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Effect of preparation method on the properties of potato starch acetates with an equal degree of substitution☆

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ABSTRACT

Acetylated retrograded starch is one of the forms of resistant starch (RS3/4). Apart from the known resistance to amylolysis, it is characterized by the capability to form viscous pastes. Properties of this type of acetates are mainly determined by the degree of substitution and raw material used for esterification.

The objective of this study was to produce starch acetates with a degree of substitution DS = 0.1 from native potato starch and retrograded potato starch, and to compare selected properties of the resultant preparations.

Retrograded starch was produced by freezing pastes with concentrations of 1, 4, 10, 18 or 30 g/100 g. Starch acetates with a degree of substitution DS ~ 0.1 were produced from native or retrograded starch through acetylation with various doses of acetic acid anhydride (6.5–26.0 cm^3/100 g of starch). The preparations produced were characterized by various properties. A positive correlation was observed between resistance to amylolysis and the number of acetyl groups at C2 and C3 the produced starch acetates.

1. Introduction

Starch – as one the most abundant polysaccharides in nature – has been widely applied in both the food and non-food industries. Yet, in its native form starch has low industrial applicability. Depending on demands and mode of utilization, most of the starch produced is subjected to successive physical and chemical modifications. These modifications enable obtaining starch preparations with different structure and properties. The change of starch structure by means of physical and chemical modifications may affect a decrease in its susceptibility to amylolytic degradation. One of the groups of modified preparations used in recent years as food additives includes preparations of resistant starch that have been reported to play a health-promoting role (Laguna, Salvador, Sanz, & Fiszman, 2011; Perera, Meda, & Tyler, 2010), as the so-called prebiotics (Angioloni & Collar, 2011; Scarminio, Fruet, Witaicenis, Rall, & Di Stasi, 2012). One of the forms of resistant starch is retrograded starch (RS3) produced as a result of physical modification of starch (Haralampu, 2000; Zhou & Lim, 2012). Retrogradation is a process defined as the linking of starch chains into ordered structures being crystalline in character. Properties of the resultant retrograded starch are determined by, among other things, the origin and type of starch, conditions of retrogradation and presence of other compounds (Funami et al., 2008; Korus, Witczak, Juszczak, & Ziobro, 2008; Silverio, Fredriksson, Andersson, Eliasson, & Aman, 2000; Zhou, Wang, Zhang, Du, & Zhou, 2008). The chemical modification of starch also leads to the production of resistant starch which is referred to as RS4 fraction. Acetylation, hydroxypropylation, phosphorylation, roasting with glycine, cross-linking with epichlorohydrin or saturation with iron ions are chemical modifications that increase starch resistance to amylolysis (Juansang, Puttanlek, Rungsardtsardt, Puncha-arnon, & Uttapap, 2012; Leszczyński, 2004). Acetylation of retrograded starch has bee shown to enable obtaining preparations of resistant starch RS3/4 with high resistance to the activity of amylolytic enzymes (Kapelko, Zięba, & Michalski, 2012a; Zięba, Szumny, & Kapelko, 2011b) and characterized by the capability to form viscous pastes (Kapelko, Zięba, & Michalski, 2012a; Zięba, Juszczak, & Gryszkin, 2011). The process of starch acetylation is determined by a number of factors. Both the degree and site of substitution with acetyl groups depend on, among other things, the origin (Mirmoghtadaie, Kadivar, & Shahedi, 2009) and form of starch (Kapelko, Zięba, Golachowski, & Gryszkin, 2012), size of starch granules (Mirmoghtadaie et al., 2009), degree of crystallinity (Golachowski, 2003), amylose content (Mirmoghtadaie et al., 2009), and conditions of the acetylation process (González & Pérez, 2002).

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The objective of this study was to preparation starch acetates with a degree of substitution DS = 0.1 from native potato starch and retrograded potato starch, and to compare selected properties of the resultant preparations.

2. Materials and methods

2.1. Materials

The initial experimental material was Superior Standard potato starch produced by PEPEES Łomża in the year 2010 (Poland). Starch was acetylated with analytically pure acetic acid anhydride purchased from POCH SA Gliwice (Poland).

2.2. Production of preparations of acetylated retrograded starch

Five-kilogram portions of starch suspensions in water with concentrations of 1, 4, 10, 18, or 30 g/100 g were prepared from native potato starch. The suspensions were heated to a temperature of ca. 70 °C for 30 min, with continuous stirring until paste thickening that made starch sedimentation impossible. Next, the suspensions were left for 6 h in a water bath (Memmert, Germany) at a temperature of 94 °C for complete starch pasting. The successively produced portions of pastes were left for 12 h to cool to a temperature of 20 °C, and then 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 the 5 kg portion has reached ca. 5 °C). The precipitated starch with a spongy structure was rinsed with distilled water, dried in an air flow dryer (Memmert, Germany) at a temperature of 35 °C for 24 h, ground and sifted through a sieve 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 native starch and the produced preparations of retrograded starch were subjected to the acetylation process with acetic acid anhydride under conditions provided by Zięba et al. (2011b). The preparations were acetylated with various doses of acetic acid anhydride in order to produce modified preparations with a degree of substitution DS ~ 0.1. The resultant preparations were denoted as: Ns/0.1a – acetylated native starch; R1/0.1a, R4/0.1a, R10/0.1a, R18/0.1a, or R30/0.1a – acetylated retrograded starch (a digit that follows "R" denotes the concentration of starch paste the preparation was made of).

2.3. Determination of amylose content with the Morrison's method (Morrison & Laignelet, 1983)

The content of amylose was determined with the iodometric method after dissolution of starch samples in a solution of dimethyl sulfoxide and urea. The absorbance was measured against a reference sample (not containing starch), 15 min after iodine solution was added, using a CECIL CE 2010 spectrophotometer (Cecil Instruments, England) at a wavelength of 635 nm.

2.4. Determination of swelling power and solubility in water with a temperature of 80 °C (Golachowski & Brzeski, 2001; Richter, Augustat, & Schierbaum, 1968)

From a preparation of retrograded starch, an aqueous suspension was prepared that contained 1 g of starch per 100 g of the solution. The suspension was next shaken in a water bath for 30 min at a temperature of 80 °C (Memmert, Germany). Afterwards, the mixture was cooled to a temperature of 20 °C and centrifuged for 30 min using a Biofuge 28RS Heraeus Sepatech centrifuge (Germany) with an acceleration of 22,500 × g. The separated supernatant was determined for dry matter content with the gravimetric method, whereas the precipitate left in the centrifuge tubes was weighed.

2.5. Determination of resistance to the activity of amyloglucosidase (Zięba et al., 2011b)

Starch suspensions were prepared that were heated under continuous stirring until the boiling point, and then cooled to a temperature of 37 °C, at which the samples were hydrolyzed with amyloglucosidase (Amigase by Genecor, Denmark). The enzyme's concentration was adjusted so as to enable the complete saccharification of gelatinized native starch after 120 min of the process. The content of free glucose was determined spectrophotometrically using a CECIL CE 2010 spectrophotometer (Cecil Instruments, England) at a wavelength of $\lambda = 500$ nm, applying a reagent for glucose concentration assay by Biosystem (Spain), containing glucose oxidase and peroxidase.

2.6. Determination of pasting characteristics with the use of Brabender viscograph (Zięba, Kapelko, & Gryszkin, 2007)

The pasting characteristics was determined with a Brabender viscograph (Germany), using a 700 cmg measuring can. In a measuring vessel of the viscograph, starch suspension (450 mL) was prepared from native potato starch in the concentration 4 g of starch per 100 g of the solution. The suspension was heated to a temperature of 40 °C/min with the rate of 75 rpm. Next, it was kept at this temperature for 10 min. Afterwards, the solution was heated with the rate of 1.5 °C/min until it has reached 94 °C. After 10 min of mixture keeping at this temperature, it was cooled to 30 °C with the rate of 1.5 °C/min, and kept at this temperature for another 10 min.

2.7. Determination of flow curves of pastes with a Haake oscillatory-rotational viscosimeter (Zięba et al., 2011)

For determinations, suspensions were prepared that contained 5 g of starch per 100 g of the solution. The suspensions were heated at a temperature of 96 °C for 30 min under continuous stirring. The analysis was conducted using an RS 6000 Rheostress oscillatory-rotational viscosimeter by Haake (Germany). Flow curves of the pastes were determined at a temperature of 50 °C in a system of coaxial cylinders (Z38AL type), with a shear rate range of $1–300\ s^{-1}$. The flow curves determined were described with the Oswald de Waele's and Casson's equations.

2.8. Determination of thermal characteristics of pasting with the DSC technique (Zięba et al., 2011b)

The determination was carried out with the use of a DSC 922E differential scanning calorimeter by Mettler Toledo (Germany). Before the measurement, the apparatus was calibrated using iodine and zinc samples. Starch preparations (10 mg per dry matter basis) were weighted out into semi-pressure crucibles (ME-29990), to which bidistilled water was added in a ratio of 3:1 (water:starch), finally the crucibles were closed and conditioned at a temperature of 25 °C for 30 min. The analysis was performed in a temperature range of 20–100 °C, with a heating rate of 10 °C/min.

2.9. Determination of the chemical structure with the method of nuclear molecular resonance ^{1}H NMR (Zięba, Szumny, & Kapelko, 2011a)

The analyzed starch preparations were dissolved in DMSO-d6 in the quantity of 10 mg per 0.6 mL. Analyses were carried out at a temperature of 25 °C. Spectra were prepared at the Laboratory of NMR Structural Studies, Chemical Faculty, Wrocław Technical University, on a Bruker Avance II 600 MHz spectrometer (Germany). The total degree of starch substitution with acetyl residues was determined based on the methodology described by Matti et al. (2004).

The partial substitution with acetic acid residues at particular carbon atoms was computed based on ratios of sizes of the registered signals (peaks). Integration of an acetyl group signal at carbon atoms 2 and 3 at 1206 Hz was adopted as 1.

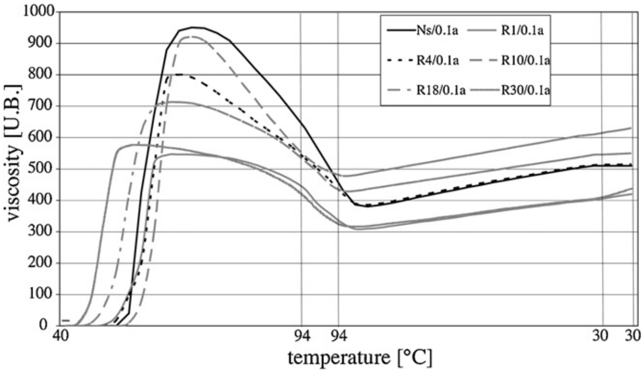

Fig. 1. Characteristics of paste formation determined with a Brabender viscograph.

2.10. Statistical analysis

Results of analyses were subjected to the statistical analysis using a package of the Statistica 10.0 PL software. Based on statistical computations (from at least three parallel replications of particular assays), values of the least significant differences were calculated, equations of flow curves were determined and a Pearson's correlation coefficient was computed. 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

Starch industry is producing, on a commercial scale, acetylated potato starch that is characterized by a low degree of substitution with acetic acid residues, not exceeding 0.1 (Zięba et al., 2011b). In the conducted experiment, preparations of acetylated starch with an equal degree of substitution (ca. 0.1) were produced from native starch and from preparations of retrograded starch produced from pastes with different concentrations. Differences in the quantity of acetic acid anhydride used for esterification (Table 1) point to their various susceptibility to chemical modification. Presumably, it results from a diversified structure of the retrograded starch preparations produced. Alike dependencies were reported by authors of this manuscript in their previous works (Kapelko, Zięba, Golachowski, et al., 2012b; Zięba et al., 2007, 2011a, 2011b).

In native potato starch, the content of amylose usually accounts for 25–30 g/100 g (Pycia, Juszczak, Gałkowska, & Witczak, 2012). The conducted esterification caused a decrease in amylose content (Table 1). This dependency was also noted by other authors (Gunaratne & Corke, 2007). Amylose content in the analyzed preparations of acetylated retrograded starch was lower than in the native starch and was observed to diminish along with an increasing concentration of starch paste subjected to retrogradation. An exception was the R10/0.1a preparation. The various susceptibility of amylose to the likely hydrolysis during chemical modification may point to considerable differences in the structure of starch crystallites formed during retrogradation. Acetylation of starch, both of the native and retrograded one, causes an increase of its swelling power and solubility in water (Zięba et al., 2011).Values of both these characteristics of starch acetates with an equal degree of substitution fitted within wide ranges (swelling power from 39.3 to 98.6 g/g, solubility from 26.7 to 58.4 g/100 g), which indicates the production method to have an impact on the structure and properties of resultant preparations. Alike differences refer to preparations resistance to the action of amyloglucosidase (18.51–42.03 g/100 g). The significant effect of production method on amylose content, swelling power, solubility in water and resistance of acetylated retrograded potato starch was reported in the authors' previous work (Kapelko, Zięba, & Michalski, 2012).

The resistance of acetylated retrograded potato starch results from both retrogradation and chemical modification, and thereby this starch was referred to by the authors as RS3/4 starch (Kapelko, Zięba, & Michalski, 2012). Apart from significant resistance, this starch is characterized by the capability to form viscous pastes (Kapelko, Zięba, & Michalski, 2012; Zięba et al., 2011). The preparations' pasting characteristics determined with the use of a Brabender viscograph (Fig. 1) and flow curves of the prepared pastes (Fig. 2) confirm this capability of the starch acetates produced in the study. At the early stage of pasting, the highest viscosity was noted for the paste made of acetylated native starch. The maximum viscosity of pastes prepared from acetylated retrograded starch was lower by 5–42% than that of the paste produced from acetylated native starch. The viscosity of all pastes after cooling (at a temperature of 30 °C) was fluctuating in a significantly narrower range (405–610 U.B.). The highest viscosity was determined for the paste made of R10/0.1a preparation, whereas the lowest one – for pastes made of R1/0.1a and R30/0.1a preparations. All pastes examined exhibited the non-Newtonian, shear-thinning flow with a tendency towards yield stress (Fig. 2). Different methods of retrograded starch production had a significant effect on rheological properties of the pastes prepared. The pastes made of acetylated retrograded starch were characterized by a significantly lower value of consistency coefficient and yield stress according to the Casson's model (being a measure of viscosity at the initial stage

Table 1

Dose of acetic acid anhydride, degree of substitution, amylose content, swelling power, solubility, and resistance to amyloglucosidase activity of acetylated native starch and preparations of acetylated retrograded starch with a degree of substitution DS ∼ 0.1.

Type of preparation	Dose of acetic acid anhydride [cm^3/100 g]	DS	Amylose content [g/100 g]	Swelling power [g/g]	Solubility [g/100 g]	Resistance [g/100 g]
Ns/0.1a	13.0	0.09 ± 0.00	20.2 ± 0.14	39.3 ± 0.09	26.7 ± 0.01	13.51 ± 0.07
R1/0.1a	13.0	0.10 ± 0.00	16.4 ± 0.06	51.5 ± 0.02	37.1 ± 0.10	25.13 ± 0.12
R4/0.1a	13.0	0.11 ± 0.00	15.8 ± 0.15	62.8 ± 0.04	53.8 ± 0.05	33.68 ± 0.09
R10/0.1a	6.5	0.09 ± 0.00	17.6 ± 0.09	70.7 ± 0.04	58.4 ± 0.01	28.05 ± 0.05
R18/0.1a	13.0	0.09 ± 0.00	13.6 ± 0.21	58.9 ± 0.04	49.9 ± 0.04	40.77 ± 0.14
R30/0.1a	26.0	0.09 ± 0.00	7.7 ± 0.09	98.6 ± 0.03	39.5 ± 0.06	42.03 ± 0.10
LSD$_{0.05}$	–	–	0.24	0.31	0.09	0.46

Mean values from three replications ± standard deviations, LSD$_{0.05}$ – least significant differences.

Table 2
Mathematical parameters describing the flow curves of pastes prepared from acetylated native starch and preparations of acetylated retrograded starch.

Type of preparation	Model of Ostwald de Waele			Model of Casson ($n = 0.5$)		
	K [Pa s^n]	n	R^2	τ_{oC} [Pa]	η_C [Pa s]	R^2
Ns/0.1a	23.45 ± 1.79	0.44 ± 0.00	0.99	31.39 ± 1.56	0.135 ± 0.019	0.96
R1/0.1a	1.51 ± 0.13	0.82 ± 0.05	0.99	2.60 ± 0.14	0.094 ± 0.002	0.98
R4/0.1a	3.23 ± 0.10	0.75 ± 0.01	1.00	5.11 ± 0.21	0.130 ± 0.000	0.97
R10/0.1a	4.66 ± 0.88	0.44 ± 0.02	1.00	8.53 ± 0.16	0.187 ± 0.006	0.99
R18/0.1a	4.54 ± 0.06	0.54 ± 0.00	1.00	7.20 ± 0.07	0.150 ± 0.001	0.97
R30/0.1a	2.34 ± 0.20	0.59 ± 0.01	0.95	3.30 ± 0.03	0.179 ± 0.002	0.98
LSD$_{0.05}$	0.67	0.05	–	0.22	0.005	–

Mean values from three replications ± standard deviations, LSD$_{0.05}$ – least significant differences.

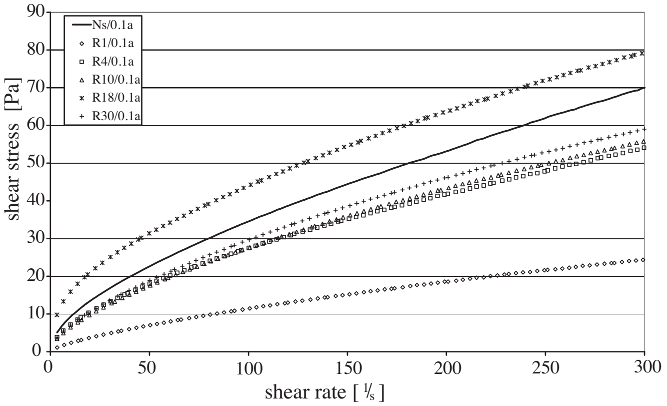

Fig. 2. Flow curves of pastes prepared from acetylated native starch and preparations of acetylated retrograded starch.

of shearing) compared to the paste produced from acetylated native starch (Table 2). This indicates that it forms pastes with a significantly lower initial viscosity when compared to acetylated native starch. Opposite observations were made in the case of Casson's plastic viscosity which is a measure of paste resistance to shear forces. The pastes produced from R10/0.1a, R18/0.1a and R30/0.1a preparations were characterized by higher (the paste from R4/0.1a – by comparable, and the paste from R1/0.1a – by lower) viscosity than the paste made of Ns/0.1a starch. This type of rheological properties of pastes, namely low initial viscosity and high resistance to shear forces during technological treatments, may receive a positive feedback in technological practice. The high variability of the rheological properties of pastes made of acetylated retrograded starch with different methods had been reported by authors of this manuscript in their previous works (Kapelko, Zięba, & Michalski, 2012; Zięba et al., 2011).

Thermal parameters of native acetylated starch gelatinization depend on the type of starch (Gunaratne & Corke, 2007) and on the degree of substitution with acetic acid residues (Golachowski, 2003; Kapelko, Zięba, & Michalski, 2012). Table 3 presents parameters of phase transition of acetylated native starch gelatinization and of solubilization (re-gelatinization) of acetylated retrograded starch preparations with a degree of substitution ~0.1. The native acetylated starch was characterized by a significantly higher initial pasting temperature (on average by 6.4 °C) and by over twofold higher phase transition heat than the acetates produced from retrograded starch. Similar dependencies resulting from differences in the structure of native (granular) starch and acetylated retrograded starch produced under various conditions had been described in a previous work of the authors (Zięba et al., 2011b). Alike course of thermal characteristics of retrograded starch acetates produced from pastes with different concentrations, being in opposition to the high differentiation of the above-discussed preparations, indirectly negates the hypothesis on considerable differences in the structure of the analyzed preparations.

In order to determine differences in the chemical structure of preparations produced in the study, use was made of a high-performance technique of nuclear magnetic resonance ^{1}H NMR. In the earlier study, based on ^{1}H NMR, ^{13}C NMR and HSQC spectra, the authors were determining values of chemical shifts of acetates with a different degree of substitution produced under various conditions from native or retrograded starch. All acetates produced from native starch were characterized by identical values of chemical shifts. Likewise the acetates of retrograded starch, in the case of which the read out signal did not differ from the signals of acetates produced from native starch (Zięba et al., 2011a, 2011b). The ^{1}H NMR analysis involved the ratio of acetate groups substitution at carbon atom 6 to the total substitution at carbon atoms 2 and 3 (Fig. 3). In the case of starch with a low degree of substitution (below 0.1), the esterification reaction proceeds more intensively on the I-order hydroxyl groups compared to the II-order groups (Leszczyński, 2004; Mężyński, 1972), which explains a high number of acetyl groups substituted at carbon atom 6 (Table 4). The varying contribution of the I-order carboxyl group and II-order carboxyl groups in the substitution points to differences in the chemical

Table 3
Parameters of phase transition of acetylated native starch and preparation of acetylated retrograded starch determined from thermal characteristics (DSC).

Type of preparation	Initial temperature of gelatinization [°C]	Endotherm maximum temperature [°C]	Final temperature of gelatinization [°C]	Heat of phase transition [J/g]
Ns/0.1a	54.11 ± 0.06	60.35 ± 0.24	68.61 ± 0.17	12.62 ± 0.03
R1/0.1a	47.46 ± 0.10	57.42 ± 0.18	68.42 ± 0.03	5.23 ± 0.04
R4/0.1a	46.89 ± 0.09	54.28 ± 0.02	63.70 ± 0.14	4.08 ± 0.02
R10/0.1a	47.28 ± 0.04	56.64 ± 0.04	67.90 ± 0.03	5.39 ± 0.01
R18/0.1a	49.36 ± 0.11	56.97 ± 0.01	63.61 ± 0.19	5.98 ± 0.06
R30/0.1a	47.38 ± 0.08	56.82 ± 0.15	69.54 ± 0.32	4.97 ± 0.05
LSD$_{0.05}$	0.14	0.24	0.31	0.07

Mean values from three replications ± standard deviations, LSD$_{0.05}$ – least significant differences.

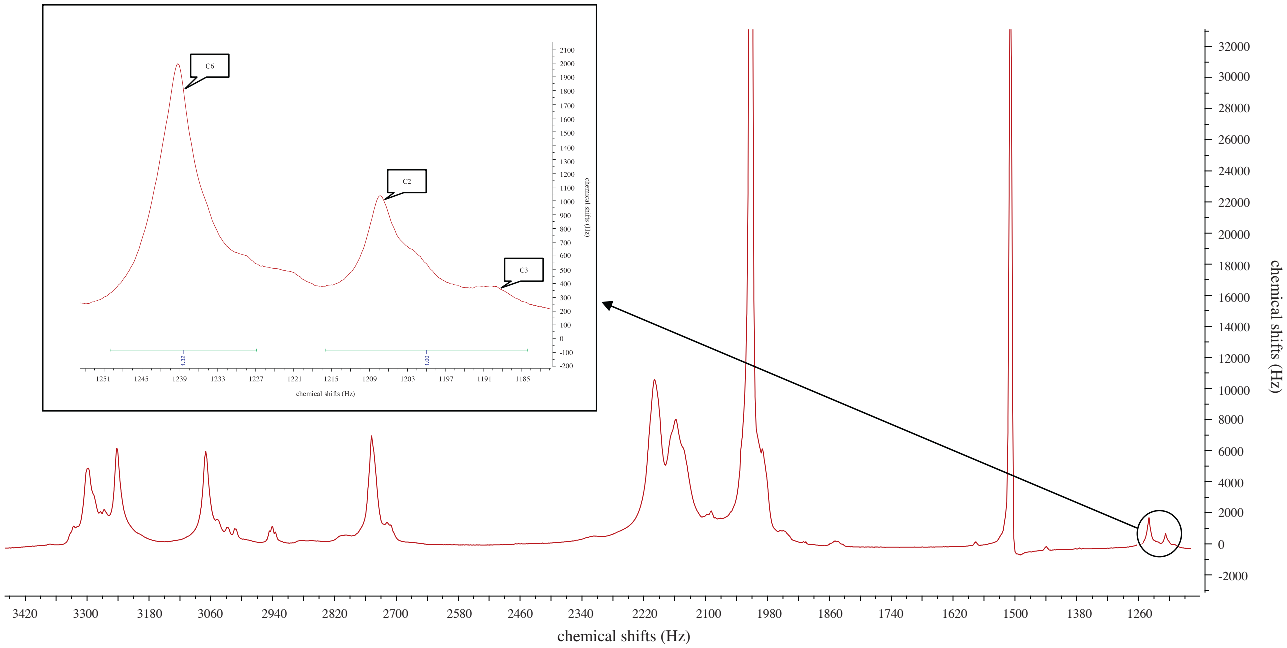

Fig. 3. Fragment of a spectrum of nuclear magnetic resonance ^{1}H NMR of the acetylated preparation of retrograded starch.

Table 4
Content of acetyl groups at the 2, 3, and 6. carbon atom of acetylated native starch and preparations of acetylated retrograded starch with a degree of substitution DS ~ 0.1.

Type of preparation	Contribution of $CH_3(CO)O$— proton signal at carbon atoms	
	C-6	C-2 and C-3
Ns/0.1a	53.70	46.30
R1/0.1a	56.90	43.10
R4a/0.1	47.92	52.08
R10/0.1a	50.00	50.00
R18/0.1a	44.75	55.25
R30/0.1a	49.49	50.51

structure of the produced starch esters with an equal total degree of substitution (~0.1). The number of groups substituted at carbon atoms 2 and 3 (that are located next to the 1,4-glycosidic bond being hydrolyzed) is, presumably, one of the reasons behind differences in the susceptibility of acetylated retrograded starch to amylolysis (Zięba et al., 2011a, 2011b). However, differences in the total degree of acetylated starch substitution makes explicit confirmation of this hypothesis impossible. The positive correlation determined in this study between resistance of the preparations with the same degree of substitution (~0.1) to amylolysis and the number of acetyl groups at carbon atoms 2 and 3 confirms the above assumptions.

4. Conclusion

Starch acetates produced from native potato starch and from retrograded potato starch, and having an equal degree of substitution (ca. 0.1), were found to differ in their properties. Different methods of their preparation (various contents of pastes used to produce retrograded starch and different doses of acetic acid anhydride used for starch acetylation) resulted in the production of acetates with a differentiated degree of substitution with acetic acid residues at carbon atoms 2, 3 and 6. The significant effect of the substitution site on the properties of produced starch acetates is indicated by the determined positive correlation between resistance to amylolysis and the number of acetyl groups substituted at carbon atoms 2 and 3.

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