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Microwave-assisted boration of potato starch

Summary — Granular potato starch was successfully borated with boric acid and sodium tetraborate decahydrate (borax) in a microwave-assisted solid state reaction. Products of starch boration reached (dependently on the conditions of the process) the maximal value of the degree of esterification (*DE*) equal to 0.27 when boric acid was applied, and 0.18 when borax was used. DTA, TG, DTG and FT-IR methods revealed that boration of starch provided boron esters or borate complexes. High-pressure size exclusion chromatography (HPSEC), DSC and X-ray diffraction showed that although the boration of starch caused changes in its macrostructure, the thermal stability of borated starch was enhanced even by 20 ^{o}C when compared with native product, with larger stability exhibited by complexes than by esters. The thermal stability of the borated starch increased with an increase in *DE*. After modification, granularity of starch was retained, as was indicated by the scanning electron microscopy.
Key words: starch borates, solid state reaction, microwave assisted synthesis, structure, thermal stability.

BORANOWANIE SKROBI ZIEMNIACZANEJ W POLU MIKROFALOWYM
Streszczenie — Ziarnistą skrobię ziemniaczaną boranowano za pomocą kwasu borowego i dziesięciowodnego tetraboranu sodu (boraksu) w reakcji wspomaganej mikrofalami. Określono wpływ stosunku skrobia: czynnik borujący oraz czasu trwania i mocy naświetlenia na stopień estryfikacji (*DE*) produktów (tabela 1). Maksymalna osiągnięta wartość *DE* w próbkach skrobi boranowanej H_3BO_3 wyniosła 0,27, a boranowanej boraksem 0,18. Wyniki uzyskane metodami DTA, TG, DTG oraz FT-IR (rys. 2—8) wykazały, że produkty boranowania stanowiły estry oraz kompleksy (Schemat A). Na podstawie wyników badań z zastosowaniem wysokociśnieniowej chromatografii żelowej (HPSEC) (rys. 1), DSC (rys. 9 i 10), oraz dyfraktometrii promieni X (rys. 11, 12) ustalono, że chociaż skrobia miała zmienione właściwości fizykochemiczne (tabele 1 i 3) i jej struktura krystaliczna była zaburzona, to stabilność termiczna tak zmodyfikowanej skrobi wzrosła nawet o 20 ^{o}C w stosunku do skrobi natywnej. Stabilność ta zależała od wartości *DE* — zwiększała się wraz z jej wzrostem (Tabela 2). Ziarnista struktura skrobi po reakcji boranowania została zachowana, co stwierdzono metodą SEM (rys. 13).
Słowa kluczowe: borany skrobiowe, reakcja w ciele stałym, synteza mikrofalowa, struktura, termostabilność.

Boric acid has a wide range of applications. It is commonly used as a preservative in weatherproof wood and fireproof fabrics, leather, carpets, as an additive in china manufacturing, nickel plating, printing, dyeing, and steel hardening. For its biological activity it serves as insecticide, especially against cockroaches and black carpet beetles, and as astringent and antiseptic. It also shows antibacterial and antifungal properties. For decades it was used as hygienic aid, but for its toxicity its use is now limited, especially in contact with children [1—3].

Boric acid for cosmetic and hygienic was frequently offered in the form of suspensions with starch [4, 5]. Because of the interaction of this acid with starch, its admixture causes thickening of starch pastes [6-13]. The interactions can involve hydrogen bond formation [14] as well as esterification of starch with acid. Since boric acid is a three-basic acid, crosslinking of starch can occur with the involvement of its two of three reactive groups [15]. Thus, regardless of the form of the reaction of boric acid with starch, the product would exhibit anionic properties. The latter are essential for intermolecular interactions with other macromolecules, leading, for instance, to biodegradable polysaccharide-protein binary polymers [16—28]. Interactions of such kind are indispensable to combining of polysaccharides with proteins [29].

Among starches, only potato starch is naturally anionic, because its amylopectin esterifies phosphoric acid. There are several methods of making starch anionic. Oxidation, carboxymethylation and esterification of starch with at least dibasic inorganic acids are the most

common and suitable methods for obtaining anionic starches [30, 31]. Recently, a series of papers were published on esterification of starch in microwave-assisted reactions, for example, phosphation [32, 33], magnesium sulphation [34], selenation with selenous and selenic acid salts [35], and sulphation with the SO_3.pyridine complex [36]. Such reactions were readily performed in a solid state in a wasteless manner. They could, eventually, compete with reactions carried out by convectional heating and by extrusion. Boration by extrusion has already been patented [37, 38].

In this paper microwave-assisted, solid state boration of starch with either boric acid or sodium tetraborate decahydrate (borax) is described as an alternative to boration by convectional heating or in a heat-moisture--pressure manner. The products of starch boration have been examined by a variety of physicochemical methods, and the results of measurements, together with their discussion, are presented.

EXPERIMENTAL PART

Materials

— Potato starch (13 wt. % of relative moisture content) was isolated in Potato Enterprise in Łomża (Poland);

— powder boric acid was purchased from POCh Gliwice (Poland);

— sodium tetraborate decahydrate was the product of Lach-Ner, s.r.o. (Czech Republic).

Boration

The starch/boron reagent (1:0.1 and 1:1, by weight) blends were prepared by mixing of potato starch with either boric acid or sodium tetraborate decahydrate (borax) to obtain 2 g of final blends, and thorough homogenization in a agate mortar. The blends were heated in a Samsung M1711N microwave oven at 450 and 800 W for 900, 1200 or 1800 s. Reaction products were washed on a suction filter with 30 cm^3 of ice-water and subsequently dried at 40 ^oC for 24 h.

Methods of testing

Boron determination

The samples for analyses were prepared by weighing approximately 0.125 g of samples into a 150 ml beaker, followed by an addition of 5 ml hot concentrated nitric acid (1.40 g/cm^3). This solution was transferred into a 50 ml volumetric flask and filled with triple distilled water. Boron concentration in the solutions was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (HORIZON spectrometer, Thermo-Optek). The analysis was based on synthetic standards. The boron line of 182.640 nm was measured by a two-side subtraction of the background around the line. Radiation of frequency of 27.12 MHz at 700 W was used as the power source.

Thermal analyses (TG, DTG, DTA)

The analyses were performed using 100 mg samples. They were heated in the oven in corundum crucibles, starting from room temperature up to 500 ^oC, at a rate of 10 ^oC/min. Corundum particles of Φ = 8 μm served as the standard. The fully computerized instrument of Paulik-Paulik Erdey D-1500-Q (Budapest, Hungary) was used. Analyses were run twice.

Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of either borated starch samples or their components in KBr discs were recorded in the range of 4000—500 cm^{-1} at resolution of 4 cm^{-1} using a Matson 3000 FT-IR (Madison, Wisconsin, USA) spectrophotometer.

Differential scanning calorimetry (DSC)

The samples of approximately 8 mg were sealed in an aluminum pan with water at the sample/water ratio of 1:3 (by weight) and left for 1 h for equilibration. They were then scanned at the rate of 6 ^oC/min in the temperature range of 20 to 90 ^oC. An instrument, self-assembled in the Department of Physics, Agricultural University in Cracow, was used with a water filled pan as a reference. Analyses were run three times.

High performance size exclusion chromatography (HPSEC)

100 mg of samples were moistened with 10 ml water prior to an addition of 90 ml of dimethyl sulfoxide. The mixtures were gently agitated and their temperature was gradually raised up to 60 ^oC. Agitation at that temperature was maintained for 24 h, followed by cooling of the mixture to room temperature. Resulting solutions were transparent and visually homogeneous.

The HPSEC system consisted of a pump (Shimadzu 10AC, Tokyo, Japan), an injection valve (model 7021, Rheodyne, Palo Alto, CA, USA), a guard column TSK PWH (Tosoh Corporation, Tokyo, Japan), and two connected SEC columns: TSKgel GMPWXL (300 × 7.8 mm, Tosoh Corporation, Tokyo, Japan) and TSKgel 2500 PWXL (300 × 7.8 mm, Tosoh Corporation, Tokyo, Japan). A multiangle laser light scattering detector Dawn-DSP-F (Wyatt Technology, Santa Barbara, CA, USA), equipped with a He–Ne laser light source (630.0 nm) and a differential refractive index detector (L-7490, Merck, Darmstadt, Germany) were connected to the columns. The temperature of columns was maintained at 30 ^oC. The mobile phase (0.15 M $NaNO_3$ with 0.02 % of sodium azide) was filtered through 0.2 and 0.1 ìm cellulose acetate filters (Whatman, England). The flow rate of the mobile phase and the sample injection volume were 0.4 ml/min and 100 μl, respectively. The output voltage of refractive index (RI) and light scattering (LS) at 18 angles

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were utilized for calculation of the weight-average molecular weight (M_w) and the radius of gyration (R_g), using Astra 4.73.04 software (Wyatt Technology, Santa Barbara, CA, USA). The Berry plot with third order polynomial fit was applied for the calculation of M_w and R_g values. [39,40]. The standards utilized were pullulan and two dextrans — D-580 and D-2000 — with M_w equal to 6.2×10^5 and 2.0×10^6, respectively. All separation and calibration operations were run three times. The recovery of injected samples was in the range 92—95 %.

Powder X-ray diffraction

The measurements were carried out by applying CuK_α radiation of wavelength 0.154 nm using a Philips type X'pert diffractometer. The operation setting for the diffractometer was 30 mA and 40 kV. The spectra over the range of 5.0 — 60.0^o 2θ were recorded at a scan rate of 0.02^o 2θ/s.

Scanning Electron Microscopy (SEM)

Granule morphology of starch samples was studied by scanning electron microscopy using an apparatus E-SEM XL30 (FEI Company, Eidhoven, The Netherlands), equipped with SE detector of secondary electrons. The instrument set for 15 kV accelerating voltage operated at low vacuum. The magnification range changed from 500 to 2000 times.

Solubility in water

Solubility of the samples in water was estimated according to Richter et al. [41]. Samples (100 mg) were dissolved in distilled water (8 ml) and agitated for 30 min in a water bath at temp. 25 ^{o}C and then centrifuged (4000 rpm for 5 min). The resulting transparent solution (5 ml) was transferred to a weighing dish of constant weight and dried at 120 ^{o}C to reach the constant weight.

Statistical analysis

The data obtained from the DSC thermal analysis and HPSEC chromatography were statistically analyzed by one-way analysis of variance to determine significant differences among samples, using STATGRAPHICS version 2.1 (Statistical Graphics Corporation, USA). Significance was accepted at $p < 0.05$.

RESULTS AND DISCUSSION

As it was stated in Experimental Part, boration of potato starch was carried out by microwave heating of starch blended in various proportions with either boric acid or borax. The boron reagent esterified starch; simultaneously, it was also hydrolyzed. The extent of hydrolysis resulting in a decrease in the molecular weight of the product depended on the starch/boron reagent proportion in the reaction mixture, as well as on the power and reaction time applied. Results of the boron content analyses and M_w values for the native and starch samples borated in different conditions are given in Table 1.

The degree of esterification (*DE*) did not exceed 0.27. The reaction with boric acid led to higher *DE* than the reaction with borax. *DE* increased with the amount of admixed boric acid and the applied power of the microwave oven, but the time prolongation of the reaction had no positive effect on *DE* value. Application of 800 W for 1200 s was optimal for the highest *DE* in the case of the reaction with borax, when *DE* = 0.18 was achieved.

There were distinct differences in the shapes of chromatograms of native and borated starch samples taken using the RI detector and LS detector diode at a 90° angle. Careful analysis of the chromatograms enabled to distinguish one, two or three regions, for which the values of M_w were calculated. An example of superimposed chromatograms taken using the LS and RI detectors for both native and borated with boric acid starch is presented in Fig. 1.

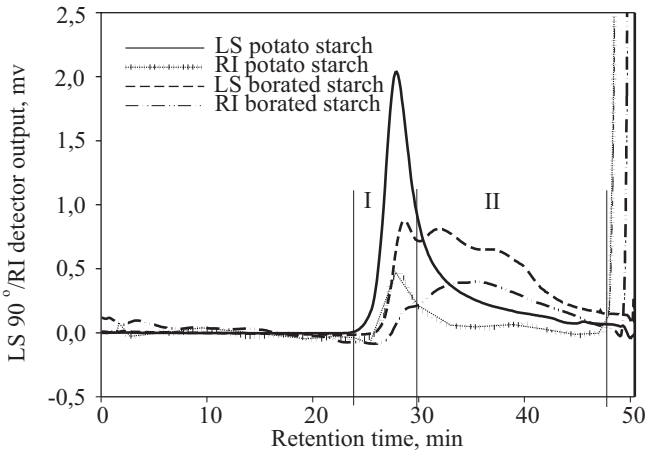

Fig. 1. An example of superimposed chromatograms of RI and LS 90° detector outputs for starch borated with boric acid (starch: boric acid = 1:0.1) at 450 W and for 1800 s (see text); chromatograms for the potato starch are shown for comparison

The boration of starch with boric acid initiated deep degradation of polysaccharide chains. This facilitated access to starch granules; therefore the reaction could progress. The M_w values of samples obtained by microwave heating of starch with borax for 900 s, applying both low and high power, differed only slightly from that of native starch. Significantly lower M_w values were observed for the samples heated for 1200 s. An increase in time of the reaction to 1800 s caused very distinct increase in the M_w values. It could be supposed that slight substitution of D-glucose units took place, followed by relatively deep degradation due to thermolysis, which gave the highest *DE*. Further microwave heating led to crosslinking of borated starch. These processes contributed to an increase in the solubility in water of the boration products (Table 1). It is suggested by this fact that all the

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T a b l e 1. Characteristics of starches borated in different conditions (mean of three measurements ± standard deviation)

Conditions of boration	Boron content, %.	$DE^{*)}$	$M_W \cdot 10^{6**)}$			Solubility in water, %	
						25 °C	40 °C
Potato starch			$8.04\pm0.7^{c,d}$			0.48	0.56
Heated at: 450W for 1200 s($S_{pot.}$ 450)	—	—	12.35 ± 0.6^{e}			0.47	0.56
Heated at: 800W for 1200 s($S_{pot.}$ 800)			0.11 ± 0.0^{i}			0.32	0.52
1:0.1 starch:H_3BO_3							
Heated at 450W for:							
900s	0.08	0.015	$5.24\pm0.3^{f,g}$			0.48	1.60
1200s	0.09	0.017	0.66 ± 0.0^{i}			0.52	1.84
1800s	0.22	0.042	7.75 ± 0.5^{f}	2.95 ± 0.2^{a}		1.00	2.88
Heated at 800W for:							
900s	0.78	0.149	7.62 ± 0.5^{f}	0.98 ± 0.1^{b}		4.72	10.08
1200s	0.84	0.160	$3.98\pm0.2^{g,h}$	1.00 ± 0.1^{b}	0.79 ± 0.1^{a}	0.76	2.24
1800s	0.38	0.072	$1.85\pm0.1^{h,i}$	0.58 ± 0.0^{b}	0.73 ± 0.1^{a}	6.50	12.16
1:1 starch:H_3BO_3							
Heated at 450W for:							
900s	1.00	0.190	0.12 ± 0.1^{i}			0.96	2.88
1200s	1.05	0.200	$1.86\pm0.1^{h,i}$	0.42 ± 0.0^{b}		0.32	1.00
1800s	0.66	0.126	0.11 ± 0.0^{i}	0.02 ± 0.0^{b}		0.68	4.00
Heated at 800W for:							
900s	1.41	0.269	0.68 ± 0.1^{i}	0.11 ± 0.0^{b}		0.80	2.72
1200s	1.26	0.240	0.23 ± 0.0^{i}	0.11 ± 0.0^{b}		1.28	4.27
1800s	1.12	0.213	0.11 ± 0.0^{i}	0.11 ± 0.0^{b}		5.28	10.72
1:1 starch:borax							
Heated at 450W for:							
900s	1.01	0.075	16.44 ± 0.9^{d}			5.72	5.88
1200s	1.33	0.099	7.34 ± 0.5^{f}			7.16	7.00
1800s	0.98	0.073	19.91 ± 1.0^{c}			5.40	5.68
Heated at 800W for:							
900s	0.68	0.051	26.14 ± 1.8^{b}	18.84 ± 0.9^{c}		3.92	4.48
1200s	2.39	0.179	$1.27\pm0.1^{h,i}$			13.80	14.16
1800s	0.92	0.069	46.81 ± 2.3^{a}	19.70 ± 1.0^{c}		5.52	6.32

*) DE = degree of esterification **) Values in the columns marked with various letters are significantly different at $p < 0.05$.

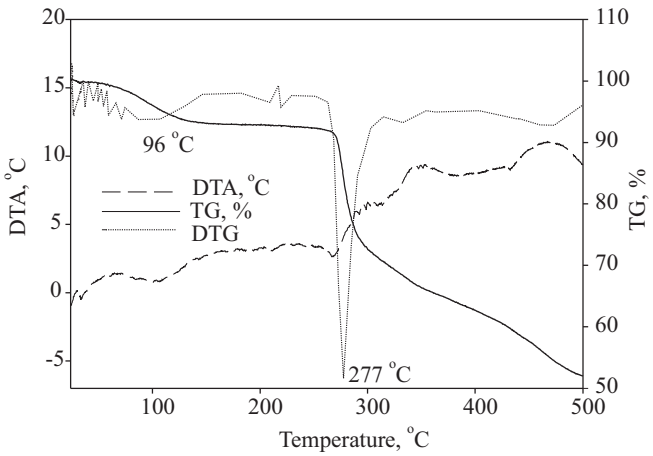

Fig. 2. Thermogram of potato starch

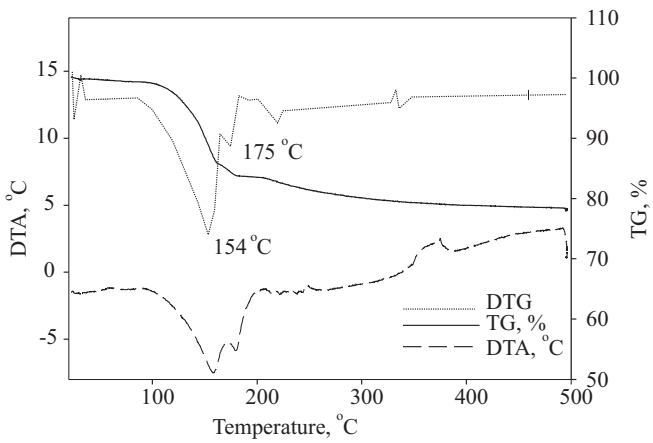

Fig. 3. Thermogram of boric acid

reactions under examination resulted in the products more hydrophilic than starch itself.

The thermal analysis proved that the reaction between the components of the blend occured. Figures 2—4 present thermograms of native potato starch, boric acid and borax, respectively.

A sharp, one-step decomposition of starch took place at 277 °C. The pattern of the diagrams of starch prior and after the microwave radiation remained, essentially, the same, with only small changes in the decomposition temperature (275 and 273 °C for 450 and 800 W, *i.e.* for S_{pot} 450 and S_{pot} 800 respectively). The

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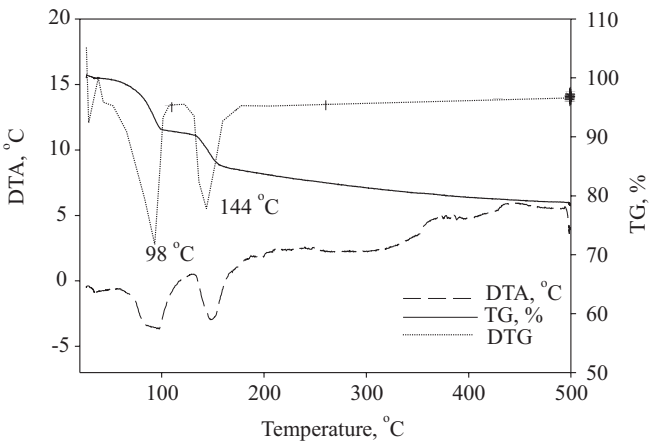

Fig. 4. Thermogram of borax

slope of the TG line became milder as the power increased (Table 2).

The thermal decomposition of boric acid occurred in two steps. The major peak value at around 154 °C was due to the first dehydration of boric acid, and the minor one appearing at around 176 °C was due to the second dehydration and transformation to B_2O_3.

Borax, in the process of heating up to the temperature of 260 °C, gradually lost four water molecules: two at the temperature of 98 °C, and another two at 144 °C. Above 260 °C it remained stable up to 500 °C.

The boron atom in boric acid outer electronic shell with a vaconcy and thus can be considered as an electron-deficient atom. The boron atom is, therefore, very reactive to any group which can donate electrons and thereby stabilize the boron atom. For this reason, boric acid (I) functions as an electron acceptor, giving the tetrahedral borate $B(OH)_4^-$ anion. Thus starch, as a polyalcohol, can react with this acid to form esters [(III), (V)] and complexes [(IV, (VI)] (see Scheme A). The starch can form complexes also with borax what will be discussed in further text.

Decomposition of the starch boration products prepared from the samples containing small doses of boric acid (starch: boric acid = 1:0.1) proceeded in two steps,

T a b l e 2. Comparison of the thermal properties of native potato starch (S_{pot}), boric acid, borax and borated starches in the temperature range of 25—500 °C

Sample	Weight loss (%) in the temperature range*):				DTG (°C)		
	25—260 °C	260—307 °C	Slope (tg α)	307—496 °C			
PS native	7.9	20.5		19.4	96		
$S_{pot.}$ 450 (heated at 450 W for 900 s)	2.0	25.1	2.32	20.1			277
$S_{pot.}$ 800 (heated at 450 W for 900 s)	2.0	23.4	1.26	20.8			275
H_3BO_3	18.9	1.1	1.14	1.7		154	273
$Na_2B_4O_7 \cdot 10H_2O$	19.0	0.9		1.8	98	144	175
1:0.1 starch:H_3BO_3							
Heated at 450W for:							
900s	6.0 (8.9)	19.7 (18.7)	0.70	20.1 (17.8)	99	275	
1200s	9.2 (8.9)	18.4 (18.7)	0.70	22.4 (17.8)	103	272	
1800s	9.7 (8.9)	17.5 (18.7)	0.49	20.1 (17.8)	89	274	
Heated at 800W for:							
900s	7.9 (8.9)	16.0 (18.7)	0.69	17.9 (17.8)	108	282	
1200s	6.4 (8.9)	9.2 (18.7)	0.63	17.1 (17.8)	98	278	325
1800s	7.1 (8.9)	18.2 (18.7)	0.59	19.5 (17.8)	96	279	
1:1 starch:H_3BO_3							
Heated at 450W for:							
900s	9.7 (13.4)	12.4 (10.8)	0.45	18.1 (10.6)	93	282	312
1200s	8.5 (13.4)	15.7 (10.8)	0.57	18.2 (10.6)	94	274	307
1800s	11.2 (13.4)	14.8 (10.8)	0.46	18.1 (10.6)	96	282	317
Heated at 800W for:							
900s	6.3 (13.4)	14.9 (10.8)	0.47	18.3 (10.6)	105	281	315
1200s	10.3 (13.4)	14.0 (10.8)	0.48	17.4 (10.6)	94	282	307
1800s	5.1 (13.4)	16.9 (10.8)	0.75	17.8 (10.6)	103	282	320
1:1 starch:$Na_2B_4O_7 \cdot 10H_2O$							
Heated at 450W for:							
900s	4.4 (13.5)	14.6 (10.7)	0.38	14.1 (10.6)		287	
1200s	6.0 (13.5)	14.7 (10.7)	0.29	15.9 (10.6)		288	
1800s	5.0 (13.5)	15.5 (10.7)	0.46	16.9 (10.6)		289	
Heated at 800W for:							
900s	4.8 (13.5)	15.3 (10.7)	0.39	13.7 (10.6)		286	
1200s	5.6 (13.5)	10.1 (10.7)	0.17	9.9 (10.6)		296	
1800s	4.6 (13.5)	14.0 (10.7)	0.48	1.4 (10.6)		289	

*) Weight loss calculated from experiments with individual components is given in parentheses.

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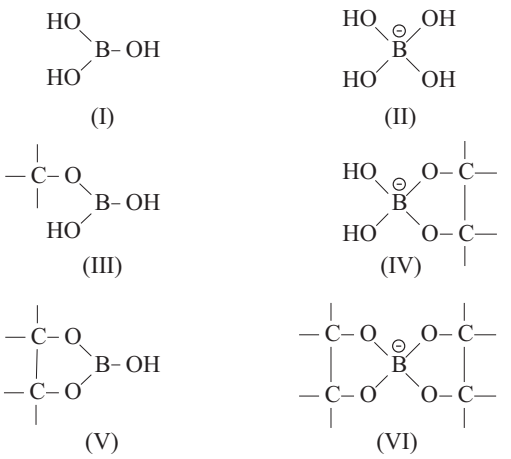

Scheme A. Chemical structures of boric acid (I), borate anion (II), their esters (III, V) and complexes (V, VI)

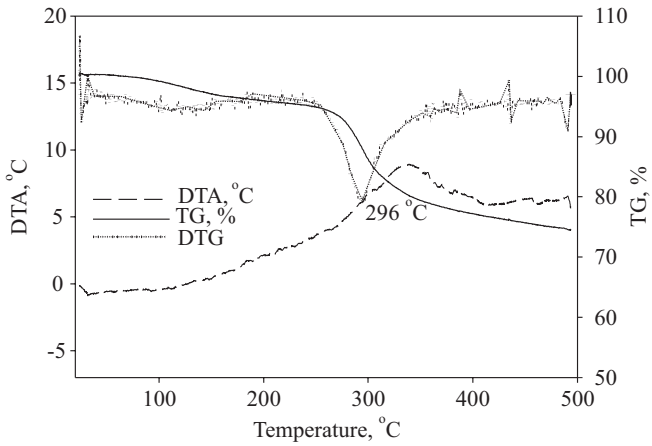

Fig. 6. Thermogram of starch borated with borax at proportions 1:1 for the microwave heating time of 1200 s and the power of 800 W

and it only slightly differed from that of native starch. The first weight loss of such starch boration product corresponded to the loss of one water molecule. It means that one hydroxyl group of the D-glucose units reacted with one of the three reaction centers of boric acid, forming a product of monoesterification. When a larger dose of the boric acid was used (starch: boric acid = 1:1), three thermal effects were observed namely at 94 °C, 287 °C and 307 °C (Fig. 5). The actual weight loss measured within the range 25 to 260 °C did not reach, and within the range 260 to 307 °C exceeded the respective value calculated from the thermograms of particular components of the products.

An increase in the dose of boric acid caused a shift in the decomposition point of starch (the second weight loss) to higher temperature (277 °C ε 282 °C), suggesting that some crosslinking might occur. The slopes of the TG line corresponding to particular decomposition steps revealed that borated starch decomposed less readily than native starch. These results, obtained for two different doses of boric acid, showed that esterification gave two types of borates.

Microwave heating of starch with borax provided novel products. An example thermogram is shown in Fig. 6. The main decomposition step appeared at a temperature 296 °C, that means by around 20 °C higher than that of the native starch decomposition (277 °C), suggesting that crosslinking took place. The resulting products held less water, and decomposed at a lower rate than the products obtained by the boration with boric acid (compare TG — lines in Fig. 5 and 6).

The FT-IR spectra of the native potato starch (c) and the starch borated with higher dose (1:1)of boric acid (b) are shown in Fig. 7. The bands resulting from the OH stretching vibration of B–O–H at 3225 cm^{-1} [42], the asymmetric B–O stretching vibrations at 1464 cm^{-1}, and

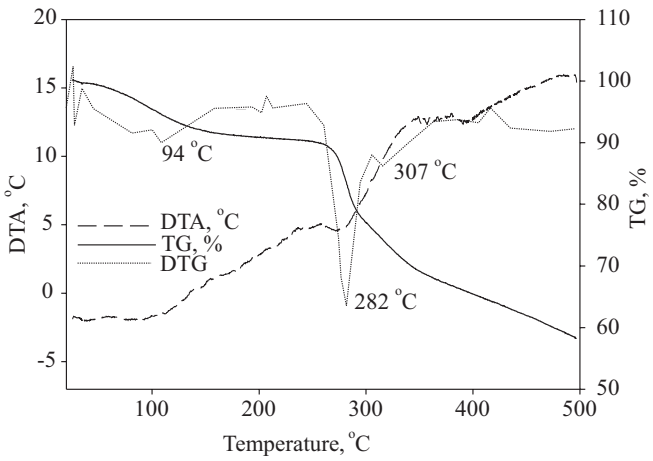

Fig. 5. Thermogram of starch borated with boric acid at proportions 1:1, for the microwave heating time of 1200 s and the power of 800 W

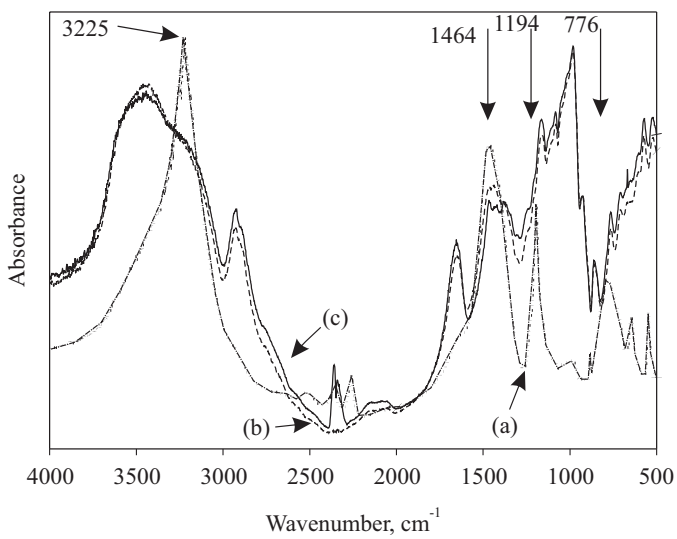

Fig. 7. FT-IR spectra of 1:1 physical mixture of starch and boric acid (a), and the resulting product of boration carried out at 450 W and for 1200 s (b); potato starch spectrum is shown for comparison (c)

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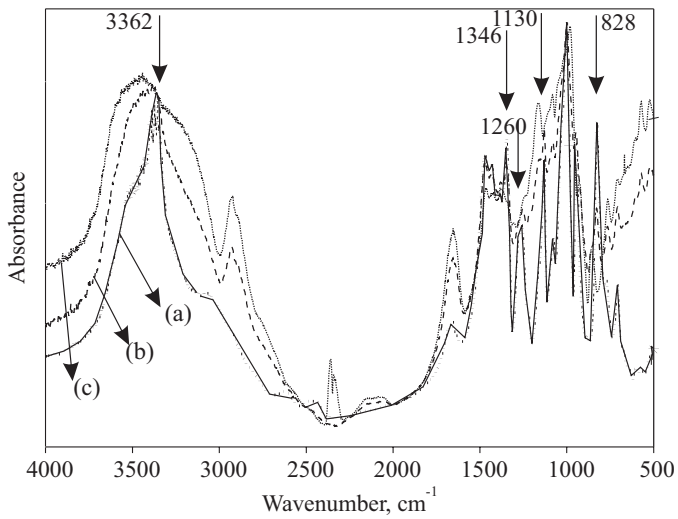

Fig. 8. FT-IR spectra of 1:1 physical mixture of starch and borax (a), and the resulting product of boration carried out at 450 W for 1200s (b); potato starch spectrum is shown for comparison (c)

the in-plane B–O–H bending vibrations at 1194 cm^{-1}, characteristic for the trigonal planar molecule of free boric acid [43], could be well observed in the spectrum of the physical mixture of starch and boric acid (a). In this spectrum, there was an additional broad peak at 776 cm^{-1} that could arise either from the symmetric B—O stretching vibrations characteristic for the tetrahedral borate $B(OH)_4^-$ anion, or the out-of-plane B–O–H bending vibrations (the overlapping of these bands makes the data analysis difficult). Only the band at 1464 cm^{-1}, shifted to 1437 cm^{-1}, was clearly observed in the spectrum of the starch borated with boric acid (b), while the others were not.

These results indicated the formation of esters [see structures (III) and/or (V) in Scheme A]. The comparison of FT-IR spectrum of the physical mixture of starch and boric acid with that of the boration product, within the range 3600—3000 cm^{-1}, revealed the formation of intramolecular hydrogen bonds in the latter one. It seems that the possibility of hydrogen bonding between the D-glucose units and borate hydroxyls could attribute to the better thermal stability of the esters.

In the FT-IR spectrum of the starch borated with borax [Fig. 8, (b)], peaks resulting from B–O and C–O–B–O–C stretching vibrations at 1346 cm^{-1} and 1260 cm^{-1}, respectively, and also the asymmetric B–O stretching vibrations at 1130 cm^{-1} (triangular) and 828 cm^{-1} (te-

Table 3. Results of DSC investigations of potato starch and its borated derivatives (mean of three measurements ± standard deviation)*)

Sample	T_o, °C**)	T_p, °C	T_c, °C	ΔH, J/g
Potato starch	$59.2\pm0.2^{c,d}$	$65.4\pm0.3^{a,b}$	65.9 ± 0.4^{c}	12.9 ± 0.3^{a}
Spot. 450 (heated at 450 W for 900 s)	$55.2\pm0.2^{h,i}$	$62.3\pm0.3^{f,g}$	n.g.***)	$11.3\pm0.2^{a,b,c,d,e}$
Spot. 800 (heated at 450 W for 900 s)	51.2 ± 0.4^{l}	$64.0\pm0.4^{c,d}$	n.g.	1.8 ± 0.3^{j}
1:0.1 starch:H_3BO_3				
Heated at 450W for:				
900s	62.6 ± 0.1^{a}	$64.8\pm0.2^{b,c}$	67.3 ± 0.1^{b}	$10.6\pm0.2^{d,e,f}$
1200s	62.4 ± 0.4^{a}	$65.2\pm0.2^{a,b}$	$68.1\pm0.2^{a,b}$	$12.0\pm0.0^{a,b,c}$
1800s	62.3 ± 0.4^{a}	$65.1\pm0.2^{a,b}$	67.6 ± 0.2^{b}	$10.2\pm0.1^{d,e,f}$
Heated at 800W for:				
900s	$56.2\pm0.4^{g,h}$	60.2 ± 0.1^{i}	63.4 ± 0.1^{e}	$9.1\pm1.0^{f,g,h}$
1200s	$57.7\pm0.2^{e,f}$	$60.9\pm0.4^{h,i}$	63.7 ± 0.5^{e}	$12.1\pm0.6^{a,b}$
1800s	$58.2\pm0.3^{d,e,f}$	$61.8\pm0.2^{g,h}$	64.8 ± 0.1^{d}	$9.5\pm0.5^{f,g}$
1:1 starch:H_3BO_3				
Heated at 450W for:				
900s	63.0 ± 0.1^{a}	65.8 ± 0.0^{a}	68.8 ± 0.0^{a}	$11.6\pm0.5^{a,b,c,d}$
1200s	61.0 ± 0.4^{b}	$63.9\pm0.2^{d,e}$	67.1 ± 0.2^{b}	$12.7\pm0.1^{a,b}$
1800s	59.5 ± 0.5^{c}	$63.3\pm0.4^{e,f}$	67.1 ± 0.3^{b}	$11.5\pm0.4^{a,b,c,d,e}$
Heated at 800W for:				
900s	$57.0\pm0.1^{f,g}$	$61.0\pm0.1^{h,i}$	$64.5\pm0.4^{d,e}$	$11.3\pm0.2^{b,c,d,e}$
1200s	$58.3\pm0.2^{c,d,e}$	$61.5\pm0.0^{g,h}$	$64.1\pm0.1^{d,e}$	$10.0\pm0.6^{d,e,f}$
1800s	$58.0\pm0.2^{d,e,f}$	$63.9\pm0.3^{d,e}$	$60.9\pm0.3^{h,i}$	$10.4\pm0.3^{c,d,e,f}$
1:1 starch:borax				
Heated at 450W for:				
900s	53.9±0.1j,k	56.3 ± 0.2^{l}	59.9 ± 0.2^{g}	$9.9\pm0.3^{e,f}$
1200s	54.9±0.3i,j	$57.0\pm0.3^{k,l}$	59.8 ± 0.2^{g}	$9.0\pm0.2^{f,g,h}$
1800s	55.4±0.4h,i	$57.8\pm0.1^{j,k}$	$60.5\pm0.4^{f,g}$	$10.3\pm0.3^{d,e,f}$
Heated at 800W for:				
900s	56.1±0.3g,h,i	58.6 ± 0.3^{j}	61.5 ± 0.3^{f}	$8.1\pm0.2^{g,h}$
1200s	53.4±0.4k	56.3 ± 0.2^{l}	59.9 ± 0.2^{g}	5.4 ± 0.4^{i}
1800s	55.0±0.2i,j	58.1 ± 0.2^{j}	61.4 ± 0.3^{f}	7.6 ± 0.1^{h}

*) Values in the columns marked with various letters are significantly different at $p < 0.05$.
**) Temperature of: T_o — onset, T_p — peak, T_c — conclusion; ΔH — melting, enthalpy.
***) n.g. = Not given.

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trahedral) [44], occur. All these bands were absent in the spectrum of native starch (c). Moreover, the band at 994 cm^{-1} observed in the starch spectrum (C–O–H bending) was shifted to 1000 cm^{-1}, indicated that the OH groups of starch took part in the hydrogen bond formation.

Crosslinking of starch with borating agent involving pairs of *cis*- hydroxyl groups of two D-glucose units, at positions 2 and 3, has been noted previously [15, 37, 38]. The results discussed above, obtained for starch borated with borax, suggested the formation of two types of borate complexes — structures (IV) and (VI) in Scheme A.

Steric hindrance can explain increased stability of such products, resulting from DSC investigations of starch and starch boration products, summarized in Table 3. The reaction of starch with borating agent led to a decrease in melting temperatures and enthalpies (application of 450 W) with respect to those for native potato starch, with more considerable effects observed when borax was applied. However, the application of 800 W power during the reaction resulted in a significant increase in the melting enthalpy values of all samples when compared to the control one. Figs. 9 and 10 demonstrate DSC thermograms of the starch boration products when the power of 450 and 800 W was applied,

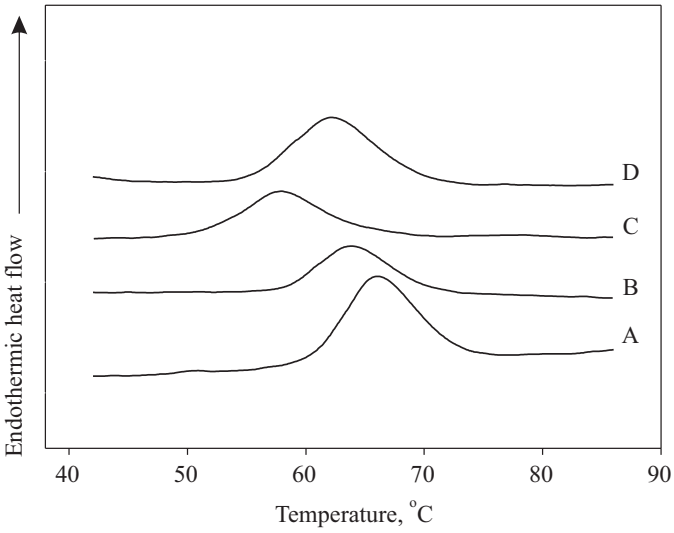

Fig. 9. DSC thermograms of the starch borated with boric acid (B) and borax (C) (starch: borating agent = 1:1) at 450 W for 1800 s; potato starch prior (A) and after (D) heating under identical conditions are added for comparison.

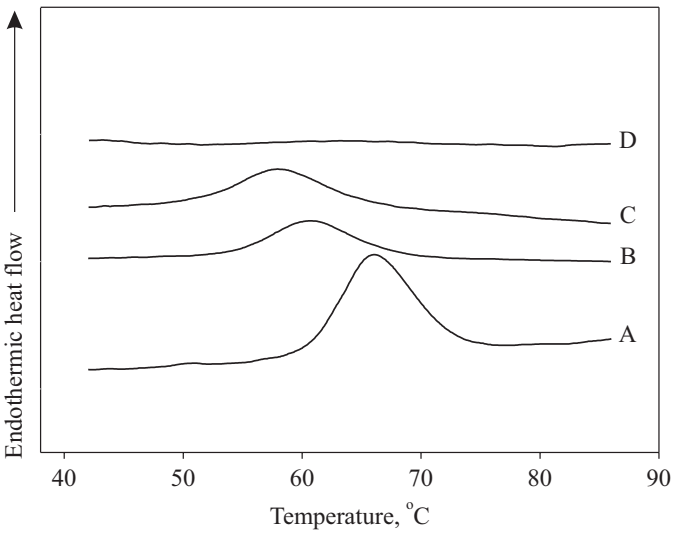

Fig. 10. DSC thermograms of the starch borated with boric acid (B) and borax (C) (starch: borating agent = 1:1) at 800 W for 1800 s; potato starch diagrams prior (A) and after (D) heating under identical conditions are added for comparison.

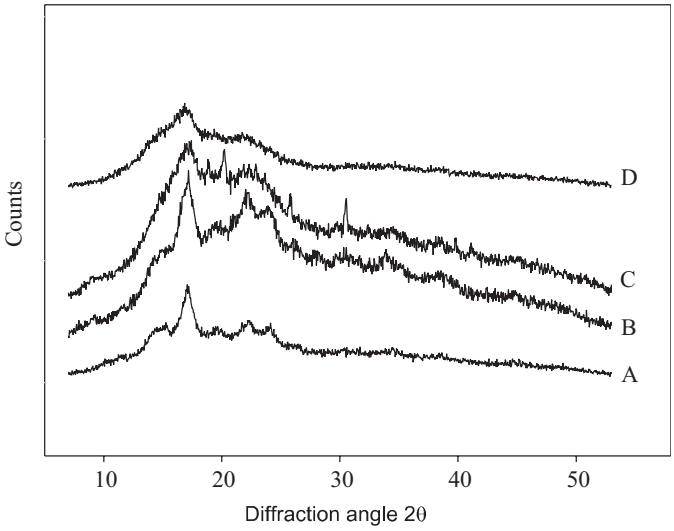

Fig. 11. Powder X-ray diffraction patterns of the starch borated with boric acid (B) and borax (C) (starch: borating agent = 1:1) at 450 W for 1800 s; potato starch patterns prior (A) and after (D) of heating under identical conditions are added for comparison.

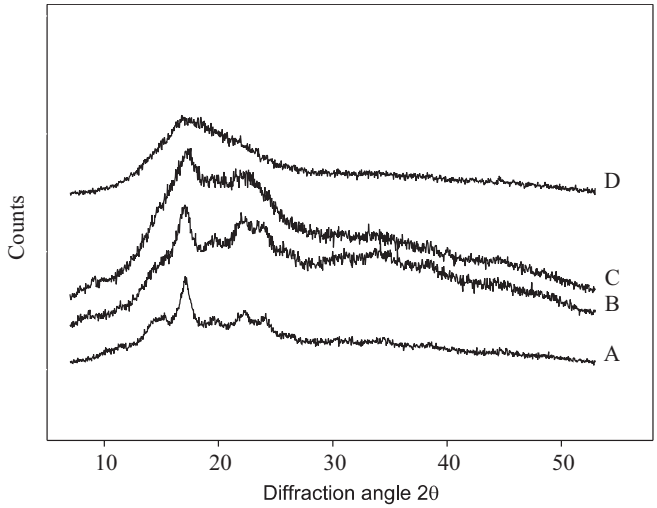

Fig. 12. Powder X-ray diffraction patterns of the starch borated with boric acid (B) and borax (C) (starch: borating agent = 1:1) at 800 W for 1800 s; potato starch patterns prior (A) and after (D) heating under identical conditions are added for comparison.

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respectively, for different borating agents used in the same doses. It could be seen that the peaks of a phase transition of borated starches (C and D) was in both cases shifted towards a low temperature range, particularly when borax was used as a borating agent (c).

X-ray diffraction patterns of the samples are shown in Figs. 11 and 12.

The microwave heating of a control sample of native starch resulted in progressive flattening of contours in both DSC and X-ray patterns with increasing power of radiation. Disorder in granules and decrease in their cristallinity where observed by us also in the case of illumination of potato starch with green and red linearly polarized light [45]. Ultimately, at the power of 800 W, only a very weak peak of phase transition, and a diffused diffraction peak, can be observed. Granules of starch heated at 800 W lost their shape, and the granule deterioration process is illustrated in SEM images (Fig. 13B). These observations indicated the destruction of native starch and the loss of its crystallinity because of heating, while the boration of starch evidently led to the limitation of this destruction. Diffractograms of the boration products had distinct sharp diffraction peaks. However, the diffraction revealed differences in intensity and sharpness in the recorded patterns among the samples borated with boric acid and those borated with borax.

Physical properties, such as melting temperature, are linked to the changes in the crystalline structure [46]. Hence, the differences seen in the DSC and X-ray diffraction diagrams (compare Fig. 9 with Fig. 11, and Fig. 10 with Fig. 12) indicated insignificant changes in the crystallinity of the samples of starch borated with boric acid, and more pronounced decrease in the crystallinity in the case of borax used as a borating agent.

The esterification of starch with boric acid could occur mainly in the amorphous regions of starch granules. This promoted swelling in these regions and, thus, disrupted the crystalline phase which melted at a lower temperature than that of unmodified starch. These phenomena could occur in the products prepared with a small doses of boric acid. An increase in the melting temperature and enthalpy when a larger dose of boric acid was used could be due to the reduced mobility of amorphous chains in the starch granule, as a result of the formation of intramolecular bonds. The surface of starch granules borated with boric acid was coarse, with partial protuberances (Fig. 13C). It could suggest that granules swelled to a certain extent and in this way boric acid could penetrate granules.

Additionally, the boration conducted for 1800 s led to granules' fusion, no matter if boric acid or borax was applied (Fig. 13, C and D). The fusion of borated starch granules could be attributed to the introduction of hydrophilic groups to the starch molecules, which resulted in increasing role of hydrogen bonding. On the other hand, reactions of granular starch proceeded first of all

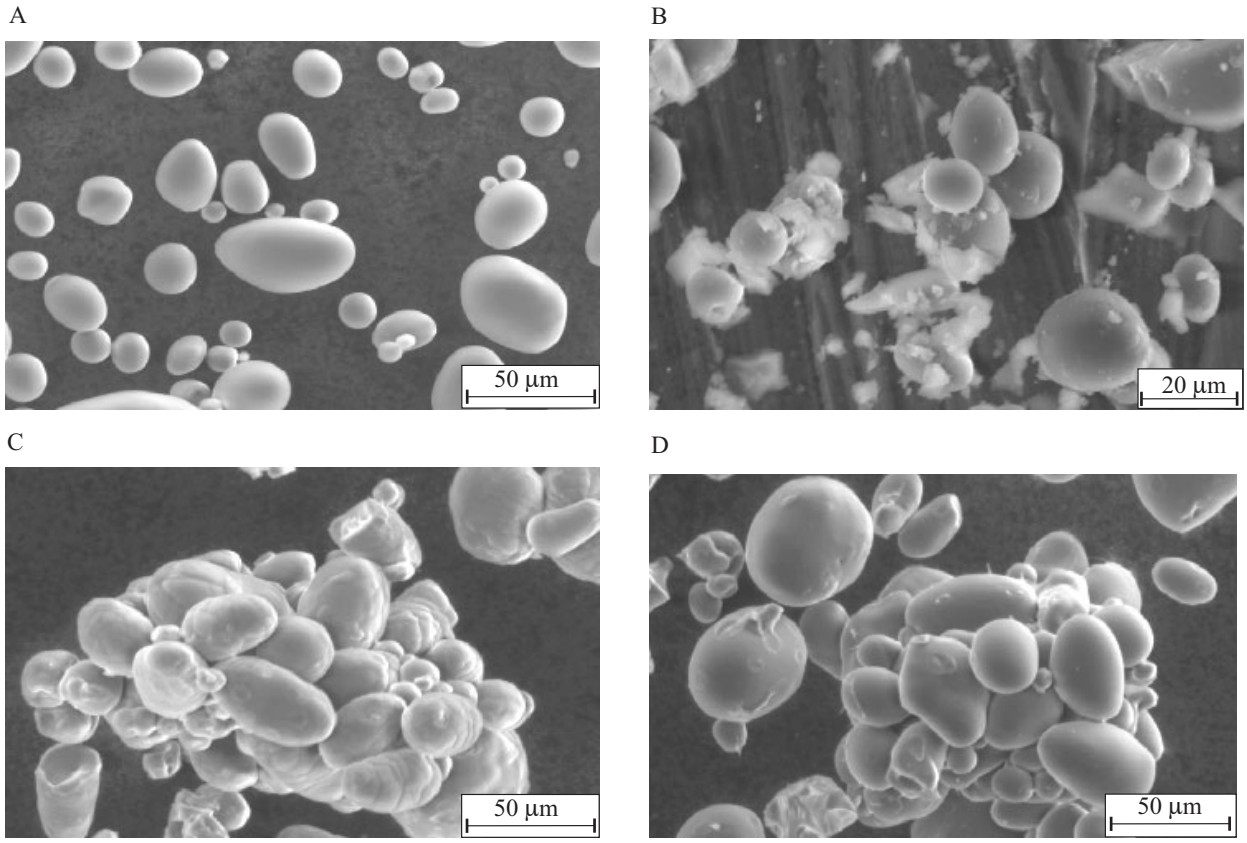

Fig. 13. SEM images of potato starch prior (A) and after (B) microwave radiation at 800 W for 1800 s, and of the starch borated with boric acid (C) and borax (D) (starch: borating agent = 1:1) under the same heating condition.

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on the surface, involving the exudation of the granule interior content which is usually present on the granule surface [47]. The extended reaction time had no positive effect on *DE*; thus, fusion might be the result of the surface gelatinization of non-reacted portion of polysaccharide in response to the microwave heating in the presence of the borating agent.

The formation of complexes [Scheme A, (V) and (VI)] during the boration of starch with borax was due to the alkaline character of the reacting mixture, caused by the presence of borax and water therein. The necessity of alkaline conditions for strong complex formation has been previously confirmed by using NMR [48]. In such conditions plastification of individual granules of starch took place, which was reflected by the results of DSC and X-ray analyses.

CONCLUSIONS

The microwave-assisted, solid state reactions of starch with boric acid or borax proved to be an efficient method of starch boration. Depending on the initial ratio of starch and borating agent, two types of boron esters or borate complexes (Scheme A) were formed. It turned out that the process of esterification of starch led to smaller changes in the internal structure of starch and their physical properties than the process of its complexation. However, the granular character of starch was retained in both processes. Boration of starch increased its thermal stability compared to native starch, with larger stability exhibited by complexes rather than esters.

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