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SMALL GRANULE POTATO STARCH, STRUCTURE AND USABILITY

Summary

Small granule potato starch (SGPS) produced by "Wielkopolskie Przedsiębiorstwo Przemysłu Ziemniaczanego" during potato starch production season 1999 was investigated to evaluate its physicochemical properties, structure and usability. SPGS was used as a raw material for different modification processes typically applied in the Polish starch industry to obtain both food and non-food products. The obtained preparations were compared with industrial products: food grade modified starches E 1403, E 1404, E 1412, E 1414 and E 1422, as well as two types of preparations for paper industry - oxidised starch for wet end application and corrugated board adhesive.

The experimental and reference starch samples were examined by chemical analysis, rheological methods, scanning electron microscopy and X-ray diffractometry. Textural parameters of deserts prepared by means of food grade modified starches as well as some specific functional properties of industrial preparations were investigated.

It was found that SPGS like standard potato starch contained quite small amounts of inorganic impurities as well as crude fibre, revealed similar rheological properties but relatively low crystallinity. SGPS due to its unique physicochemical properties could be recommend as a raw material for the production of corrugated board adhesive. Reactivity of SGPS towards sodium hypochlorite was found lower as compare to standard one. On the contrary susceptibility of SGPS to crosslinking with sodium trimetaphosphate seemed to be higher than of standard starch. The texture of food grade modified starches much differed from standard counterparts, which make possible to extent the assortment of these type products.

Introduction

Small granule fractions of potato, wheat and corn starches are characterised by the largest real surface, volume of pores and their average diameter. Fractions of small starch granules were also characterised by higher content of total phosphorus, crude protein and amylose as well as lower capability of swelling and solubility than large

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starch granules [1]. Similar observation have been made by Gambuś et al. on their investigations of triticale starch [6]. Small granules of triticale starch are characterised by higher total phosphorus content, gelatinisation temperature and maximum viscosity, but lower water binding, solubility and intrinsic viscosity. Particularly high attention was paid to differences between small and high granule fractions in wheat especially regarding pasting properties and fat content [3, 10]. The amounts of lipid per granule tend to be proportional to the granule surface areas of the larger granules, but proportional to the volumes of the smaller granules [10]. Potato starch reveals especially low fat and protein contents as compared to cereal starches [13]. Consequently these substances located mainly in the surface layer of starch granules probably are not the main factor differentiating properties of starch fractions in relation to granules size. Small granules of potato starch undergo more extensive phosphorylation in reaction with trimethaphoshate than big ones [5].

Materials and methods

Small granule potato starch fraction (SGPS) produced by "Wielkopolskie Przedsiębiorstwo Przemysłu Ziemniaczanego" during potato starch production season 1999 as well as potato starch "Superior Standard" were used as raw materials.

Modification reactions

Food grade modified starches were prepared according to technologies applied in Polish starch industry elaborated by Starch and Potato Products Research Laboratory team i.e.:

- E 1403 – bleached starch, industrial product "Skrobia budyniowa" made by WPPZ Luboń according to [11];
- E 1404 – oxidised starch, industrial product "Skrobia żelująca" made by WPPZ Luboń, according to [11];
- E 1412 – distarch phosphate, industrial product "Lubostat" made by WPPZ Luboń, according to [15];
- E 1414 – acetylated distarch phosphate, industrial product "Lubosol" made by WPPZ Luboń, according to [15];
- E 1422 – acetylated distarch adipate, industrial product "Zagęstnik AD" made by WPPZ Luboń, according to [8].

Industrial starch preparations were prepared according to technologies applied in Polish starch industry elaborated by Starch and Potato Products Research Laboratory team i.e.:

- oxidised starch for wet end application, industrial product "Oxamyl" made by WPPZ Luboń, according to [12].

- corrugated board adhesive, industrial product “Spoiwo do tektury falistej 50S” made by WPPZ Luboń, according to [9]. Corrugated board adhesive was prepared in two types containing different amounts (10% and 12%) of the carrier.

Analytical methods

Granule size distribution

Granule size distribution was measured automatically with Scanning Photo Sedimentograph FRITSCH analystette 20 (Germany) in water as a suspension liquid. The particle size distribution was calculated from the measured sinking speed of solids in suspension. In order to perform this analysis properly, the densities of sample and sedimentation liquid as well as dynamic viscosity of sedimentation liquid had to be exactly known.

Microscopic examinations

The structure of potato starch granules has been studied with SEM. The samples of starch preparations were applied on metal discs on specimen holder and than they were coated with gold in vacuum evaporator JEOL JEE 400. The obtained specimens were observed in JSM 5200 scanning electron microscope.

X-ray diffractometry

X-ray diffractometry was carried out with a TUR 62 Carl Zeiss X-ray diffractometer under the following conditions: X-ray tube CuKα (Ni filter); voltage 30 kV; current 15 mA; scanning from $\Theta = 2°$ to $18°$.

Chemical analysis

Ash content was determined according to EN ISO 3593 standard, crude fibre content according to ISO 5498 standard, and carboxyl groups content according to Joint FAO/WHO Expert Committee Recommendations [4].

Rheological properties

The course of gelatinisation was monitored with a Brabender viscograph under the following conditions: measuring cartridge 0.07 Nm; heating/cooling rate 1.5°C/min; thermostating at 95°C – 30 minutes.

The viscosity of oxidised starch preparations were measured with a Brookfield Digital Viscometer Model DVII, at 50 rpm, for the 10% solutions, prepared at 90°C for 20 minutes and then cooled to the temperature of 50°C.

The viscosity of corrugated board adhesive were determined with Ford Cup No 4, for the suspensions containing one part of starch preparation and four parts of water previously stirred for about 30 minutes.

Sedimentation of suspensions of corrugated board adhesive

The suspensions of corrugated board adhesive prepared for the viscosity measurements were allowed to sedimentation for 24 hours. Then the sedimentation rate defined as a ratio of the clear fluid height to the whole fluid height (expressed in percent) was calculated.

Texture analysis

Two types of the desserts were prepared using both standard and small granule preparations i.e.:

- pudding type (according to the Polish standard PN-A-74723) were prepared using starch preparations E 1403, E 1412, E 1414 and E 1422,
- gel type (according to the industrial standard ZN-84/MRiBŻ-I-09/89) – were prepared using E 1404.

The textural parameters of deserts were measured using TA-XT2 texture analyser (Stable Micro System UK) with 35-mm diameter cylinder aluminium probe. The original TPA curves were interpreted in terms of five textural parameters, two measured and three calculated: hardness (N), – adhesiveness (Ns), cohesiveness, springiness and gumminess [N].

Results and discussion

Small granule potato starch revealed significantly different granule size distribution from the standard ones (Fig. 1). Medium diameter of standard potato starch was of about 40 µm whereas small granule type of about 15 µm what made it similar to typical corn starch. In spite of that, pasting properties (Fig. 2) and X-ray diffraction pattern (Fig. 3) made it typical for potato starch. However, remarkable differences in pasting properties of small granules and standard potato starch could be observed (Fig. 2). Small granule potato starch started to paste at the temperature of about 5 centigrade lower than standard starch, and reached higher values of peak viscosity. The viscosity after cooling to 25°C was also higher in case of small granule starch.

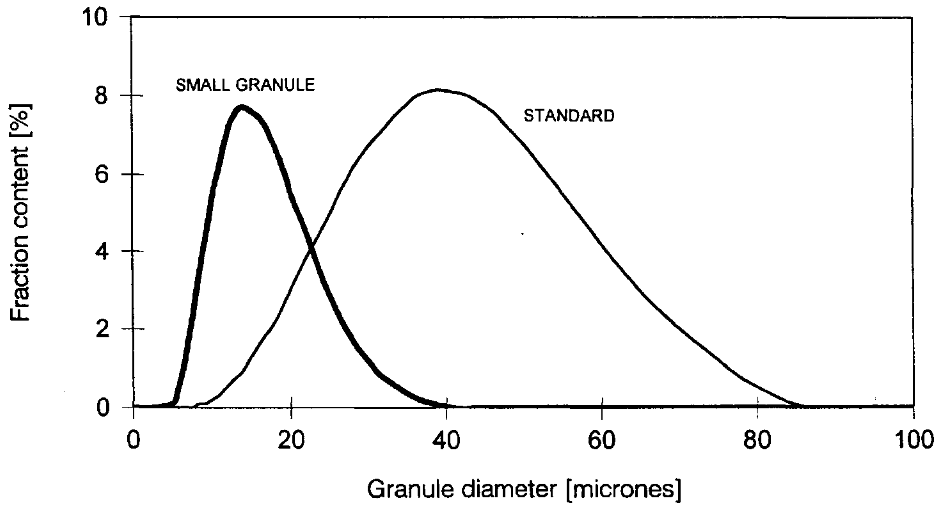

Fig. 1. Granule size distribution of small granule and standard potato starch.

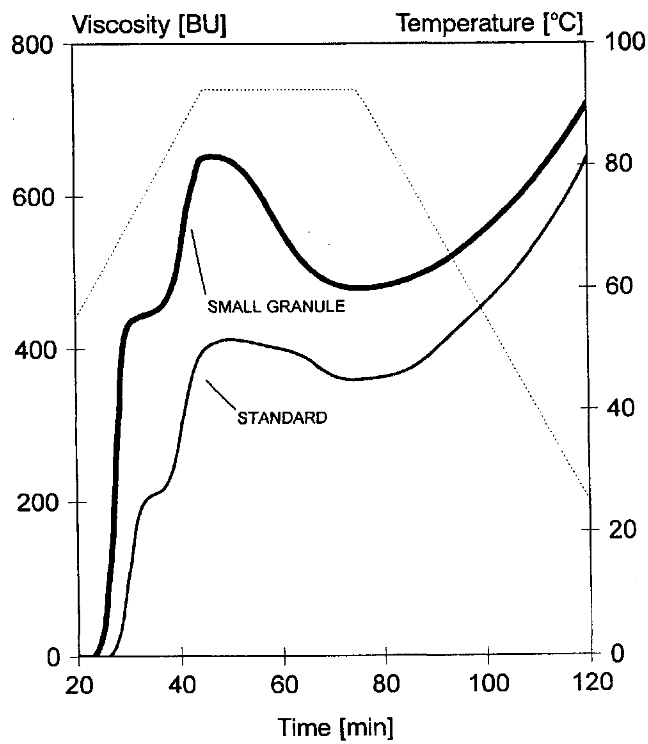

Fig. 2. Brabender viscosity curves (c=3,3%) of potato starch: S – standard; D – small granule.

Small granule and standard starch samples revealed the same B type of X-ray diffraction pattern typical of potato starch (Fig. 3), but a significant difference in their relative crystallinity seemed to be the most important observation. Small granule potato starch exhibited rather low degree of crystallinity what may be associated with a maturity of starch granules. According to Gambuś et al [7] the small starch grains are synthesised in cereal kernel mainly during late-waxy phase. Short time of growing of small granules could be the reason of their chaotic organisation and consequently smaller crystallinity. In spite of that SEM analysis did not pointed to any damages of the granules surface (Fig. 4).

The chemical analysis of standard and small granule potato starch (Table 1) proved that purification processes performed in WPPZ Luboń were satisfactory. Ash

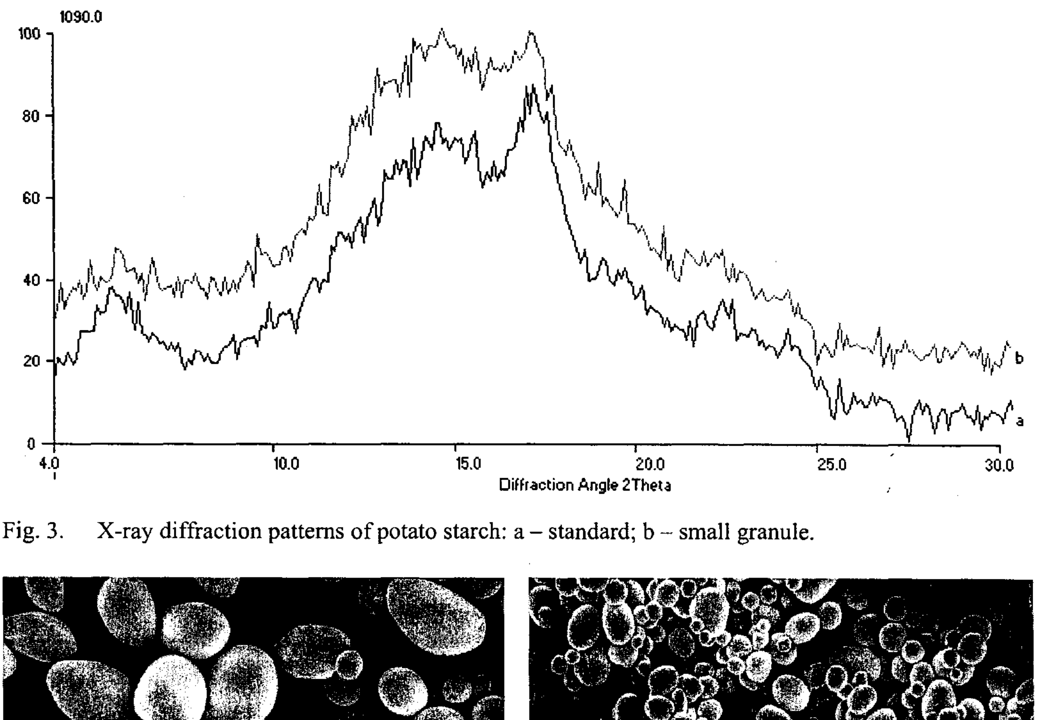

Fig. 3. X-ray diffraction patterns of potato starch: a – standard; b – small granule.

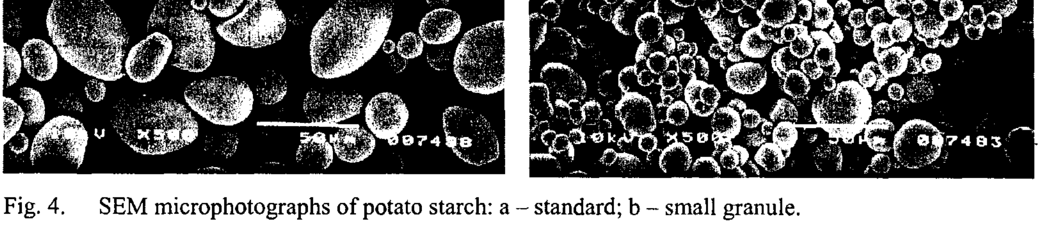

Fig. 4. SEM microphotographs of potato starch: a – standard; b – small granule.

as well as fibre content revealed similar level in both types of starch and were typical for high-grade potato starch. These observations were confirmed by SEM analysis (Fig. 4). Both types of starch did not contain any impurities, which can be visible in microphotographs.

Table 1

Some physicochemical properties of small granule and standard potato starch.

Type of raw material	Chemical analysis of native starch		Parameters of oxidised starch for wet end application	
	Ash content [%]	Crude fibre content [%]	Viscosity of 10% solution of the preparation [mPas]	Carboxyl groups content in the preparation [%]
Standard potato starch	0,30	0,02	56	0,436
Small granule potato starch	0,35	0,02	98	0,406

These differences in physicochemical properties caused significant differences in usability of two types of potato starch. For example, Stein-Hall type corrugated board adhesive contained the same amounts of carrier and different types of potato starch revealed very similar viscosity values, but significantly different tendency to sedimentation (Fig. 5). These made small granule potato starch an excellent raw material for the production of Stein-Hall type corrugated board adhesive. Also reactivity of SGPS towards sodium hypochlorite (Table 1) much differed as compare to standard starch. The difference between degree of substitution with carboxyl groups was found remarkable, but the difference between viscosity was so high that made these two products useful in quite different uses.

The application of native small granule for the preparation of pudding type desserts pointed to significant differences in sensory properties of these products as compare to desserts made from standard potato starch. These sensory observations were confirmed by texture analysis (Fig. 6-9). Small granule potato starch gave pudding type desserts of significantly lower hardness, cohesiveness and guminess but far higher adhesiveness. Consequently using of small granule potato starch as a raw material instead of standard could make possible to obtain the whole range of new food grade starch preparations. This hypothesis was fully confirmed by further investigations. The technologies applied by Polish starch processing factories for the production food grade modified potato starch preparations were simply used in laboratory in aim to obtain small granule counterparts. As the result five new types of food modified potato starch were obtained. All new modified food starches significantly differed in texture as compare to standard counterparts. It should be emphasised that the way of changes was not simply and was difficult to predict. All types of small granule modified starches gave desserts of higher adhesiveness than standard preparations (Fig. 7). This phenomenon was observed also in case of native starches. Hardness of desserts made from small granule preparations were higher in case of E 1403 and E 1414, but smaller in case of E 1404, E 1412, E 1422 (Fig. 6). It could be not classified in terms of type of modification reaction. Similar statements could be made in case of cohesiveness and guminess. Cohesiveness of desserts made from small granule preparations was higher in case of E 1404 and E 1412 but smaller in case of E 1403, E 1414 and E 1422 (Fig. 8). Guminess of desserts made from small granule preparations was higher in case of E 1403, E 1404 and E 1414 but smaller in case of E 1412 and E 1422 (Fig. 9).

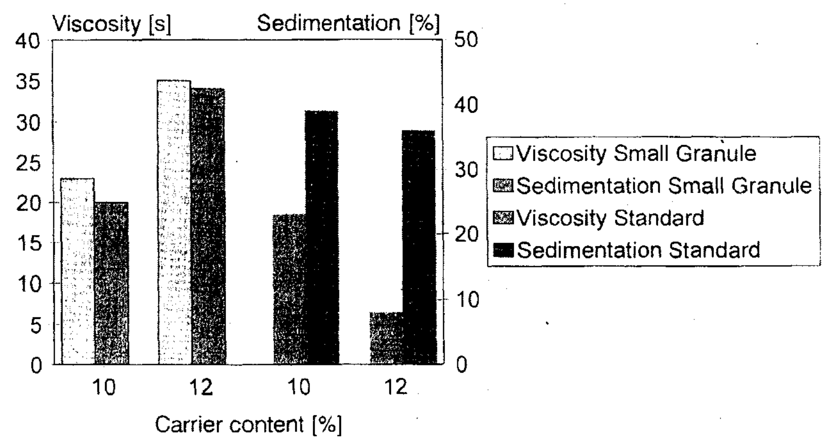

Fig. 5. Viscosity and sedimentation of Stein-Hall type corrugated board adhesive.

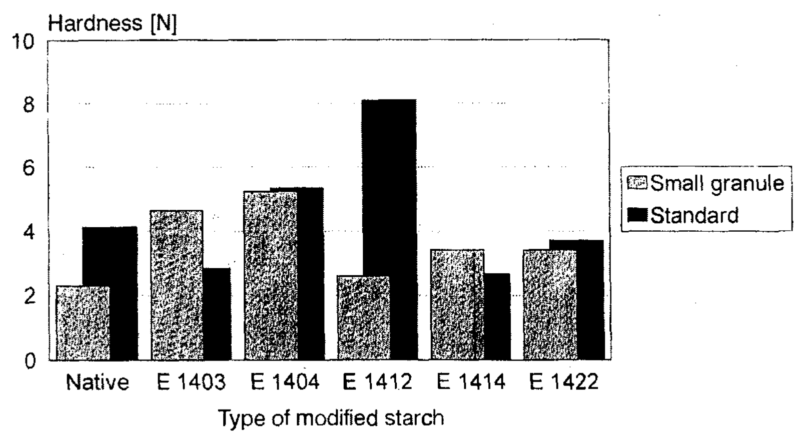

Fig. 6. Hardness of pudding type (raw materials: native starch, E 1403, E 1412, E 1414, E 1422) and gel type (raw material - E 1403) desserts made using standard and small granule raw materials.

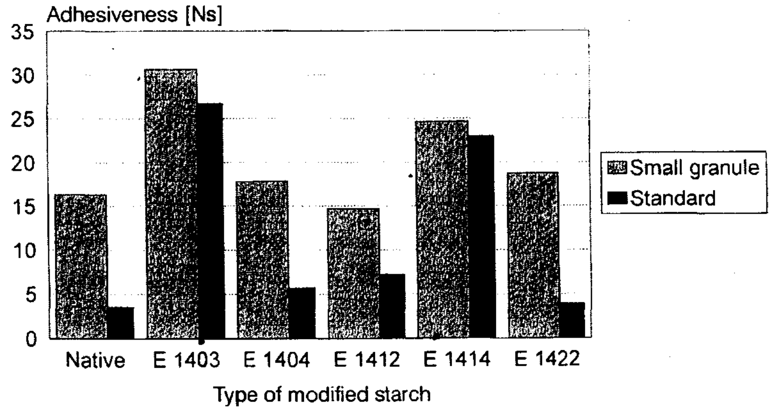

Fig. 7. Adhesiveness of pudding type (raw materials: native starch, E 1403, E 1412, E 1414, E 1422) and gel type (raw material - E 1403) desserts made using standard and small granule raw materials.

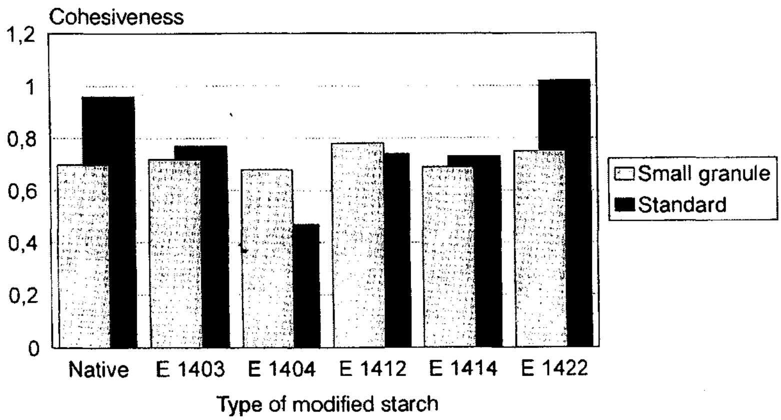

Fig. 8. Cohesiveness of pudding type (raw materials: native starch, E 1403, E 1412, E 1414, E 1422) and gel type (raw material - E 1403) desserts made using standard and small granule raw materials.

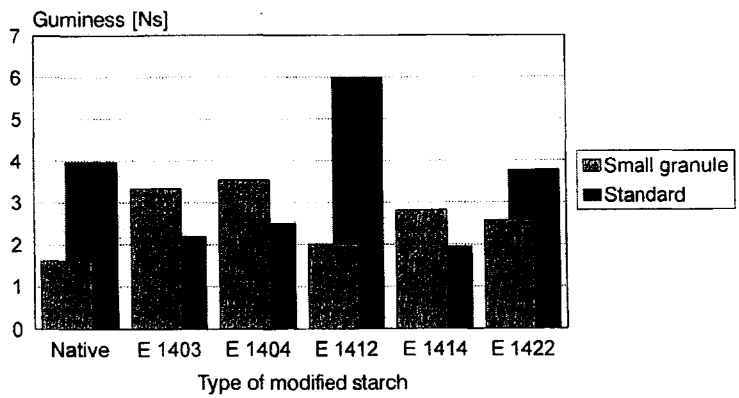

Fig. 9. Guminess of pudding type (raw materials: native starch, E 1403, E 1412, E 1414, E 1422) and gel type (raw material - E 1403) desserts made using standard and small granule raw materials.

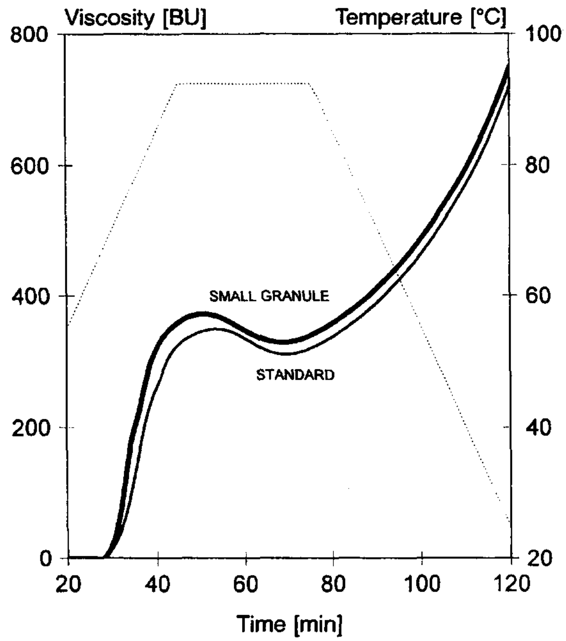

Fig. 10. Brabender viscosity curves (c = 3,3%) of E 1403 preparation made from: S – standard; D – small granule potato starch.

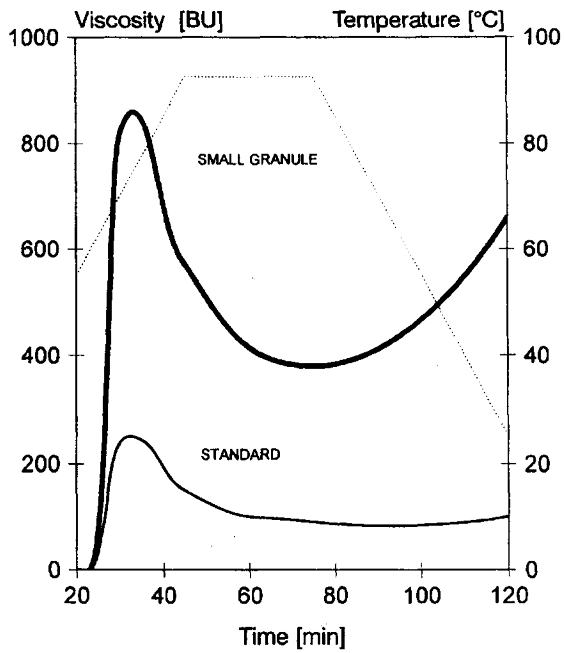

Fig. 11. Brabender viscosity curves (c = 6,0%) of E 1404 preparation made from: S – standard; D – small granule potato starch.

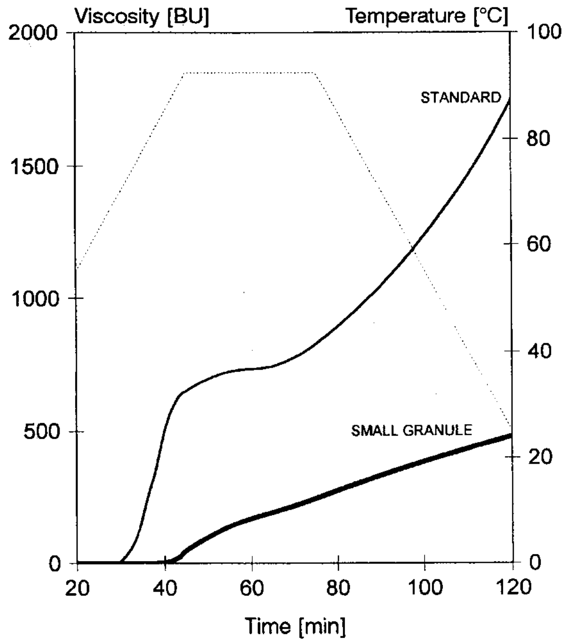

Fig. 12. Brabender viscosity curves (c = 3,3%) of E 1412 preparation made from: S – standard; D – small granule potato starch.

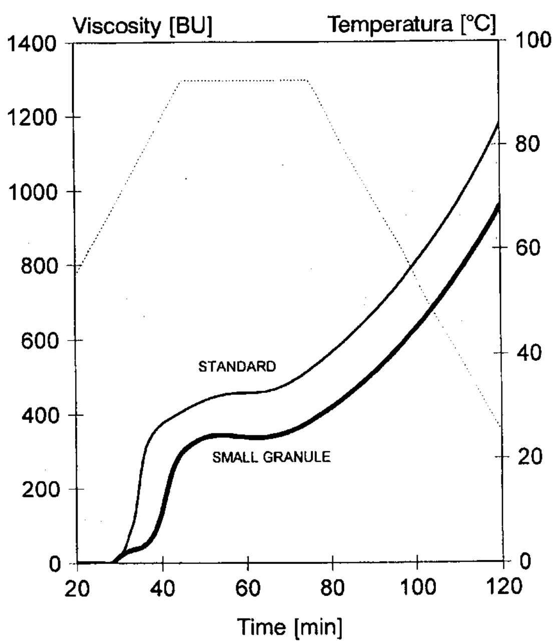

Fig. 13. Brabender viscosity curves (c = 3,3%) of E 1414 preparation made from: S – standard; D – small granule potato starch.

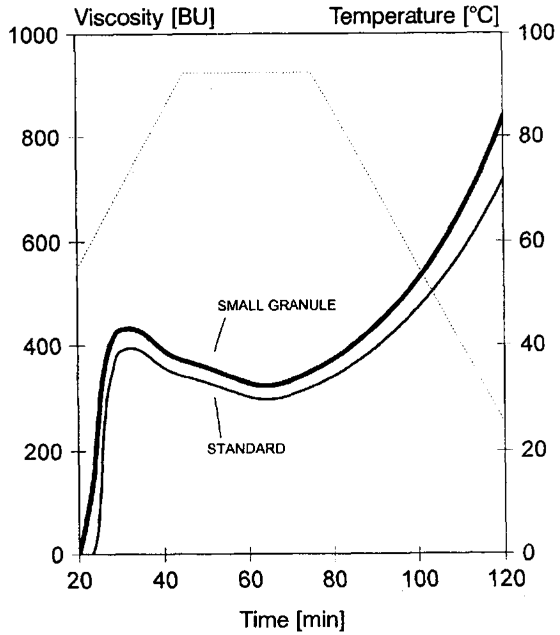

Fig. 14. Brabender viscosity curves (c = 3,3%) of E 1422 preparation made from: S – standard; D – small granule potato starch.

Observation more easily subjected to classification could be made on study of pasting properties (Fig.10-14). SGPS and standard bleached starch E 1403 preparations, which were only slightly chemically changed, revealed almost the same pasting properties (Fig. 10). Brabender viscosity curves of E 1403 preparation only slightly differed from pasting curves of native starches (Fig. 2). Pasting properties of small granule and standard oxidised E 1404 preparations differed significantly, especially in terms of viscosity (Fig. 11). Significant difference in Brabender viscosity of two types E 1404 starches corresponded to the difference in viscosity of oxidised starch preparation for paper industry (Table 1). Both, food grade oxidised starch as well as oxidised starch for wet end application made from SGPS revealed much higher viscosity than standard counterparts. This phenomenon as well as degree of substitution with carboxyl groups pointed to a lower reactivity of small granule potato starch towards sodium hypochlorite than standard preparations. On the contrary, susceptibility of SGPS to crosslinking with sodium trimetaphosphate seemed to be higher than these of standards. Small granule E 1412 preparation revealed significantly higher pasting temperature and more restricted type of swelling characteristic than standard counterpart that unquestionable pointed to higher degree of crosslinking of preparation made from small granule starch as compare to standards (Fig. 12). Similar but less pronounced differences could be observed in case of acetylated distarch phosphate E 1414 preparations (Fig. 13). That could be caused by stabilising effect of acetyl groups. Acetylated distarch adipate E 1422, preparation of higher acetyl groups content than E 1414, made from small granule raw material revealed even smaller pasting temperature than standard counterpart (Fig. 14). All observations regarding rheological and functional properties of chemically modified starches showed that SGPS due to its physicochemical properties could be used as a raw material for the production of a whole range of new starch preparations. However, simple application of present existing industrial procedures seemed to be impossible due to unforeseeable character of the reactivity of SGPS.

References

[1] Achremowicz B., Fortuna T., Januszewska R., Juszczak L., Kielski A., Pałasiński M.: Wpływ wielkości ziarn skrobiowych na ich porowatość. Żywność. Technologia. Jakość, 1997, **3(12)**, 28-35.

[2] Boruch M.: Physico-chemical modification of potato starch with different grain size, Acta Alimentaria Polonica, 1985, **11**, 43.

[3] Dengate H.N., Meredith P.: The Pasting Characteristic of Various Sizes of Starch Granule from Wheat. Starch/Stärke, 1978, **36**, 305-309.

[4] FAO Food and Nutrition Paper (1997). Rome, 91-109.

[5] Fortuna T., Juszczak L., Pałasiński M. Fosforylacja skrobi ziemniaczanej rozsegregowanej pod względem wielkości ziaren. Żywność, 2000, **4(25) Supl.**, 91-98.

[6] Gambuś H., Nowotna A., Krawontka J:. Effect of triticale starch graininess on its physico-chemical properties. Pol. J. Food Nutr. Sci., 1993, **2/43**, 25.

[7] Gambuś H., Gumul D., Tuszyński T., Walczycka M.: Starch from immature cereal kernels as an improver of bread. Żywność, 2000, **2 (23) Suppl.**, 72-83.

[8] Lewandowicz G., Walkowski A., Szymańska G., Gzyl P., Mączyński M. (1993). Sposób otrzymywania skrobiowego środka zagęszczającego przeznaczonego do celów spożywczych. Projekt wynalazczy nr 1/93 z dnia 04.01.1993.

[9] Lewandowicz G., Walkowski A., Voelkel E.: Sposób produkcji kleju do tektury falistej. Polish Patent Application P. 323 900, 1997.

[10] Meredith P., Dengate H.N., Morrison W.R.: The lipids of various Sizes of Wheat Starch Granules. Starch/Stärke, 1978, **30**, 119-125.

[11] Mężyński L., Szymankiewicz A.: Sposób otrzymywania skrobi modyfikowanej. Polish Patent No 132 401, 1986.

[12] Mężyński L., Ślawski M.: Sposób otrzymywania skrobiowego środka klejącego. Polish Patent No 144 862, 1989.

[13] Swinkles J.J.M.: Composition and Properties of Commercial Native Starches. Starch/Stärke, 1985, **37**, 1-5.

[14] Walkowski A., Lewandowicz G., Szymańska G., Gzyl P., Mączyński M., Urbaniak G.: Sposób otrzymywania skrobi o ustabilizowanej lepkości. Projekt wynalazczy nr 6/93 z dnia 12.08.1993.

[15] Walkowski A., Lewandowicz G., Szymańska G., Gzyl P., Mączyński M.: Sposób otrzymywania spożywczego zagęstnika skrobiowego FREMIX. Projekt wynalazczy nr 5/95 z dnia 25.10.1995.

DROBNOZIARNISTA SKROBIA ZIEMNIACZANA – STRUKTURA I WŁAŚCIWOŚCI UŻYTKOWE

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

Zbadano strukturę oraz właściwości fizykochemiczne i użytkowe drobnoziarnistej skrobi ziemniaczanej (SGPS), wyprodukowanej w Wielkopolskim Przedsiębiorstwie Przemysłu Ziemniaczanego w toku kampanii ziemniaczanej w roku 1999. SGPS użyto jako surowca do laboratoryjnej syntezy wybranych spożywczych i niespożywczych skrobi modyfikowanych, produkowanych przez polskie zakłady ziemniaczane. Otrzymane preparaty były porównywane z produktami handlowymi: spożywczymi skrobiami modyfikowanymi E 1403, E 1404, E 1412, E 1414 i E 1422 oraz z dwoma preparatami stosowanymi w przemyśle papierniczym – skrobią utlenioną do powierzchniowego zaklejania papieru oraz klejem do produkcji tektury falistej.

Badane preparaty poddano analizie chemicznej, określono ich właściwości reologiczne, a także przebadano strukturę krystaliczną i mikroskopową. Określono ponadto parametry tekstury a także wybrane, specyficzne właściwości użytkowe preparatów dla przemysłu papierniczego.

Stwierdzono, że SGPS zawiera podobne ilości popiołu i włókna surowego jak standardowa skrobia ziemniaczana, podobne właściwości reologiczne, ale niższą krystaliczność względną. Ze względu na swe unikalne właściwości fizykochemiczne, SGPS może być zalecana do produkcji kleju do tektury falistej. Reaktywność SGPS w stosunku do podchlorynu sodu jest niższa niż skrobi standardowej, natomiast w stosunku do trimetafosforanu sodu – wyższa. Parametry tekstury spożywczych skrobi modyfikowanych, otrzymanych z SGPS jako surowca, różnią się znacznie od standardowych odpowiedników. Stwarza to możliwość produkcji całej gamy nowych produktów dla przemysłu spożywczego.