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Esterification of starch with sodium selenite and selenate

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Abstract

Granular potato starch was esterified with selenous and selenic acid sodium salts in the microwave assisted solid state reaction. Degree of esterification (DE) in both cases did not exceed 3.01×10^{-2}. Reaction with selenite provided higher DE. DE increased with the applied power of the microwave oven but increased amount of admixed selenium reagents had no positive effect upon DE. The thermal stability of products was higher than that of native starch. The esterification retained granularity of starch but the crystallinity of granules partly ceased as indicated by scanning electron microscopy (SEM) and X-ray diffractometry, respectively.

Keywords: Granular starch; Potato starch; Starch selenate; Starch selenite; Solid state reaction

1. Introduction

Starch, containing primary and secondary hydroxyl groups in its glucose units, readily esterifies inorganic and organic acids (Tomasik & Schilling, 2004; Tomasik, Fiedorowicz, & Para, 2004). Recent papers demonstrated the esterification of starch with sodium bismuthate in the solid state reaction providing starch bismuthate (Bączkowicz, Wojtowicz, Anderegg, Schilling, & Tomasik, 2003). Such reaction with magnesium hydrogen sulphate provided magnesium sulphated starch (Staroszczyk & Tomasik, 2005).

Selenium is one of the most interesting elements for its clinical and environmental effects. This element has been recognized as an essential micronutrient and antioxidant in the human and animal diet (Hamilton, 2004; Tapiero, Townsend, & Tew, 2003; Young, Nahapetian, & Janghorbani, 1982). Thus, in this study potato starch was esterified in the microwave induced reaction with sodium either selenite or selenate in order to prepare esters, potential sources of biologically available, released in controlled manner, selenium. Resulting products were characterized by means of the thermal analysis (TG/DTG/DTA), differential scanning calorimetry, high performance size exclusion chromatography equipped with multiangle laser light scattering (MALLS) detector and a differential refractive index detector, powder X-ray diffraction, and scanning electron microscopy.

2. Experimental part

2.1. Preparation method

Native potato starch (isolated in Potato Enterprise, Łomża, Poland in 2004), containing 4.7% moisture (10 g) was blended with either sodium selenite or sodium selenate (both min 98%), purchased from Sigma Germany. Amount of used selenium reagent was adjusted to have either the 1:1 or 1:0.1 molar D-glucose unit:selenium compound ratio.

The blends were thoroughly homogenized and situated in the microwave oven (Samsung M1711N, 2450 MHz) set, depending on the experiment, either for 450 or 800 W. In every case heating lasted 20 min. After the reaction was

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completed, the reaction mixture was cooled to room temperature and washed on the suction filter with ice-cold water (20 cm^3) followed by drying at 30 °C. Neither sodium selenite nor sodium selenate was found in the last portions of filtrates.

2.2. Determination of selenium

Samples (0.5 g) were mineralized under pressure in concentrated nitric acid (4 cm^3) in a microwave system (Mars Xpress, CEM GmbH, Kamp-Lintfort, Germany) at, subsequently, 50, 80, 100, 120, 150 °C for 120 s at each temperature and, finally, at 170 °C for 300 s. After cooling to room temperature the samples were filled with deionised water to the volume of 15 cm^3 and subjected to analysis with Atomic Absorption Spectrometer (Varian SpectrAA220FS, Victoria, Australia) equipped with automatic SIPS20 system of the sample injection. The calibration curve in the region of 0–50 mg/dm^3 provided absorbance in the 0–0.06 interval. Estimations were run in triplicates.

2.3. Thermogravimetry (TG) and differential thermogravimetry (DTG)

The analyses were performed on 100 mg samples. They were heated in the open in corundum crucibles from room temperature to 450 °C. The 10 °C/min rate of the temperature increase was applied. Corundum particles having $\phi = 8$ μm were used as the standard. The instrument of Paulik-Paulik Erdey D-1500-Q (Budapest, Hungary) was used. Analyses were run in duplicates.

2.4. Differential scanning calorimetry (DSC)

Measurements were performed on 10 mg samples sealed in aluminum pan with water in the 1:3 w/w ratio and heated in the range of 20–90 °C with the rate of 6 °C/min. Capsule filled with water served as a reference. Instrument self-assembled in Department of Physics was used. Measurements were run in triplicates.

2.5. High performance size exclusion chromatography (HPSEC)

A sample (100 mg) was placed in a 100 cm^3 measuring flask containing 10 cm^3 deionised water, the whole was gently agitated followed by addition of dimethyl sulfoxide (60 cm^3). The flask was heated up to 60 °C and the agitation at that temperature was maintained for 24 h. The resulting clear solution was cooled to 25 °C and dimethyl sulfoxide (90 cm^3) was added.

High performance size exclusion column chromatography (HPSEC) system consisted of a pump (Shimadzu 10AC, Tokyo, Japan), an injection valve (model 7021, Rheodyne, Palo Alto, USA), a guard column (TSK PWH, Tosoh Corporation, Tokyo, Japan), and two connected together SEC columns TSKgel GMPWXL (7.8 × 300 mm, Tosoh Corporation, Tokyo, Japan) and TSK Gel 2000 PW (7.8 × 300 mm, Tosoh Corporation, Tokyo, Japan). A multiangle laser light scattering detector Dawn-DSP-F (Wyatt Technology, Santa Barbara CA, USA), equipped with He–Ne laser emitting light with wavelength 630.0 nm and a differential refractive index detector (L-7490, Merck, Darmstad, Germany) were connected to the columns. Columns were maintained at 50 °C and RI detector at 30 °C. The mobile phase (0.15 M $NaNO_3$ with 0.02% sodium azide) was filtered subsequently through 0.2 and 0.1 μm cellulose acetate filters (Whatman, England). Flow rate of mobile phase was 0.4 cm^3 min^{-1}. The output voltage of refractive index (RI) and light scattering (LS) at 18 angles was used for calculation of the weight-average molecular weight (M_w) and radius of gyration (R_g) using Astra 4.73.04 software (Wyatt Technology, Santa Barbara CA, USA). One hundred microlitre samples were injected. The Berry plot (Aberle, Burchard, Vorwerg, & Radosta, 1994; Bello-Perez, Paredes-Lopez, Roger, & Colonna, 1996) with third order polynomial fit was applied for the calculation of M_w and R_g values. The recoveries of injected samples were between 92% and 95%.

2.5.1. Calibration of detector

Calibration constant for the RI detector was determined by injection of five (0.05–0.50 mg cm^{-3}) aqueous NaCl solutions of known concentration into the detector. Output voltage from the detector was collected by Rical 2 software (Wyatt Technology, Santa Barbara CA, USA) and calibration constant was calculated from the slope of the $fn = c\,dn/dc$ vs. voltage graph. The following values of dn/dc (change in refractive index with concentration) were used in calculation of the average molecular weight (M_w) and radii of gyration (R_g): pullulan 0.148, dextran 0.142, and starch 0.146. LS calibration constant for the diode at 90° was available from the LS intensity of toluene. Normalization of the response of the photodiodes arranged around the scattering cell to the diode at 90° was carried out using BSA. One pullulan and two dextran standards were applied for the accuracy test of the calibration.

The recovery of injected standards exceeded 95%. Determined M_w were 9.9×10^5, 6.2×10^5, 2.0×10^6 for pullulan P-100, dextrans D-580, and D-2000, respectively. These estimations were in good match with those given by the manufacturer (9.8×10^5, 5.8×10^5, and 2.0×10^6, respectively). All separation and calibration operations were run in duplicates.

2.6. Scanning electron microscopy (SEM)

Micrograms of 500× magnitude were taken with a E-SEM XL 30 (FEI Company, Eidhoven, The Netherlands) microscope equipped with a SE detector of secondary electrons. The instrument set for 20 kV accelerating voltage operated at low vacuum. The working distance was 7.5 mm.

2.7. Powder X-ray diffraction

The measurements were carried out using Cu K_{α} radiation of wavelength 0.154 nm on a Phillips 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° 2θ were recorded at a scan rate of 0.02 2θ/s.

3. Results and discussion

Selenation of potato starch was carried out on microwave heating of starch blended with varying amount of sodium selenite or selenate. Results of the elemental analysis (Table 1) revealed that, in both cases, degree of the esterification (DE) did not exceed 3.01×10^{-2}. The reaction with selenite provided higher DE. DE increased with the applied power of the microwave oven but increased amount of admixed selenium reagents had no positive effect upon DE. A generally low DE likely resulted from the solid state character of those reactions. Selenium reagents could not penetrate into the granule interior leaving it unreacted. Moreover, the facilitating the first step of esterification electron gap at the selenium atom of selenate and selenite was reduced by possible hybridization with participation of d-orbitals of that atom and, in a consequence, extension of the outer valence shell from octet into decet. It made the selenium atom a relatively poor site for nucleophilic attack from the hydroxyl groups of the D-glucose units. Together with the steric effect, more pronounced in case of selenate it explained better results in selenition than in selenation.

The thermal analysis provided evidence for the reaction between the components of the blend. Thermogram of native potato starch (Fig. 1) revealed the one step decomposition of that starch at 277 °C. Its exposure to the microwave radiation slightly decreased temperature of the decomposition (to 275 °C). Moreover, the slope of the TG line turned milder as the applied power increased (Table 2). The pattern of the diagrams remained essentially the same.

Table 1
Determination of the degree of esterification in selenated starches

Reaction mixture	Amount of selenium in the product (mg)		DE[a] $\times 10^{-3}$
	Calculated[b]	Found	
1:0.1 starch:Na_2SeO_4(450 W)	44.61	0.01	0.15
1:0.1 starch:Na_2SeO_4(800 W)	44.61	0.84	18.89
1:1 starch:Na_2SeO_4(450 W)	253.89	0.07	0.26
1:1 starch:Na_2SeO_4(800 W)	253.89	1.36	5.36
1:0.1 starch:Na_2SeO_3(450 W)	45.12	0.01	0.21
1:0.1 starch:Na_2SeO_3(800 W)	45.12	1.36	30.14
1:1 starch:Na_2SeO_3(450 W)	267.66	0.01	0.04
1:1 starch:Na_2SeO_3(800 W)	267.66	2.46	9.18

[a] Degree of esterification.
[b] Assuming 100% reaction yield.

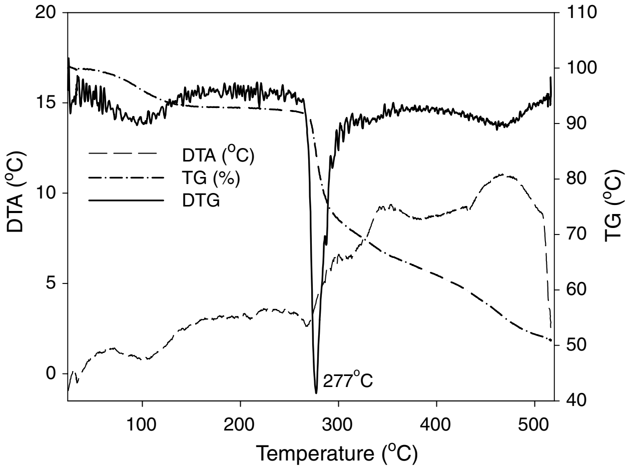

Fig. 1. Thermograms of native potato starch.

Table 2
Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis of native potato starch (PS) and its selenate and selenite esters

Sample	TG			DTG[a] (°C)
	Temperature range (°C)	Weight loss (%)	Slope (TG α)	
PS: native	25–157	4.7		
	257–310	46.6	2.32	273
Heated at: 450 W	25–157	1.2		
	257–310	25.7	1.26	275
800 W	25–157	1.0		
	256–310	24.1	1.14	273sh
Selenates				
1:0.1 at: 450 W	25–156	4.2		
	256–309	25.5	1.70	282
800 W	25–157	3.4		
	257–309	23.8	1.54	283
1:1 at: 450 W	25–157	4.6		
	257–309	24.7	1.68	288
800 W	25–156	5.2		
	257–309	24.3	1.32	284sh, 287
Selenites				
1:0.1 at: 450 W	25–156	3.3		
	257–310	24.2	1.53	290, 293sh
800 W	25–157	4.0		
	256–322	23.5	0.82	297sh, 300
1:1 at: 450 W	25–156	6.3		
	257–309	24.0	1.61	278
800 W	25–157	3.2		
	257–320	22.8	0.79	297sh, 300

[a] sh denotes a shoulder.

The thermal stability of selenate ester of starch was higher than that of native starch (Fig. 2). The increase in the thermal stability of the products did not depend on the irradiation energy applied and amounted to 5 and 10 °C for small and large initial doses of selenate, respectively.

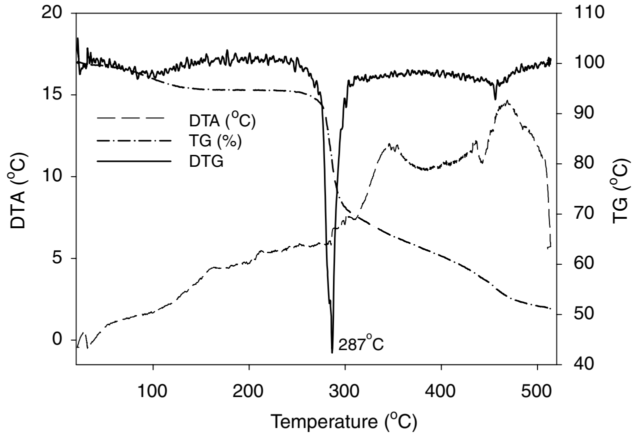

Fig. 2. Thermograms of native potato starch blended at proportion 1:1 with selenate and heated with 800 W energy.

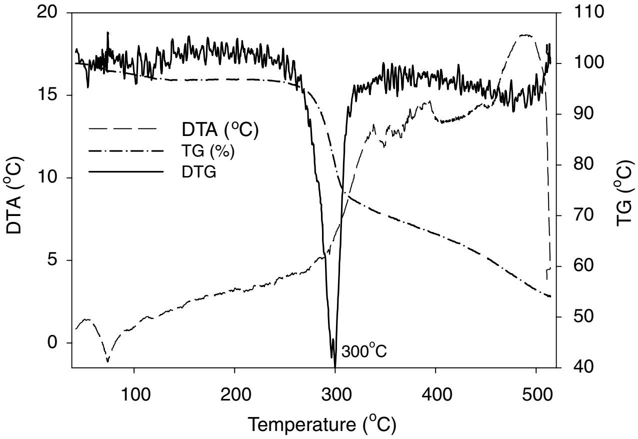

Fig. 3. Thermograms of native potato starch blended at proportion 1:1 with selenite and heated with 800 W energy.

In case of the selenite ester of starch (Fig. 3) that increase depended on the applied power of the oven, and for small doses of selenite it reached 13 and 23 °C for 450 and 800 W, respectively, and for large selenite doses 2 and 23 °C, respectively. Such changes of the thermal properties on the esterification could result from the hydrogen bond interactions between introduced selenite and selenate moieties, (1) and (2), and the hydroxyl groups of the D-glucose units (D-Glc). Crosslinking could also be involved providing products of the structures (3) and (4), respectively. The latter was formerly proposed as the structural factor in bismuthated (Bączkowicz et al., 2003) and phosphated (Tomasik & Schilling, 2004) starches. Thus, crosslinking of starch through the esterification with involvement of two reaction centres of dibasic mineral acids might be common. The intra- or inter-molecular character of that crosslinking as well as which hydroxyl groups of the D-glucose units esterified selenium reagents remained unknown.

An insight in Table 2 revealed that after the esterification, the thermal stability of starch increased. Starch selenite was more stable than starch selenate. An increase in the thermal stability could result from developed inter- and intra-molecular hydrogen bonds involving the hydroxyl groups and selenite and selenate group oxygen atoms. Esterifying crosslinking could also be a factor. In respect to starch, the weight loss in particular decomposition steps of the selenite and selenate esters decreased by approximately the same magnitude. Based on the slope of the TG line in particular decomposition steps selenates decomposed with a higher rate than selenites. Such changes in the thermal properties of esters again suggest that esterification might result in crosslinking of starch.

The microwave heating of the control sample of potato starch resulted in a decrease in the phase transition enthalpy with the increase in applied power of the microwave oven (Table 3). The magnitude of the effect of the phase transition decreased with the heating power applied and, finally, there was very weak phase transition observed in the product heated at 800 W. Molecular weight of the reaction products was always lower than that of original starch but almost always higher than that of plain starch heated

Table 3
DSC calorimetric parameters and weight-average molecular weight (M_w) for potato starch and its selenite and selenate esters

Sample	Starch gelatinization			$M_w \times 10^6$
	T_o (°C)[a]	T_p (°C)[b]	ΔH (J/g)[c]	
Native potato starch (PS)	59.2	65.4	12.9	18.04 ± 0.00
PS at 450 W	55.2	62.3	11.3	12.35 ± 0.00
PS at 800 W	51.2	64.0	1.8	0.11 ± 0.01
Starch:Selenium compound				
1:0.1 Selenate at 450 W	56.2	62.4	11.1	14.94 ± 0.00
1:1 Selenate at 450 W	56.2	62.8	11.7	9.01 ± 0.03
1:0.1 Selenite at 450 W	57.3	63.0	12.8	15.93 ± 0.01
1:1 Selenite 450 W	57.0	62.8	11.6	10.22 ± 0.07
1:0.1 Selenate 800 W	51.2	57.3	4.9	1.53 ± 0.01
1:1 Selenate 800 W	49.5	57.3	6.7	2.01 ± 0.02
1:0.1 Selenite 800 W	54.6	60.9	9.3	9.08 ± 0.05
1:1 Selenite 800 W	55.0	60.6	8.9	8.81 ± 0.03

[a] The onset temperature.

[b] The peak temperature.

[c] The phase transition (melting) enthalpy. The precision of all estimations did not exceed beyond ±10% of determined value.

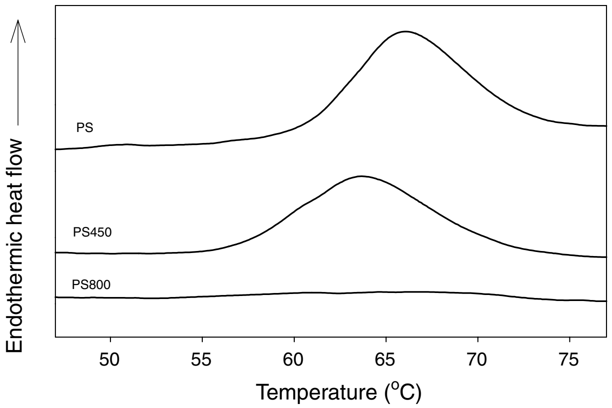

Fig. 4. DSC thermograms of native potato starch (PS) and microwave heated starch with 450 W (PS450) and 800 W (PS800) energy.

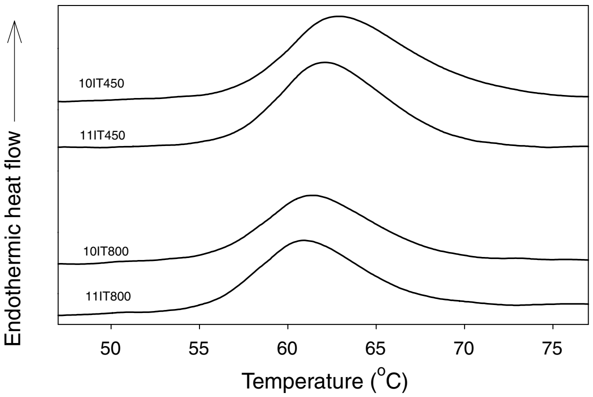

Fig. 6. DSC thermograms of starch blended with selenite at proportions 1:0.1 (10) and 1:1 (11) and heated at 450 W and 800 W.

under identical reaction conditions (Table 3). It could be an additional argument speaking in favour of esterifying crosslinking with selenite and selenate, however, assisted with increasing with the applied power and exposition time, destruction of starch (Fig. 4). The reaction at the high power of the oven resulted in an increase in the molecular weight, more pronounced for selenite than for selenate derivatives.

The enthalpy of the phase transition of starch blends with selenates after heating at 450 W practically remained unaffected whereas an insignificant increase in enthalpy was noted for selenite. The DSC thermograms of the starch blends with selenite (Fig. 5) and selenate (Fig. 6) revealed that in the first case the blend proportion and power applied had stronger effect on the temperature of the phase transition than in the second case.

Application of 800 W to all blends resulted in the decrease in the phase transition enthalpy in respect to those of heated at 450 W, but the significant increase as compare to that of control. The change of the power of the oven from 450 to 800 W resulted in a decrease in the phase transition temperature. In the case of selenate heated with starch it decreased below that for control sample. These changes might also advocate for crosslinking on the esterification, although the M_w magnitudes after esterification decreased. The degradation of starch on any its processing is common, even on its graft polymerisation, obviously performed for production of starch derivatives of higher molecular weight than original starch.

The diffractogram of native potato starch displayed the typical B-type pattern. Differences observed in the diffraction patterns of the control samples of starch heated at 450 or 800 W indicated a collapse at the crystallinity, more pronounced for starch heated at 800 than 450 W. The admixture of either selenite or selenate inhibited the thermal decomposition of the starch matrix as shown by sharper diffraction patterns (Fig. 7).

The peak at about 17° 2θ, which represented monoclinic crystal system characteristic for the B-type starch, was intensive for Se(IV) and week for Se(VI) containing starches.

Regardless of the conditions applied, the processing of starch without selenium reagents retained its granularity.

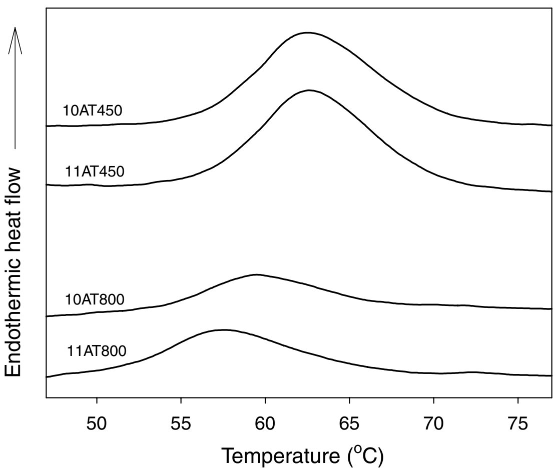

Fig. 5. DSC thermograms of starch blended with selenate at proportions 1:0.1 (10) and 1:1 (11) and heated at 450 W and 800 W.

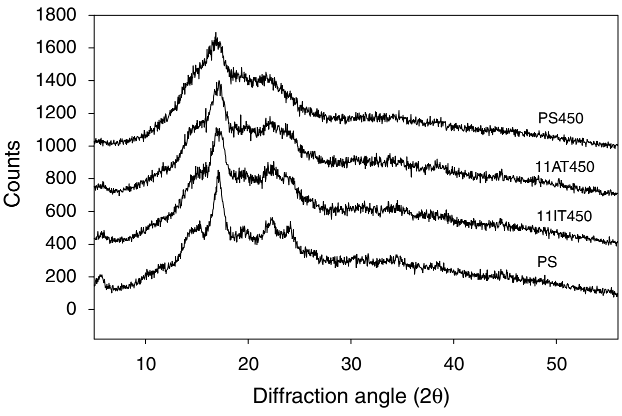

Fig. 7. Powder X-ray diffractograms of native potato starch (PS) prior and after 20 min heating and at 450 W (PS450) as well as the reaction products resulting from heating under identical conditions with selenite (IT) and selenate (AT) (PS: selenium compound = 1:1).

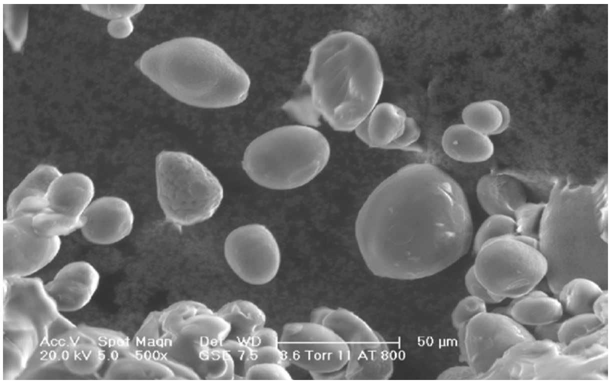

Fig. 8. SEM image of starch granules heated 20 min at 800 W with sodium selenate in the 1:1 (w/w) blend.

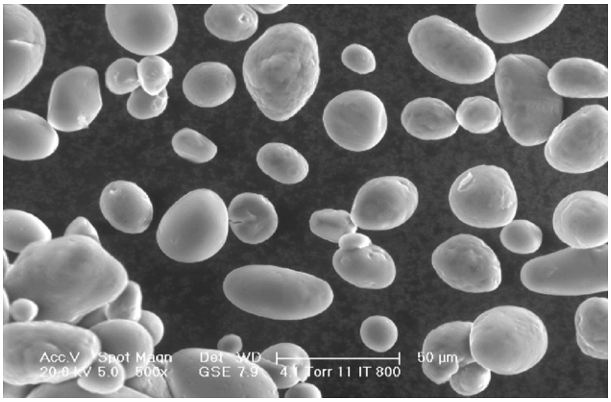

Fig. 9. SEM image of starch granules heated 20 min at 800 W with sodium selenite in the 1:1 (w/w) blend.

No coarseness or damage was observed on the surface of the potato starch granules. The granule surface appeared smooth, oval, and irregularly shaped. In both selenation reactions, with selenate and selenite, granularity of the products was retained (Fig. 8). However, after heating of starch blends with selenite the granules were aggregated and after heating with selenate more amorphous material surrounded granule. Small deformations seen on the surface of granules could indicate that granules swelled to a certain extent and the selenium reagent could penetrate granules (Fig. 9).

Inspection of the powder X-ray diffractograms of the reaction products showed that the crystallinity of the granules significantly decreased.

The heating at 800 W obviously was critical for the crystallinity of starch granules. The esterification inhibited, to a certain extent that degradation. The esterification with selenate was more starch structure conserving than that with selenite (Fig. 10). Throughout this paper, evidences for crosslinking esterification of starch were collected. Simultaneously, observed gelatinization of selenated starches could, apparently, contradict suggested crosslinking. One should pay attention that granularity of starch was retained on that esterification. Thus, the random esterification could occur on the granule surface and in selected regions of the granule interior. Non-esterified portion of the granule material could gelatinize.

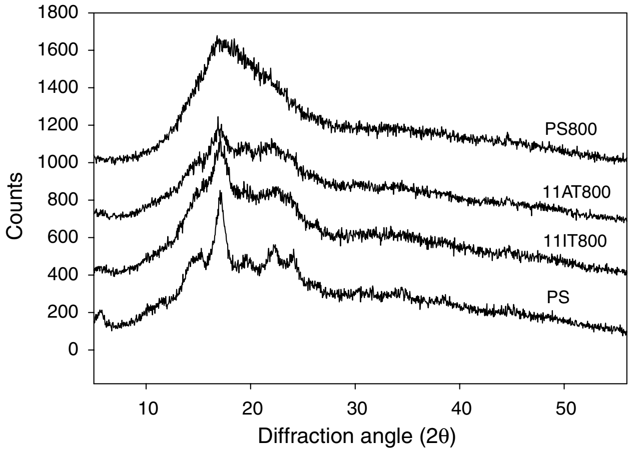

Fig. 10. Powder X-ray diffractograms of native potato starch (PS) prior and after 20 min heating at 800 W (PS800) as well as the reaction products resulting from heating under identical conditions with selenite (IT) and selenate (AT) (PS: selenium compound = 1:1).

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