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Specific Physical and Chemical Properties of Potato Starch

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ABSTRACT

Potato starch offers several unique properties essential for nutrition, and numerous non-nutritional applications. First of all, it is the sole native starch of anionic character. For that reason, potato starch combines, for instance, with proteins forming various complexes considered as potential biodegradable plastics. Potato starch is, practically, the sole starch variety containing a considerable amount of organically bound phosphorous. Hence, potatoes are an important source of phosphorous in a diet poor in fish. Potato starch distinguishes itself from other starches in the size of its granules which reach up to 150 µm in their diameter. Regular potato starch contains up to 27% amylose but, recently, also almost purely amylopectin (so-called waxy) starch and starches of enhanced content of amylose, so-called hylon starches, have become available through genetic modifications. Regular starches also contain up to 1.5% protein. While looking for a good source of protein suitable for the synthesis of spidroin (protein of the spider net) attention has been paid to genetic modifications of potatoes to replace genetically modified goat milk as a superior source of that protein. Potato starch granules swell much more readily than granules of other starches and resulting gels are much more viscous than gels of the same concentration from other starches. Specific properties of potato starch are manifested in results of several physical modifications such as gelatinization, thermolysis and pyrolysis, deep freezing, high pressure, ultrasounds, electromagnetic radiation (ionizing x-ray, neutron, α, β, and γ microwaves, ultraviolet, visible linearly polarized, infrared), low pressure glow plasma, corona discharges, the solvent effect. The unique properties of potato starch are also revealed in physicochemical modifications, that is, formation of the Werner type complexes with metal ions, all surface sorption, capillary, inclusion and channel complexes, and numerous chemical and enzymatic modifications.

Keywords: exceptionality, functionality, modifications, properties, structure

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PRESENT AND FUTURE SIGNIFICANCE OF POTATO STARCH

Throughout the world, potato (*Solanum tuberosum*) lost its leading position as a source of starch. Its lead position on the list is now taken by wheat and corn, and the commercial significance of cassava (tapioca, mandioca, yucca) starch steadily grows (Bergthaller 2004). Nevertheless, among others, because of the unique properties of its starch, potato is an invariantly important starchy plant. Recently, there has been a focus (Scheller *et al*. 2001; Scheller and Conrad 2006; Abdeeva *et al*. 2007) on potato as a plant which, after genetic modification, might offer protein suitable for synthesis of spidroin (protein of the spider net).

Potato starch is, perhaps, the most readily isolable starch. It can easily be purified from other components of tubers and may be the purest commercially available starch. Potato varieties can be divided into low- (≤20% starch) and high-starch content (≥20% starch) groups. Water, protein, lipids and mineral salts are the other components of potato tubers. A sparse amount of those components remain in isolated starch. The level of those components is usually lower than in other starches (**Table 1**).

The low-starch varieties are willingly used in human nutrition whereas the high starch content varieties are used as a fodder and industrial source of starch. Apart from potato tubers, also starch isolated from tubers presents a considerable value in food technology as well as in non-nutritional applications. On isolation of starch problems are encountered as the potato tuber juice, a waste, contains a group of surface active components, the saponins causing serious foaming. There were attempts to utilize tuber juice as a natural, good quality detergent (Bączkowicz and Tomasik 1985; Tomasik *et al*. 1986).

SPECIFICITY OF POTATO STARCH

Structure

Potato starch is a mixture of two polysaccharides, namely lower molecular weight amylose and higher molecular weight amylopectin. Typically, starch from genetically unmodified potato varieties contains from 17 to 22% amylose. Because of consumer demand for starch of different functional properties, potatoes have been subjected to genetic modifications towards starches enriched in amylose (Hylon

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Invited Review

Table 1 Granule size and level of some natural impurities in selected starch varieties (from Nowotny 1969; Gunaratne and Hoover 2002; Moorthy 2002; Tomasik 2002).

Starch variety	Granule size (µm)	Content (%)		
		Protein	Lipids	Phosphorus[a]
Cassava	3-54	0.115	0.06-1.54	0.007-0.012
Maize	10-30	0.32	0.60	0.020
Potato	1-100	0.15	0.06	0.076
Rice	2-10	up to 2.82	Up to 1.00	0.007
Wheat	2-38	0.24	0.36	0.045

[a] In cassava and potato starches phosphorous is bound in form of ester of phosphoric acid in the 6-CH_2OH groups of the α-D-glucose units of amylopectin. In other starches it resides in form of inorganic phosphates and component of glycoproteins.

starches with ~70% amylose) and in amylopectin (waxy starch with ~99% amylopectin). Amylose is chiefly a linear polymer of 1→4-bonded α-D-glucose units but sometimes amyloses with few short chain branches are encountered. The molecular weight (MW) of amylose in starches varies from ~500 anhydroglucose units for high amylose maize starch up to over 6000 anhydroglucose units for potato amylose. Amylopectin is a branched polymer of α-D-glucose units. These units within chains are 1→4 bonded and in the site of branching the 1→6 bond is involved. The MW of amylopectin reaches almost 3,000,000,000 anhydroglucose units (waxy-rice starch). The MW of amylopectin is unrelated to the origin of starch (Jane 2004).

Amylopectin of tuber starches, that is, that from potato, sweet potato, cassava and yams, particularly from potato, is distinguishable from cereal amylopectin in so-called organically bound phosphorus. Some 6-CH_2OH groups of side chain α–D-glucose units esterify phosphoric acid. Various sources report a different density of localization of such groups. Their average number is one ester group per every 8-12 α–D-glucose units in the outer branches.

Native starches have a granular structure. Potato starch has granules of the largest size among all known starches. That size spreads over the range of 5 to 150 µm (Seidemann 1966; Jane *et al.* 1994). **Table 1** presents size of granules from the most common starches. Since the size of potato starch granules covers a broad range, fractions of the same starch separated according to granule dimension fractionated granular starch can offer essentially different properties. Indeed, for instance, the smallest granules contain the highest level of phosphorus. Logically, also the content of metal cations (Na, K, Mg, Ca) is higher in the smallest granules. Granule size had a negligible effect on their amylose and amylopectin content (Noda 2007).

Some plants, for instance sorghum and corn contain perforated starch granules (Huber and BeMiller 1997, 2001). Pores and cavities can be observed in granules of other cereal starches such as rye, barley and wheat (Fannon *et al.* 1992, 1993). The nature of the pores and cavities remains unclear. In some cases the perforation seems to be a genetic property and in the other channels and cavities could be formed on the action of enzymes on starch isolation. Treatment of granules of rice starch varieties with low-pressure cold plasma (Lii *et al.* 2002) and corona discharges (Lii *et al.* 2003) produced cavities on the surface layer of those granules. That effect was interpreted as the destruction of either lower MW polysaccharide components of the granule envelope or incorporation of protein therein. Such treatment of potato starch granules did not produce such effects. Thus far, perforated potato starch granules have never been observed. High pressure treatment, ultrasonication and swelling of granular potato, cassava, maize and rice starches (Tomasik *et al.* 2004) revealed differences in the structure of envelopes of those granules. Ultrasound applied cracked only the largest granules of potato starch. Smaller granules of that starch and granules of other starches remained intact. Swelling of soaking granules in water and high pressure up to 1 GPa caused cracking of the envelopes. Cracks of those envelopes in potato, rice and cassava starch granules occurred in some preferred directions showing some anisotropy in the structure of envelopes whereas envelopes of maize starch cracked in non-specific directions. Electron microscopic images of sliced granules showed that the thickness of the potato starch granule envelopes varied between 1 and 1.5 µm whereas thickness of envelopes of granules of maize, cassava and rice starch granules was hardly 0.29-0.70, 0.11-0.23 and 0.05-0.10 µm, respectively.

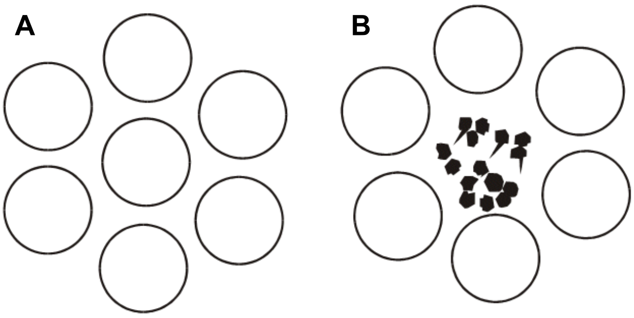

Fig. 1 Schematic view of cross-section of double helices in A- and B-type starches. Black points in right structure represent water molecules. Copied from **Tomasik P** (2002) Food saccharides – structure and transformations. In: Sikorski ZE (Ed) *Food Chemistry*, Wydawnictwo Naukowo-Techniczne, Warszawa pp 106-170 (in Polish), ©2002 with kind permission from Wydawnictwo Naukowo-Techniczne, Warsaw.

The interior of starch granules contains a number of concentric rings of a certain state of crystallinity with the space between them filled with amorphous layers. Crystalline and amorphous layers are built of entangled amylose and amylopectin (Gallant *et al.* 1997). Both layers have a so-called blocklet structure. Concentric layers could be observed earlier on micrographs of partly enzymatically digested starch granules (Tegge 1988) and blocklets could be seen on micrographs of starch smashed under 1.2 GPa pressure (Kudła and Tomasik 1992). Such a structure is common for starch granules regardless of their botanical origin. Some differences appear in the structure of crystalline layers of cereal starches, tuber starches, and sago starch from the bark of sago palm. Their crystalline structures are characterized as A-, B- and C, i.e. (A+B)-type, respectively (Imberty *et al.* 1991). The crystallographic types distinguish between one another in ordering of amylose helices therein (**Fig. 1**).

The presence of phosphoric acid esterified by potato amylopectin is one of the most important properties making potato starch unique. In nutrition, potato is an alternative to fish and legumes as a source of readily metabolized phosphorus. Native potato starch appears in the form of salts of metals residing in the soil. Thus, potato starch is chiefly a source of sodium, potassium, magnesium and/or calcium salt. These salts dissociate in aqueous solution and, as such, starch becomes anionic, that is, it may play a role of ion exchanger. Negative charges on the polyelectrolyte provide interactions with protein, for instance, either with milk casein (Zaleska *et al.* 2001a; Grega *et al.* 2003) or whey protein isolate (Zaleska *et al.* 2001b), providing complexes of various potential applications, such as meat substitutes (Tolstoguzov 2007) and biodegradable materials. Starches from other sources being non-dissociating polysaccharides do not combine with protein into complexes (Korolczuk *et al.* 1996).

Physical modifications

Regardless of their origin, starches are multidentate *O*-ligands of metal ions and they form Werner type complexes (Lii *et al.* 2001, 2002; Ciesielski *et al.* 2003; Ciesielski and Tomasik 2003a, 2003b, 2004a). Potato starch is distinguished from other starches as the phosphoric acid moiety also binds metal ions (Leszczyński 1985; Ciesielski and Tomasik 2004b). For that reason, potato starch and potato amylopectin more willingly then other starches form clathrates in which water is arrested. The rate of thermal decomposition of potato starch metal complexes is slightly lower than that of metal complexes of other starches.

Apart from the Werner-type complexes, starch forms several other complexes with inorganic (Tomasik and Schilling 1998a) and organic (Tomasik and Schilling 1998b) guest molecules. They are surface sorption, capillary, and inclusion complexes. Inclusion complexes involve either amylose and/or amylopectin which coil into helices arresting some molecules which fit the dimension of the channels of helices. Reaction with KI_5 results in the formation of a blue complex with amylose and a purple complex with amylopectin, delivering perhaps the most common example of starch inclusion complexes. The absorption wavelength of the complexes depends on number of turns of each of six α-D-glucose units of either amylose or outer branches of amylopectin enveloping the bar of the I_5^- ion. More turns in such a complex shift the wavelength of absorption towards a higher value.

Another kind of inclusion complex is formed by whole granules. On swelling, the amorphous content of the granule interior is exuded to the granule surface leaving empty domains inside granules available for various guest molecules. Because granular potato starch swells easily, it is superior in its formation of microcapsules with various guest molecules (Polaczek *et al.* 2000; Korus *et al.* 2003; Kapuśniak and Tomasik 2006). **Table 2** presents the efficiency of microencapsulation of lipids in three granular starches.

Water absorption by granular starches depends on their botanical origin. It decreases in the order (Schierbaum 1960): potato > wheat > cassava > maize > rice, and in the same order decreases integrated heat of sorption of those starches (Schierbaum and Taeufel 1962).

Swelling of granules is the first stage leading to gelatinization. A comparative study (Lii *et al.* 2003c) revealed that potato starch granules swell by several orders faster than other starches (see **Fig. 2**). The water-saturation capacity of potato starch is considerably higher than other starches (**Table 3**).

Table 2 Yield (%) of encapsulation of lipids in starch granules. From: **Kapuśniak J, Tomasik P** (2006) Lipid encapsulation in starch, *Journal of Microencapsulation* **23**, 341-348, ©2006 with kind permission from Taylor and Francis Ltd.

Starch	**Lipids**[a]					
	OA	**SA**	**LA**	**EO**	**MS**	**EL**
Potato	88.7	91.3	84.6	62.1	93.6	62.4
Waxy maize	10.8	91.6	n.e.[b]	50.3	94.1	59.3
Cassava	43.1	89.3	39.0	48.2	89.5	48.4

[a] OA – *cis*-9-octadecenoic acid; SA – octadecanoic acid; LA – *cis,cis*-9,12-octadecadienoctanoic acid; EO – ethyl OA; MS – methyl SA; LE – ethyl LA.
[b] Not estimated.

Table 3 Water saturation capacity (WSC), temperature of gelation (Tg) and visocity (η) of gels of most common starches.

Starch variety	**WSC**[a] **(g/g dry residue)**	**T_g (°C)**	**η (cPs)**[c]
Cassava	42.4	65-70	650 (6%)
Maize	39.9	75-80	265 (5%)
Potato	50.9	56-68	3000 (4%)
Rice	40.5	61-78	
Wheat	39.9	59-85	

[a] From Tomasik and Schilling (1998a)
[b] From Tegge (1988) p 55.
[c] From Muzimbaranda and Tomasik (1994). In parentheses, the concentration of the gel is given.

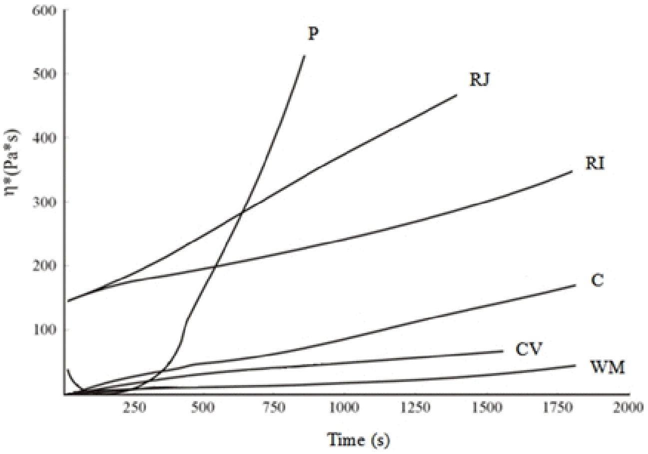

Fig. 2 Changes in time of complex viscosity of suspensions of granular starches soaked in saturated aqueous NaCl solutions. Notation of starches: P – potato; RJ – rice japonica; RI – rice indica; C – corn; CV – cassava; WM – waxy maize. From: **Lii CY, Tomasik P, Yen MT, Lai VM-F** (2003b) Granular starches as dietary fibre and natural microcapsules. *International Journal of Food Science and Technology* **38**, 677-685, ©2003 with kind permission from Wiley-Blackwell.

Gels are, perhaps, the most common products from starch and gelatinization is the most common process performed on starch. Because of phosphoric acid moieties in amylopectin, gelatinization behavior of potato starch is quite distinct from other starches (Yamada *et al.* 1987). From a practical point of view, the temperature of gelatinization (**Table 3**), viscosity and strength of gels and their stability, i.e. resistance to crystallization (retrogradation), are key parameters. Gelatinization temperature depends on the molecular structure of amylopectin, on the amylose-to-amylopectin and crystalline-to-amorphous fraction ratios and on the content of lipids and phosphorus (Gunarate and Hoover 2002). Among common starches, potato starch belongs to those with the lowest temperature of gelatinization and, at the same time, it produces gels of the highest viscosity when gels made of aqueous suspensions of equal concentration of starches of various botanical origins are compared. Smaller potato starch granules provided gels with lower peak viscosity, which, however, developed at higher temperature (Noda 2007). Retrogradation results from the crystallization of starch polysaccharides which slowly and mutually reorient in solution to form hydrogen bonded double helices. Amylose is more mobile in solution and, therefore, it crystallizes considerably faster, even within hours, than amylopectin, crystallization of which can take weeks. Stability to retrogradation is a function of the molecular weight of both starch polysaccharides, the temperature of storage of gels and the presence of ionizing salts and is basically independent of starch variety. However, there might be a difference in the polymorphism of double helices formed. Cereal starches usually develop A-type polymorphism of the crystals whereas unperturbed retrogradetion of potato starch leads to B-type double helices (Jane 2004). Retrogradation of potato starch is low compared to maize and wheat starch which retrograde relatively quickly. Only gels of potato starch are very clear whereas gels of maize, wheat and other starches are opaque and cloudy, respectively (Richter *et al.* 1969).

Dextrins are another common product made of starches (Tomasik *et al.* 1989). They are products of limited depolymerization of starch. In principle, there are two ways from starch to dextrins. One is an acid-catalyzed process and the other is a thermal polymerization (roasting) leading to pyrodextrins called British gums. Dextrins resulting from both

Table 4 Dextrinization of potato, maize, and rice starches to British gums (from Cernani 1951).

Temp. (°C)	Extinction (%)			Aqueous solubility (%)			Reducing sugars (mg Cu/g)		
	Potato	Maize	Rice	Potato	Maize	Rice	Potato	Maize	Rice
100	0	0	0	0.22	0.35	0.23	0.80	1.90	0.60
120	0	0	0	0.19	0.63	0.49	0.30	0.80	0.55
140	16.6	8.3	3.3	5.78	4.94	2.03	3.10	3.30	1.50
160	23.3	13.3	13.3	83.68	75.75	52.75	19.10	15.00	15.30
180	66.6	43.3	51.7	57.80	82.50	77.31	33.50	34.00	39.60
200	95.3	66.3	90	2.92	6.80	3.01	8.90	14.50	7.80

Table 5 Thermal stability of some starches in terms of number of spins *n* generated on roasting. From: **Ciesielski W, Tomasik P** (1996) Starch radicals. Part I. Thermolysis of plain starch. *Carbohydrate Polymers* **31**, 205-210, ©1996 with kind permission from Elsevier.

Temp. (°C)	Roasting time (min)	***n* x 10^{15}/g Starch variety**					
		Cassava	Maize	Oat	Potato	Waxy maize	Wheat
285	90	None	None	10	None	None	None
	120	None	1	20	None	2	6
300	90	6	None	10	5	3	2
	120	7	3	30	6	2	3

Table 6 Weight average molecular weight (M_w) and radii of gyration (R_G) of native and polarized light illuminated waxy corn, potato and sago starches (from Fiedorowicz *et al.* 2001, 2004, 2007).

Illumination time (h)	M_w x $10^{7\,a}$			R_G (nm)[a]	
	Whole peak	Amylopectin	Amylose	Amylopectin	Amylose
Waxy corn starch					
0	9.43	14.45	1.36	161.1	111.1
5	6.13	12.19	0.48	173.9	83.7
15	2.44	5.80	0.35	117.6	55.3
25	2.76	7.60	0.35	134.0	70.8
50	2.77	6.74	0.97	131.2	64.9
Potato starch					
0	12.30	21.30	0.59	207.0	123.7
5	11.99	18.90	0.44	192.9	98.5
15	10.87	14.87	0.35	141.5	69.4
25	11.30	18.97	0.41	146.6	71.4
50	12.87	19.69	0.49	207.1	91.9
Sago starch					
0	1.734	1.781	1.713	69.5	80.4
5	1.370	1.520	1.164	69.5	74.6
15	1.843	1.913	1.780	79.2	81.3
25	1.371	1.604	1.123	79.0	82.0
50	1.280	1.320	1.231	77.6	83.0

[a] Range of uncertainty of all results does not exceed 0.5% of given value.

processes are not equivalent to one another. The source of dextrins is very essential for the quality of the final product. Cassava is a superior source for dextrins. Unfortunately, potato starch is not a favored source for this purpose. The major concern is the unpleasant odor developed by potato starch on dextrinisation, particularly on a deep acid-catalyzed depolymerization and on roasting to British gums. That odor can be partly masked with Bergamot oil. Usually, roasting is carried out in the open. Stability of starch to roasting expressed in terms of darkening of the resulting British gums, their aqueous solubility and reducibility is specific for given botanical origin as shown in **Table 4**. Among three compared starches, potato, maize and rice, potato starch resulted in the darkest British gums. British gums from all three starches began to char at about 170°C but charring of potato starch was the fastest as shown by a rapid decrease in aqueous solubility of those gums above 170°C.

Odor, color, solubility, acidity (pH) and viscosity of aqueous solutions of dextrins and stability in time can be controlled by the atmosphere in which roasting is performed (Pałasiński *et al.* 1986; Tomasik *et al.* 1986). Dextrins deigned under nitrogen are most water soluble.

Pyrolysis of starches produces a heavy distillate as well as gaseous products. Their yield depends not only on starch botanical origin but also on a variety within a given origin. Thus, from pyrolysis at 1000°C potato starch delivers 76.7 to 48.6% heavy distillate and rice, maize and wheat starches 77.5-72.4, 71.15 and 74.5-73.0% of that product, respectively (Picon 1953).

Acid-catalysed hydrolysis of starch is the most common way of their dextrinization but also a thermal treatment of starch and starchy plants is a common way of their processing on production of dextrins and on food preparation. Such kind of treatment evokes free radical processes leading to stable saccharide free radicals. In comparative studies (Ciesielski and Tomasik 1996), in contrast to several other starches, potato starch appeared stable on roasting at 285°C for 2 hours (**Table 5**).

Starch has been subjected to numerous physical modifications with involvement less common, non-conventional sources of energy (Tomasik and Zaranyika 1995). In every case, even under very mild conditions offered by infrared heating, depolymerization of the polysaccharides takes place although in case of action of polarized light and ultrahigh pressure depolymerization is accompanied by repolymerization. Systematic comparative studies on the effect of a given treatment upon starches of various botanical origins are mostly lacking. Different properties of starches have to be taken into account depending on the applied source of energy. For instance, in case of 3×10^8 Pa pressure applied on granular starches the size and shape of granules controlled measured plastic flow (Paronen and Juslin 1983) whereas the effect of white linearly polarized light depended mainly on the crystallinity of granules. **Table 6** presents changes in the average MW and radii of gyration of potato, waxy maize and sago starches illuminated in aqueous suspension with white, linearly polarized light.

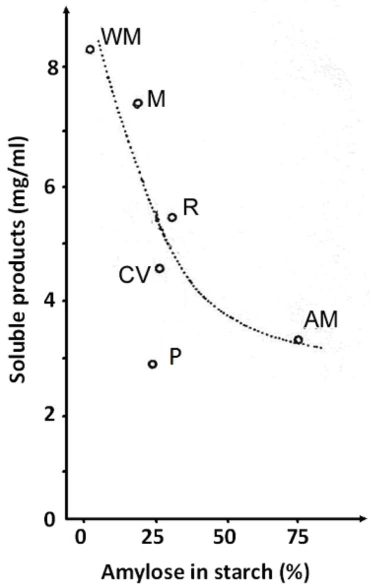

Fig. 3 Effect of irradiation of granular starches with identical dose of γ-rays expressed as aqueous solubility of radiodextrins. Notation of starches: WM – waxy maize; M – maize; R – rice; CV – cassava; P – potato; AM – amylomaize. From: **Raffi JJ, Agnel JPL, Thierry CJ, Freaville CM, Saint-Lebe LR** (1981b) Study of gamma-irradiated starches derived from different foodstuffs: a way for extrapolating wholesomeness data. *Journal of Agricultural and Food Chemistry* **29**, 1227-1232, ©1981 with kind permission from the American Chemical Society.

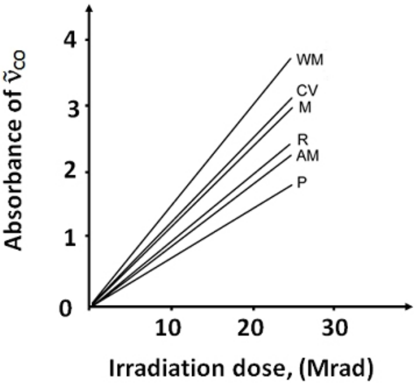

Fig. 4 Effect of irradiation of granular starches with identical dose of γ-rays expressed as the content of produced carbonyl compounds. Notation of starches: WM – waxy maize; M – maize; R – rice; CV– cassava; P – potato; AM – amylomaize. From: **Raffi J, Agnel PL, Dauberte B, d'Urbal M, Saint-Lebe L** (1981a) Gamma radiolysis of starches derived from different foodstuffs. Part II. Study of induced acidities. *Starch/Staerke* **33**, 235-240, ©1981 with kind permission from Wiley-VCH Verlag.

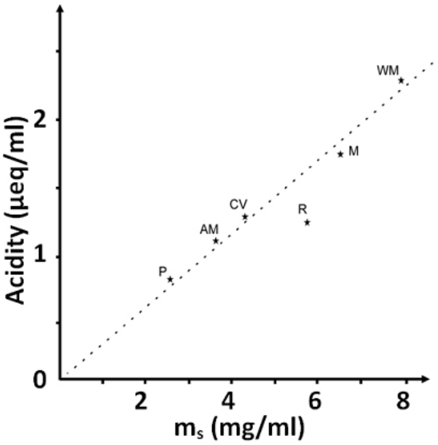

Fig. 5 Effect of irradiation of granular starches with identical dose of γ-rays expressed as acidity of aqueous solutions of radiodextrins. Notation of starches: WM – waxy maize; M – maize; R – rice; CV– cassava P – potato; AM –amylomaize. From: **Raffi JJ, Agnel JPL, Thierry CJ, Freaville CM, Saint-Lebe LR** (1981b) Study of gamma-irradiated starches derived from different foodstuffs: a way for extrapolating wholesomeness data. *Journal of Agricultural and Food Chemistry* **29**, 1227-1232, ©1981 with kind permission from the American Chemical Society.

One could interpret the results in terms of depolymerization of starch polysaccharides within the first period of illumination. Chiefly amylopectin was depolymerized. Short chains split from amylopectin repolymerized in the subsequent illumination periods into linear amylose-like polysaccharide. Potato starch as the most crystalline starch suffered such changes most willingly (Fiedorowicz *et al.* 2001, 2002, 2004, 2007).

Well documented are the effects of ionizing radiation upon starches of different origin. The degree of damage of the structure depends on the origin of the starch, on the applied source and on the dose of radiation (see **Table** 7). **Figs. 3-5** show that potato starch is least susceptible to γ–radiation by producing water-soluble dextrins, their acidity, and carbonyl compounds formed.

Multiple deep freezing in liquid nitrogen and thawing of moist potato starch resulted in modification of granule surfaces (**Fig. 6**) and an increase in the crystallinity (**Fig. 7**) of the granule structure. Such treatment facilitated the rehydration of granules but insignificantly influenced the temperature of gelatinization and viscosity of gels from starch treated in this way (Krok *et al.* 2000; Szymońska *et al.* 2000; Szymońska and Wodnicka 2005). However, such loosening of the internal structure of granules and their envelope provided easy mechanical disintegration of granules into nanostarch (Szymońska and Tomasik 2005; Szymońska 2005, 2007; Szymońska and Tomasik 2007a, 2007b) with the majority of the fraction of particles being 20 nm in size (**Fig. 8**).

Such treatment of cassava, maize and oat starch provided much milder modification of granules and making nanostarch from them was not so successful (Szymońska, pers. comm.).

Microwave radiation also devastates starch. Because of the principle of the action of microwaves on water molecules, changes in starch granules should be positively dependent on the water content in granules. Comparative studies (Muzimbaranda and Tomasik 1994) carried out on cassava, maize and potato starch showed that it is not quite so (**Table 8**). In the first 5 min of heating, the temperature of

Table 7 Effect of exposure of potato (P), maize (M) and wheat (W) starches to neutrons and γ-radiation (from Samec 1963).

Property	Type of exposure								
	None			Neutrons			γ-Rays		
	P	M	W	P	M	W	P	M	W
Viscosity (t/t_1)	2.46	1.30	1.40	1.37	1.21	1.03	1.10	1.11	1.06
Reducing value (% of maltose)	0.13	0.37	0.36	0.39	0.69	0.73	2.16	2.50	2.31
Iodine binding (%)	4.04	3.57	4.08	3.36	3.57	3.53	3.93	3.23	3.69
pH	6.2	4.0	5.75	5.0	3.9	5.6	4.0	4.9	3.3
Av. molecular weight $\times 10^3$	166	1037.7	1045	151.4	476.6	503.1	79.5	275.6	261.8
β-Amylolytic index	77.93	76.98	70.70	75.09	75.02	71.72	76.81	86.17	75.75

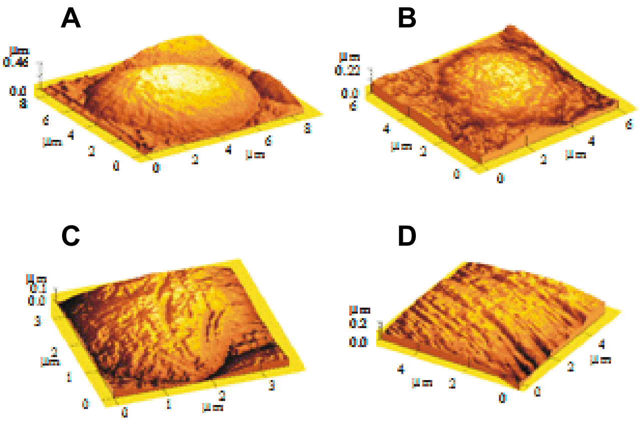

Fig. 6 The nc-AFM image of deep-frozen potato starch granule. A: original; **B–D**: frozen in a water suspension. **B** – 1x, **C** – 2x, **D** – 5x. From: **Szymońska J** (2005) Changes in structure and functional properties of potato starch in low-temperature modifications. *Zeszyty Naukowe Akademii Rolniczej im. Hugona Kołłątaja w Krakowie, Ser. Rozprawy* **424 (308)**, 3-114 (in Polish), ©2005 with kind permission from author and the Editorial Office of the Agricultural University of Cracow.

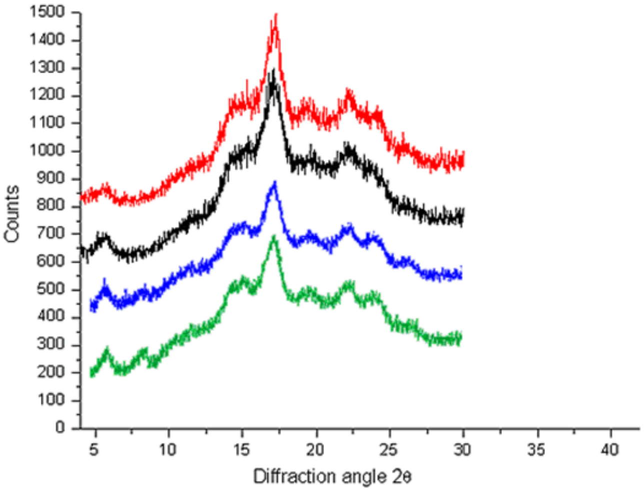

Fig. 7 Powder X-ray diffractograms of potato starch granules. From the top: after 10 deep-freezing and thawing cycles; after 5 deep-freezing and thawing cycles; after a single deep-freezing and thawing cycles; non-frozen. From: **Szymońska J** (2005) Changes in structure and functional properties of potato starch in low-temperature modifications. *Zeszyty Naukowe Akademii Rolniczej im. Hugona Kołłątaja w Krakowie, Ser. Rozprawy* **424 (308)**, 3-114 (in Polish), ©2005 with kind permission from author and the Editorial Office of the Agricultural University of Cracow.

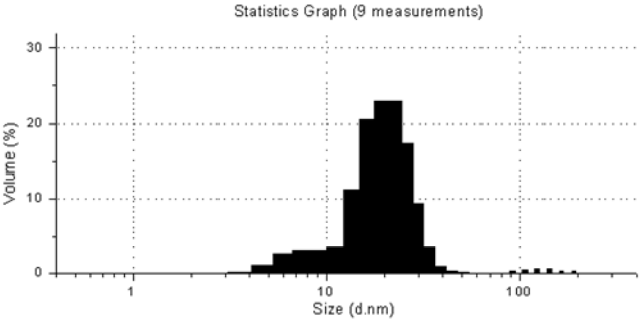

Fig. 8 Particle size distribution in nanostarch prepared according to Szymońska and Tomasik (2005). From: **Szymońska J, Tomasik P** (2007) Properties of potato starch nanoparticles. In: Lazos ES (Ed) *Proceedings of 5th International Congress of Food Technology* (Vol 2), Hellenic Association of Food Technologists, Thessaloniki, pp 170-175, ©2007 with kind permission from the Hellenic Association of Food Technologists, Thessaloniki.

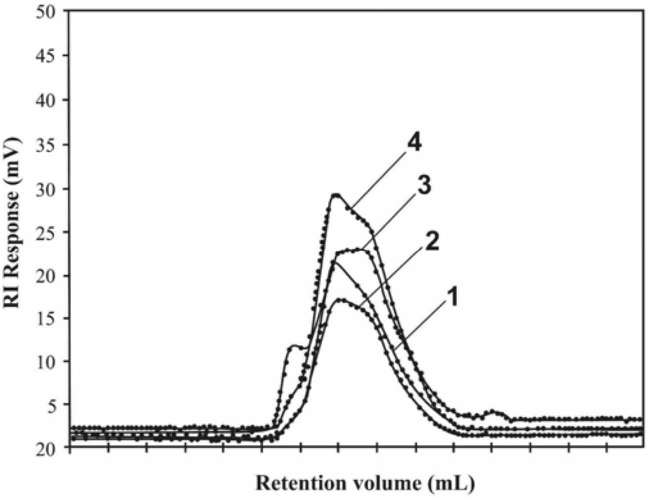

Fig. 9 Effect of low-pressure glow hydrogen (2), oxygen (3), and ammonia (4) plasma on potato starch. Line 1 is for non-treated, native potato starch. From: **Lii CY, Liao CD, Stobiński L, Tomasik P** (2002b) Effect of hydrogen, oxygen, and ammonia low-pressure glow plasma on granular starches. *Carbohydrate Polymers* **49**, 449-456, ©2002 with kind permission from Elsevier.

gelatinization decreased but viscosity of gel from that starch remained the same as that from non-treated starch. It seems likely that the granular structure of that starch was made more loose favoring swelling and gelatinization, and just extended heating resulted in depolymerization. The two other starches depolymerized instantly already within first 5 min of heating. The rate of depolymerization of potato starch was, however, faster as indicated by the viscosity of gels designed from irradiated starches.

Low pressure glow plasma enjoys many applications. Among others, it causes depolymerization of high-molecular weight materials and etches surface of materials, preferably in sites with some defects. **Table 9** shows that low-pressure air glow plasma depolymerized granular starch. Among a series of cereal and tuber starches, tuber starches (cassava and potato) appeared to be more sensitive to such treatment. Under the exposure conditions applied, their MW was reduced by approximately 50% whereas the average MW of all tested cereal starches except for *japonica* rice was reduced by approximately 30%. The granules of *japonica* rice appeared to be extremely sensitive to glow-plasma and its average MW was reduced by 75% (Lii *et al*. 2002a).

For cassava and potato starches, low-pressure hydrogen and ammonia glow-plasma appeared to be least and most destructive, respectively, whereas the effect of air, hydrogen, oxygen, and ammonia plasma was specific for particular cereal starch variety (**Table 9**) (Lii *et al*. 2002b). Analysis of profiles of the MW distribution assessed by HPLC indicated that regardless of the type of plasma applied, it was more fatal for amylopectin than for amylose. Comparatively, in the case of potato starch, ammonia plasma was least fatal for amylopectin (**Fig. 9**).

Experiments with low-pressure ethylene glow plasma (Lii *et al*. 2002c) revealed that potato starch was significantly more deteriorated than cassava starch, and cereal starches were even more resistant. Over *indica* rice starch, ethylene underwent graft polymerization to starch and over other starches it solely homopolymerized. *Indica* rice underwent graft polymerization with ethylene whereas over other starches ethylene homopolymerized. On exposure to corona discharges potato starch responded stronger than cassava starch. The resistance of the latter resembled that of cereal starches (**Table 10**) (Lii *et al*. 2003).

As in the case of glow plasmas, corona discharges preferably degraded amylopectin in both tubers and the majority of cereal starches but in both rice starch varieties amylose was preferably depolymerized.

Starches are frequently used as a food texturizer. Blending starches with other polysaccharide hydrocolloids may

Table 8 Effect of exposition to microwaves (middle low energy) upon granular cassava, maize and potato starches. From: **Muzimbaranda C, Tomasik P** (1994) Microwaves in physical and chemical modification of starch. *Starch/Starke* **46**, 469-474, ©1994 with kind permission from Wiley-VCH Verlag.

Starch variety	Moisture content (%)	Exposition time (min)	Gel		Gelation temp. (°C)	Appearance
			Concentration (%)	Viscosity (cPs)		
Cassava	10.2	0	6	650	70	-
		5		475	68	No change
		10		90	68	Brownish
		15		<10	68	Charred in 30%
Maize	10.3	0	5	265	80-85	-
		5		100	70	Yellowish
		10		60	70	Brownish
		15		<10	70	Charring started
Potato	14.3	0	4	3000	70	-
		5		3000	63	No change
		10		140	63	Brownish
		15		40	60	Charring started

Table 9 Molecular weight average (M_w Av), intrinsic viscosity (η_{int}) and radius of gyration (R) of original and low pressure glow plasma exposed starches. From: **Lii CY, Liao CD, Stobiński L, Tomasik P** (2002b) Effect of hydrogen, oxygen, and ammonia low-pressure glow plasma on granular starches. *Carbohydrate Polymers* **49**, 449-456, ©2002 with kind permission from Elsevier.

Starch variety	Type of plasma	M_w Av × 10^7	Extent of changes (%)	η_{int} (dl/g)	R (nm)
Cassava	None	9.35	-	0.52	75.68
	Air	4.93	47.3	0.45	49.87
	Hydrogen	5.79	38.1	0.40	58.15
	Oxygen	4.52	51.7	0.45	45.44
	Ammonia	1.59	83.0	0.44	31.91
Maize	None	8.68	-	0.31	57.49
	Air	5.34	38.5	0.26	25.49
	Hydrogen	3.75	56.2	0.33	42.34
	Oxygen	2.61	69.6	0.31	33.81
	Ammonia	3.12	64.1	0.35	47.10
Potato	None	7.73	-	0.43	53.11
	Air	3.68	52.4	0.34	33.46
	Hydrogen	5.63	27.2	0.35	46.18
	Oxygen	2.72	64.8	0.31	38.67
	Ammonia	1.95	74.8	0.59	47.52
Rice japonica	None	13.70	-	0.32	76.45
	Air	3.89	78.9	0.25	27.48
	Hydrogen	7.99	41.7	0.33	60.06
	Oxygen	6.00	56.2	0.25	54.26
	Ammonia	3.21	76.6	0.38	46.98
Wheat	None	7.09	-	0.32	52.13
	Air	5.11	27.9	0.42	56.93
	Hydrogen	4.22	40.5	0.26	40.49
	Oxygen	3.85	45.7	0.38	40.80
	Ammonia	3.96	44.1	0.43	50.54

Table 10 Effect of exposure of starches to corona discharges. From: **Lii CY, Liao CD, Stobiński L, Tomasik P** (2003a) Effect of corona discharges on granular starches *Journal of Food, Agriculture and Environment* **1**, 143-149, ©2003 with kind permission from WFL.

Starch origin		M_w Av x 10^6	η_{int} (dl/g)	R (nm)
Cassava	Native	94.65	0.60	92.81
	Exposed	82.92	0.52	80.25
Maize	Native	56.80	0.40	21.62
	Exposed	44.79	0.32	20.98
Potato	Native	64.54	0.55	63.39
	Exposed	34.04	0.47	51.57
Rice japonica	Native	90.77	0.41	76.18
	Exposed	72.55	0.43	75.82
Wheat	Native	51.20	0.44	59.57
	Exposed	37.86	0.48	57.25

provide better rheological properties at an overall lower concentration of a texturizer. To a certain extent, the results of composing blends can be predicted in a qualitative and quantitative sense (Kowalski *et al.* 2008). Since potato starch is an anionic polysaccharide, it should not be blended with other anionic hydrocolloids as they show a tendency to mutual repulsion and a separated phase system is formed. That is well illustrated in the case of potato starch–xanthan gum combinations used in thickening of sweet and sour sauces. Non-ionic oat starch blended with anionic xanthan gum performed much more efficiently than blends of potato starch with xanthan gum (Gibiński *et al.* 2006) (**Fig. 10**).

Because the feeling of the mouth depends on the macrostructure of foodstuff (Szczesniak and Farkas 1962; Kokini *et al.* 1977; Hill *et al.* 1996; Ferry *et al.* 2006) more structurally disordered potato starch–xanthan gum blends performed poorly in the sensory analysis tests against better organized in solution blends of oat starch with xanthan gum. This observation was confirmed in the case of blends of xanthan gum with other starches (Sikora *et al.* 2008). Kowalski *et al.* (2008) studied the rheology of cassava, corn, oat and potato starches, all blended with Arabic, carob, guar, karaya and xanthan gums and with κ-carrageenan. In the case of potato starch gel an admixture of carob gum provided a blend of viscosity higher than that of original potato starch gel and that viscosity increased with the concentration of the admixed gum. Also an admixture of karaya gum provided a slight increase in the original viscosity of potato starch gel but it decreased with the concentration of that gum in the blend. Admixture of remained gels resulted in a decrease of the viscosity, particularly pronounced in the case of anionic carrageenan and xanthan gum. Gels of cassava, corn and oat starches usually reacted positively to the admixture of gums. In all cases, admixture of carrageenan provided an insignificant effect.

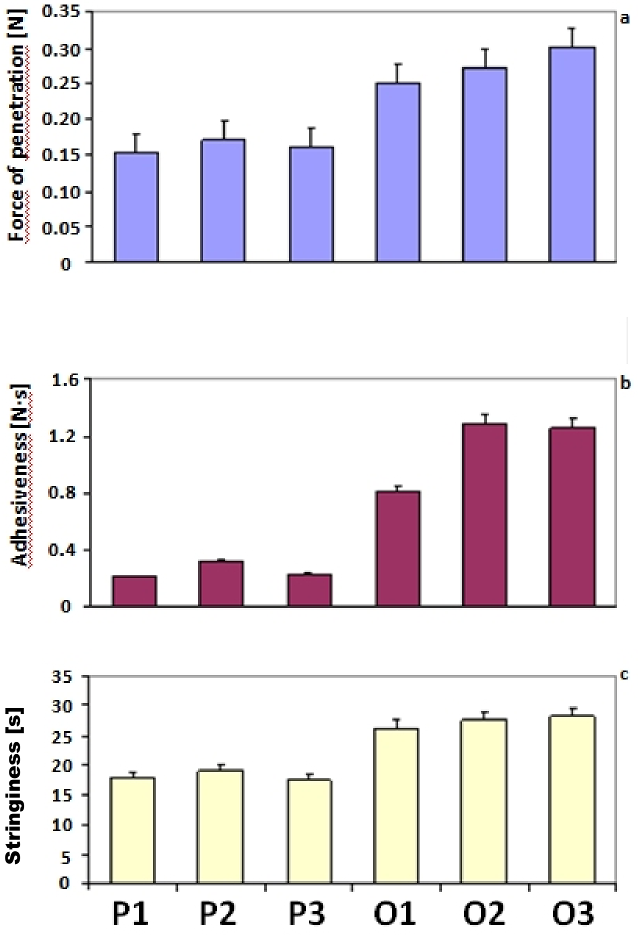

Fig. 10 Effect of blending potato starch (P), oat starch (OS) with xanthan gum (XG) in the proportion 3% of any starch and 0.1, 0.2 and 0.3 % of XG upon force of penetration (a), adhesivness (b), and stringiness (c) of resulting blends. From: **Gibiński M, Kowalski S, Sady M, Krawontka J, Tomasik P, Sikora M** (2006) Thickening of sweet and sour sauces with various polysaccharide combinations. *Journal of Food Engineering* **75**, 407-414, ©2006 with kind permission from Elsevier.

Table 11 Selected parameters from pasting characteristics (RVA) of acid-catalyzed hydrolysis of starches[a]. From: **Nadiha MZ, Karim AA** (2007) Comparative resistance of various starches towards acid treatment. *Proceedings of Starch Update 2007*, National Center for Genetic Engineering and Biotechnology (NCGEB), Pathumthani, Bangkok, Thailand, pp 109-114, ©2007 with kind permission from authors and NCGEB, Bangkok.

Starch variety	Hydrolysis period (days)	Peak viscosity (Pa.s)[b]/%	Pasting temp. (°C)
Maize	0 (native)	153.7	80
	15	37.3	73
	30	8.3	75
Potato	0 (native)	798.3	66
	15	0.56	70
	30	0.65	72
Sago	0 (native)	160.2	76
	15	7.00	77
	30	4.10	80

[a] With 0.1% hydrochloric acid at room temp.

[b] Peak viscosity values of native starches are followed by values presenting percent of original viscosity after hydrolysis for a given period.

Chemical modifications

Chemical reactions of starch (Tomasik and Schilling 2004; Tomasik *et al.* 2004) require the contact of reagents. When granular starch is reacted, the reaction can involve polysaccharides constituting the granule envelope as well as granule interior. In the latter case, penetration of the reagent into the granule becomes an essential factor. The majority of microscopic images of granular starch show granules with a clean, smooth surface. However, when granules are simultaneously illuminated with a beam of a polarized light and a perpendicular beam of red laser (so-called Crossed Light Beam Microscopy, CLBM technique) (Starzyk *et al.* 2001) exudations from the granule interior become visible on their surface. Likely, it is a result of swelling granules in the stage of their isolation. Therefore, several reactions of granular starch are possible, as material in the exudations is well exposed to reagents and the interior of granules can be more readily penetrated by reagents. The method of Huber and BeMiller (2001) provides the localization of the reaction sites in starch. They have been found on the surface as well as in the interior of granules. A series of thermal solid state reactions of granular starch was reported i.e. formation of *O*-metal salts (Tomasik *et al.* 2000, 2001; Bączkowicz *et al.* 2003), esters of inorganic acids (Lewandowicz *et al.* 2000; Jyothi *et al.* 2005; Staroszczyk and Tomasik 2005; Mao *et al.* 2006; Staroszczyk *et al.* 2007a, 2007b), esters of organic acids (Kapuśniak *et al.* 1999, 2001; Xing *et al.* 2006) and derivatives resulting from reactions of starch with nitrogen derivatives of carbonic and thiocarbonic acids (Siemion and Kozioł 2004; Siemion *et al.* 2004, 2005a, 2005b, 2006). In these reactions the exuded surface material was preferably attacked by reagents. Thus, logically, when reactions involve granular starch, potato starch which swells most readily should be most reactive. Crosslinking granular starch with phosphoryl chloride proceeded exclusively on the external surface of granules (Gray and BeMiller 2004).

According to Blennow *et al.* (2000), on phosphation of starch the degree of phosphation was correlated with chain length distribution in granules. Therefore, results of reactions of starches of different botanical origin could be associated with specific chain length distribution of their polysaccharides. One may not exclude that such a finding is common for other reactions. According to Jane *et al.* (2004), the reactivity of starch might be due to the internal structure of starch granules. Using Confocal Laser-light Scanning Microscopy they showed that among three varieties of corn starch, green banana and potato starch, the latter had the most ordered and compact structure, and thus the reaction of that starch with epichlorohydrin required the longest reaction period to be completed.

Acid-catalyzed hydrolysis of starch is, perhaps, the most common chemical reaction of starch. It is usually carried out under non-aggressive conditions. The role of the origin of starch can be readily observed. Perhaps the most recent comparative data in **Table 11** documents that potato starch undergoes proton-catalyzed hydrolysis more readily than maize and sago starches (Nadiha and Karim 2007). Perhaps, it is associated with the susceptibility of that starch to swelling. On hydrolysis of granular starch with ethanolic hydrochloric acid, potato starch reacted with a higher rate than corn starch. Potato starch hydrolyzed stepwise whereas hydrolysis of corn starch proceeded monotonously (Chang and Lin 2002).

When reactions involve aggressive reagents, for instance, either nitration or sulphation, the origin of starch is no longer important (Guisley 1978). The same was observed on acylation of starch with very reactive acyl chlorides whereas acylation with less reactive acyl anhydrides showed that all cassava, wheat, rice and potato starches reacted at the same rate but maize starch reacted more rapidly (Smith and Treadway 1944; Lohmar and Rist 1950). The role of the origin of starch in oxidation appears dependent on the oxidant used. Kinetics of the oxidation of various starches with sodium hypochlorite in the pH range of 7.5 to 11.0 was practically independent of the origin of starch (Schmorak *et al.* 1962). Under drastic conditions of oxidation, the origin is meaningless for the final result although accompanying processes such as hydrolysis and esterification depend on it. Perhaps the effect of the origin is associated with the affinity of the given starch to hydrolysis

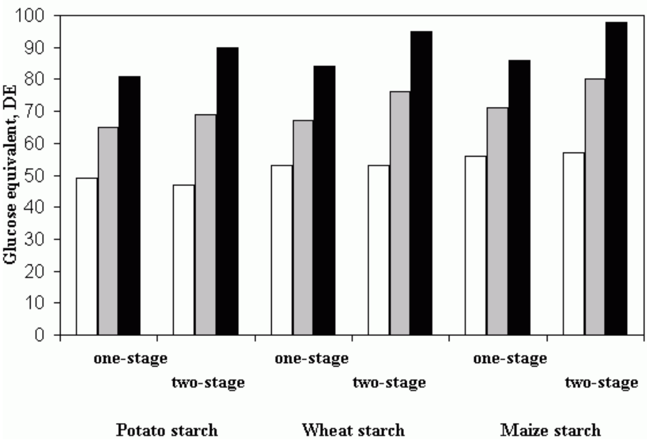

Fig. 11 One- and two-step hydrolysis of starches with α-amylase. White, grey and black fields denote results after processes lasting 24, 48, and 72 h. From: **Słomińska L, Wiśniewska D, Grześkowiak A** (2003) Liquefaction of starch by thermostable alpha-amylase. *Acta Scientiarum Polonorum, Technologia Alimentaria* **2** **(2)**, 17-26, ©2003 with kind permission from University of Life Sciences in Poznań, Poland.

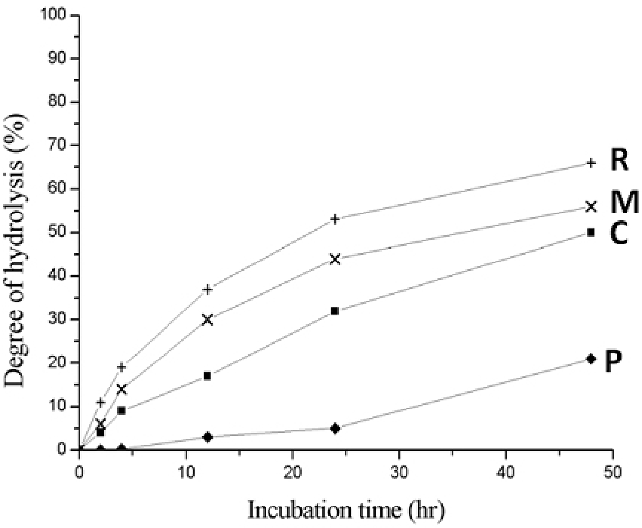

Fig. 12 Degree of hydrolysis of various starches treated with granular starch hydrolysis enzyme. Starches: R –high amylose rice; P – potato; C – cassava; M – maize. From: **Piachomkwan K, Wunsunksri R, Wanlapatit S, Chatakanonda P, Sriroth K** (2007) Application of granular starch hydrolyzing enzymes for ethanol production. In: Tomasik P, Yuryev VP, Bertoft E (Eds) *Starch: Progress in Basic and Applied Science*, Polish Society of Food Technologists (PSFT), Małopolska Branch, Cracow, pp 183-190, ©2007 with kind per-mission from authors and PSFT, Cracow.

(Tomasik and Schilling 2004). Potato starch also undergoes glycerolysis more readily than wheat and rice starch (Tuzuki 1941).

Exchange of metal cations into hydrogen in the phosphoric acid moiety of amylopectin to produce hydrogen starch (Winkler 1956) is a specific reaction for potato starch. Hydrogen starch is unstable do to autohydrolysis.

Enzymatic modifications

Enzymatic reactions of starch involve several types of enzymes leading to products of hydrolysis splitting α–1,4– and/or α–1,4–glycosidic bonds, reduction, oxidation, branching, cyclization and so on (Bielecki 2004). Słomińska *et al.* (2003) compared hydrolysis of three starch varieties with α-amylase (α-amylolysis). Processes were carried out either directly in one stage or in two stages involving subsequently liquefaction of starch followed by saccharification. **Fig. 11** shows that the rate of hydrolysis depends on the mode of saccharification, the time of the process, and also on starch variety. Generally, the two-stage process in a given time provided a higher yield of the final product. In both one- and two-step processes corn starch hydrolyzed at a higher rate than wheat and, finally, potato starch. In the case of potato starch, glucoamylase more readily digested small granules (Noda 2007).

Thus, potato starch appeared to be the most resistant to α-amylolysis. This property is essential in nutrition. There is a focus on so-called resistant starch (RS) stable to enzymatic digestion improving in such a manner the functioning of the large bowel and intestine. Among three starches, pea, potato and wheat tested *in vivo* in rats, potato starch provided best parameters of caecal digesta such as caecum wall, and caecal digesta both wet mass and dry matter. That starch provided the best removal of lower fatty acids from those animals (Wronkowska and Soral-Śmietana 2004). However, the susceptibility of starches obviously depends on reaction conditions and the enzyme applied. Comparative α-amylolysis of waxy maize, maize, wheat, cassava and potato starches in low water system degree of destruction of those starches fall in the order: waxy maize < maize < wheat < cassava < potato. This order was controlled by ability of particular starches to swell (Tester and Sommerville 2001). Piachomkwan *et al.* (2007) hydrolyzed starches using granular starch hydrolyzing enzymes from Danisco. They found that potato starch was most resistant to hydrolysis up to the 40th hour of the process. After that time high amylose maize starch became most resistant (**Fig. 12**).

However, results from several other authors show that the higher resistance of potato starch to enzymatic digestion is not so univocal. It depends on the type of enzyme and reaction conditions. A comparative study of hydrolysis of various starches with hydrolases in aqueous two-phase systems (Karakatsanis *et al.* 1998) showed that the resistance of starches to α-amylase digesting them at 40°C to D-glucose falls in the order: rice > corn > barley > wheat > soluble starch > potato. However, that order changed with temperature into wheat > barley > rice > potato > corn > soluble starch and soluble starch > potato > rice > wheat > barley > corn at 60 and 70°C, respectively. When α-amylase and glucoamylase were applied jointly, at 40°C corn starch appeared to be a superior source for D-glucose and potato starch the best source for manufacture of maltose. Similar results were collected on hydrolysis with α-amylase in heterogenic systems (Anger *et al.* 1994). In experiments with β-amylase and amyloglucosidase potato starch was uniformly more resistant than wheat, rice, and maize starches (Kearsley and Nketsia-Taibri 1979). When starches were cooked prior to hydrolysis potato starch appeared to be the most susceptible to α–amylolysis and the order of susceptibility was: corn amylose < hylon corn starch < waxy maize starch < corn starch < potato starch (Rendleman 2000). Thermostable α-amylase provided almost identical results of hydrolysis for potato, corn and tapioca starches (Słomińska *et al.* 2003)

Usually, maize starch is superior for manufacturing syrups for isomerization of D-glucose to D-fructose. Selection of right enzymes and reaction conditions provided best results in case of potato starch, although maize, wheat and tapioca starches were only slightly worse sources (Aschengreen *et al.* 1979). These and numerous other studies, see for instance Lorentz and Kulp (1982) and Planchot *et al.* (1997), lead to the conclusion that crystallinity of starches is the crucial factor governing susceptibility of starches to α-amylolysis.

PERSPECTIVES

Because of its unique properties, potato starch will continuously play important role in nutrition and in nonnutritive applications. The most essential properties offered by that starch are its purity, anionic character and susceptibility to swelling. Clear gels of high penetration force and viscosity designed at starch concentration lower than in case of other starch variety is a beneficial property. Polysaccharide –

polysaccharide blends offer novel approach to the texture of foodstuffs and blends for non-nutritional purposes (Sikora *et al*. 2007; Baranowska *et al*. 2008; Kowalski *et al*. 2008; Sikora *et al*. 2008).

Pyrodextrins from potato starch might appear interesting, commonly available radioprotectivae (Tomasik *et al.* 2008).

Developments in instrumental structural analysis provide more exact insight into effect of the climate and breeding conditions upon amylose/amylopectin ratio and subtle structure of both starch polysaccharides e.g. their molecular weight profile, number of branches and their length. Such information would be very useful for more precise designing various functional properties of products either developed from that starch or containing it as one of the components.

Functional properties and applications of hylon and waxy potato starches still remain unrecognized. In spite of numerous chemical modifications of potato starch (Tomasik *et al*. 2004; Tomasik and Schilling 2004) such modifications should still be considered fascinating area of penetration in looking for novel biodegradable materials. Recent developments in nanotechnology indicate that admixture of various nanoparticles to polysaccharides produces novel composites of improved mechanical properties, lower aqueous solubility and resistance to enzymatic digestion (Polaczek *et al*. 2007; Khachatryan *et al*. 2008).

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