PIOTR TOMASIK[1], WOJCIECH CIESIELSKI[2], MAREK SIKORA[3],
BEATA SYCHOWSKA[3]

THERMAL STARCH TRANSFORMATIONS

Abstract

Studies on the radical, thermal decomposition of 11 starch varieties revealed that among amaranthus, cassava, oat, maize, waxy maize, rye, triticale, two varieties of potato and two varieties of wheat starch the oat starch was least stable and waxy maize starch was the most stable. The stability determination was based on the free radical count in the EPR spectra. The radicals appeared to be very stable against air as well as water and alcohol used for extraction of dextrins resulting from the thermolysis of starch. Simulations of the EPR spectra for 12 glucosyl radicals and the comparison of experimental and simulated spectra led to the conclusion that the delocalization of unpaired spin as well as steric hindrances are responsible for that stability.

In order to prepare novel dextrins of increased water binding capacity accompanied by low aqueous solubility thermolysis of starch was carried out under nitrogen, carbon dioxide, ammonia and hydrogen sulfide. The conventional and microwave heating of plain starch and its blends with formaldehyde, carboxyamides and esters were tested. The results are compared and discussed.

A majority of starch derivatizations involves elevated temperature as the source of energy. Starch containing foodstuffs are usually treated for consumption by either cooking, frying or roasting. Also the most common industrial starch modification which turns starch into dextrins frequently requires an elevated temperature, and eventually catalysts. Depending on the reaction conditions the derivatization proceeds according either to ionic or radical mechanisms.

It is well known that temperature above 200°C applied to mono- and oligosaccharides results in their radical decomposition [1]. Therefore, a considerable attention has been paid to the radical character of thermally processed food and food ingredients prepared thermally from saccharides, for instance, caramels. The most recent studies [2] have revealed that such evidently radical containing products are not mutagenic. The radicals are very stable, and when generated in starch as well as in

[1] Department of Chemistry, University of Agriculture, Cracow, Poland
[2] Institute of Chemistry, Teachers Training College, Czestochowa, Poland
[3] Department of Carbohydrate Technology, University of Agriculture, Cracow, Poland

cellulose only randomly add to polysaccharides and crosslink them [3]. Radicals can also be generated from polysaccharides on heating but neither their properties nor structure are well recognized.

Our studies on thermolysis of 11 varieties of starch up to 325°C for 30 to 120 min. revealed that radicals appeared when starch turned very dark brown. The radical count (number of spins) in starch of various origin dependent on the roasting temperature and time is given in Table 1.

Table 1

Number of spins, n, in starch of various origin[a], $n \cdot 1015/g$[b]

Temp.	Time	$n \cdot 10^{15}/g$										
°C	min	PM	PD	T	O	WE	R	WH	M	C	WM	A
285	90				10							
	120			5	20	6	8	4	1		2	
300	90	5	7	2	10	2	2	6		6	3	5
	120	6	10	3	30	3	4	5	3	7	2	5
325	60				4							
	90	40	10	4	80	3	4	70	2	10	4	12
	120	200	80	8	1000	40	60	600	7	50	10	40

[a] PM and PD – potato starch of two origins; T – triticale starch; O – oat starch; WE and WH wheat starch of two origins; R – rye starch; M – maize starch; WM – waxy maize starch; C – cassava starch; A – amaranthus starch.

[b] $CuSO_4$ was taken as the standard.

One may see that oat starch was the least thermally stable, and both triticale and maize starch were the most stable in terms of the number of spins generated. This stability was in no relation to the amylose-to-amylopectin ratio because the number of spins in dextrins resulting from waxy maize starch should take a terminal position in the order of either decreasing or increasing spin count. The presence of noneluted ingredients such as protein and/or lipids in form of native starch complexes could have an essential influence on the thermal stability of starch. Proteins, as thermally unstable readily decomposed and accelerated the thermal generation of radicals from starch. It might be deduced from the significant weight loss of the oat starch on heating. The loss reached 40 % within 90 min heating at 285°C and almost 80 % after 120 min. heating at 325°C. This behavior of oat starch was unique because other starch varieties did not loose their weight on such heating. The stability of maize starch might result from the presence of lipids which resided in form surface and helical amylose com-

plexes. Distinctly more thermally stable lipids and their complexation to starch inhibited its thermal decomposition.

The analysis of the UVVIS absorption spectra of iodine complexes of resulting dextrins revealed that the extention of the damage of starch matrix as well as its macromolecules were proportional neither to time nor to temperature of roasting. Relevant information was brought by the observation of the shift of the absorption maximum around 625 nm in the visible spectra of the iodine complexes as well as the ratio of absorbance measured at 625 and 545 nm (Table 2).

Table 2

Selected characteristics of the visible spectra of iodine complexes with roasted starch

Roasting conditions		625 nm-band nm	A_{625}/A_{545}	$(A_{625}/A_{545})_0 - A_{625}/A_{545}$[a]
Temp.,°C	Time, min			
Potato starch				
unprocessed		626	1.51	
170	30	645	1.63	-0.12
	60	625	1.71	-0.20
	90	625	1.68	-0.17
	120	625	1.62	-0.11
250	30	625	1.61	-0.10
	60	625	1.51	0.00
	120	588	1.03	0.48
270	30	613	1.51	0.00
	60	613	1.49	0.02
	90	588	0.94	0.57
	120	no band		
285	30	581	1.07	0.44
	60	585	1.51	0.36
	90	no band		
300	30	581	1.07	0.44
	60	no band		
325	30	578	0.86	0.65
Oat starch				
unprocessed		583	0.88	
170	30	575	0.92	-0.04
	60	571	0.84	0.04
	90	588	1.00	-0.12
	120	571	0.95	-0.07
250	30	595	1.08	-0.20
	60	581	0.92	-0.04
	90	no band		
270	30	588	0.91	-0.03
	60	575	0.87	0.01

	90	no band		
285	30	515	0.54	0.34
	60	no band		
300	30	543	0.62	0.26
	60	no band		
325	30	no band		
Maize starch				
unprocessed		598	1.06	
170	30	568	0.90	0.16
	60	588	1.10	-0.04
	90	588	1.11	-0.05
	120	588	0.95	0.09
250	30	562	0.88	0.18
	60	538	0.79	0.27
	120	556	0.65	0.41
270	30	588	1.00	0.06
	60	588	1.16	-0.10
	90	543	0.67	0.39
	120	543	0.69	0.37
285	30	565	0.82	0.24
	60	543	0.78	0.28
	90	588	1.08	-0.02
	120	no band		
300	30	588	1.04	0.02
	60	no band		
325	30	521	0.62	0.44
	60	no band		
Waxy maize starch				
unprocessed		614	1.20	
170	30	613	1.36	-0.16
	60	613	1.35	-0.15
	90	613	1.44	-0.24
	120	613	1.26	-0.06
250	30	588	0.97	0.25
	60	599	1.21	-0.01
	90	566	0.67	0.57
	120	566	0.79	0.41
270	30	588	1.02	0.08
	60	606	1.18	0.02
	90	543	0.66	0.54
	120	no band		
285	30	513	0.51	0.69
	60	549	0.71	0.49
	90	no band		
300	30	575	0.78	0.42
	60	no band		
325	30	515	0.48	0.72
	60	543	0.59	0.61

[a] $(A_{625}/A_{545})_0$ is the ratio for unprocessed starch.

The blue shift of the 625 nm-band signalized the damage of the starch structure to dextrins. The increase of the A_{625}/A_{545} ratio in respect to the original value spoke in favor of the priority of amylopectin in thermally decomposition. Neither the position shift of the 625 nm-band nor the A_{625}/A_{545} absorbance ratio variation were monotonous with the treatment time and temperature increase being a possible result of a repolymerization and reversion. The total damage of the starch structure into dextrins took place at temperatures lower than these required for the generation of radicals.

The radicals from starch were unusally stable. They survived a several months long air exposure and extraction with such hydroxylic solvents as cold (24 h) and hot (30 min) water as well as hot ethanol (24 h), although in an extreme case the concentration of unpaired spins decreased even by 80% (Fig. 1)
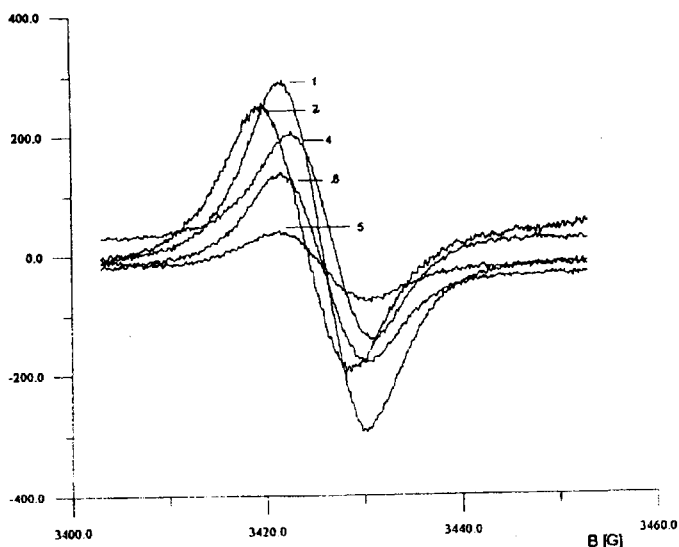
Fig. 1. Spin count decrease in roasted potato starch after extraction: 1 – sample (14.1 mg) prior to extraction; 2 – sample (13.8 mg) treated with cold water followed by evaporation to dryness (nonfiltered); 3 – dry sample (8.1 mg) after extraction (30 min) with hot water; 4 – dry sample (0.14.3 mg) after extraction (24 h) with cold water; 5 – dry sample (15.3 mg) after extraction (24 h) with hot ethanol.

This phenomenon could be explained as the result of either perfect delocalization of unpaired spin within the glucose unit radicals or/and steric hindrance of the unpaired spin from approaching spin scavenger. A simulation of EPR spectra for all possible glucosyl radicals (Fig. 2) was carried out with and without an assumption of intermolecular spin-spin interactions, respectively.

The resemblance of experimental spectra and those simulated under the intermolecular spin-spin interaction condition and lack of such similarity when this
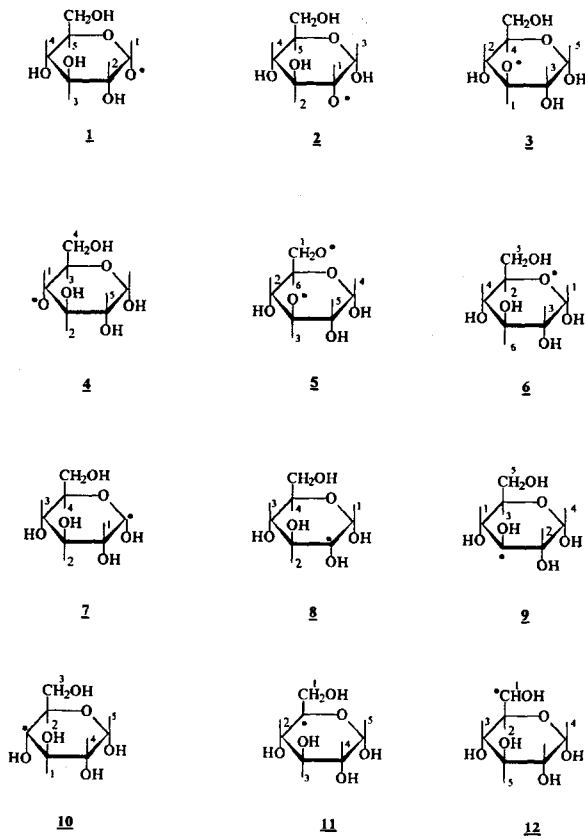
Fig. 2. Radicals for which the simulation of the EPR spectra wascarried out.

assumption was rejected (Fig. 3), pointed to an essential role of a migration of un-paired spins within the structure in the stabilization of radicals.

The thermal transformations of starch are commonly used for industrial manufac-ture of dextrins. Starch can be processed either as a plain material or with some catalysts added. There was also published a variety of laboratory procedures of dex-trinization. Pyrolysis of starch to gaseous and liquid products was also described in the literature [4].

Since more than decade a great concern is noted about biodegradable plastics. Starch and its modificates are utilized as components of such materials [5]. Such and other modern applications developed studies on a facile starch modifications providing more hydrophobic products and, simultaneously, with a higher water binding capacity. Their electric compatibility to proteins is also an essential factor.
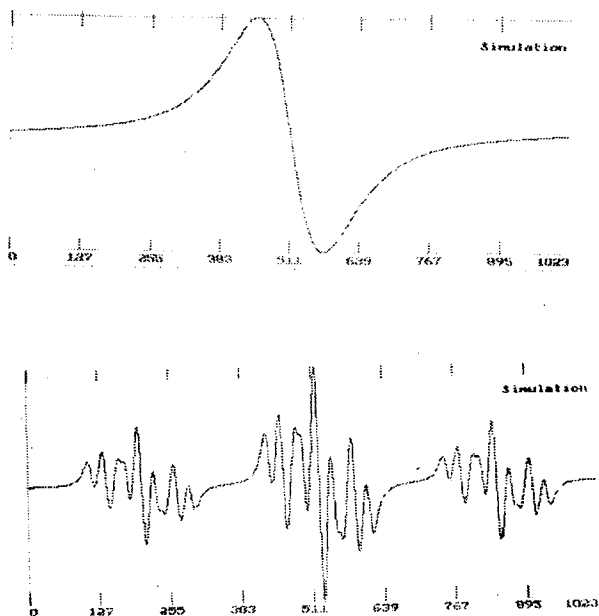
Fig. 3. Example of the EPR spectra simulated under assumption of the spin-spin interactions (left) and lack of such interactions (right). Compare the results with experimental spectra in Fig. 4.
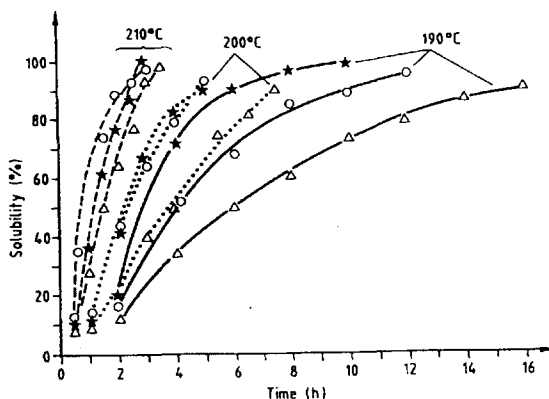
Fig. 4. The dextrinization course of potato starch under variable roasting conditions presented in terms of the aqueous solubility increase resulting dextrins with the rosting time (circles – in the air; stars – under nitrogen; triangles – under CO_2) (after [6]).

We have considered microwave heating of starch either plain or with certain reagents as well as conventional heating of starch in a oxygen-free atmosphere.

The latest group of experiments involved the starch dextrinization under nitrogen and carbon dioxide [6, 7], ammonia [8, 9] and hydrogen sulfide [10].

Table 3

Solubility, viscosity of 40 % aq. solutions and degree of thickening of British gums prepared under nitrogen, carbon dioxide, and in the air after twelveth hour of roasting at 190°C (according to [6])

Atmosphere	Solubility, %	Viscosity of 40 % aq. solutions (cP)	Degree of thickening
Air	90.0	173.0	165.0
Nitrogen	90.7	351.0	164.0
CO$_2$	90.6	1534.0	531.0

Fig. 4 [6] shows that the dextrinization carried out under CO$_2$ provided the least soluble dextrins which, simultaneously, differed from dextrins prepared under nitrogen and in the air in the viscosity of their aqueous solutions and degree of their thickening (Table 3).
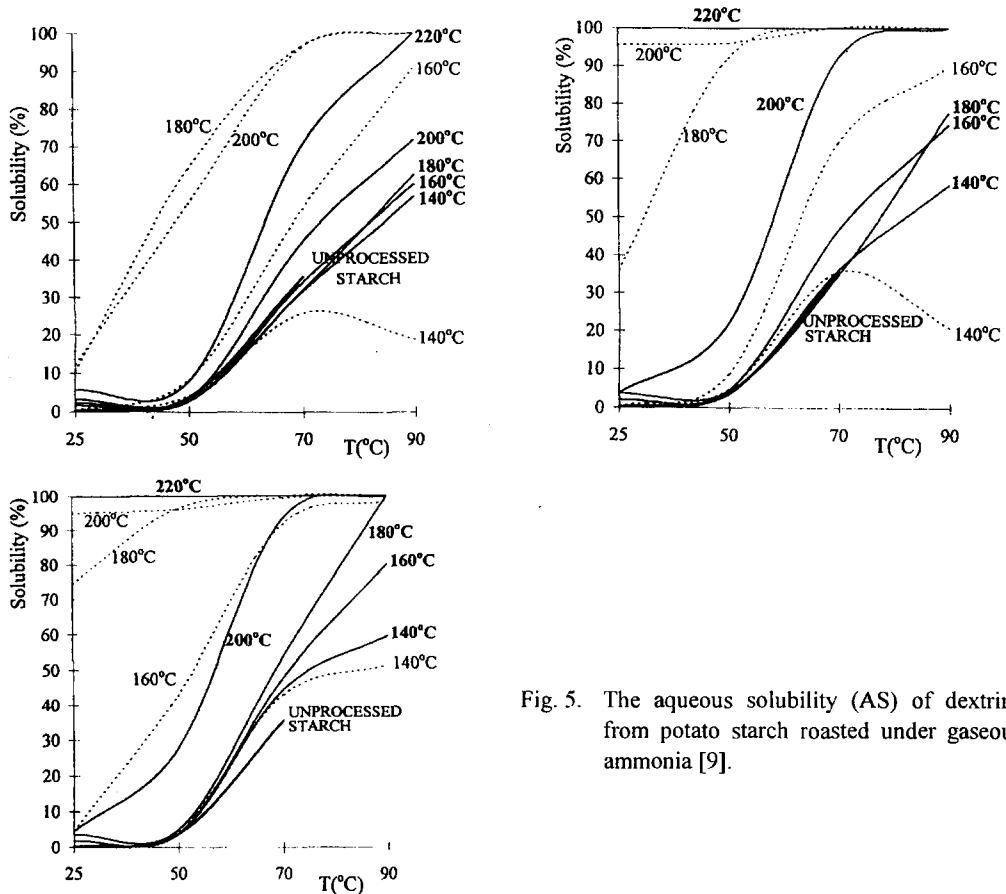
Fig. 5.   The aqueous solubility (AS) of dextrins from potato starch roasted under gaseous ammonia [9].

These dextrins were acidic (pH 5.28 to 4.11) and for this sake their isoelectric point could be suitable for the formation of complexes with proteins.

Ammonia as the atmosphere of thermolysis retarded the polisaccharide destruction. Resulting dextrins, especially these prepared between 180 and 200°C had lower solubility (AS) and higher water binding capacity (WBC) as the corresponding products thermolyzed in the air (Figs. 5 and 6, respectively).
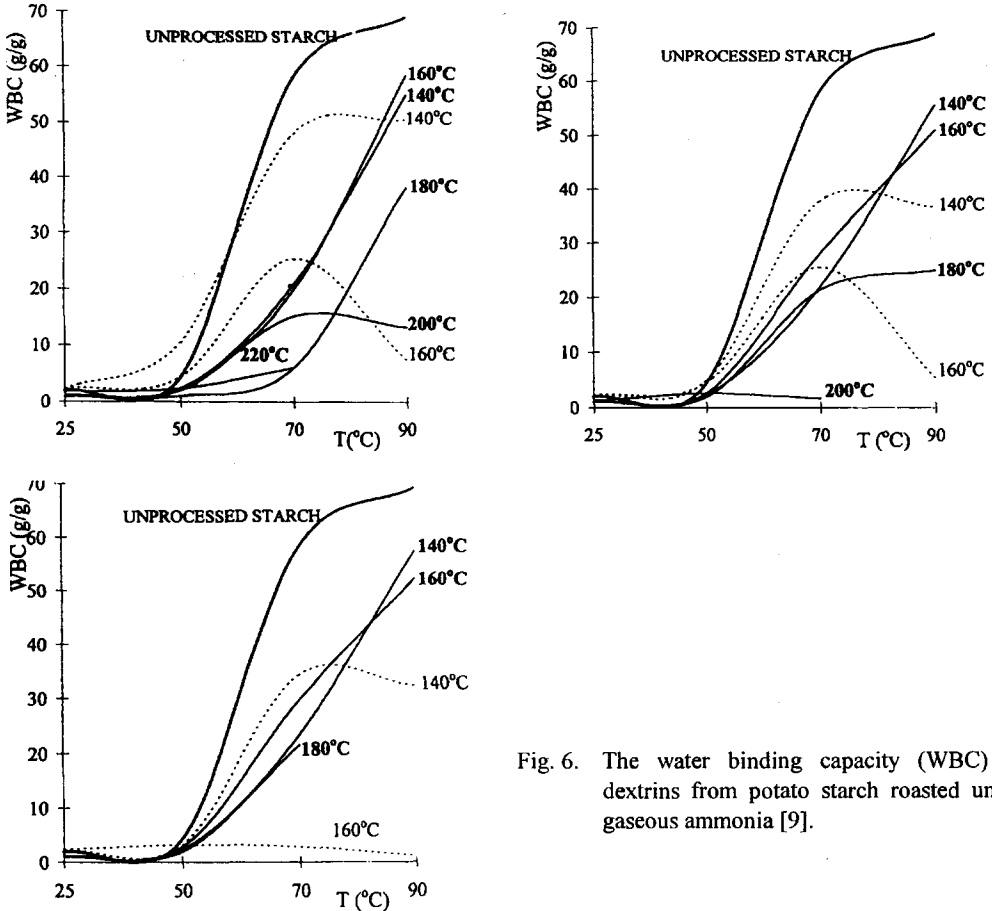
Fig. 6. The water binding capacity (WBC) of dextrins from potato starch roasted under gaseous ammonia [9].

Ammonia practically did not add to starch and only dextrins prepared in extremal conditions (220°C, 6 h) contained residual nitrogen (0.48 %) bound to starch. pH of these dextrins was between 7.00 and 5.80. Also hydrogen sulfide as the thermolysis atmosphere provided dextrins of suitable AS – temperature and WBC – temperature profiles (Figs. 7 and 8).
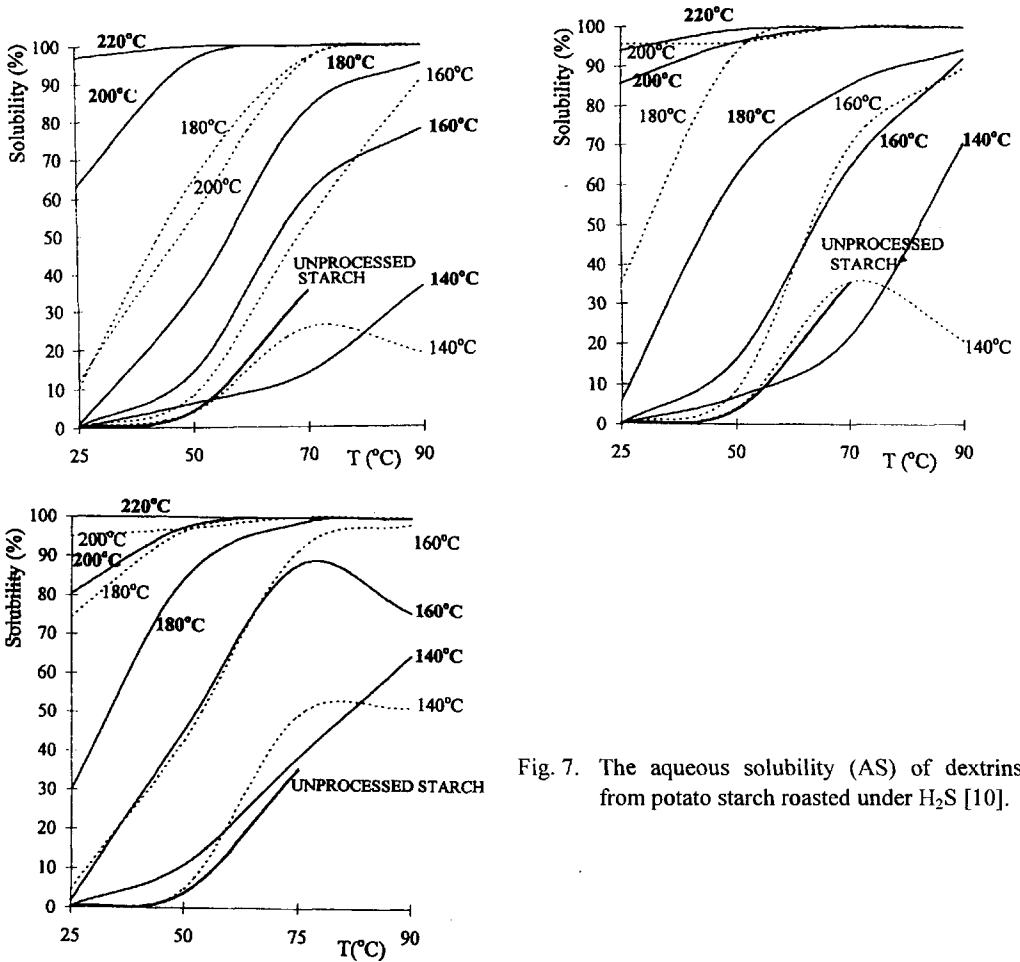
Fig. 7. The aqueous solubility (AS) of dextrins from potato starch roasted under H_2S [10].

Contrary to ammonia H_2S added to polysaccharide which after thermolysis contained from 0.4 to 0.9 % S. pH of these product varied form 5.25 to 4.0.

Our experiments with microwave thermolysis of starch involved plain, solid starch, starch sols, starch – formaldehyde mixtures [11] as well as starch blends with one of urea, (U), formamide, (FA), dimethylformamide, (DMF), phthalimide, (PI), ethhyl benzoate (EB) and dimethyl phthalate (DP) as well as a group of α-hydroxy and α-amino acids [lactic, (LA), tartaric, (TA), and citric (CA) acids as well as leucine, (Leu), serine, (Ser), asparagine, (Asn), and glutamic acid (GluA)].
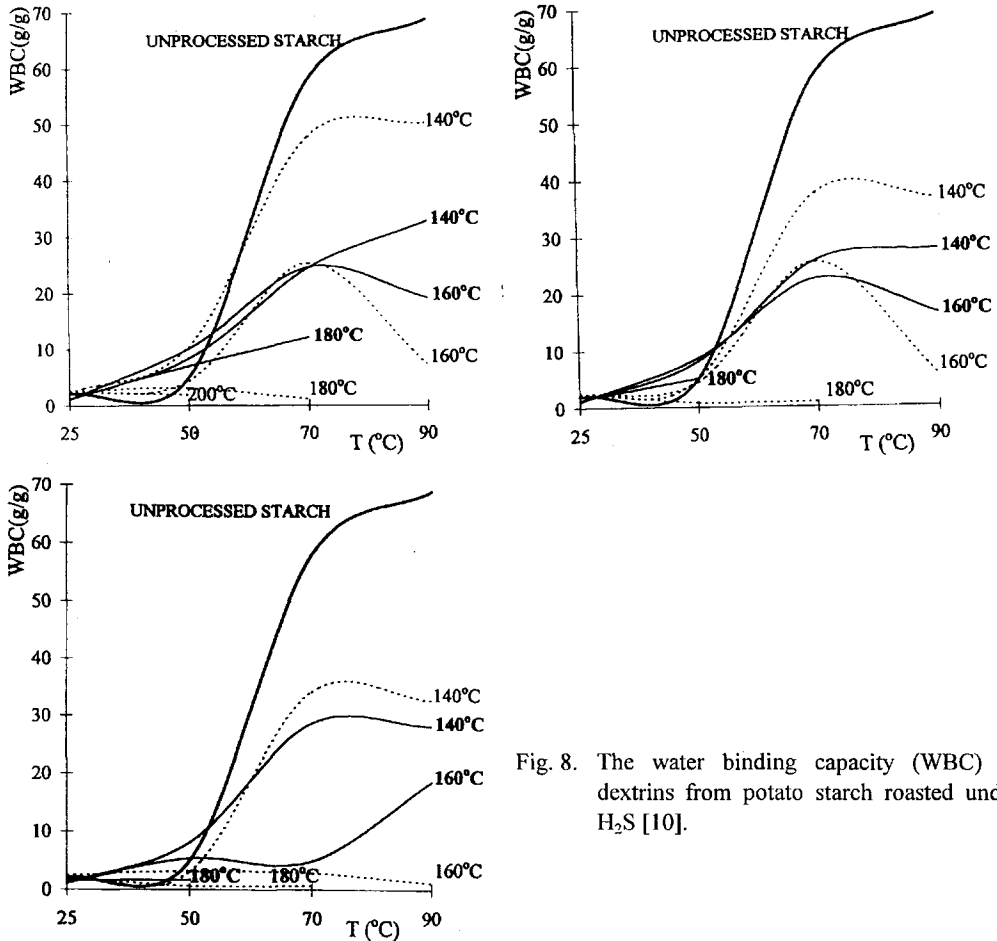
Fig. 8. The water binding capacity (WBC) of dextrins from potato starch roasted under H_2S [10].

The irradiation of air dried cassava, maize and potato starch showed their fast destruction even by the irradiation with the middle low energy. Fig. 9 shows the decrease of the viscosity of gels made of such gels.

The 15 min. irradiation of 4 % starch slurries with the middle low energy provided a dirty brown opaque gel of low reversion from maize starch, gummy clear product of low reversion from potato starch, and milky tixotropic stiff gel from cassava starch.

The starch crosslinking with formaldehyde on microwave irradiation was very successful. The reaction which required an acid catalyst when carried out on conventional heating was over without any catalyst within 5 to 20 min. of irradiation with low energy. The reaction time was dependent on the starch variety and volume of formaldehyde added as shown in Table 4 in terms of the viscosity of gels made of such products.
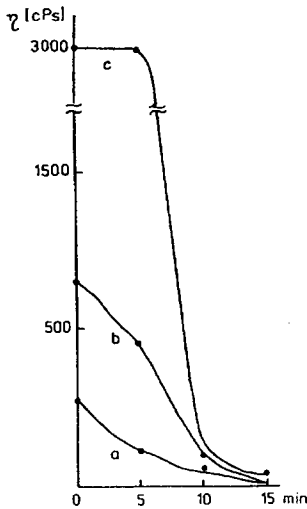
Fig. 9. The viscosity decrease of 5 % gels made of air-dried maize (a), cassava (b) and potato (c) starch irradiated for variable period with middle low energy microwaves (after [11]).

On microwave irradiation starch could also be crosslinked with acetylene. Hydrogen peroxide was used as the catalyst. The product of crosslinking of maize starch contained one double bond per 42 glucose units whereas the products from crosslinking of potato and cassava starch contained one double bond per 5 and 10 glucose units, respectively. In spite of crosslinking starch deteriorated to a significant extent under the reaction conditions (20 min. with low energy, 6 % of H_2O_2 added) and the gels made of the products had a low viscosity.

α-Hydroxy and α-amino acids added to starch prior to its irradiation with microwaves, except lactic acid which is liquid, practically did not dissociate under reaction conditions. They reacted with starch possibly by an addition hindering the macromolecule from deterioration. As shown in Figs. 10 and 11 such

Table 4

Viscosities, cP, at 25°C of 4-5 % gels made of starch crosslinked with 40 % aq. formaldehyde on irradiation with low energy [11].

| Irradiation	Gel viscosity at 25°C, cP (gel. conc., %)		
time, min.	Maize	Potato	Cassava
1 weight % added			
0		330 (5)	280 (4)
5	650 (5)	4400 (5)	445 (5)
10	610 (5)	5200 (5)	370 (5)
15		3200 (5)	
2 weight % added			
5	480 (5)	1900 (4)	400 (4)
10	330 (5)	1900 (4)	330 (4)
20		2100 (4)	
25		800 (4)	
5 weight % added			
5	270 (5)	1200 (4)	800 (4)
10	365 (5)	1400 (4)	300 (3)
15	140 (5)	800 (3)	
10 weight % added			
5	170 (5)	1250 (4)	400 (4)
10	365 (5)	1300 (4)	400 (3)
15	270 (5)	1250 (3)	95 (1)

treatment increased WBC and, at the same time, hydrophobized starch. The products were anionic. α-Hydroxy acids gave better results in terms of all AS, WBC and pH. The latest decreased in the case of tartaric acid up to 2.7.

Carrying the reactions with amides and esters we assumed that the reaction of transesterification could be likely. In this manner amides and esters could act as acylating agents.

The microwave irradiation of potato starch blends with all esters and amides but phthalimide produced more hydrophobic dextrins with enhanced WBC which, however, in none of the cases exceeded 6 g of H_2O per 100 g of the product at 30°C as shown in Figs. 10 and 11.
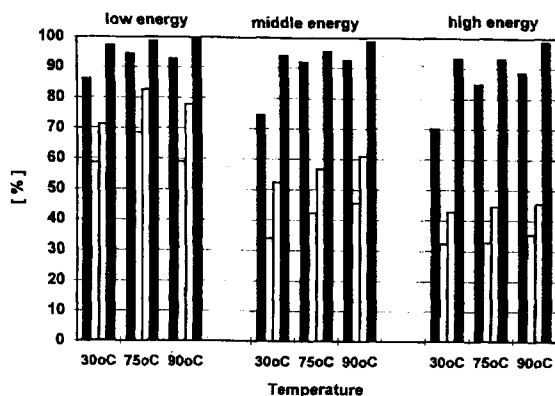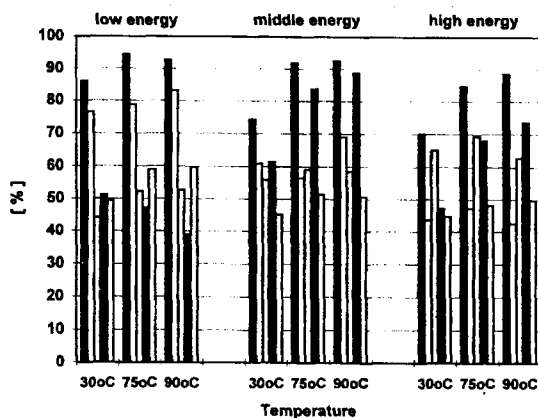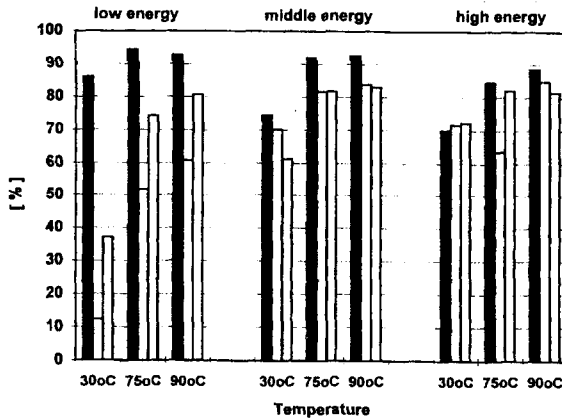

Fig. 10a. The aqueous solubility (AS) of dextrins from potato starch roasted with: 1 – α-hydroxy acids (columns from the left: plain starch, citric acid, tartaric acid, and lactic acid); 2 – α-amino acids (column from the left: plain starch, glutamic acid, asparagine, leucine and serine);
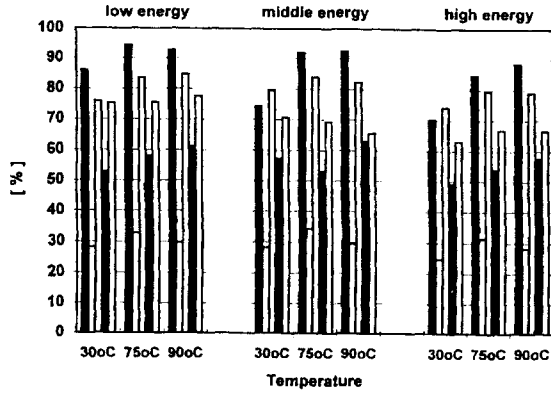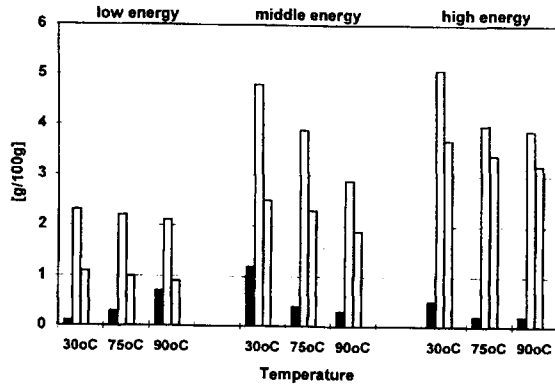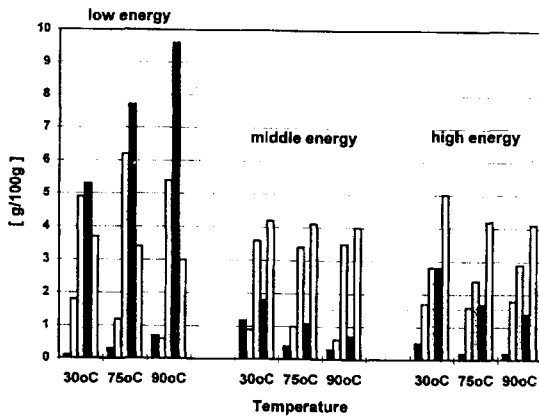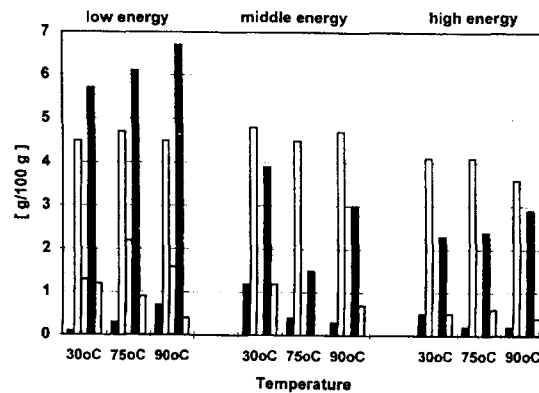
Fig. 10b. The aqueous solubility (AS) of dextrins from potato starch roasted with: 3 – amides (columns from the left: plain starch, urea, phthalimide, dimethylformamide, formamide); 4 – esters (columns from the left: plain starch, ethyl benzoate, dimethylphthalate). The 10 min irradiation with low, middle low and high energy microwaves in every case.
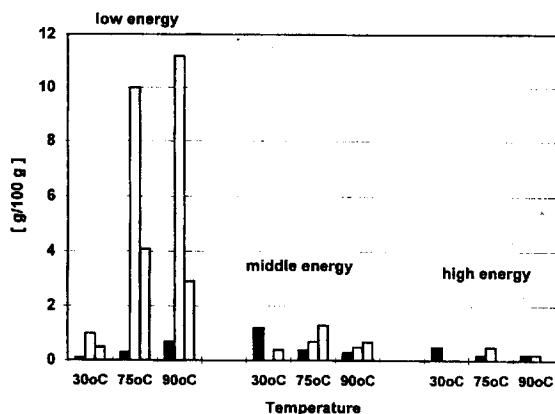
Fig. 11a. The water binding capacity (WBC) of dextrins from potato starch roasted with α-hydroxy and α-amino acids as well as with amides and esters (see Fig. 10 for notation).

Fig. 11b. The water binding capacity (WBC) of dextrins from potato starch roasted with α-hydroxy and α-amino acids as well as with amides and esters (see Fig. 10 for notation).

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TERMICZNE PRZEKSZTAŁCENIA SKROBI

Streszczenie

Badania nad rodnikowym, termicznym rozkładem 11 odmian skrobi wykazały, że spośród skrobi z amarantusa, tapioki, owsa, kukurydzy, kukurydzy woskowej, żyta, triticale, dwu odmian skrobi ziemniaczanej i dwu odmian skrobi pszennej skrobia owsiana jest najmniej trwała, a skrobia kukurydziana woskowa jest najtrwalsza. Trwałość określono na podstawie liczby wolnych rodników wykazanych widmami EPR. Rodniki te były bardzo trwałe w kontakcie z powietrzem, wodą i alkoholem, którymi ekstrahowano powstające w trakcie termolizy dekstryny. Symulacja widm EPR dla 12 rodników gliukozy-

lowych i porównanie tych widm z widmem doświadczalnym doprowadziły do wniosku, że za trwałość rodników odpowiada delokalizacja niesparowanych spinów oraz osłony sferyczne.

W celu przygotowania nowych dekstryn o podwyższonej zdolności wiązania wody i obniżonej rozpuszczalności w wodzie termolizowano skrobię pod azotem, dwutlenkiem węgla, w amoniaku i siarkowodorem. Badano też sieciowanie skrobi formaldehydem, karboksyamidami i estrami przez ogrzewanie mieszanin reakcyjnych w polu mikrofalowym.