stopień retrogradacji kleików skrobiowych przechowywanych przez trzy dni w temp. +20°C (NIR; po 1. dniu = 1,1, 2. dniu = 1,4, 3. dniu = 0,7)

Summarizing the results it could be concluded that the lower enzymatic activity of rye flour used for starch isolation (higher FN) resulted in limited degradation of glucans, which enhanced starch retrogradation. In case of rye starches, the higher retrogradation susceptibility of 'Amilo' in comparison to 'Dańkowskie Złote' was caused by higher amylose content and increased length of its chains. Despite of the significant differences in the content of phospholipids in particular rye starches, the amount of these components did not influence degree of starch retrogradation, as it was already observed by Gudmundsson and Eliasson [1991]. In case of rye starches the process was mainly affected by the amounts of linear starch glucans, which leached out during gelatinization susceptible to retrogradation, and the length of their chains.

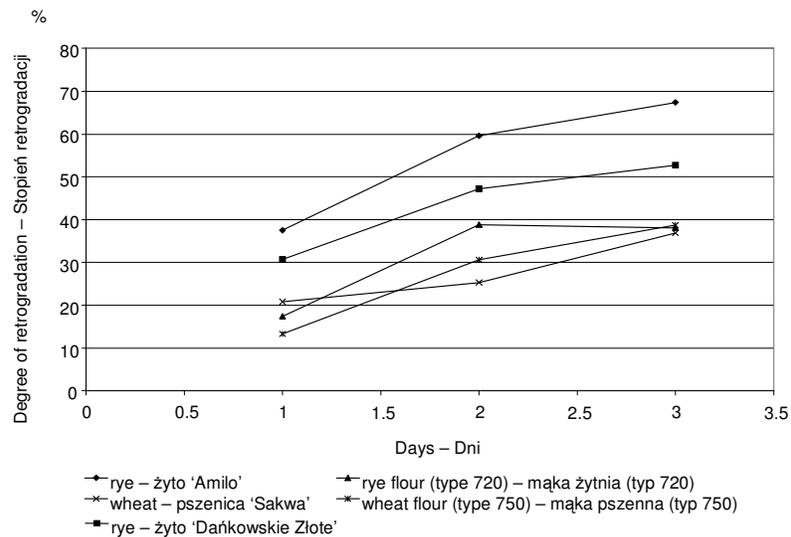


Fig. 2. Degree of retrogradation of starch paste stored for three days at +8°C (LSD; after 1 day = 3.3, 2 day = 8.8, 3 day = 2.3)

Rys. 2. Stopień retrogradacji kleików skrobiowych przechowywanych przez trzy dni w +8°C (NIR; po 1. dniu = 3,3, 2. dniu = 8,8, 3. dniu = 2,3)

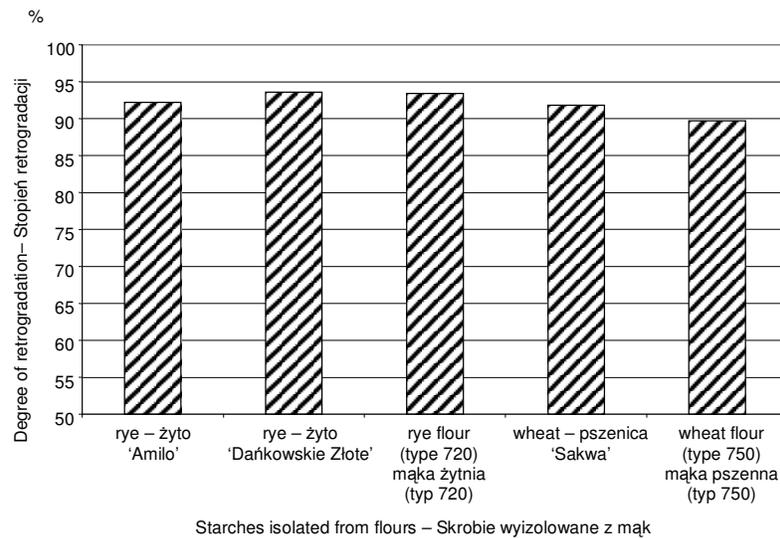


Fig. 3. Degree of retrogradation of starch paste stored 24 h at -20°C (LSD = 1.7)

Rys. 3. Stopień retrogradacji kleików skrobiowych przechowywanych przez 24 h w -20°C (NIR = 1,7)

Wheat starches exhibited similar degree of retrogradation, but lower from rye, which resulted from comparable enzymatic activity of flours and corresponding amount of amylose and Mw of AM. Lower retrogradation susceptibility of this starch in comparison to rye, was result of higher content of phospholipids, what is in agreement with Lin and Czuchajowska [1998] and other authors [Gudmundsson and Eliasson 1991].

Because starch retrogradation is one of the most important factors in bread ageing, high retrogradation susceptibility of rye starch 'Amilo' variety should have negative impact on the baking characteristics of its flour. Preliminary baking studies on whole-meal prepared from this variety do not confirm such conclusion. It seems that good quality of bread obtained from 'Amilo' is due to the high content of pentosans in the flour. Studies on this subject will be continued.

CONCLUSIONS

1. Despite of the similar enzymatic activity of flour from rye variety 'Amilo' and wheat, the isolated starches differ significantly in a degree of retrogradation.
2. Starch isolated from flour from rye variety 'Amilo', which displays very low amylolytic activity, contains starch with highest amounts of amylose and high retrogradation susceptibility.
3. Flour from rye variety 'Dańkowskie Żłote' and commercial rye flour type 720, that have higher amylolytic activity in comparison to 'Amilo', contain starch with lower amounts of amylose and reduced retrogradation susceptibility.
4. Wheat starch display lower degree of retrogradation in comparison to rye, because of larger amounts of phosphorus (phospholipids).

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RETROGRADACJA KLEIKÓW SKROBI ŻYTNIJ

Streszczenie. Podatność na retrogradację skrobi określa przydatność konsumencką produktów żywnościowych bogatych w ten polimer. Skrobia wyizolowana z mąki otrzymanej przez zmielenie ziarna żyta odmiany 'Amilo', która wykazuje bardzo małą aktywność enzymatyczną, charakteryzuje się największą zawartością amylozy i cechuje się największym stopniem podatności na retrogradację. Mąka z żyta odmiany 'Dańkowskie Złote' i mąka handlowa typu 720, które wykazywały większą aktywność amylolytyczną w porównaniu 'Amilo', zawierają skrobię z mniejszą ilością amylozy i charakteryzują się mniejszą podatnością na retrogradację. Skrobia pszenna wykazuje mniejszy stopień retrogradacji w porównaniu z żytnią ze względu na większą ilość fosforu (fosfolipidów).

Słowa kluczowe: żyto, skrobia żytnia, pentozany, fosfor, stopień retrogradacji

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