Post-print of: Staroszczyk H., Fiedorowicz M., Opalińska-Piskorz J., Tylingo R.: Rheology of potato starch chemically modified with microwave-assisted reactions. LWT-FOOD SCIENCE AND TECHNOLOGY. Vol. 53, iss. 1 (2013), p. 249-254. DOI: 10.1016/j.lwt.2013.01.009

Rheology of potato starch chemically modified with microwave-assisted reactions

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abstract

Native potato starch was sulfated, selenated, borated, silicated and zincatated by means of microwave-assisted reactions with varying doses of relevant reagents. Resulting products were characterized involving rheological behavior of pastes, their weight-average molecular weight (M_w), and radius of gyration (R_g). Most of the pastes showed shear-thinning behavior, with the flow behavior index (n) below unity. The pastes of starch sulfated and borated with boric acid exhibited n higher than native potato starch paste. They had significantly lower consistency index (K) and plastic viscosity (η_c) and no yield stress (σ_{oc}). M_w values of these starches were considerably reduced. The pastes of starch selenate, borate after borax, and silicate after silicic acid, with n lower than native potato starch, had similarly lower K and η_c but, simultaneously, they showed non-zero σ_{oc} values, and σ_{oc}, M_w and R_g of starch selenate were reagent concentration dependent. Also magnitudes of n, K, η_c, σ_{oc}, M_w and R_g of pastes of starch silicate after sodium metasilicate and zincatate were reagent concentration dependent. While their n rose with concentration, K and η_c significantly decreased, and σ_{oc} ceased. The effect of temperature on the apparent viscosity of modified starch pastes followed Arrhenius equation.

Keywords: Boration, Selenation, Silication, Sulfation, Zincatation, Paste rheology

1. Introduction

Apart from cellulose, starch is the most common and the most readily available polysaccharide. Modern technologies offer a high yield extraction of pure starch from diverse plants making this polymer one of the most versatile among raw plant materials. Numerous physical (Tomasik, Wiejak & Pałasiński, 1989; Tomasik & Zaranyika, 1995), physicochemical (Tomasik & Schilling, 1998a, 1998b), chemical (Tomasik & Schilling, 2004) and enzymatic (Tomasik & Horton, 2013) techniques converting starch to several useful derivatives considerably extend the range of its applications.

Chemical modification of starch with at least dibasic acids, their anhydrides and salts, provides ester-type derivatives of starch of anionic properties (Tomasik & Schilling, 2004). Such properties are crucial for intermolecular interactions with other, oppositely charged macromolecules, for instance, with proteins. In such manner binary systems are formed which combine properties of both partners (Najgebauer, Grega, Sady, & Tomasik, 2003; Najgebauer, Grega, Sady, & Tomasik, 2004; Rutiaga et al., 2005; Tolstoguzov, 1986; Zaleska, Ring, & Tomasik, 2000; Zaleska, Ring, & Tomasik, 2001a, 2001b). Enjoying with a wide potential application, biodegradable polysaccharide-protein materials can be derived from them, and modified starch can contribute to the improvement of their functional properties (Lacroix, 2009; Rutiaga et al., 2005). Because even the smallest change in molecular conformation and structure of starch due to its modification can result in dramatic changes in its physicochemical properties (Djakovic & Dokic, 1972), any control of final properties of starch-based products a good knowledge of the influence of starch modification on its properties is indispensable.

It was found that microwave irradiation offers a facile synthesis of starch esters (Kaur, Ariffin, Bhat, & Karim, 2012), including inorganic starch esters such as phosphates produced usually by roasting relevant reagents (Lewandowicz et al., 2000; Mao, Wang, Meng, Zhang, & Zheng, 2006). Although microwave-assisted preparation of sulfated (Staroszczyk, Fiedorowicz, Zhong, Janas, & Tomasik, 2007), borated (Staroszczyk, 2009a), selenated (Staroszczyk, Tomasik, Janas, & Poreda, 2007), silicated (Staroszczyk, 2009b; Staroszczyk & Janas, 2010a), and zincatated (Staroszczyk & Janas, 2010b) starch has also been extensively studied, there is no information on the rheological properties of these starch derivatives. Such data are important for their handling, processing and utilization. Therefore, in this paper an influence of modification of potato starch with the pyridine × SO_3 complex, sodium selenite and sodium selenate, boric acid, sodium tetraborate decahydrate (borax),

http://dx.doi.org/10.1016/j.lwt.2013.01.009

sodium metasilicate, silicic acid and generated *in situ* sodium tetrahydroxozincate on starch rheological behavior and changes in its weight-average molecular weight is presented.

2. Materials and methods

2.1. Materials

Native potato starch, of moisture content either 4.5 or 13.0 g/100 g, was isolated in Potato Enterprise in Łomża (Poland). Pyridine × SO_3 complex (Merck, Darmstadt, Germany), minimum 98% sodium selenite and minimum 98% sodium selenate (Sigma, Steinheim, Germany), boric acid (POCH S.A., Gliwice, Poland), sodium tetraborate decahydrate (borax) (Lach-Ner s.r.o., Neratovice, Czech Republic), over 97% sodium metasilicate pentahydrate (Fluka, Zwijndrecht, Netherlands) and over 99% powder silicic acid hydrate (Fluka, Zwijndrecht, Netherlands) were used as reagents. Sodium tetrahydroxozincate was prepared *in situ* from zinc oxide (Sigma—Aldrich, Poznan, Poland) and sodium hydroxide (P.P.H. Stanlab, Lublin, Poland) following procedure of Staroszczyk & Janas, 2010b.

2.2. Preparation of starch derivatives

As previously described in our papers (Staroszczyk, 2009a,b; Staroszczyk, Fiedorowicz, et al., 2007; Staroszczyk & Janas, 2010a,b, Staroszczyk, Tomasik, et al., 2007), native potato starch was blended with a given reagent at selected molar D-glucose unit: inorganic reagent ration and the blends after a thorough homogenization were placed in a microwave oven (Samsung M1711N, 2450 MHz). Applied energy of 180, 300, 450, 700 and 800 W and time of exposition ranging from 1 to 30 min were combined depending on reagent used and experiment as given in Table 1. After the reactions were completed, the starch selenation and boration products were cooled to room temperature, washed on the suction filter with ice-cold water (30 mL) and dried at 40 °C. The starch sulfation products were dissolved in aq. K_2CO_3 solution (8 g/100 g), precipitated with ethanol, washed with petrol ether on filters and dried at 40 °C. The starch silication with silicic acid products were shaken with ammonia solution (20 mL), followed by drying at 30 °C. The products of starch silication with sodium metasilicate and starch zincatation were analyzed without any purification. The pH level of starch modification products was measured in solutions prepared for viscosity investigations.

2.3. Rheological measurements

Granular starch suspensions (3 g/100 mL) were gently stirred for 15 min at room temperature and then 30 min heated at 95 °C in a water bath shaker to avoid the starch particles sedimentation and agglomeration. Prepared hot pastes were placed into Brookfield Digital Model DVIII Ultra viscometer (Middleboro, MA, USA) equipped with temperature-controlled bath, and their rheological properties were tested. All rheological measurements were performed in triplicates.

To determine the rheological properties under steady shear rate conditions, the hot pastes were cooled down to 25 °C in the measuring system, kept in this temperature for 30 min, and then shear stress produced by shearing at rates ranging from 0.1 to 330 s^{-1}, resulting from 0.08 to 250 rpm of the spindle SC4-18 was recorded.

To determine the effect of temperature upon rheological properties, the hot pastes were cooled down to 80 °C in the measuring system, equilibrated at this temperature for 10 min before the first measurement was taken, and then the apparent viscosity at constant shear rate of 0.34 or 84 s^{-1}, given by 1 or 250 rpm of the spindle SC4-27, respectively, in the temperature range of 80—20 °C was measured.

2.4. HPSEC-MALLS-RI

Starch samples (100 mg) were moistened with 10 mL water, prior to an addition of 90 mL of dimethyl sulfoxide, and then the mixtures were gently agitated, while their temperature was gradually increased to 60 °C. Agitation at latter temperature was maintained for 24 h, followed by cooling to room temperature and injection of the resulting transparent and visually homogeneous solutions onto the high performance size exclusion column chromatography (HPSEC) system, by means of which the weight-average molecular weight (M_w) and the radius of gyration (R_g) of starch samples were measured.

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 2500 PWXL (300 × 7.8 mm, Tosoh Corporation, Tokyo, Japan). A multi-angle laser light scattering detector Dawn-DSP-F (Wyatt Technology, Sta. Barbara, CA, USA) and a differential refractive index detector L-7490 (Merck, Darmstadt, Germany) were connected to the columns. The temperature of columns was maintained at 50 °C, and that of the refractive index (RI) detector — at 35 °C. The mobile phase used in measurements was 0.15 M $NaNO_3$ with 0.02% NaN_3, filtered off through 0.2 and 0.1 μm cellulose acetate filters (Whatman, England), and the flow rate and the sample injection volume were 0.4 mL/min and 100 μL, respectively. The output voltages of the RI and light scattering (LS), at 18 angles, were used for calculation of the M_w and R_g, using Astra 4.73.04 software (Wyatt Technology, Santa Barbara, CA, USA). The calculations were carried out by using the Berry plot with the third order polynomial (Aberle, Burchard, Vorwerg, & Radosta, 1994; Bello-Perez, Paredes-Lopez, Roger, & Colonna, 1996).

The recovery of all the injected standards used for calibration was over 95%, and the determined M_w values were 9.9×10^5 for pullulan P-100, and 6.2×10^5 and 2.0×10^6 for dextrans D-580 and D-2000, respectively. These values well matched 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 triplicates.

2.5. Statistical analysis

The data obtained 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 $p < 0.05$.

3. Results and discussion

3.1. Rheological properties

The rheological properties of starch pastes were analyzed in terms of the power law described by the equation:

$$\sigma = K\dot{\gamma}^n, \tag{1}$$

where σ is the shear stress (Pa),$\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency index (Pa · s^n), and n is the flow behavior index (dimensionless), and the Casson model defined by the relation:

$$\sqrt{\sigma} = K_{oc} + K_c\sqrt{\dot{\gamma}}, \tag{2}$$

in which $(K_c)^2$ is the Casson plastic viscosity (η_c). The Casson model (2) provides determination of the yield stress (σ_{oc}). The latter was determined as the square of the intercept (K_{oc}) from linear regression of square roots of shear rate — shear stress data.

Table 1
Effect of the microwave-assisted modification on rheological properties, weight—average molecular weight, radius of gyration, and pH of potato starch (PS).

Sample[a] (reaction conditions)[b]	Power law			Casson model			Arrhenius equation			$M_w \times 10^6$	R_g (nm)	pH
	K (mPas^n)	n (−)	R^2	σ_{oc} (Pa)	η_c (mPas)	R^2	A (mPas)	E_a (kJ/mol)	R^2			
PS (none)	380.40	0.43	0.990	0.71	1389.00	0.973	25.53	16.82	0.990	18.04[d]	94.9	6.5
(180 W, 5 min)	313.30	0.22	0.986	1.42	409.20	0.995	86.49	11.68	0.988	18.00	88.2	6.4
(300 W, 1 min)	325.00	0.22	0.983	1.43	448.80	0.986	85.60	11.65	0.995	17.57	77.9	6.3
(700 W, 1 min)	284.60	0.31	0.987	0.88	669.00	0.996	90.02	11.49	0.995	18.60	77.2	6.4
(800 W, 5 min)	384.60	0.43	0.984	0.75	682.00	0.974	68.72	11.60	0.995	16.37	78.2	6.3
(450 W, 20 min)	17.50	0.49	0.989	0.22	10.20	0.989	100.48	10.74	0.994	12.35[d]	65.9	6.1
(450 W, 30 min)	15.70	0.53	0.983	0.19	9.67	0.984	83.10	10.39	0.994	12.22	68.3	6.1
(800 W, 20 min)	0.13	1.03	0.970	0.00	1.97	0.691	0.29	8.18	0.985	0.11[d]	24.7	4.7
PS: pyridine × SO_3 complex (180 W, 5 min)												
1:0.1	1.32	0.72	0.996	0.06	1.35	0.996	0.02	12.76	0.997	3.90	89.8	5.4
1:0.75	0.27	0.87	0.990	0.01	1.03	0.990	0.27	2.88	0.996	0.07	49.1	5.5
PS: pyridine × SO_3 complex (300 W, 1 min)												
1:0.1	2.29	0.63	0.994	0.11	1.08	0.994	0.41	6.41	0.995	4.90	69.2	5.6
1:0.75	5.89	0.49	0.978	0.24	0.84	0.979	0.04	11.32	0.989	0.26	70.2	5.6
PS:selenite (450 W, 20 min)												
1:0.1	255.60	0.31	0.944	0.83	539.50	0.941	78.26	10.79	0.977	15.93[d]	83.0	7.2
1:1	278.40	0.39	0.942	0.67	811.30	0.935	80.64	10.53	0.997	10.22[d]	62.8	7.2
PS:selenite (800 W, 20 min)												
1:0.1	69.30	0.16	0.985	1.21	0.16	0.986	71.52	10.24	0.990	9.08[d]	72.6	6.8
1:1	92.50	0.39	0.993	0.44	94.20	0.987	79.84	9.28	0.998	8.81[d]	73.3	6.6
PS:selenate (450 W, 20 min)												
1:0.1	250.50	0.35	0.959	0.66	692.80	0.965	24.29	13.85	0.988	14.94[d]	77.7	6.5
1:1	88.90	0.28	0.986	0.31	175.50	0.990	96.54	10.14	0.980	9.01[d]	76.7	6.3
PS:selenate (800 W, 20 min)												
1:0.1	36.40	0.25	0.989	0.84	0.33	0.990	0.09	26.84	0.979	1.53[d]	54.0	6.3
1:1	40.80	0.33	0.989	0.23	28.30	0.985	27.39	12.50	0.921	2.01[d]	51.8	6.2
PS:boric acid (450 W, 20 min)												
1:0.1	14.00	0.50	0.993	0.17	7.04	0.993	0.07	12.88	0.992	0.66	96.3	5.6
1:1	0.20	0.99	0.994	0.00	1.86	0.994	0.30	8.46	0.914	1.81	213.3	5.0
PS:boric acid (800 W, 20 min)												
1:0.1	1.01	0.74	0.995	0.05	1.25	0.996	0.01	16.27	0.990	1.00	109.6	5.5
1:1	1.00	0.70	0.998	0.05	0.87	0.998	0.25	6.70	0.990	0.11	47.6	5.3
PS:borax (450 W, 20 min)												
1:1	113.80	0.24	0.981	1.40	6.17	0.984	0.06	27.80	0.941	7.34[e]	56.5	7.6
PS:borax (800 W, 20 min)												
1:1	58.70	0.30	0.978	0.74	5.76	0.980	0.13	14.77	0.997	1.27[e]	96.9	7.6
PS:silicate (450 W, 30 min)												
1:0.1	131.40	0.31	0.987	0.41	297.70	0.980	52.46	10.85	0.995	7.01	62.1	7.7
1:1	0.03	1.23	0.979	0.02	1.93	0.622	0.61	5.30	0.877	16.24	60.6	7.9
PS:silicate (800 W, 5 min)												
1:0.1	303.00	0.46	0.956	0.51	1178.00	0.949	16.28	13.57	0.994	8.74	66.2	7.8
1:1	0.72	0.79	0.995	0.03	1.38	0.995	0.83	3.64	0.853	3.19	54.7	7.9
PS:silicic acid (450 W, 20 min)												
1:1	198.90	0.38	0.994	0.98	186.90	0.987	0.58	22.17	0.953	11.13	60.1	7.2
PS:silicic acid (800 W, 20 min)												
1:1	214.40	0.09	0.989	2.94	0.10	0.989	0.03	16.12	0.986	Nd[c]	Nd[c]	7.4
PS:zincate (450 W, 30 min)												
1:0.1	275.20	0.39	0.955	0.64	837.00	0.995	242.26	6.02	0.881	13.60	70.1	7.7
1:0.5	9.10	0.89	0.985	0.04	15.80	0.955	42.95	9.46	0.952	2.43	42.1	7.9
PS:zincate (700 W, 1 min)												
1:0.1	572.90	0.42	0.935	1.24	1784.00	0.933	79.84	11.47	0.987	19.64	100.8	7.7
1:0.5	6.30	0.72	0.991	0.05	13.30	0.991	11.94	12.08	0.990	0.56	28.4	7.9

[a] PS: modifying reagent initial ratio.
[b] Power and time of microwave irradiation.
[c] Not determined.
[d] Staroszczyk, Fiedorowicz, et al., 2007.
[e] Staroszczyk (2009a).

The Arrhenius equation (3) was used for consideration of the viscosity—temperature relationships:

$$\eta_a = A \cdot \exp\left(\frac{E_a}{RT}\right), \tag{3}$$

where η_a is the apparent viscosity (Pa · s) at constant shear rate, A is a constant (Pa · s), T is absolute temperature (K), R is the gaseous constant (8.3144 J/mol K), and E_a is the activation energy (kJ/mol). The magnitudes of E_a and A were determined from a regression analysis of the ln η_a vs. 1000/T dependence.

The shear stress (σ) versus shear rate ($\dot{\gamma}$) data determined at 25 °C revealed that all starch pastes followed the power law (1) with determination coefficients $R^2 = 0.935–0.998$. According to this model, apparent viscosity, i.e. $\sigma/\dot{\gamma}$, decreased with increasing shear rate, with the flow behavior index (n) almost always below unity (Table 1). Since $n < 1$ points to non-Newtonian flow when fluid becomes thinner with the shear rate increase (Holdsworth, 1971; Rao, 1999; Schramm, 1994), all starch pastes with $n < 1$ were pseudoplastic. The lower value of n they had, the more shear-thinning behavior they exhibited, and, in turn, the higher value of n they had, their viscosity was less dependent on changes of the shear rate. Typical Newtonian flow is exhibited by fluids of low molecular weight, and the molecular interactions lead to non-Newtonian flow behavior (Holdsworth, 1971). Therefore, likely the higher values of n recorded for plain starch exposed for a longer time to microwaves and starches either sulfated or borated with boric acid pointed to depolymerization of starch polysaccharides. The pH values of these starch samples were in the range of 4.7–5.6. The shear-thinning behavior of starch pastes with the lower values of n could be ascribed to disentangling, stretching and ultimately breaking of long polysaccharide chains in the starch network produced by increasing shear rates (Bhandari, Singhal, & Kale, 2002; Schramm, 1994). Such behavior showed starches either selenated, silicated with silicic acid or borated with borax. Their pH values were in the range of 6.2–7.6.

The n values of pastes of starch silicated with sodium metasilicate and zincatated with sodium tetrahydroxozincate were reagent concentration dependent. That parameter was close to n of unprocessed starch paste when a low concentration of the modifier was applied (1:0.1 potato starch: modifier initial ratio), and rose when its concentration increased. The pH values of these starch samples were in the range of 7.7–7.9.

Both, sulfur trioxide coordinated to pyridine and boric acid could contribute to hydrolysis of starch matrix. In contrast to it, esterification with hydrolyzing salts of strong base and weak acids, i.e. with the sodium all selenite, selenate, tetraborate, metasilicate and zincic acids produced sodium hydroxide. As long as the microwave-assisted modification of starch proceeded in the solid-state that hydroxide remained non-dissociated. However, on pasting, solution turned alkaline initiating degradation of starch under alkaline conditions assisted by oxidation (Tomasik & Schilling, 2004).

The rheological data obtained under steady shear conditions indicated that in pastes from plain starch irradiated for a short-time only slight changes of the consistency index (K), only 2–3 fold decrease in the plastic viscosity (η_c), and an increase in the yield stress (σ_{oc}) could be observed. Pastes after a prolonged irradiation exhibited a marked decrease in all three rheological parameters (Table 1). It was a result of deeper degradation of polysaccharide molecules. As the longer chains form network of significantly higher number of intermolecular bonds, they required much larger external forces to overcome the forces forming the network and, therefore, they have the much larger internal resistance to the flow, reflected by higher viscosity (Schramm, 1994). Likely, the prolonged irradiation of starch reduced the number of intermolecular bonds remaining in the network, hence the starch pastes had significantly lower K, η_c and σ_{oc} being less resistant to shearing.

Pastes of modified starches, with n higher than n of native potato starch paste, i.e. pastes of starch sulfated and borated with boric acid, had significantly lower parameters K and η_c than the pastes of native and microwave irradiated starches. Their yield stress completely cesased. In contrast to them, the pastes with n lower than that of native potato starch, i.e. pastes of starch selenated, borated with borax and silicated with silicic acid, had, in fact, lower K and η_c parameters than of native potato starch. However, their K values were significantly higher than the respective values for irradiated plain starch and they all showed yield stress values. The magnitudes of K, η_c and σ_{oc} parameters of pastes of starch silicated with sodium metasilicate and zincatated with sodium tetrahydroxozincate, as well as their n, were reagent concentration dependent and significantly decreased with an increase in a dose of the reagent.

From these observations one can assume that extra intensive intermolecular association took place in the starch network after its selenation, boration with borax and silication with silicic acid. Unlike the weakened shear-thinning behavior of pastes of starch sulfated and borated with boric acid, starch pastes mentioned above had strengthened shear-thinning behavior, with the yield stress values higher than these observed for starch microwave irradiated without any reagent. The high shear-thinning behavior of pastes of starch silicated with sodium metasilicate and zincatated with sodium tetrahydroxozincate with low doses of reagents resembled those of starch selenated, borated with borax and silicated with silicic acid. On the contrary, the weakened shear-thinning behavior of pastes of these starches modified with high doses of reagents were similar to those of starch sulfated and borated with boric acid. Therefore, likely sodium metasilicate and sodium tetrahydroxozincate used in low concentrations resulted in increased intermolecular associations in starch network, while used in high concentrations contributed to degradation of polysaccharide chains of starch.

3.1.1. *Effect of temperature on apparent viscosity*

Table 2 shows the effect of microwave-assisted modification of starch on apparent viscosity (η_a) of its pastes within the temperature range of 80–20 °C, determined at constant shear rate of 0.34 s^{-1}. Presented data demonstrate that decrease in temperature from 80 to 20 °C of pastes from all starches modified for 20 min at 450 W as well as plain starch irradiated in such manner resulted in an increase in η_a.

The paste of native potato starch had the higher activation energy (E_a) than the pastes from all starches processed on short irradiation. Prolonged irradiation in some cases resulted in increase in E_a over that for the paste from native starch (Table 1). Thus, the increase in viscosity with decrease in temperature was always more pronounced in native than in short-time processed starch pastes. Increase in E_a was associated with a higher sensitivity of viscosity to temperature (Holdsworth, 1971).

Table 2

Effect of the microwave-assisted selenation of potato starch (PS) on apparent viscosity ($\eta_{a,}$ mPas)[a] of its pastes at temperature range of 80–20 °C, determined at shear rate of 0.34 s^{-1}. The values in a particular lines and columns marked with various characters (a–f) and (A–G), respectively, differ significantly at $p < 0.05$.

Temperature (°C)	PS		PS: selenite[b] (450 W, 20 min)[c]		PS: selenate[b] (450 W, 20 min)[c]	
	Native	450 W, 20 min[c]	1:0.1	1:1	1:0.1	1:1
80	$7354 \pm 355^{d,A}$	$3903 \pm 260^{c,A}$	$2540 \pm 111^{a,A}$	$2878 \pm 73^{b,A}$	$2392 \pm 268^{a,A}$	$2608 \pm 94^{a,b,A}$
70	$9588 \pm 13^{e,B}$	$4298 \pm 16^{d,B}$	$3281 \pm 19^{c,B}$	$3222 \pm 12^{b,B}$	$2988 \pm 17^{a,B}$	$3213 \pm 47^{b,B}$
60	$11{,}736 \pm 16^{e,C}$	$4797 \pm 11^{d,C}$	$3897 \pm 25^{c,C}$	$3634 \pm 28^{a,C}$	$3618 \pm 12^{a,C}$	$3773 \pm 25^{b,C}$
50	$11{,}448 \pm 12^{f,D}$	$5364 \pm 23^{e,D}$	$4511 \pm 17^{d,D}$	$4106 \pm 45^{a,D}$	$4262 \pm 17^{b,D}$	$4312 \pm 31^{c,D}$
40	$15{,}764 \pm 11^{f,E}$	$6444 \pm 25^{e,E}$	$5144 \pm 12^{d,E}$	$4703 \pm 19^{a,E}$	$5085 \pm 10^{c,E}$	$4867 \pm 16^{b,E}$
30	$19{,}692 \pm 12^{f,F}$	$7218 \pm 25^{e,F}$	$5764 \pm 22^{c,F}$	$5317 \pm 21^{a,F}$	$6123 \pm 19^{d,F}$	$5460 \pm 25^{b,F}$
20	$25{,}776 \pm 11^{f,G}$	8065 ± 22^{eG}	$6315 \pm 12^{c,G}$	$5961 \pm 16^{b,G}$	$6788 \pm 19^{d,G}$	$5935 \pm 11^{a,G}$

[a] Means of two measurements ± standard deviation.

[b] PS: selenating reagent initial ratio.

[c] The power and time of the microwave irradiation.

3.2. *Molecular weight distribution*

In chromatogram of native potato starch two regions could be distinguished. They could be attributed to amylopectin and amylose fraction (Fig. 1). Profiles of the most chromatograms for processed starches generally resembled that of native starch but some of them differed in retention times and shapes of peaks. Therefore, the weight-average molecular weight (M_w) and radius of gyration (R_g) were calculated for the whole complicated peak of eluate of particular samples (Table 1).

Increasing time of microwave irradiation gradually decreased M_w and R_g of native potato starch (Table 1). Although in the chromatogram profiles of irradiated starch samples (Fig.1) two regions attributed to two appropriate fractions could be still distinguished, the plots of the differential molar distribution for these samples (Fig. 2) revealed that the irradiation reduced the amylopectin fraction due to its partial fragmentation.

Chemical modification of starch produced derivatives of M_w and R_g lower than that original of native potato starch (Table 1). Solely starch zincatated for 1 min at 700 W with lower dose of sodium hydroxozincate demonstrated increased M_w and R_g. The most substantial reduction of M_w was observed in the samples of starch sulfated and borated with boric acid. The M_w values of these starches were even by two orders of magnitude lower than that of native potato starch. It is worth noting, however, that the changes in the M_w values of starch borated with boric acid did not entail changes in the R_g values, which were in some cases higher than R_g value of native potato starch. The M_w and R_g values of all the other modified starches depended on the concentration of reagent applied and were often higher than that of starch irradiated in appropriate conditions when lower dose of reagent was applied, and decreased when its concentration increased.

Extent of destruction of polysaccharides on modification increased with doses of reagents. An examples of chromatogram profiles of modified starch samples are presented in Figs. 3 and 4. One could see that in the RI patterns of samples of starch modified with lower dose of reagent amylopectin and amylose fractions could be distinguished but in the RI patterns of samples modified with its higher dose division into the two fractions completely vanished in favor of one peak located in the range between the peaks ascribed in chromatogram of unprocessed starch to amylopectin and amylose (Figs. 3 and 4). Thus, as the silication and zincatation of starch progressed, fraction of larger molecules of starch decreased whereas that of small molecules increased. Plots of the differential molar distribution for these samples (Fig. 5) confirmed that the number of molecules of the amylopectin fraction was reduced on the modification. However, considerable fragmentation of amylopectin chains took place only in the case of starch zincatated with higher dose of sodium hydroxozincate. Similar effect was observed in case of starch esterified with inorganic acids (Lewandowicz et al., 2000). The phenomenon was interpreted as the result of degradation and simultaneous crosslinking. The latter was previously proven on selenation (Staroszczyk, Tomasik, et al., 2007), boration (Staroszczyk, 2009a), silication (Staroszczyk, 2009b; Staroszczyk & Janas, 2010a) and zincatation (Staroszczyk & Janas, 2010b) of starches. While the degradation of starch occurred particularly as a result of starch sulfation and boration with boric acid, crosslinking appeared especially on starch modification with the sodium salts of selenite, selenate, tetraborate, metasilicate and zincic acids with lower dose of reagent used. It means that such doses of the reagents were to a high extent consumed in the crosslinking process and concentration of NaOH was too low to promote decomposition of the starch polysaccharides.

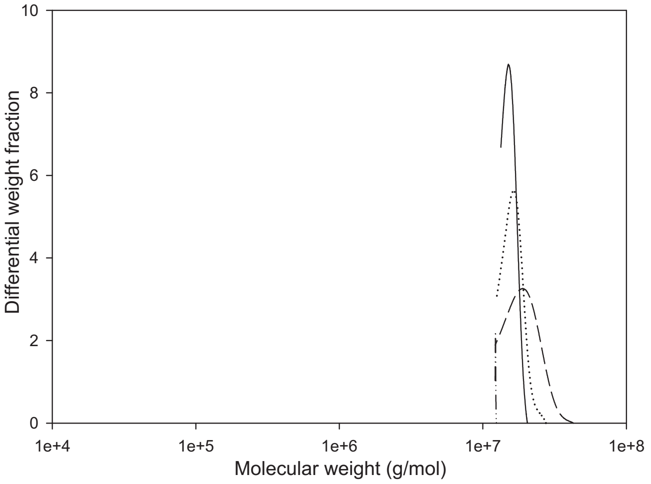

Fig. 2. Plots of differential weight fraction versus molar mass for native potato starch (————) and starch microwave irradiated at 700 W for 1 min (– – –), at 800 W for 5 min (••••••), and at 450 W for 30 min (– •• – ••).

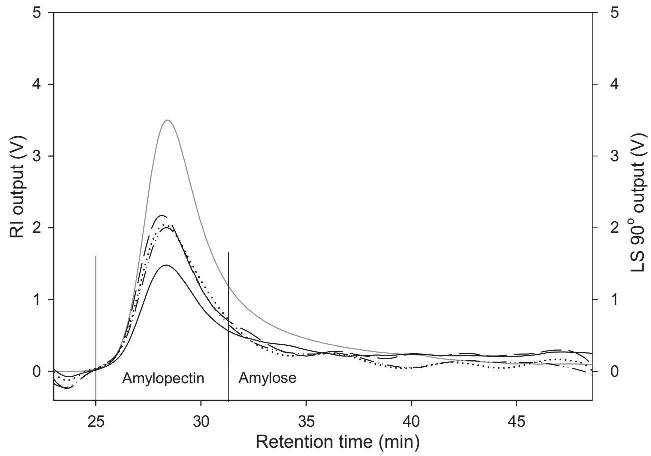

Fig. 1. Chromatograms of RI (————) and LS 90° (————) detector outputs for native potato starch and example chromatograms of RI detector output for samples of starch microwave irradiated at 700 W for 1 min (– – –), at 800 W for 5 min (••••••), and at 450 W for 30 min (– •• – ••).

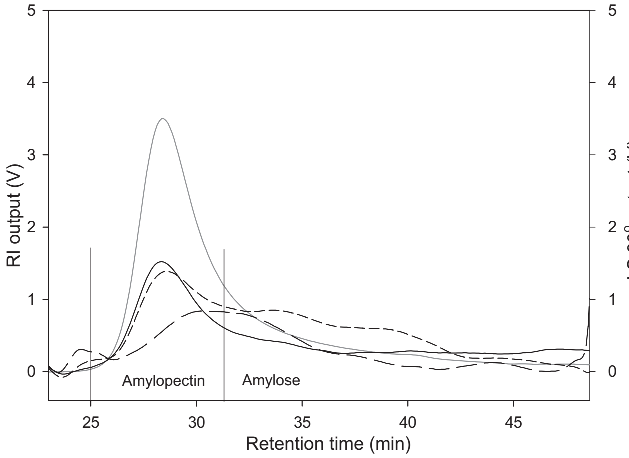

Fig. 3. Chromatograms of RI detector output for starch silicated at 450 W for 30 min with sodium metasilicate: 1:0.1 (– – –) and 1:1 (— —) starch: silicating agent initial ratio. Chromatogram of RI (————) and LS 90° (————) detector outputs for native potato starch are shown for comparison.

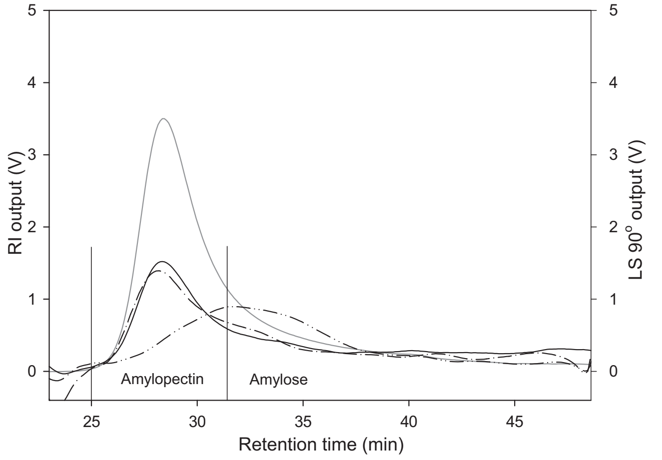

Fig. 4. Chromatograms of RI detector output for starch zincatated at 450 W for 30 min with sodium tetrahydroxozincate: 1:0.1 (– • – •) and 1:0.5 (– •• – ••) starch: zincatating agent initial ratio. Chromatogram of RI (————) and LS 90° (————) detector outputs for native potato starch are shown for comparison.

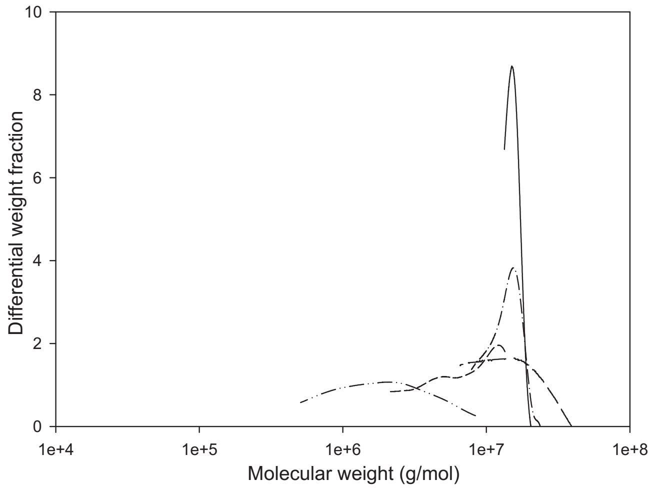

Fig. 5. Plots of differential weight fraction versus molar mass for starch silicated with sodium metasilicate: 1:0.1 (– – –) and 1:1 (— —) starch: silicating agent initial ratio and zincatated with sodium tetrahydroxozincate: 1:0.1 (– • – •) and 1:0.5 (– •• – ••) starch: zincatating agent initial ratio, in all cases at 450 W for 30 min. Plot for native potato starch (————) is shown for comparison.

4. Conclusions

1. On starch sulfation and boration with boric acid proton-catalyzed decomposition of starch polysaccharides dominates. It results in a significant decrease of the starch paste viscosity and in the examined parameters K in the power law model, and σ_{oc} and η_c in the Casson model.
2. On starch silication with silicic acid as well as on selenation, boration with borax and zincatation decomposition of starch polysaccharides is assisted by crosslinking. At lower doses of modifying reagents crosslinking prevails whereas at higher doses decomposition dominates. Such modifications result in decrease in the starch paste viscosity as well as K and η_c. The σ_{oc} values of pastes of those starches are mostly higher than that of native potato starch.
3. In the pastes resulting from these starches decomposition can be caused by pH > 7 originating from NaOH liberated on the modifications.

Acknowledgements

This research was supported by the Polish Ministry of Science and Higher Education under Grant No. NN 312 205 436.

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