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Selected novel materials from polysaccharides

Summary — Blending of starch with some polysaccharide gums can provide complexes improving flow behavior and textural properties of starch pastes. Either deep freezing and thawing or controlled soaking of starch granules in water improves their surface sorption and is making them effective natural microcapsules. The efficient microencapsulation can also be achieved by a rapid microwave heating of granular starch in suspension of the compounds microencapsulation of which is attempted. The microwave heating of starch blended with generated *in situ* $Mg(HSO_4)_2$ as well as Na_2SeO_3 or Na_2SeO_4 provided a wasteless, solid state esterification of starch. Magnesium salts of starch sulphate are potential plasticizers for hydraulic binders, and selenated starch can be considered as a source of bioacceptable selenium for yeast and other organisms. The oxidation of starch with periodate with electrochemical recovery of periodate provided an easy access to dialdehyde starch. It was transformed into starch dialdehyde dihydrazone, dioxime, disemicarbazone, and dithiosemicarbazone. These derivatives bind numerous metal ions forming complexes. Dialdehyde starch disemicarbazone applied to a soil contaminated with heavy metals inhibited heavy metal uptake by maize grown on that soil.
Key words: starch, plant gums, starch esters, dialdehyde starch.

WYBRANE NOWE MATERIAŁY Z POLISACHARYDÓW
Streszczenie — Mieszanie skrobi z wybranymi gumami polisacharydowymi [wzory (I)—(V)] prowadzi do powstania kompleksów polepszających płynięcie i teksturę kleików skrobiowych (rys. 1—4). Głębokie zamrażanie i rozmrażanie lub kontrolowane pęcznienie ziarenek skrobiowych w wodzie polepsza ich właściwości sorpcyjne i pozwala wykorzystywać je jako naturalne mikrokapsułki (tabela 1, rys. 5 i 6). Efektywne mikrokapsułkowanie można też osiągnąć przez szybkie ogrzanie ziarenek skrobiowych w zawiesinie związku, który zamierza się mikrokapsułkować (rys. 7). Mikrofalowe ogrzewanie skrobi z generowanym *in situ* $Mg(HSO_4)_2$ jak również z Na_2SeO_3 i Na_2SeO_4 prowadzi do jej bezodpadowego zestryfikowania [wzory (V) i (VI)]. Reakcje przebiegają w fazie stałej. Sól magnezowa siarczanu skrobi jest potencjalnym plastyfikatorem zapraw hydraulicznych, a selenowane skrobie mogą być źródłem przyswajalnego selenu dla drożdży i innych organizmów. Utlenianie skrobi perjodanami z równoczesną elektrochemiczną regeneracją perjodanu prowadzi do prostego otrzymania skrobi dialdehydowej, którą następnie przekształca się w dihydrazon, dioksym, disemikarbazon i ditiosemikarbazon. Te pochodne skrobi dialdehydowej tworzą kompleksy wiążąc jony metali ciężkich wychwytywane z roztworów wodnych.
Słowa kluczowe: skrobia, gumy roślinne, estry skrobiowe, skrobia dialdehydowa.

FIELDS OF APPLICATION OF POLYSACCHARIDES

Except deserted areas, polysaccharides are distributed around the globe as structural and storage materials in flora and fauna. Currently, approximately 97 % of available polysaccharides in their either native or physically, physicochemically or chemically modified forms are used for nutrition [1]. For the last decade of XX century the polysaccharides are noted as versatile, biodegradable, and renewable sources for chemical industry. Among over 100 natural polysaccharides available commercially, the starch, cellulose, and pectins are these most commonly utilized. A vast majority of numerous solutions offering physical [2—4], physicochemical [5, 6], chemical [7—9], and enzymatic [10] modifications of starch for non-nutritive purposes, are economically non-feasible. Because of the role of polysaccharides as the major source for chemical industry in this century, there is a global call for novel technologies providing more refined methods of the utilization of polysaccharides and novel materials originating from them. They should be competitive to the materials produced from the minerals.

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Frequently, polysaccharides are used as fillers, sizes and texturising agents. Their functional properties, mainly flow behavior, hardness, fracture, adhesion, springiness, cohesiveness, resilience, and stringiness, the textural parameters, used to be controlled by concentration, temperature, and chemical modifications of polysaccharides. Applications of polysaccharides such as starch [11, 12], cellulose [13], sawdust (cellulose + lignin) [14] are common to various biodegradable plastics in which they reside either as non-bounded or physically bounded components of those composites. Starch, the most common polysaccharide, is subjected to numerous chemical modifications [7—9] but, recently, also in Poland, chitin and the product of its hydrolysis — chitosan, attract an increasing attention [15, 16].

In this paper the possibility of controlling such properties by blending of various polysaccharides is demonstrated.

A surface sorption of granular starch is one of essential properties of that material. For this property starch is sometimes used as a stationary phase in chromatography [6]. The sorption of solvents on the surface of starch granules is the preliminary step of the swelling phenomenon of granules, and the latter controls many physical properties and reactivity of granular starch. In this paper a facile physical modification of the sorption ability of granular starch is reported. The modification involves a multiple deep freezing and thawing of starch granules. Controlled swelling of starch granules results in exudation of amorphous parts of the granule interior. In this manner, empty domains formed inside starch granules provide microencapsulation of various guest molecules [17]. In this paper a facile and efficient microencapsulation of lipids in granular starch is presented.

A wasteless chemical modification of granular starch is exemplified in this paper by its microwave assisted solid state esterification with developed *in situ* magnesium hydrosulfate, with sodium selenate(IV) or sodium selenate(VI).

Dialdehyde starch is one of the most intriguing products of specific oxidation of starch. Unfortunately, the sole oxidants suitable for the oxidation are either fairly expensive periodates or currently eliminated from the use lead tetracetate. Recently elaborated oxidation of starch with periodates with its electrochemical recovery [18] opened an access to dialdehyde starch of moderate degree of oxidation. Thus, dihydrazones [19], dioximes [20], disemicarbazones [21], and dithiosemicarbazones [22] of starch dialdehyde were prepared as potential ligands in metal complexes. Such properties of those compounds were proven pointing to them as potential traps for heavy metals from liquid waste and soil. Results of related studies are briefly discussed in this paper.

Recently, several very efficient depressants for selective flotation of galena-chalcosite ores were developed from starch [23—26]. Ligation properties of those dialdehyde starch derivatives in respect to various metals suggested that also these starch derivatives could act as depressants for such ore. In this paper, also results of those studies are quoted. Finally, the role of the derivatives and their metal complexes as growth stimulants for maize is presented here.

POLYSACCHARIDE BLENDS FOR CONTROLLING FLOW BEHAVIOR AND TEXTURE [27]

Rheological studies of 3—5 % blends of gelatinized potato starch with 0.05 and 0.2 % of either karaya [formula (I)], carob [formula (II)], or [formula (III)] arabic gum prepared from hot aqueous solutions of the components showed that the effect of the additive depends on its nature and concentration. Arabic (Fig. 1) and karaya gums decreased the pseudoplasticity (a shear thinning effect, that is deviation from linearity of the shear stress *vs.* shear rate relationship towards a concave down func-
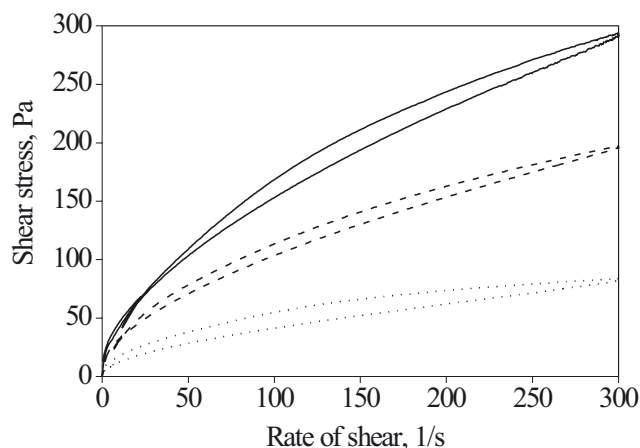

Fig. 1. Flow behavior of the blends composed of potato starch (PS) paste with arabic gum (AG): solid line — 5 wt. % of PS, dashed line — 4.95 wt. % of PS + 0.05 wt. % of AG, dotted line — 4.8 wt. % of PS + 0.2 wt. % of AG [27]

Fig. 2. Flow behavior of the blends composed of potato starch (PS) paste with carob gum (CG): solid line — 5 wt. % of PS, dashed line — 4.95 wt. % of PS + 0.05 wt. % of CG, dotted line — 4.8 wt. % of PS + 0.2 wt. % of CG [27]
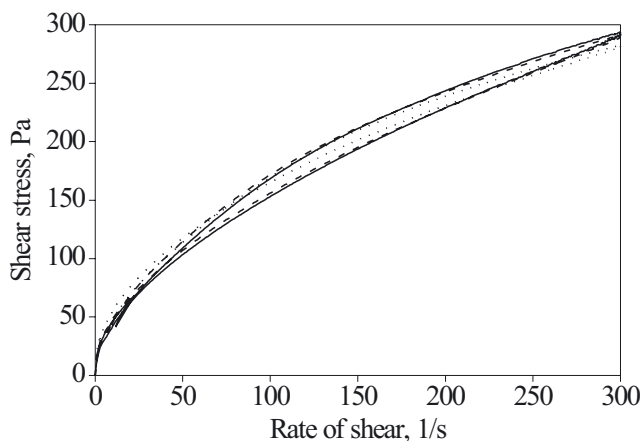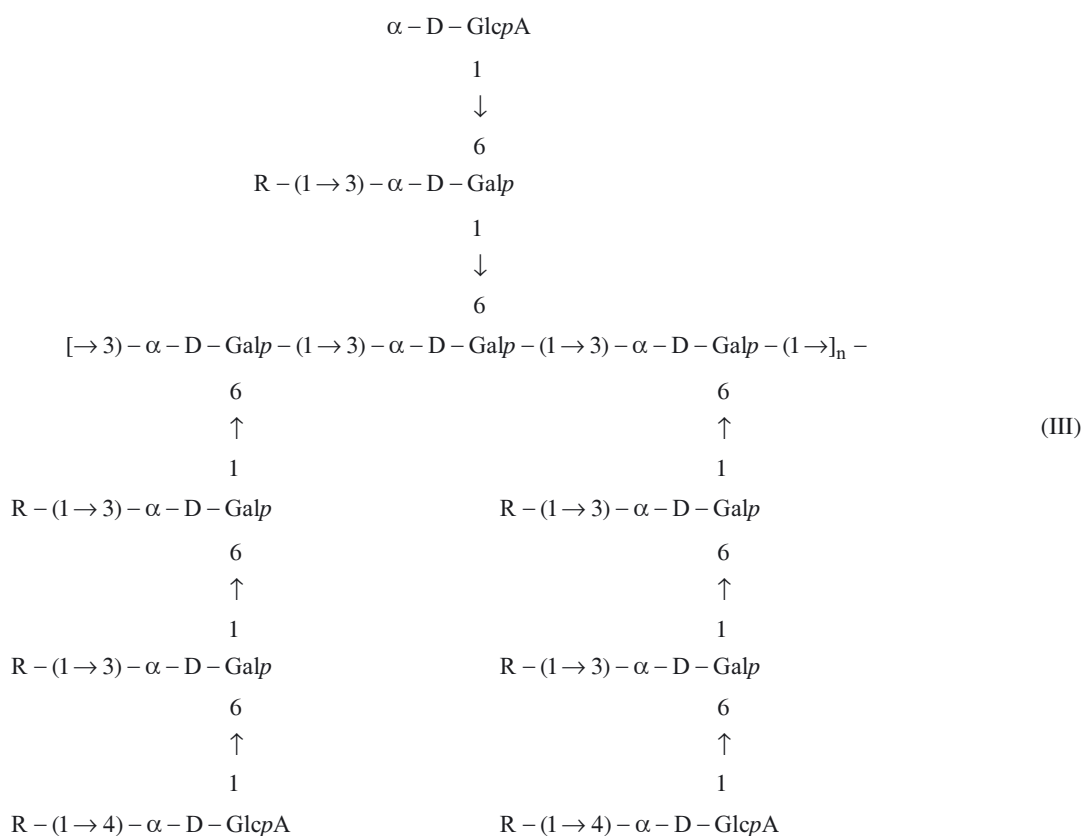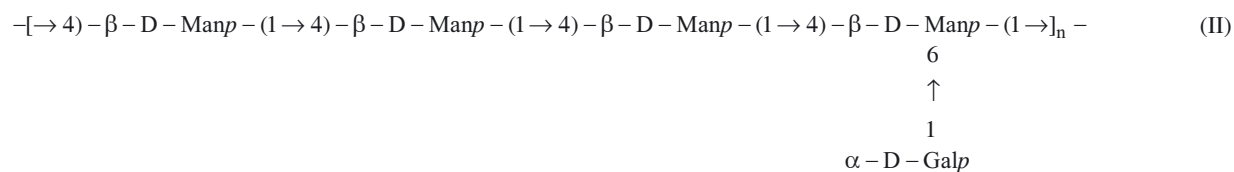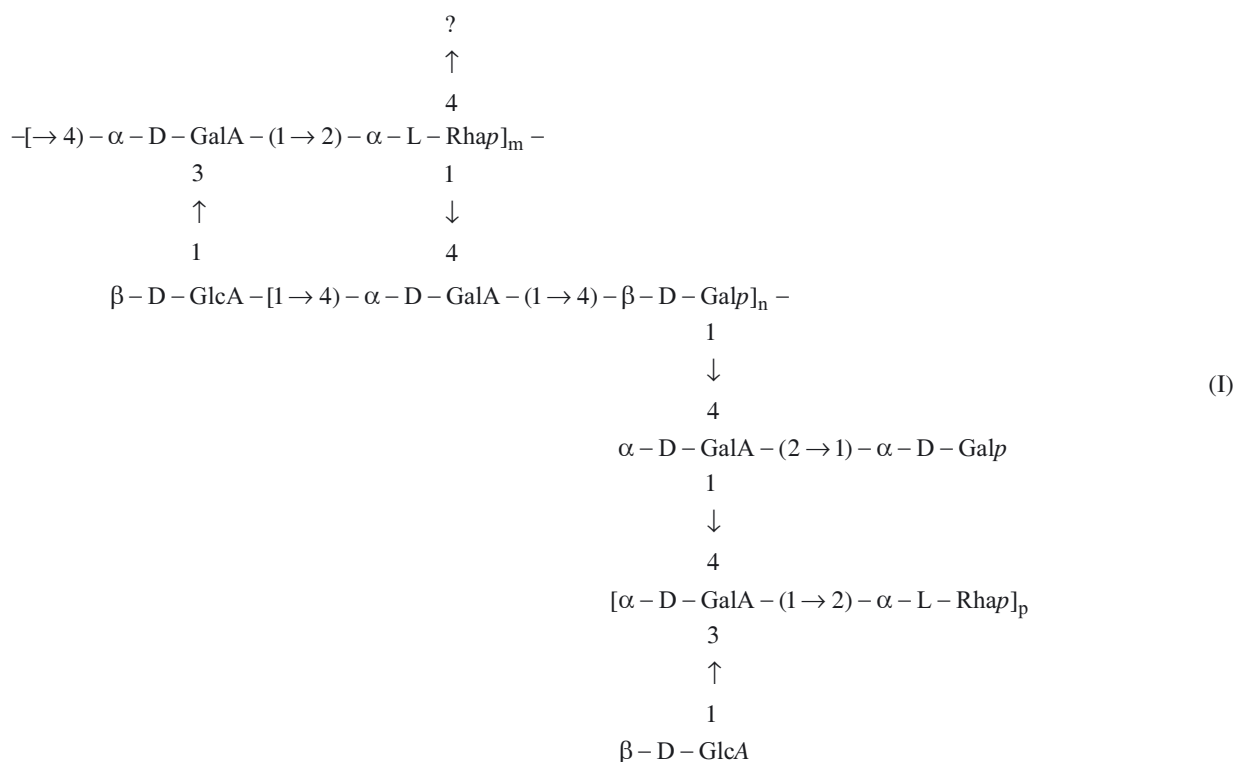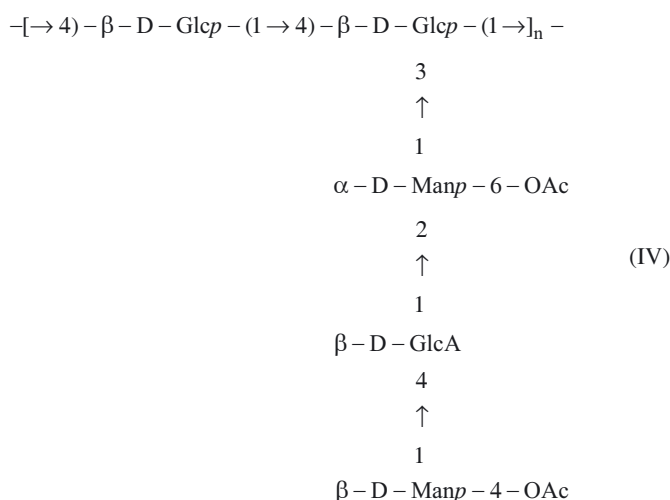
$$
\begin{array}{c}
? \\
\uparrow \\
4
\end{array}
$$

$$-[\to 4)-\alpha-\mathrm{D}-\mathrm{GalA}-(1\to 2)-\alpha-\mathrm{L}-\mathrm{Rha}p]_m-$$

$$
\begin{array}{cc}
3 & 1 \\
\uparrow & \downarrow \\
1 & 4
\end{array}
$$

$$\beta-\mathrm{D}-\mathrm{GlcA}-[1\to 4)-\alpha-\mathrm{D}-\mathrm{GalA}-(1\to 4)-\beta-\mathrm{D}-\mathrm{Gal}p]_n-$$

$$
\begin{array}{c}
1 \\
\downarrow \\
4
\end{array}
$$

$$\alpha-\mathrm{D}-\mathrm{GalA}-(2\to 1)-\alpha-\mathrm{D}-\mathrm{Gal}p$$

$$
\begin{array}{c}
1 \\
\downarrow \\
4
\end{array}
$$

$$[\alpha-\mathrm{D}-\mathrm{GalA}-(1\to 2)-\alpha-\mathrm{L}-\mathrm{Rha}p]_p$$

$$
\begin{array}{c}
3 \\
\uparrow \\
1
\end{array}
$$

$$\beta-\mathrm{D}-\mathrm{Glc}A$$

(I)

$$-[\to 4)-\beta-\mathrm{D}-\mathrm{Man}p-(1\to 4)-\beta-\mathrm{D}-\mathrm{Man}p-(1\to 4)-\beta-\mathrm{D}-\mathrm{Man}p-(1\to 4)-\beta-\mathrm{D}-\mathrm{Man}p-(1\to]_n-$$

(II)

$$
\begin{array}{c}
6 \\
\uparrow \\
1
\end{array}
$$

$$\alpha-\mathrm{D}-\mathrm{Gal}p$$

$$\alpha-\mathrm{D}-\mathrm{Glc}p\mathrm{A}$$

$$
\begin{array}{c}
1 \\
\downarrow \\
6
\end{array}
$$

$$\mathrm{R}-(1\to 3)-\alpha-\mathrm{D}-\mathrm{Gal}p$$

$$
\begin{array}{c}
1 \\
\downarrow \\
6
\end{array}
$$

$$[\to 3)-\alpha-\mathrm{D}-\mathrm{Gal}p-(1\to 3)-\alpha-\mathrm{D}-\mathrm{Gal}p-(1\to 3)-\alpha-\mathrm{D}-\mathrm{Gal}p-(1\to]_n-$$

$$
\begin{array}{ccc}
6 & & 6 \\
\uparrow & & \uparrow \\
1 & & 1
\end{array}
$$

(III)

$$\mathrm{R}-(1\to 3)-\alpha-\mathrm{D}-\mathrm{Gal}p \qquad \mathrm{R}-(1\to 3)-\alpha-\mathrm{D}-\mathrm{Gal}p$$

$$
\begin{array}{ccc}
6 & & 6 \\
\uparrow & & \uparrow \\
1 & & 1
\end{array}
$$

$$\mathrm{R}-(1\to 3)-\alpha-\mathrm{D}-\mathrm{Gal}p \qquad \mathrm{R}-(1\to 3)-\alpha-\mathrm{D}-\mathrm{Gal}p$$

$$
\begin{array}{ccc}
6 & & 6 \\
\uparrow & & \uparrow \\
1 & & 1
\end{array}
$$

$$\mathrm{R}-(1\to 4)-\alpha-\mathrm{D}-\mathrm{Glc}p\mathrm{A} \qquad \mathrm{R}-(1\to 4)-\alpha-\mathrm{D}-\mathrm{Glc}p\mathrm{A}$$

$$\mathrm{R}=\mathrm{L}-\mathrm{Rha}p,\ \mathrm{L}-\mathrm{Ara}f,\ \mathrm{D}-\mathrm{Gal}p-(1\to 3)-\mathrm{L}-\mathrm{Ara}f,\ \mathrm{L}-\mathrm{Ara}p-(1\to 3)-\mathrm{L}-\mathrm{Ara}f$$

tion) of starch gel and that decrease was deeper when the concentration of the gum added increased. The effect of the addition of carob gum was opposite but rather weak (Fig. 2). Thixotropic measurements showed that added arabic and karaya gums decreased the area of the surface of thixotropy by approximately 10 %, whereas carob gum increased that area by 27 %.

Results of blending upon flow behavior and texture depends also on the botanical variety of starch and added gum. Among many botanical varieties of starch, potato starch is the sole anionic starch. Among three gums, effect of whose was discussed above, arabic gum is also anionic. In the case of blending two anionic components lack of electrical compatibility could be anticipated. The latter could affect flow behavior and textural

$$-[\rightarrow 4)-\beta-D-Glcp-(1\rightarrow 4)-\beta-D-Glcp-(1\rightarrow]_n-$$

$$
\begin{array}{c}
3 \\
\uparrow \\
1 \\
\alpha-D-Manp-6-OAc \\
2 \\
\uparrow \qquad\qquad (IV)\\
1 \\
\beta-D-GlcA \\
4 \\
\uparrow \\
1 \\
\beta-D-Manp-4-OAc
\end{array}
$$

parameters. Such assumption was proven in the studies of behavior of the blends of anionic potato starch with anionic xanthan gum [formula (IV), in 40 % of the molecules the 6-CH$_2$OH group in the β-D-Manp-4-OAc unit is acylated with pyruvic acid which cyclizes with the 4-OAc group in that unit into -6-CH$_2$O-C(COOH) (Me)--O-4-] and non-ionic oat starch with that gum. Figures 3 and 4 shows essential differences in penetration force
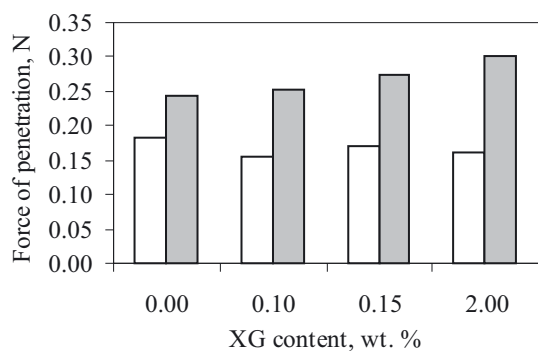

Fig. 3. *The force of penetration of pastes composed of 3 wt. % potato starch (white column) or 3 wt. % of oat starch (grey column) with various content of xanthan gum (XG) as an additive* [27]
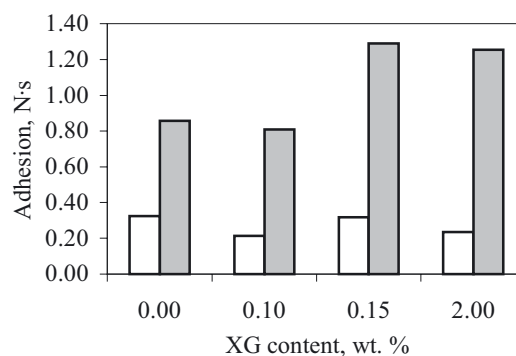

Fig. 4. *Adhesion of pastes composed of 3 wt. % of potato starch (white column) or 3 wt. % of oat starch (grey column) with various content of xanthan gum (XG) as an additive* [27]

and adhesion respectively, of the blends with both starches. As anticipated, distinctly higher penetration force and adhesion were observed for the blends of xanthan gum with oat starch than for the blends of potato starch and xanthan gum. It showed more efficient, unperturbed by repulsion of negative charges complexing interactions in the first case.

PHYSICAL MODIFICATION OF THE GRANULES

The effect of freezing-thawing processes on structure of starch granules was studied [28]. Native, granular potato starch containing 13 wt. % of humidity and oven-dried (130 °C for 2 h) was frozen in aqueous suspensions (either 1:1.5 v/v or 1:1 v/v) by immersing in liquid nitrogen or deep freezer at -26 °C followed by thawing. Such processes were consecutively repeated up to 10 times. Then the processed starch was dried in a vacuum dessicator and subjected to the further studies, that is investigation of changes on the surface of granules [confocal atomic force microscope (AFM)], crystallinity [wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS)], specific surface, porosity (BET isotherm, the helium method), density of granules, wettability and susceptibility to alpha-amylolysis.

The freezing-thawing produced the most pronounced changes on the surface of granules. Oval polysaccharide elements, so-called blocklets, tightly packed on the surface gradually separated arranging regularly ordered rows. Already after the fifth freezing-thawing cycle a clear layered structure of the granule envelope could be observed (Fig. 5). The 30—40 nm interlayer distance was a multiplicity of the dimension of the double polysaccharide helices (18 nm) and fits proposed models of the structure of starch granules [29—33]. These changes are accompanied by irreversible reorganization of the interior of the granules. Crystallinity of the granules increased and, at the same time, their density decreased as the result of evacuation of amorphous content of the granule interior caused by swelling during the granule processing.

a)

b)

c)

d)
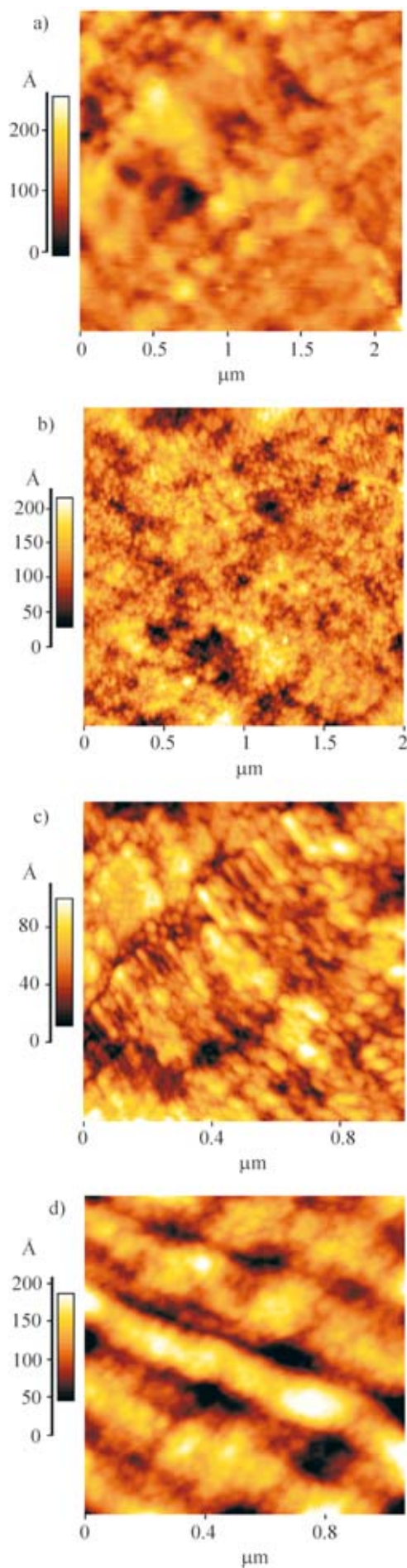
T a b l e 1. **Effect of freezing-thawing cycles upon selected properties of the surface of the potato starch granules**

Starch sample[*]	Humidity, %	Specific surface area S_{BET} m²/g	Total volume of micro- and mesopores 10^{-4}, cm³/g	Pore diameter nm
Dried, non-frozen	7.9	0.66 ± 0.02	2.1	1.3
Dried, frozen 1 time	11.7	1.11 ± 0.06	10.1	3.6
Dried, frozen 5 times	13.1	1.35 ± 0.06	9.0	2.7
Dried, frozen 10 times	10.1	1.54 ± 0.04	9.0	2.3
Native, non-frozen	13.1	0.36 ± 0.004	below detection limit	below detection limit
Native, frozen 1 time	11.9	1.18 ± 0.02	7.3	2.5
Native, frozen 5 times	12.0	1.27 ± 0.06	6.4	2.0
Native, frozen 10 times	11.3	1.45 ± 0.02	11.2	3.1

[*] In every case a rapid freezing was applied for 1:1 v/v starch to water samples.

Subsequent deep freezing — thawing cycles resulted in an increase in the specific area of starch granules, size of pores (Table 1), sorption of gases, wettability, and susceptibility to enzymatic hydrolysis [17]. Figure 6 presents the effect of multiple freezing and thawing upon the granule wettability expressed as a square of the penetration distance. The results demonstrated effects of loosening of the granule structure. One of such effects
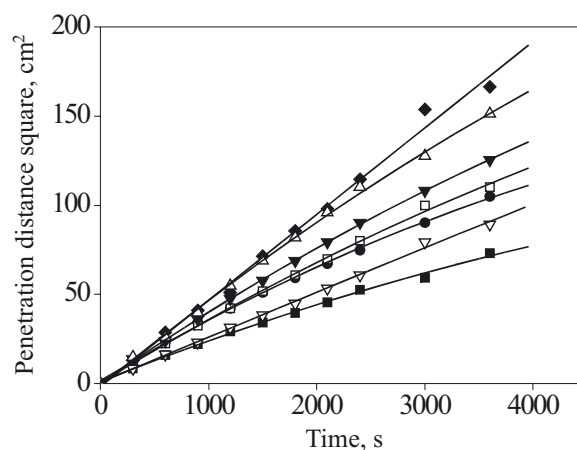
Fig. 6. Increase in penetration distance square of potato starch granules frozen and thawed in aqueous suspension [17]. Denotations: ♦ — rapidly frozen once (water:starch 1:1.5 v/v); △ — slowly frozen 5 times; ▼ — rapidly frozen 10 times; □ — rapidly frozen 5 times; ● — rapidly frozen once (water:starch 1:1 v/v); ▽ — slowly frozen 10 times; ■ — non-frozen

◄――――

Fig. 5. Effect of multiple deep freezing of granular potato starch visualized by non-contact AFM micrographs [28]; a) not frozen, b) once frozen, c) twice frozen, d) five times frozen sample

could be caused by controlled swelling of starch granules in water. It resulted in the formation of empty domains inside the granules available for encapsulation of many potential guest molecules.
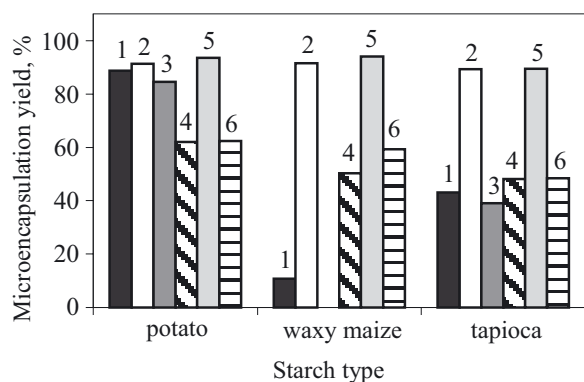

Fig. 7. Yield of microencapsulation of selected lipids in granular potato waxy maize or tapioca starches [34]; 1 — oleic acid, 2 — stearic acid, 3 — linoleic acid, 4 — ethyl oleate, 5 — methyl stearate, 6 — ethyl linoleate

Recently, it was shown [34] that microencapsulation of lipids in granular starch could be caused by a rapid, that is microwave heating of granular starch immersed in the lipids. Prolonged heating of such blends resulted in esterification of the lipid fatty acids and transesterification of the lipid fatty acid esters with starch. Figure 7 presents the yield of the microencapsulation of lipids in granular potato starch.

NOVEL CHEMICAL MODIFICATIONS OF STARCH

Magnesium salts of sulfated starch

A solid state, wasteless synthesis of the products was performed by either microwave or convectional heating of granular starch with $Mg(HSO_4)_2$ [34, 35]. That salt was generated *in situ* from magnesium sulfate and catalytic amount of conc. H_2SO_4. The products which are mono- and diester [formula (V) and (VI) respectively] were considered as potential plasticizers for hydraulic binders.

(V)

(VI)
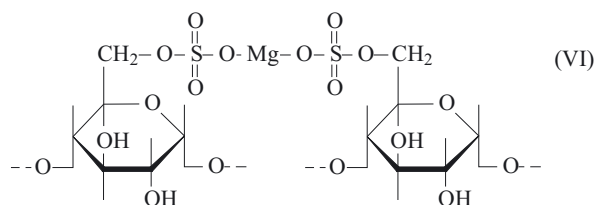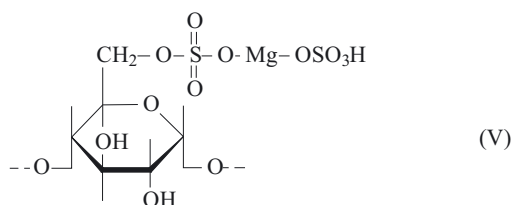
Esters of starch with selenic(IV) and (VI) acids

The solid state, wasteless microwave assisted reaction of granular potato starch with sodium selenate(IV) [$Na_2(SiO_3)$] and (VI) [$Na_2(SiO_4)$] provided starch esters of corresponding acids [37]. The optimized reaction conditions involve 1:0.1 (w/w) starch: selenium reagent ratio and 20 min heating in the microwave oven set for 800 W. The reaction with selenate(IV) proceeded more readily than the reaction with selenate(VI). The products were considered A as the slowly releasing Se preparations, nutrient for yeast cultures, and anionic starch for the protein-containing biodegradable plastics.

Dialdehyde starch (DAS)

An improved synthesis of DAS [18] opened an access to a cheap product. It induced more detailed study on its structure and reactivity. The applicability of resulting DAS starch depends on the degree of its oxidation but any attempt to increase it leads to decrease in the degree of polymerization of the product. Hence the study was performed to provide a link between both parameters by estimation of differences in the degree of crystallinity and distribution of molecular weights of resulting dextrins and structural units of amylopectin in the products of 5 to 25 % degree of oxidation. The most oxidized samples were amorphous. Under the reaction conditions providing 5 % oxidized DAS starch, the molecular weight of the product was already reduced by half in respect to that determined for original starch ($\overline{M}_w = 30 \cdot 10^6$). In 25 % oxidized DAS, the molecules of $\overline{M}_w < 1 \cdot 10^3$ predominated. The decrease in $\overline{M}_w$ provided better water solubility.

The aldehyde groups in DAS exhibited reactivity typical for aldehydes. Thus, dihydrazones [19], dioximes [20], disemicarbazones [21], and dithiosemicarbazones [22] of 25 % oxidized DAS could readily be prepared. They were tested for their ability for ligation of the ions of Ca, Cd, Co(II), Cu(II), Fe(II), Mg, Mn(II), Ni(II), Pb(II), and Zn. That ability was diverse in respect to particular DAS derivatives and particular cations [19—23].

These DAS derivatives were checked as immobilizers of heavy metals in soil under conditions of pot experiments in greenhouse [38]. The soil was intoxicated with the combination of the following salts (in parentheses their concentrations in mg/kg soil were given): 3 CdSO$_4$ · 8 H$_2$O (2), CuSO$_4$ · 5 H$_2$O (75), NiSO$_4$ · 7 H$_2$O (50), ZnSO$_4$ · 7 H$_2$O (250), Pb(NO$_3$)$_2$ (150). In each experiment 20 g of derivative was applied for 1 kg of soil. Maize planted in so contaminated soil, after 50 days produced hardly 20 % of the crops achieved from non-intoxicated soil. DAS dithiosemicarbazone and dioxime did not protect cultivated maize from bioaccumulation of heavy metals and the yield of crops decreased. In contrast to them, DAS disemicarbazide did not affect the yield of

crop but reduced the heavy metal uptake in above-
-ground parts and roots of the plants.

The application of DAS derivatives in attempted se-
lective flotation of mixed chalcosite-galena ores and
their concentrates failed.

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