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Properties of retrograded and acetylated starch produced via starch extrusion or starch hydrolysis with pullulanase

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ABSTRACT

The aim of the present study was to determine the impact of serial modifications of starch, including firstly starch extrusion or hydrolysis with pullulanase, followed by retrogradation (through freezing and defrosting of pastes) and acetylation (under industrial conditions), on its susceptibility to amylolysis. The method of production had a significant effect on properties of the resultant preparations, whilst the direction and extent of changes depended on the type of modification applied. In the produced starch esters, the degree of substitution, expressed by the per cent of acetylation, ranged from 3.1 to 4.4 g/100 g. The acetylation had a significant impact on contents of elements determined with the atomic emission spectrometry, as it contributed to an increased Na content and decreased contents of Ca and K. The DSC thermal characteristics enabled concluding that the modifications caused an increase in temperatures and a decrease in heat of transition (or its lack). The acetylation of retrograded starch preparations increased their solubility in water and water absorbability. The modifications were found to exert various effects on the rheological properties of pastes determined based on the Brabender's pasting characteristics and flow curves determined with the use of an oscillatory-rotating viscosimeter. All starch acetates produced were characterized by ca. 40% resistance to amylolysis.

1. Introduction

Starch is one of the most common natural polymers. Properties of native starch mostly influenced by its botanical origin which determines the structure and size of amylose and amylopectin molecules, the shape and size of starch granules, and contents of amylose, lipids, protein or elements. Under industrial conditions, desired properties of starch are achieved via modifications with enzymatic, physical or chemical methods. The most up-to-date modified preparations used as food additives include preparations of resistant starch (RS – resistant starch). They are characterized by reduced digestibility in man's body, which allows them to play the role of a prebiotic. The reduced susceptibility of starch to enzymatic degradation may be achieved through its retrogradation. This processes occurs under chilled conditions, when chains of gelatinized starch begin to aggregate into ordered structures, and may be intensified through freezing and defrosting (Leszczyński, 2004; Lewandowicz & Soral-Śmietana, 2004) or through hydrolysis of branched links in amylopectin (Guraya, James, & Champagne, 2001). Acetylation, phosphorylation, hydroxypropylation, crosslinking with epichlorohydrin, saturation with iron ions, or roasting with glycin are chemical modifications that increase starch resistance to amylolysis (Juansang, Puttanlek, Rungsardtsardt, Puncha-arnon, & Uttapap, 2012; Leszczyński, 2004). Studies have shown that acetylation of retrograded starch resulted in the production of starch preparations characterized by high resistance to the activity of amylolytic enzymes (Kapelko, Zięba, & Michalski, 2012; Zięba et al., 2011c). The diminished digestibility of starch may additionally result from physicochemical interactions with lipids penetrating to the interior of an amylose helix (Nebesny, Rosicka, & Tkaczyk, 2005). In turn, the processes of starch quenching at increased temperature and humidity (Würsch, 1999), roasting (Zięba, Kapelko, Gryszkin, & Brzozowska, 2010) or extrusion (Unlu & Faller, 1998) are physical methods applied to increase starch resistance. It seems interesting from the cognitive point of view to determine the effect of a series of modifications on starch susceptibility to amylolysis.

The aim of the present study was, therefore, to establish the impact of starch modifications, including firstly starch extrusion or hydrolysis with pullulanase followed by retrogradation and acetylation, on its susceptibility to amylolysis, and to determine selected properties of the resultant modified preparations.

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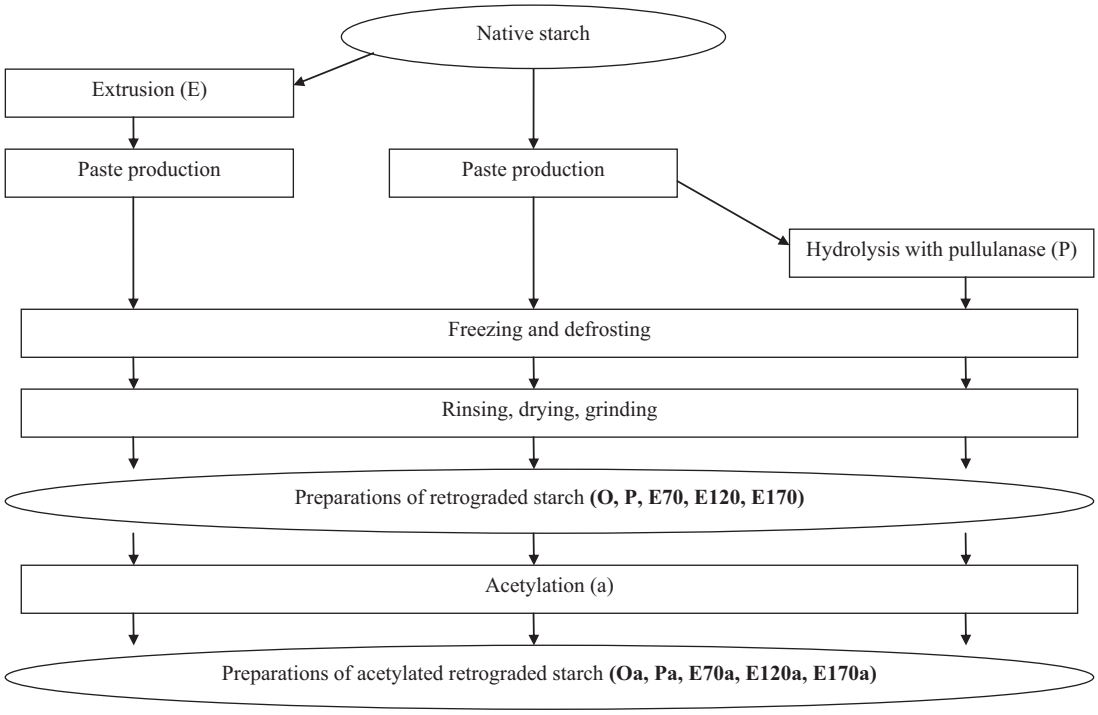

Fig. 1. Scheme of the production process of starch preparations.

2. Materials and methods

2.1. Production of preparations

The experimental material was Superior Standard potato starch produced in the year 2010 by PPZ Company in Niechlów (Poland). It was modified according to the scheme presented in Fig. 1 (symbols of preparations provided in brackets were further used in the text). Starch moistened to a moisture content of 25 g/100 g was extruded in a laboratory single-screw extruder DN 20 (Brabender, Germany) using the following temperatures: 60–65–70 °C, 100–110–120 °C or 150–160–170 °C, a screw with a compression ratio of 2:1, extruder revolution of 180 rpm, a nozzle 3 mm in diameter, and a knife granulator. Starch paste with the concentration of 10 g/100 g was prepared from all types of extruded starch and from native starch (Kapelko, Zięba, Golachowski, & Gryszkin, 2012). The paste from native starch was divided into two portions, one of which was hydrolyzed with pullulanase (Promozyme by Genecor, Denmark) at a temperature of 70 °C. Conditions of the hydrolysis process were adjusted so as to assure the maximum activity of the enzyme. The applied dose of the enzyme was three-fold higher and duration of the hydrolysis process was two-fold longer than respective parameters applied in the food industry. The pastes were left at a temperature of 20 °C till the next day, and then 5 kg portions were frozen in a freezer (Bosch, Poland) for three days at −20 °C and defrosted for two days at 20 °C (until the internal temperature in 5-kg portion has reached ca. 5 °C). The precipitated modified potato starch with a spongy structure was rinsed three times with distilled water, dried in an air flow dryer (Memmert, Germany) at 35 °C for 24 h, ground and sieved through a screen with a mesh diameter of 400 μm. The samples were packed in tightly-closed polyethylene containers and left until analyzed at a temperature of 20 °C.

The process of acetylation was conducted analogously to that applied in Polish starch production plants using a threefold higher volume of water due to the significant swelling of retrograded starch preparations (Zięba, Szumny, & Kapelko, 2011b). In brief, 200 g of starch (converted to dry matter) were weighed into a reactor vessel, which was then filled up with distilled water to the total weight of 1230 g. Next, with constant stirring and pH maintained at 8–9 (using 3 g/100 g NaOH solution), 26.2 cm^3 of acetic acid anhydride were instilled into the vessel. When the whole volume of the anhydride was added, the mixture was left for 15 min and then acidified with a solution of HCl (10 g/100 g) to pH 5.4. Acetylated starch was rinsed with distilled water to remove residues of reagents, then dried at a temperature not exceeding 35 °C, ground and sieved through a screen with a mesh diameter of 400 μm.

2.2. Analyses

Analyses were carried out for the produced preparations of retrograded starch (O, E70, E120, E170, P) and their acetylated modified preparations (Oa, E70a, E120a, E170a, Pa).

2.2.1. Determination of the percentage of acetylation with the titration method

The preparations (10 g) were weighed into a conical flask. The flask was filled with 65 mL of distilled water and the mixture was neutralized by adding a few drops of 0.01 M NaOH in the presence of phenolphthalein until pale pink color maintained for ca. 1 min. Next, 25 mL of 0.5 M NaOH was added and blended at ca. 25 °C for 35 min. The resultant mixture was titrated with 0.5 M HCl (Golachowski, 2003). The percentage of acetylation was calculated according to the method of Wurzburg (Wurzburg, 1964):

$$\text{Per cent of acetylation} = \frac{(S_Z - S_P)\,N_A \times 0.043 \times 100}{a}\ [\text{g}/100\text{g}]$$

where: S_Z – quantity of titrated HCl solution used for titration of 25 cm^3 of 0.5 M NaOH solution [cm^3], S_P – quantity of titrated HCl solution used for titration of the experimental sample [cm^3], N_A – acid titer, and a – weight of starch (converted to dry matter).

2.2.2. Determination of the contents of selected macroelements through mineralization

The samples were mineralized with concentrated nitric (V) acid and concentrated hydrogen peroxide in a closed microwave system MARS 5 (CEM Corporation, United Kingdom) (PN-EN 13805, 2003). Contents of Ca, Na and K were determined according to standard procedures (AOAC, 1990 and PN-EN 14084, 2004), in acetylene-air flame using an atomic absorption spectrometer SpectraAA with a AA240FS system (Varian).

2.2.3. Determination of water absorbability and solubility in water

The samples were assayed for water absorbability and solubility in water at 80 °C according to the method described by Richter, Augustat, and Schierbaum (1968).

2.2.4. Determination of thermal characteristics using DSC technique

Thermal characteristics of pasting was determined with the use of a differential scanning calorimeter DSC 822^e (Mettler Toledo, Germany) at the temperature of 30–200 °C and a heating rate of 10 °C/min. The analyses were carried out in ME-29990 pressure vessels using 10 mg weighed portion of starch (converted to dry matter) and 30 μL of water and an empty reference vessel (Zięba et al., 2011b).

2.2.5. Determination of pasting properties

Pasting properties of 6 g/100 g (converted to dry matter) aqueous starch suspensions were determined with the use of a Brabender viscograph (Germany). The analysis was carried out in a measuring vessel (700 cmg type) at a stirring rate of 75 rpm. The suspension was heated from a temperature of 40–94 °C at the rate of 1.5 °C/min, and then kept at this temperature for 10 min. The resultant paste was cooled to 30 °C (1.5 °C/min) and kept at this temperature for 10 min (Kapelko, Zięba, Golachowski, et al., 2012).

2.2.6. Determination of the flow curves of pastes

Suspensions containing 5 g of starch per 100 g of the solution were prepared for this determination. Flow curves of pastes were determined at a temperature of 50 °C with the use of an oscillating-rotational RS 6000 Rheostress viscometer (Haake, Germany) in a shearing rate range of 0–300 s^{-1}, applying coaxial cylinders (Z38) with a single slot used as a measuring element (Zięba, Juszczak, & Gryszkin, 2011a). The flow curves were described with rheological model:

– Ostwald de Waele : $\tau = K \times \dot{\gamma}^n$ (1)

where: $\dot{\gamma}$ – shear rate (s^{-1}), τ – shear stress (Pa), K – consistency coefficient (Pa s^n), n – flow behavior index.

2.2.7. Determination of the dynamics of saccharification by amyloglucosidase

The starch preparations were determined for saccharification dynamics after production and after pasting (heating) at a temperature of 100 °C using amyloglucosidase enzyme (amigase by Genecor, Denmark). The quantity of free glucose was determined colorimetrically using a reagent for glucose concentration assay (Biosystem, Spain) that contained glucose oxidase and peroxidase. The analysis was conducted according to the following procedure: acetate buffer (pH = 4.5) was added to the suspension of starch preparation. The flask was placed in a water bath (Memmert, Germany) with a shaker and at a temperature of 37 °C, and the enzyme's solution was added to the sample. The concentration of the enzyme was adjusted so as to achieve complete saccharification of gelatinized native starch after 120 min of the process. After each hour of the process, 5 mL of a hydrolysate was collected for centrifugation (MPW Instrumenta, Poland) that was run at 1825 × g for 5 min. The resultant supernatant was collected from the centrifuged sample, mixed with a reagent by Biosystem company, and incubated at 20 °C for 15 min. Afterwards, absorbance was measured with the use of a CECIL CE 2010 colorimeter (Cecil Instruments, England) at the wavelength of λ = 500 nm. The reagent with acetate buffer served as a blank sample. The content of glucose was read out from a standard curve prepared as above with the use of glucose solutions (analytically pure). The degree of saccharification was computed in respect of the theoretical glucose content resulting from the complete saccharification of the weighed portion of starch. The result of hydrolysis was found ultimate when no differences were observed between three subsequent results (Zięba et al., 2011a).

2.3. Statistical analysis

The results obtained in the study were analyzed statistically using Statistica 10.0 PL software package. Based on statistical computations (from at least three parallel replications), values of the least significant differences and standard deviations were calculated, and equations of flow curves were determined. For statistical evaluation, the results were subjected to one-way analysis of variance at a significance level of 0.05. Values of the least significant difference (LSD) between the means were computed using the Duncan's test at a significance level of 0.05.

3. Results and discussion

Acetylated potato starch produced on the industrial scale in starch production plants is characterized by low (not exceeding 2.5 g/100 g) substitution with acetic acid residues (Zięba et al., 2011a). In the reported study, the preparations of retrograded starch were characterized by higher susceptibility to acetylation (Table 1). Most likely, it results from greater porosity of retrograded starch compared to native potato starch, having a compact granular structure (Zięba et al., 2011b), and therefore from better penetration of the reagent though starch structures during modification. The significantly higher susceptibility of retrograded starch to acetylation, compared to native starch, has already been reported in our previous work (Zięba et al., 2011c).

The preparations of retrograded starch produced in this research were characterized by a low content of sodium and potassium, and by a relatively higher content of calcium (Table 1). As a result of the acetylation process, a decrease was observed in calcium content and a significant increase in sodium content of the preparations. These changes were due to already well-known ion-exchange properties of potato starch (Rüggeberg, 1953) that result from its structure, because from the chemical point of view starch is amylophosphoric acid that forms salts with ions contained in a solution. The absorption of an individual mineral element is determined by its concentration and pH of the solution (Winkler, 1960). During the acetylation process, aside the esterification reaction, phosphoric acid was probably also saturated with sodium ions originating from the NaOH solution used to keep reaction pH between 8 and 9.

Hydrolysis with pullulanase, applied in the present study, leads to the disruption of branched α-1,6 glycosidic bonds and, consequently, to the shortening of starch chains (Ozturk, Koksel, Kahraman, & Ng, 2009). Depolymerization of starch proceeds also in the extrusion process upon the influence of temperature and shear forces and its extent is greater the higher the process temperature is (Della, Boch, Colonna, & Vergned, 1995). The preparation of retrograded starch (O) not subjected to any additional treatments during production was characterized by the lowest solubility in water with

Table 1
Physicochemical properties of starch preparations.

Type of analyses	Retrograded starch					Acetylated retrograded starch					$LSD_{0.05}$
	O	P	E70	E120	E170	Oa	Pa	E70a	E120a	E170a	
Per cent of acetylation [g/100 g]	–	–	–	–	–	$4.35^{e} \pm 0.01$	$3.10^{a} \pm 0.01$	$3.49^{c} \pm 0.01$	$3.30^{b} \pm 0.02$	$4.18^{d} \pm 0.01$	0.15
Content of K [mg/100 g]	$4.82^{d} \pm 0.01$	$1.28^{a} \pm 0.01$	$4.88^{d} \pm 0.01$	$5.93^{f} \pm 0.04$	$5.37^{e} \pm 0.15$	$1.83^{b} \pm 0.01$	$1.85^{b} \pm 0.00$	$1.90^{b} \pm 0.00$	$2.35^{c} \pm 0.01$	$1.87^{b} \pm 0.00$	0.07
Content of Ca [mg/100 g]	$36.60^{e} \pm 0.01$	$28.45^{d} \pm 0.09$	$47.21^{fg} \pm 0.56$	$47.13^{f} \pm 0.22$	$48.37^{g} \pm 0.31$	$2.16^{a} \pm 0.03$	$3.13^{ab} \pm 0.01$	$6.22^{c} \pm 0.06$	$5.59^{c} \pm 0.03$	$3.44^{b} \pm 0.01$	1.23
Content of Na [mg/100 g]	$4.02^{b} \pm 0.04$	$2.48^{a} \pm 0.02$	$3.63^{b} \pm 0.02$	$3.56^{b} \pm 0.02$	$3.39^{ab} \pm 0.01$	$25.58^{c} \pm 0.05$	$28.79^{e} \pm 0.09$	$34.42^{g} \pm 0.34$	$26.92^{d} \pm 0.13$	$30.61^{f} \pm 0.67$	1.01

Mean values from three replications ± standard deviations; $LSD_{0.05}$, least significant differences; a–g, homogenous groups related to the same analysis.

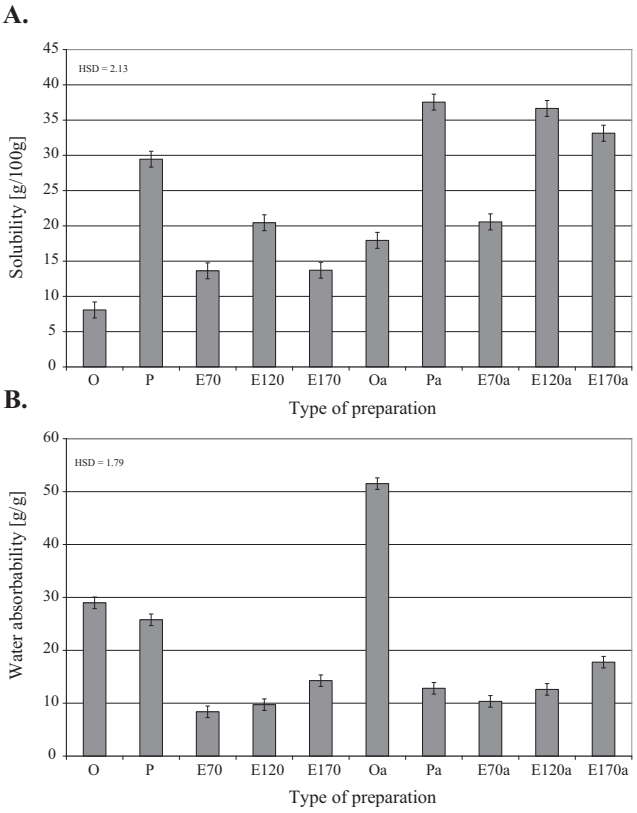

Fig. 2. Solubility in water (A) and water absorbability (B) of starch preparations.

a temperature of 80 °C (Fig. 2). All other (not modified chemically) preparations, in which enzymatic (P) or physical (E70, E120, E170) partial depolymerization of starch chains occurred during the production process, were characterized by more than two-fold higher solubility in water. The increased water solubility along with a decreasing length of chains of the modified starch is obvious. The acetylation of the retrograded starch preparations was observed to increase (by 71% on average) their solubility. Alike changes in water solubility have been reported for acetylated native starch (Raina, Singh, Bawa, & Saxena, 2006) or acetylated retrograded starch (Zięba et al., 2011a).

Physical or enzymatic modification of starch resulted in its diminished water absorbability (Fig. 2). The greatest, several times lower water absorption capability was observed in the case of extruded and retrograded starch, whereas a lesser decrease in water absorbability occurred in the case of enzymatically-hydrolyzed starch (P). During starch pasting, amylose and partly amylopectin with a low molecular weight, shift into the solution (Eliasson & Gudmundsson, 1996). The modifications used in the study, i.e. extrusion and hydrolysis with pullulanase, were likely to affect disruption of starch chains, thus increasing permeability of the produced preparations and decreasing the quantity of starch capable of absorbing water. Acetylation of native potato starch and retrograded starch preparations results in increased water absorbability (Zięba et al., 2011b). A similar dependency was observed in the described experiment. An exception was the preparation of retrograded and acetylated starch hydrolyzed with pullulanase in the production process (Pa), which was characterized by over two-fold lower water absorbability compared to the non-acetylated preparation. Probably, the P preparation contained a considerable number of simple starch chains formed during the activity of the enzyme hydrolyzing branched links in starch. The acetylation process could have led to enhanced hydrolysis of these chains, which

Table 2
Parameters of phase transition of starch preparations determined from DSC thermal characteristics.

Type of preparation	Initial temperature [°C]	Extrapolated peak [°C]	Final temperature [°C]	Heat of transition [J/g]
O	$44.72^{a} \pm 0.06$	$53.66^{a} \pm 0.18$	$66.34^{a} \pm 0.19$	$4.10^{h} \pm 0.08$
P	$61.38^{g} \pm 0.24$	$69.85^{g} \pm 1.29$	$76.04^{cd} \pm 0.23$	$0.31^{a} \pm 0.11$
E70	$58.13^{e} \pm 0.09$	$64.27^{e} \pm 0.82$	$68.95^{b} \pm 0.31$	$3.83^{g} \pm 0.24$
E120	$51.19^{c} \pm 0.12$	$58.78^{c} \pm 0.55$	$66.53^{a} \pm 0.06$	$1.99^{d} \pm 1.41$
E170	*	*	*	*
Oa	$45.95^{b} \pm 0.42$	$55.59^{b} \pm 0.35$	$66.85^{a} \pm 1.44$	$2.81^{f} \pm 0.13$
Pa	*	*	*	*
E70a	$60.09^{f} \pm 0.08$	$67.56^{f} \pm 0.87$	$79.22^{e} \pm 1.06$	$1.22^{b} \pm 0.02$
E120a	$54.77^{d} \pm 0.11$	$63.00^{d} \pm 0.09$	$75.32^{c} \pm 0.09$	$2.28^{e} \pm 0.04$
E170a	$54.72^{d} \pm 0.34$	$63.91^{de} \pm 1.30$	$76.41^{d} \pm 0.30$	$1.57^{c} \pm 0.28$
$LSD_{0.05}$	1.17	1.04	1.09	0.06

Mean values from three replications ± standard deviations; $LSD_{0.05}$, least significant differences; a–h, homogenous groups related to the same analysis.
* No transition.

resulted in increased solubility in water and diminished water absorbability of the Pa preparation.

Table 2 presents parameters of the thermal characteristics of phase transition of the starch preparations. The preparation of retrograded starch (O) was solubilized in water in a wide temperature range and with the highest heat of transition out of all analyzed preparations. Similar DSC characteristics of retrograded starches of various origin are reported in a work by Lewandowicz and Soral-Śmietana (2004). Modifications conducted during the production process of retrograded starch resulted in a decreased heat and temperature of transition or in the lack of transition (preparation E170). The value of transition heat of retrograded starch is, presumably, determined by the structure and number of starch chains arranged into double helices, which in turn are undoubtedly affected by the production method of the preparations. The effect of acetylation on transition parameters depended, to the greatest extent, on properties of starch before chemical modification. The impact of production method on DSC characteristics of acetylated preparations of retrograded starch was also observed in our previous study (Zięba et al., 2011b).

Fig. 3 presents flow curves of pastes prepared from the produced preparations of retrograded starch, and determined parameters describing them. The applied mathematical model described the determined flow curves very well ($0.99 < R^2 < 1.00$). A low value of the n coefficient points to high susceptibility of the analyzed pastes to shear thinning (Zięba et al., 2011a). The highest value of the *K* coefficient, being a measure of paste viscosity at the initial stage of shearing, was assayed for the paste from retrograded starch. Values of the *K* coefficient determined from the flow curves of the pastes produced from preparations P, E70, E120, and E170 were several times lower than these noted for the pastes made of preparation O. The method of production was also influencing pasting characteristics determined with the use of a Brabander viscosimeter (Table 3). In the entire course of characteristics, the viscosity of the paste produced from retrograded starch (O) was higher than of the pastes produced from preparations P, E70, E120, and E170. Starch hydrolysis with pullulanase and starch extrusion applied in the production process of preparations for its partial depolymerization resulted in a multi-fold decrease in pastes viscosity. Similar effects of pullulanase hydrolysis and extrusion of starch on the viscosity of pastes were reported in our previous works (Kapelko & Zięba, 2007; Zięba, Kapelko, Jacewicz, & Styczyńska, 2007).

The acetylation process, causing an increase in the viscosity of pastes produced from native starch (Golachowski, 2003), had an analogous effect on the maximum viscosity determined from the Brabender's pasting characteristics of retrograded acetylated starch (Oa). The assayed *K* coefficient and viscosity of pastes produced from the remaining preparations decreased compared to

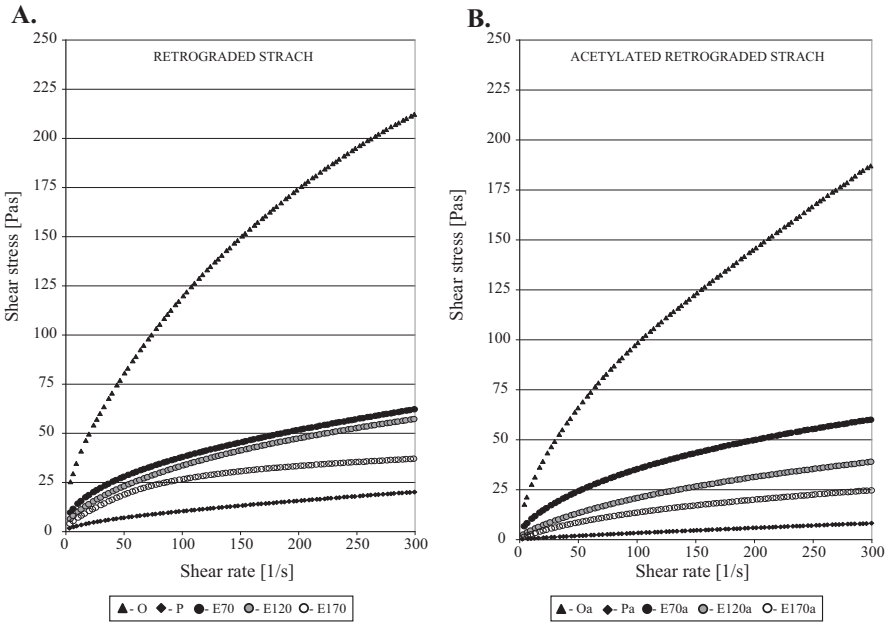

Fig. 3. Flow curves of pastes produced from starch preparations: A – retrograded starch, B – acetylated retrograded starch, and mathematical parameters describing them.

Table 3
Viscosity of pastes produced from starch preparations determined from Brabender's pasting characteristics.

Viscosity [B.U.]	Retrograded starch					Acetylated retrograded starch					$LSD_{0.05}$
	O	P	E70	E120	E170	Oa	Pa	E70a	E120a	E170a	
Maximal	$1295^{g} \pm 5$	$135^{b} \pm 5$	$425^{f} \pm 5$	$340^{d} \pm 5$	$380^{e} \pm 20$	$2015^{h} \pm 15$	$20^{a} \pm 0$	$395^{ef} \pm 15$	$270^{c} \pm 10$	$340^{d} \pm 10$	32
At temp. of 94° C	$1145^{j} \pm 5$	$130^{d} \pm 0$	$415^{h} \pm 0$	$250^{e} \pm 0$	$300^{g} \pm 10$	$950^{i} \pm 10$	$20^{a} \pm 0$	$275^{f} \pm 15$	$110^{c} \pm 5$	$80^{b} \pm 0$	20
After 10 min at temp. of 94 °C	$815^{i} \pm 0$	$105^{d} \pm 5$	$330^{g} \pm 0$	$180^{e} \pm 10$	$180^{e} \pm 10$	$690^{h} \pm 10$	$20^{a} \pm 0$	$205^{f} \pm 5$	$85^{c} \pm 0$	$45^{b} \pm 0$	11
Minimal	$810^{i} \pm 5$	$100^{d} \pm 10$	$330^{g} \pm 0$	$180^{e} \pm 0$	$180^{e} \pm 10$	$670^{h} \pm 0$	$20^{a} \pm 0$	$205^{f} \pm 5$	$85^{c} \pm 5$	$45^{b} \pm 5$	15
At temp. of 30° C	$1360^{i} \pm 0$	$190^{c} \pm 10$	$520^{g} \pm 10$	$340^{e} \pm 10$	$280^{d} \pm 20$	$1130^{h} \pm 10$	$50^{a} \pm 0$	$405^{f} \pm 0$	$190^{c} \pm 10$	$120^{b} \pm 15$	18
After 10 min at temp. of 30 °C	$1330^{j} \pm 0$	$195^{c} \pm 5$	$510^{h} \pm 10$	$335^{f} \pm 5$	$275^{d} \pm 5$	$1125^{i} \pm 30$	$50^{a} \pm 5$	$405^{g} \pm 5$	$200^{c} \pm 10$	$120^{b} \pm 10$	13

Mean values from three replications ± standard deviations; $LSD_{0.05}$, least significant differences; a–j, homogenous groups related to the same analysis.

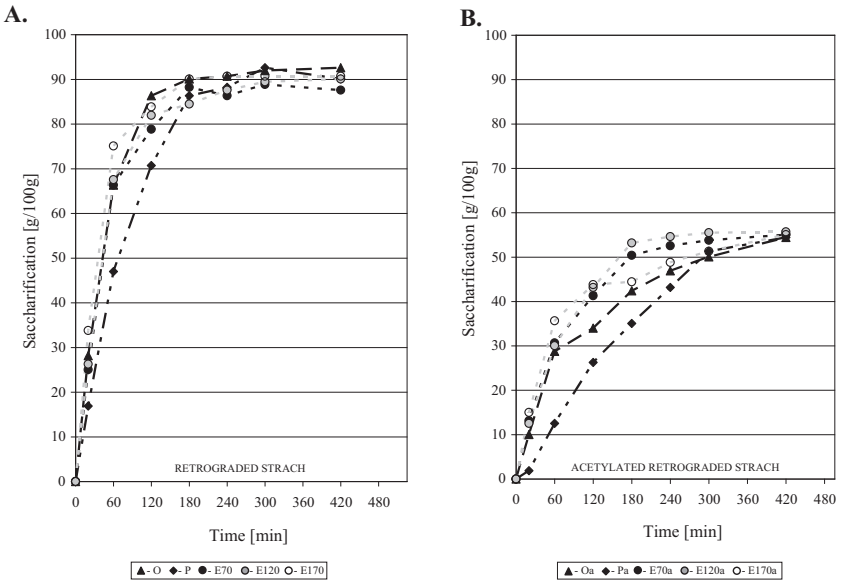

Fig. 4. Dynamics of saccharification with amyloglucosidase of non-heated (non-pasted) starch preparations: A – retrograded starch, B – acetylated retrograded starch.

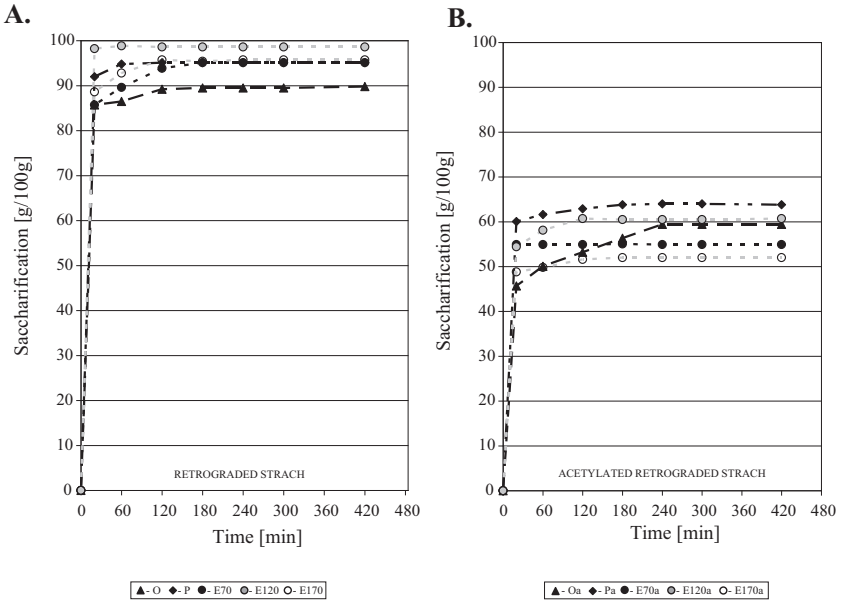

Fig. 5. Dynamics of saccharification with amyloglucosidase of heated in water (pasted) starch preparations: A – retrograded starch, B – acetylated retrograded starch.

those of preparations before acetylation. This phenomenon may be explained by successive hydrolysis of relatively short starch chains. This factor has, presumably, a greater impact on viscosity than the attachment of acetic acid residues, which usually causes an increase in pastes viscosity. The varied effects of the production methods of acetylated retrograded starch preparations on the viscosity of resultant pastes were also observed in our earlier study (Zięba et al., 2011a).

The saccharification of retrograded starch upon treatment with amyloglucosidase was significantly affected only by the chemical modification (acetylation) and preparation heating (pasting) in water before the enzymatic treatment (Figs. 4 and 5). Similar results were achieved using different methods to produce acetylated preparations of retrograded starch (Zięba, Kapelko, & Gryszkin, 2007). The degree of retrograded starch hydrolysis by amylase is at ca. 90 g/100 g (Zięba et al., 2011b). The preparations that had been heated in water before hydrolysis reached their maximum degree of saccharification practically as early as after 20 min of hydrolysis. A significantly longer (180 min) time was needed for amylolysis of the non-pasted preparations. Acetylation reduced the susceptibility of the preparations to enzymatic degradation by ca. 30 g/100 g. The course of saccharification dynamics of the preparations subjected to pasting before analysis was analogous to that of non-acetylated preparations. In contrast, the non-pasted acetylated preparations were saccharified in a significantly longer time span. They reached their maximum degree of saccharification already after ca. 30 min of amylolysis. The conducted study proves that both starch hydrolysis with pullulanase as well as starch extrusion preceding retrogradation and acetylation have no significant effect on the amylolysis of produced preparations.

4. Conclusion

The method used to produce starch preparations turned out to have a significant effect on their properties, whereas the tendency and extent of these changes depended on the type of modification applied. Both the physical (extrusion) and enzymatic (hydrolysis with pullulanase) depolymerization of starch caused an increase in water solubility and a decrease in water absorbability, heat and temperature of transition determined from the DSC characteristics as well as viscosity of the pastes produced. Extrusion and pullulanase hydrolysis of starch had no significant effect on starch susceptibility to amyloglucosidase action. The produced acetylated preparations were characterized by ca. 30% lower susceptibility to the action of amylase than the chemically unmodified preparations. The effect of acetylation on the other properties of the starch preparations was significantly dependent on their properties before acetylation.

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