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PHYSICO-CHEMICAL MODIFICATION OF POTATO STARCH WITH DIFFERENT GRAIN SIZE

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Key words: starch fraction, starch hydrolysis, oxidation, esterification and etherification of starch.

Potato starch samples separated into three fractions of different grain size (fraction I — large grains > 80 μm, fraction II — medium grains — 20-80 μm, fraction III — small grain — < 20 μm) were subjected to physico-chemical modification. It was found that the intensity of different processes varied and that the starches obtained from potatoes in different starch production plants in Poland differ significantly in the content of large and small grains.

On the very important distinctive features of potato starch is the considerable differentiation of the size and structure of its grains. It is well known that the size of potato starch grains is contained in the very wide range of 2-110 μm [14]. Apart from differences in size, the fact that differently sized potato starch grains exhibit a specifically differentiated structure [4; 13] also appears to be important. It can be seen that small grains are almost spherical in shape with a closely packed, dense interior, whereas the large grains are ellipsoidal, visibly flattened, with a strongly accented eccentric lamination. A very important element of the structure of large grains of potato starch is their loose internal structure characterized by a well-developed system of capillaries running from fissures on the grains surface down to the grain interior.

The differentiated size of potato starch grains entails the issue of the content or the share of the separate fractions with different grain size in the selected starch mass. It turns out that different starch samples usually display a differentiated content of large, medium-sized and small grains. The share of the separate fractions in the mass of differentiated grains depends on the genetical features of potatoes, on the biological and agrotechnical conditions of potato plant vegetation, and on the specific technical-technological conditions in starch production plants during the separation and refining of starch from potatoes.

In practice, certain differences and the specific characters of the given regions which have a bearing on the shaping of starch grains in potatoes combine with technological peculiarities of starch production plants frequently causing a considerable differentiation of grain size of starch obtained from potatoes grown locally in the different regions.

In the light of these well-known facts it seems interesting to determine the effect of the differentiated grain size of starch on the course and outcome of processes of physico-chemical modification of starch.

The aim of the present work is the examination of the changes of potato starch of different grain size due to the action of chemical agents, enzymes and increased temperature.

METHODS

Using the method of hydraulic classification, the potato starch sample was separated into three fractions of different grain size [4]:

— large grains (80-110 μm)
— medium-sized grains (20-80 μm)
— small grains (2-20 μm)

Samples of the fractionated starch were subjected to the following well-known processes of physico-chemical modification:

ENZYMATIC HYDROLYSIS TO GLUCOSE [8, 11, 12, 16]

Starch samples underwent a process of two-stage enzymatic hydrolysis at 30% concentration. In the first stage the starch was liquefied with the use of Novo 264 bacterial α-amylase preparation (0.05% in starch dry substance, pH 6.2). Liquefaction was done by programmed heating of the starch-and-enzyme suspension to 85°C in one hour and then maintaining the attained temperature for 2 h; the process was completed by boiling the suspension (105°C). In the second stage of hydrolysis, the liquefied starch was treated with Novo II glucoamylase (0.25% in starch dry substance, pH 4.5) at 60°C for 72 h.

DEXTRINIZATION BY ROASTING AFTER ACIDIFICATION WITH HNO_3 [5, 15, 18]

Starch samples were acidified with 10% solution HNO_3 up to pH 2.6, following which the samples were thoroughly mixed, sifted through a sieve and subjected to the process of unification by mixing in a ball grinder for 2 h. Samples thus prepared were roasted at 180°C for 3 h.

OXIDATION WITH SODIUM HYPOCHLORITE [2, 4]

A 30% water solution of starch with an addition of sodium hypochlorite (4% active chlorine in starch dry substance) was kept for 3 h at 30°C (pH 8) until the total exhaustion of active chlorine, i.e. till the decomposition of hypochlorite. After termination of the reaction, the starch was separated from the mother liquor, washed and dried.

ESTERIFICATION WITH PHOSPHATES [7, 17]

Starch samples were mixed with a water solution of a phosphates mixture ($Na_2HPO_4+NaH_2PO_4$) in the amount of 3% P_2O_5 in starch dry substance, and then a urea solution (2% urea in starch dry substance) was added. The wet starch thus prepared (ca. 50% dry substance) was mixed intensely and after sifting through a sieve was dried down to 5% water content at 50-100°C. The dried mixed preparation was roasted at 150°C for 3 h.

ETHERIFICATION WITH SODIUM MONOCHLOROACETATE [1, 3, 6]

A starch suspension in methanol (30% concentration) was alkalized with a methanol solution of NaOH up to pH 9, following which portions of sodium monochloroacetate (50% $CH_2ClCOONa$ in starch dry substance) were added to the suspension. The O-alkylation reaction was performed at 40°C for 6 h and then the starch was filtered, washed with hydrated methanol and dried.

Four selected samples of starch manufactured in 1981 by four different Polish starch production plants were also subjected to enzymatic hydrolysis, dextrinization and oxidation. The samples differ significantly in the share of large and small grains. The compared effects of physico-chemical modification of different starch samples were observed and measured in identical conditions.

DISCUSSION OF RESULTS

The results are collected in Tables 1-9.

Table 1. Grain-size composition of starches manufactured by various Polish starch producers in the 1981 season (contents expressed in %)

Grain size	Potato Industry Enterprise			
	Łomża	Głowno	Luboń	Nowogard
Large (> 80 μm)	12.0	8.3	4.2	3.4
Medium (20-80 μm)	71.5	70.9	75.0	72.5
Small (< 20 μm)	16.5	20.8	20.8	24.1

T a b l e 2. Enzymatic hydrolysis of starch to glucose

Grain fraction	Liquefaction			Saccharification		
	reducing value (DE)	viscosity (mPa · s)	glucose content (% in dry substance)	reducing value (DE)	viscosity (mPa · s)	glucose content (% in dry substance
Large	28.7	3836.4	3.7	97.8	924.8	97.4
Medium	26.9	4010.5	3.4	97.0	978.4	96.3
Small	23.1	7832.0	2.6	94.3	1636.7	91.5

Liquefaction with α-amylase (Novo 264) at enzyme dose 0.05%, pH 6.2, temperature 20-85°C; saccharification with glucoamylase (Novo II) at enzyme dose 0.25%, pH 4.5, temperature 60°C, 72 h, concentration of starch (hydrolysate) 30% dry substance.

T a b l e 3. Esterification of starch with phosphates ($Na_2HPO_4 + NaH_2PO_4$)

Grain fraction	Substitution degree (mmol/mol)	Viscosity (mPa. s)	Reducing value (mmol CHO/mol)
Large	42.4	1967.5	11.6
Medium	40.3	2050.0	10.4
Small	24.0	1325.6	7.8

Reagent roasted in presence of urea at 150°C for 3 h

T a b l e 4. O-alkylation of starch (etherification) with sodium chloroacetate

Grain fraction	Degree of etherification (mmol/mol)	Viscosity (mPa · s)	Reducing value (mmol CHO/mol)
Large	385	372.7	12.8
Medium	337	430.4	12.3
Small	193	978.2	7.4

20% suspension of starch in methanol, pH 9, temperature 40°C, time of reaction 6 h

Ta le 5. Oxidation od starch with sodium hypochlorite

Grain fraction	Viscosity (mPa · s)	CHO (mmol/100 g)	COOH (mmol/100 g)
Large	338.5	13.6	26.5
Medium	449.0	14.1	24.3
Small	568.2	12.3	18.8

pH 8, temperature 30°C, starch concentration 30%, hypochlorite dose 4% Cl in starch dry substance, reaction time 3 h

Table 6. Dextrinization of starch acidified with HNO_3

Grain fraction	Viscosity (mPa · s)	$[\alpha]_D^{20}$	Reducing value (% glucose in dry substance)	Molecular mass (M)
Large	115.3	171.0	2.08	5060
Medium	127.3	173.6	2.02	5869
Small	203.5	184.0	1.65	9165

Reaction duration — 3 h, temperature — 180°C

Table 7. Enzymatic hydrolysis

Manufacturer	Liquefaction with α-amylase			Saccharification with glucoamylase		
	reducing value (DE)	viscosity (mPa · s)	glucose cintent (% in dry substance)	reducing value (DE)	viscosity (mPa. s)	glucose content (% in dry substance)
Łomża	26.4	3921.0	3.5	98.4	959.4	97.5
Głowno	26.0	4154.5	3.7	97.8	968.0	96.8
Luboń	25.2	5741.4	3.2	96.7	1037.7	95.6
Nowogard	24.6	5972.1	3.0	95.8	1386.8	94.3

Comparison of effects of physico-chemical modification of starches from different manufacturers (of different grain-size composition)

Table 8. Dextrinization

Manufacturer	Viscosity (mPa · s)	Reducing value (% glucose in dry substance)	Molecular mass (M)
Łomża	119.5	1.90	5245
Głowno	121.9	2.05	5388
Luboń	178.4	1.82	7423
Nowogard	184.5	1.74	8172

Table 9. Oxidation with hypochlorine

Manufacturer	Viscosity (mPa · s)	Content (mmol/100 g)	
		CHO	COOH
Łomża	341.0	14.3	25.5
Głowno	345.7	12.8	24.8
Luboń	436.5	11.7	21.4
Nowogard	481.8	10.6	22.1

As expected, potato starch occurring in the form of grains of various sizes displays a markedly differentiated behaviour in chemical reactions and under the action of physical stimuli. In particular, it can be seen in all the studied cases that small grains are markedly more resistant to the action of physico-chemical factors than large grains [9, 10].

A very characteristic illustration of this fact, not reflected in the results given in the Tables, is the behaviour of starch grains during enzymatic liquefaction. Namely, as the temperature liquefied starch, increases, the large grains gelatinize when the temperature just exceeds 50°C, and at ca. 80°C there occurs full liquefaction, and a highly transparent solution results. On the other hand, the small grains gelatinize much more slowly and only in temperatures over 70°C. Even after an extended liquefaction at 85°C the paste does not turn into a transparent solution but remains very opaque and relatively immobile.

It appears that this is the reason for the clearly worse results of saccharification of starch in a solution of small grains as compared to analogous results for a large-grain sample. It is highly probable that during the process of gelatinization the starch in small grains which are much more resistant to the action of water and temperature, undergoes hydrolysis under the action of α-amylase to a small degree, and hence

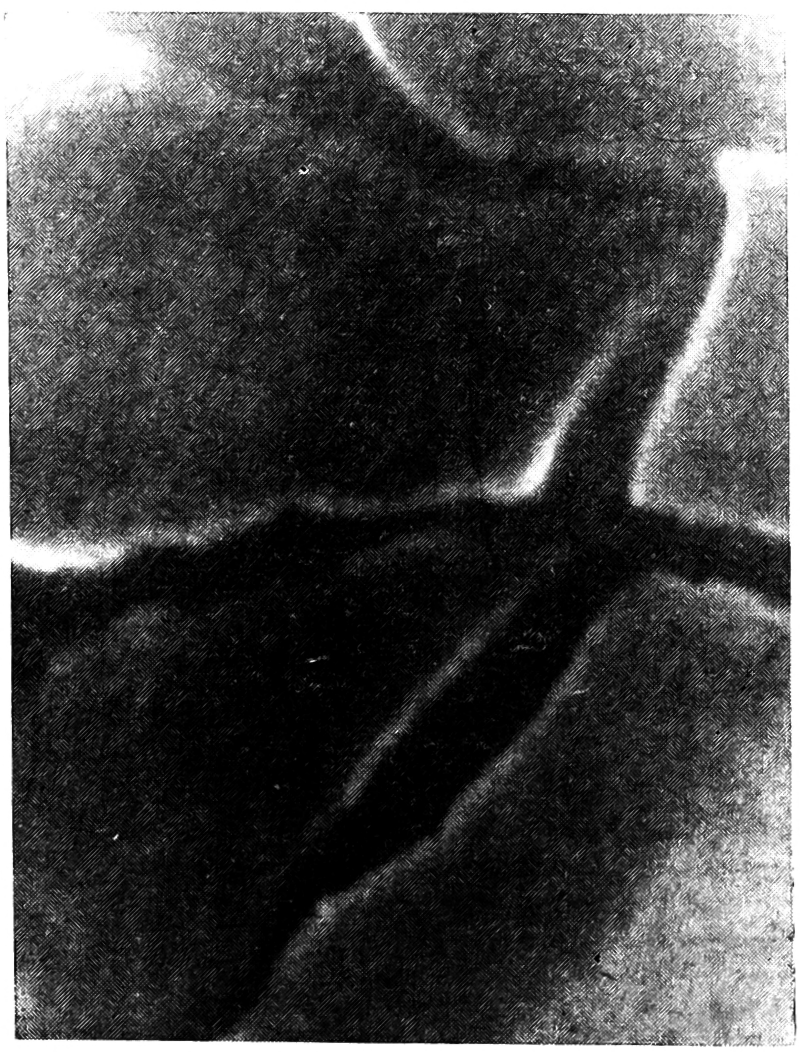

Photo 1. Large grains. Starch grain surface fragment as seen under a scanning microscope (magnification 15 000 x)

remains during saccharification in a colloidal form as large particles not easily accessible to glucoamylase. Such a course of the processes is indicated by infrequent cases of obtaining saccharified starch hydrolysates from small grains of final reducing value in excess of 90 DE and at the same time giving a colour reaction with iodine.

The remaining examples of physico-chemical modification of starch (dextrinization, esterification, etherification and oxidation) univocally confirm the claim that small grains are much more resistant to the action of physico-chemical agents than large grains. This is indicated by all the crucial indices characteristic for the given reaction of the compared samples.

Summing up the observation of behaviour of variously grained starch subjected to processes of physico-chemical modification, we must say that small starch grains, as compared with large and medium-sized ones, are much more resistant to external stimuli and are less prone to transformation. This is probably a result of the previously mentioned differences in internal structure of the large and the small grains. The large grains have a porous (spongy) structure with a very well developed surface facilitating their contact with reagents, whereas the small grains are very compact structures impeding the access of reagents to the starch mass. This is

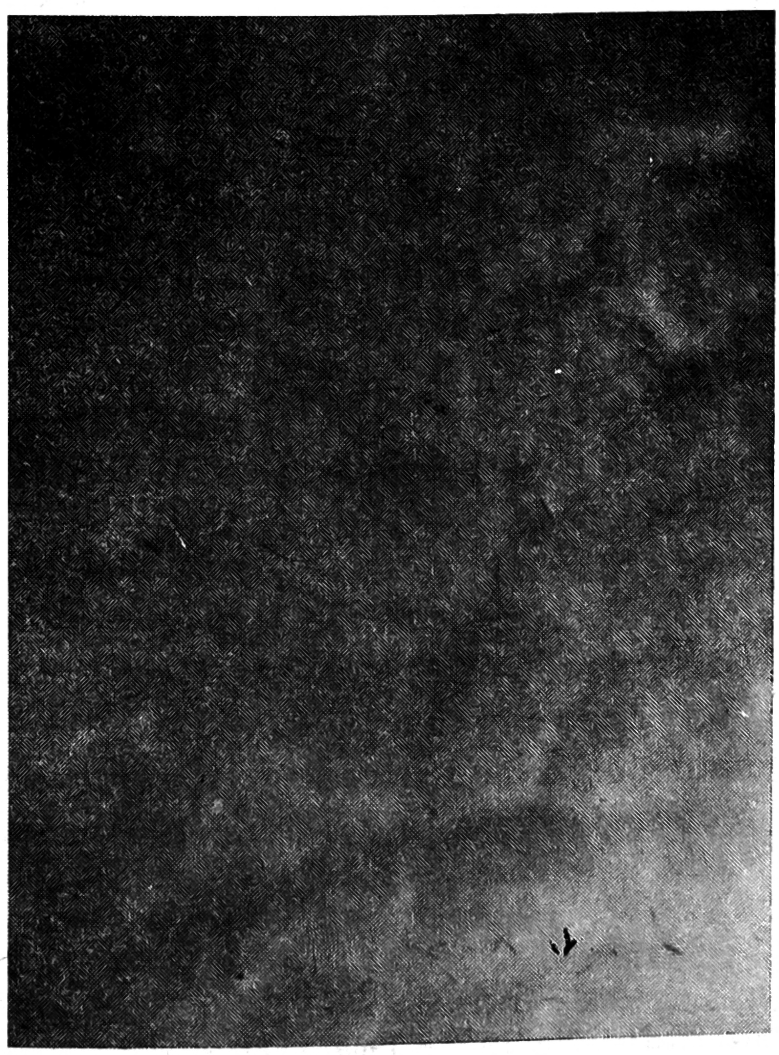

Photo 2. Small grains. Starch grain surface fragment as seen under a scanning microscope (magnification 15 000 x)

clearly visible in scanning microscope images of large and small grains (magnification 15 000 x).

It is to be expected that in view of the differentiated reactivity of starch on small and large grains, samples of commercial starch differing considerably as to the content of small grains may behave differently in various physico-chemical processes.

The performed studies and the obtained results confirm this supposition (Tables 7-9). The experiments show that starch samples containing exceptionally many small grains (> 20%) behave markedly differently in reactions. The oscillations of small-grain fraction content in different samples of commercial starch may amount to as much as 10%. The starches of such a differentiated content of variously sized grains exhibit a markedly different behaviour in most of the processes of physico-chemical modification, this observation having an obvious practical significance.

CONCLUSIONS

1. Starches obtained from potatoes in different starch production plants have different contents of large and small grains.
2. Small starch grains are much more resistant to the action of physico-chemical modification processes.
3. The starches manufactured in different plants and differing considerably as regards the share of small grains besave differently in physico-chemical stimuli than large and medium-sized grains.
4. Starches with a high content of small grains (> 20%) are much less susceptible to chemical and enzymatic reactions than starches with a low content of small grains (< 15%).
5. The products of hydrolysis and modification of starches with differentiated contents of small and large grains obtained in identical conditions have different properties.
6. Enzymatic saccharification of starch with a high content of small grains (> 20%) always results in a hydrolysate with a reduced degree of saccharification (less than 95 DE).
7. In order to unify the conditions and results of the physico-chemical modification of potato starch, it is necessary to remove from it the small grain fraction or reduce its share to less than 10% prior to modification.

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FIZYKOCHEMICZNA MODYFIKACJA SKROBI ZIEMNIACZANEJ O ZRÓŻNICOWANYM UZIARNIENIU

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S t r e s z c z e n i e

Rozdzielono na trzy frakcje próbki skrobi ziemniaczanej złożone z ziarenek dużych — frakcja I (> 80 µm), z ziarenk średnich — frakcja II (20-80 µm) i ziarenek małych — frakcja III (< 20 µm) poddano procesom fizykochemicznej modyfikacji polegającym na przemianach, jak:

1) hydroliza enzymatyczna,
2) dekstrynizacja,
3) utlenianie za pomocą podchlorynu,
4) estryfikacja za pomocą fosforanów,
5) eteryfikacja monochlorooctanem sodu.

Stwierdzono, że procesy te przebiegają z różną intensywnością, jeżeli biorą w nich udział ziarenka skrobiowe o różnej wielkości. A w szczególności zauważono, że duże ziarenka skrobiowe znacznie łatwiej ulegają przemianom i reakcjom niż ziarenka małe.

Stwierdzono również, że skrobie otrzymane z ziemniaków w różnych krochmalniach w Polsce różnią się w sposób istotny zawartością ziaren dużych i małych. Różnice te wyraźnie demonstrują się w zachowaniu takich skrobi wobec działania czynników fizykochemicznych w procesach ich modyfikacji.