

Selected Rheological Properties of RS3/4 Type Resistant Starch

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Key words: retrograded potato starch, acetylated distarch adipate, rheological properties

This study was aimed at determining the effect of acetylation degree and crosslinking of retrograded starch with adipic acid on selected rheological properties of prepared pastes and gels. The esterification of retrograded starch allowed obtaining preparations with various degrees of substitution with residues of acetic (0.7–11.2 g/100 g) and adipic acids (0.1–0.3 g/100 g). Acetylation and crosslinking caused a decrease in amylose content of the preparations (3–21 g/100 g). Solubility of the preparations in water, in a wide range of variability, was increasing along with an increasing degree of acetylation and with a decreasing degree of crosslinking (19–100 g/100 g). Values of most of the rheological coefficients determined based on the flow curves of the prepared pastes and mechanical spectra of gels ($3.5 < K < 31.5 \text{ Pa} \times \text{s}^n$, $4.2 < \tau_{0c} < 70 \text{ Pa}$, $0.26 < \lg \alpha < 0.57$) were increasing in a wide range along with increasing crosslinking of starch. Changes in the rheological properties upon the effect of double modification were not the sum of changes proceeding as a result of single modifications. Instead, interaction of both factors was observed. The conducted modifications enable modelling the properties of produced preparations.

INTRODUCTION

Starch production in 2018 is estimated to reach as many as 133.5 mln ton [Global Industry Analysts, 2015]. Industrially-produced starch is utilized only in a negligible part. Most of starch is processed using biochemical, physical and chemical methods. Modification of starch is aimed at imparting it specified physicochemical traits, respectively to the assumed mode of its potential application. One of the recent trends in its modification is the production of the so-called resistant starch which owing to reduced susceptibility to amylolysis serves a prebiotic function in a human body [Sajilata *et al.*, 2006; Zaragoza *et al.*, 2011]. Industrially, preparations of this type are produced from maize starch (“Hi-Maize” by Starch Australia Ltd.; “Hylon VII”, “Novelose 240” by National Starch and Chemical Company; “Amylomaize VII” by Cerestar Inc.; and “CrystaLean” by Opta Food Ingredients Inc.). These preparations are characterized by a significant resistance, but do not form viscous pastes [Leszczyński, 2004; Sajilata *et al.*, 2006]. Recent studies have been focused on the production of resistant starch from potato starch through its processing into retrograded form and then its chemical modification [Haralampu, 2000; Yu *et al.*, 2015]. Starches of these type are characterized by considerable resistance and undergo pasting, owing to which – apart from their basic prebiotic function – they may be potentially applied as

food additives to model the texture of food products [Song *et al.*, 2011; Yu *et al.*, 2015]. Acetylation of retrograded starch increases starch resistance to the action of amylases [Kapelko *et al.*, 2012a], whereas its crosslinking with adipic acid increases viscosity of the prepared pastes, as demonstrated in a short communication by Zięba *et al.* [2014]. In our previous work, we analyzed how changes in the degree of substitution of acetylated adipate of retrograded starch (RS $\frac{3}{4}$ type resistant starch) may affect – in a wide range – the resistance (up to ca. 70%) and pasting characteristics of the modified preparations [Kapelko-Żeberska *et al.*, 2015]. The objective of this study was, in turn, to determine the effect of the degree of acetylation and crosslinking with adipic acid of retrograded potato starch on its selected traits and on rheological properties of the prepared pastes and gels.

MATERIALS AND METHODS

Materials

The initial raw material was Superior Standard potato starch produced by PEPEES Łomża S. A. (Poland) in 2012. Starch was modified with acetic acid anhydride (analytically pure) and adipic acid (analytically pure) purchased at POCH SA Gliwice (Poland).

Production of starch preparations

Starch preparations were produced following the method described in our previous manuscript [Kapelko-Żeberska *et al.*, 2015]. Starch retrogradation was accomplished through

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the freezing of a starch paste with the concentration of 10 g/100 g at a temperature of -20°C for 3 days, followed by its defrosting at a temperature of 20°C for 2 days. The precipitated starch was flushed with distilled water, dried at 30°C for 24 h, ground, and sieved through a screen with 400 mesh size [Kapelko *et al.*, 2012].

Afterwards, the retrograded starch was subjected to double chemical modification including its acetylation and crosslinking with adipic acid. The starch was acetylated with 3.25, 6.5, 13.0, 26.0 or 52.0 mL of acetic acid anhydride per 100 g of starch, accordingly to the methodology provided by Kapelko *et al.* [2012]. In turn, crosslinking was carried out with the use of a crosslinking agent prepared by hot-dissolving 20 g of adipic acid in 80 g of acetic anhydride. As in the case of acetylation, starch was modified with various doses of the crosslinking agent, *i.e.* 0.25, 0.5, 1, 2 or 4 mL of the crosslinking agent per 100 g of starch, according to the method described by Zięba *et al.* [2014]. The resultant preparations were several times flushed with distilled water, dried and ground – analogously to the procedure of retrograded starch preparation.

Determination of the content of acetate groups

Determination of acetate groups content was conducted according to the method of Wurzburg [1987] modified by Singh & Nath [2012]. A weighted portion of starch (10 g) was transferred with distilled water (65 mL) to an Erlenmeyer flask. The suspension was neutralized against phenolphthalein with a 0.1 mol/L solution of NaOH. Afterwards, 25 mL of 0.5 mol/L NaOH were added and the sample was stirred for 35 min. Next, the solution was titrated with a 0.5 mol/L HCl solution. The degree of acetylation, expressing the number of grams of acetic acid residues in 100 g of the modified preparation, was computed from the formula:

$$A = \frac{(P_0 - P_w) \times N_k \times 0.043 \times 100}{M} \text{ [g/100 g]}$$

where: P_0 – volume (mL) of HCl solution used to titrate 25 mL of 0.5 mol/L NaOH, P_w – volume (mL) of HCl solution used to titrate the sample with acetylated starch, N_k – acid titre, and M – content (g) of starch dry matter in the sample.

Determination of the content of adipic groups

The content of adipic groups was determined according to the method developed by Zięba *et al.* [2014]. A weighted portion of the sample (1 g) was transferred with distilled water (50 mL) into an Erlenmeyer flask. Next, 1 mL of a water solution of glutaric acid and 50 mL of a 4 mol/L NaOH solution were added under continuous stirring, and the mixture was stirred by another 5 min. Afterwards, 20 mL of 12 mol/L HCL were added and the sample was cooled to 20°C . The mixture was three-fold extracted with 100 mL of ethyl acetate. After each extraction, the supernatant was decanted to an Erlenmeyer flask containing 20 g of anhydrous potassium sulfate, and the mixture was shaken for 10 min and filtrated. The solution was evaporated using a vacuum evaporator (pressure 50 mmHg, temperature 40°C). Then, 2 mL of pyridine and 1 mL

of Bis(trimethylsilyl)trifluoroacetamide (BSTFA) were added to dry residues for their complete solubilization. After 1 h, the sample was subjected to the chromatographic analysis using a PYE UNICAM series 104 gas chromatograph with a flame ionization detector (FID), a glass column ($2.1 \text{ m} \times 1.83 \text{ mm i.d.}$) packed with 5 % OV-17 on Chromosorb G/AW-DMCS with the granulation of 100/120 mesh. Separation parameters were as follows: carrier gas – nitrogen; flow rate – 40 mL/min; detector temperature – 250°C ; injector temperature – 240°C ; column temperature – 140°C ; injection volume – 0.1 μL ; and retention time – 2.8 min for glutaric acid and 4.5 min for adipic acid.

The content of adipic acid in the sample was determined based on the standard curve plotted for the samples with a known content of the acid.

Determination of amylose content with Morrison's method

Amylose content was determined according to the method elaborated by Morrison & Laignelet [1983]. A weighted portion of starch (120 mg) was dissolved in 20 mL of the solution containing: 1 part of 4 mol/L urea and 9 parts of dimethyl sulfoxide (DMSO). Then, 1 mL of the solution was collected from this sample, and 97 mL of distilled water and 2 mL of a iodine solution (2 g of potassium iodide and 0.2 g of sublimated iodine per 100 mL of the solution) were added. Absorbance of the solutions was measured 15 min after iodine solution addition, against a reference sample (not containing starch) using a CE 2010 spectrophotometer (Cecil Instruments, England) at a wavelength of 635 nm.

Determination of swelling power and water solubility at 80°C

Swelling power and solubility in water of the preparations were determined according to the method developed by Richter *et al.* [1986]. The preparation of acetylated and crosslinked retrograded starch was used to produce an aqueous suspension containing 1 g of starch per 100 g of the solution. The suspension was shaken for 30 min at 80°C . Afterwards, it was cooled to 20°C and centrifuged for 30 min using a Biofuge 28RS centrifuge (Heraeus Sepatech, Germany) with acceleration to 22,500 $\times g$. The separated supernatant was determined for dry matter content with the gravimetric method, and the precipitate remaining in the centrifuge tubes was weighed. Solubility indicates the amount of starch substance which after centrifugation is dissolved in the supernatant and is expressed in g/100 g. Swelling power determines the volume of water absorbed by the remaining part of starch and is expressed in g/g.

Starch solubility was computed according to the following formula:

$$R = \frac{dm}{a} \times 100 \text{ [g/100 g]}$$

where: R – solubility (g/100 g), dm – dry matter of supernatant (g/100 g), and a – concentration of the suspension (g/100 g).

Swelling power of starch was computed according to the following formula:

$$W = \frac{m_{\text{prec}} - b \times ((100 - R) / 100)}{b \times (100 - R)} \times 100 \text{ [g/100 g]}$$

where: W – swelling power (g water/g preparation), m_{prec} – mass of precipitate in a centrifuge test tube (g), b – weighted portion of starch in a centrifuge test tube (g), and R – solubility (g/100 g).

Determination of flow curves of pastes using Haake oscillating-rotary viscometer

Determination was conducted according to the method developed by Zięba *et al.* [2011]. Starch pastes with the concentration of 5 g/100 g were prepared by stirring the starch suspension at 96°C for 30 min. The flow curves of pastes were determined using an RS 6000 Rheostress oscillating-rotational viscosimeter (Haake, Germany). The analysis was carried out at a temperature of 50°C in the system of coaxial cylinders, at a shear rate of 1–300 s⁻¹. The determined flow curves were described with the following equations:

$$\text{Oswald de Waele: } \tau = K \times \dot{\gamma}^n$$

$$\text{Casson: } \tau = \tau_{0C}^{0.5} + (\eta_C \times \dot{\gamma})^{0.5}$$

where: τ – shear stress (Pa), K – consistency coefficient (Pa×sⁿ), $\dot{\gamma}$ – shear rate (s⁻¹), and n – flow behavior index, τ_{0C} – yield stress (Pa), η_C – Casson's plastic viscosity (Pa×s).

Determination of mechanical spectra using Haake oscillating-rotary viscometer

Mechanical spectra of starch gels were determined based on the method developed by Zięba *et al.* [2011]. Starch pastes with the concentration of 5 g/100 g were prepared analogously as in the case of flow curves determination, then cooled to a temperature of 25°C and kept at this temperature before measurement for 15 min. Determination was conducted with an RS 6000 Rheostress rheometer (Haake, Germany) in the system of coaxial cylinders (type Z38AL) at a constant deformation amplitude of 0.03, and a frequency range from 0.1 to 10 Hz. The mechanical spectra obtained allowed determining the phase shift angle tangent ($\text{tg } \alpha = G''/G'$), being a quotient of loss modulus G'' value and elasticity modulus G' value read out at the frequency of 1 Hz.

Statistical analysis

In order to determine the effect of the conducted chemical modifications on the investigated properties, the results obtained were subjected to two-way analysis of variance at a significance level of $p < 0.01$. Calculations were performed using Statistica ver. 10.0 software [StatSoft, Inc., 2011].

RESULTS AND DISCUSSION

The esterification of retrograded starch allowed obtaining preparations with degrees of substitution with residues of acetic from 0.7 to 11.2 g/100 g and adipic acid in the range of 0.1–0.3 g/100 g.

The statistical analysis demonstrated that the applied factors and their interaction had a significant effect on the ana-

lyzed properties of all preparations. A change in the value of parameters induced by the interaction of both factors (acetylation degree and crosslinking degree) was presented in the form of surface diagrams plotted following the procedure of weighted estimate with the least squares method (Figures 1–5). Graphical presentation of results is aimed at depicting the high variability of properties and possibility of their modification through changing the degree of acetylation and the degree of crosslinking.

Acetylation of potato starch causes changes in the structure of starch granules and in the degree of crystallinity [Muljana *et al.*, 2010; Diop *et al.*, 2011; Han *et al.*, 2012]. Starch depolymerization is likely to proceed during this process, which causes changes in the mean molecular weight [Berski *et al.*, 2011; Simsek *et al.*, 2012]. Both acetylation with acetic acid anhydride and crosslinking with adipic acid contributed to a decrease in amylose content of the preparations from 21 to 3 g/100 g (Figure 1). This decrease was greater along with the higher total degree of esterification. A similar tendency was observed in the case of acetylated retrograded starch [Kapelko *et al.*, 2012a]. Many works are available on the effect of changes in amylose content on starch granules subjected to esterification, however their results are not explicit. According to studies of some authors, acetylated starch contains more amylose than the native starch does [Simsek *et al.*, 2012; Singh *et al.*, 2012], whereas other authors state the opposite [Kapelko *et al.*, 2012; Emeje *et al.*, 2012; Wani *et al.*, 2012; Zięba *et al.*, 2013]. In turn, works by Akintayo *et al.* [2009] and Huang *et al.* [2007] show no significant differences in contents of amylose and amylopectin. Considerably fewer literature data concern changes in amylose content of starch subjected to the crosslinking process. Jane *et al.* [1992] report that the crosslinking of native starch does not

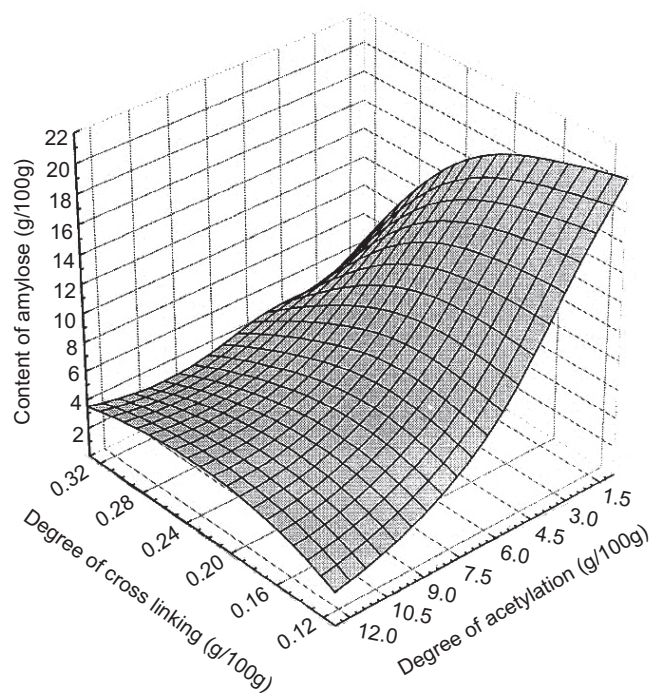


FIGURE 1. Effect of an esterification degree of the produced acetylated adipate of retrograded starch on amylose content.

induce changes in the molecular weight of amylose, which probably results from crosslinks formation only within amylopectin molecules. In turn, the crosslinking of pure amylose isolated from starch granules increases its molecular weight [Jane *et al.*, 1992]. Apparently conflicting results of studies enable speculating that the changes occurring in amylose during chemical modifications are, to a great extent, dependent on reaction conditions.

The physical properties of esterified starch, particularly its behavior in water, are determined by, *i.a.*, type of raw material and reagent applied, and process conditions including pH, temperature, and duration [Huang *et al.*, 2007; Ali, & Has-

nain, 2011; Bushra *et al.*, 2013]. The monoesters with a low degree of substitution (the maximum percentage of substitution with acetic acid residues reaches 2.5%; percentage of substitution with adipic acid residues reaches 0.135%) applied in the food industry are usually characterized by increasing solubility and swelling power along with an increasing esterification degree. A successive increase in the degree of substitution leads to a decrease in the values of these parameters [Kapelko *et al.*, 2012a; Wang, & Copeland, 2012]. Solubility of the produced preparations in water ranged from 19 to 100 g/100 g (Figure 2a). It was increasing in a wide variability range along with an increasing degree of acetylation and decreasing crosslinking with adipic acid residues. In turn, the swelling power of the preparations ranged from 0.7 to 100 g/g (Figure 2b). The high variability of swelling power values is probably due to the coupling of two modification procedures that have different effects on this characteristic.

One of the basic analyses applied to determine rheological properties of starch pastes involves determination of their flow curves. Rheological coefficients that describe the beginning of shearing at the determined flow curves include: yield stress τ_{0C} and consistency coefficient K. The τ_{0C} is a measure of stress needed to induce shearing, whereas the consistency coefficient K indicates paste viscosity at the beginning of this process. The influence of the degree of acetylation and degree of crosslinking of starch on both these coefficients had a similar course (Figure 3 and Figure 4a). The viscosity of paste at the beginning of shearing was increasing significantly at low degrees of substitution of one of the chemical modifications applied. At a low acetylation degree, both τ_{0C} and K were increasing in a wide variability range along with an increasing degree of crosslinking. A similar tendency was observed at the low degree of crosslinking with adipic acid residues and at the increasing acetylation degree. At the intermediate values

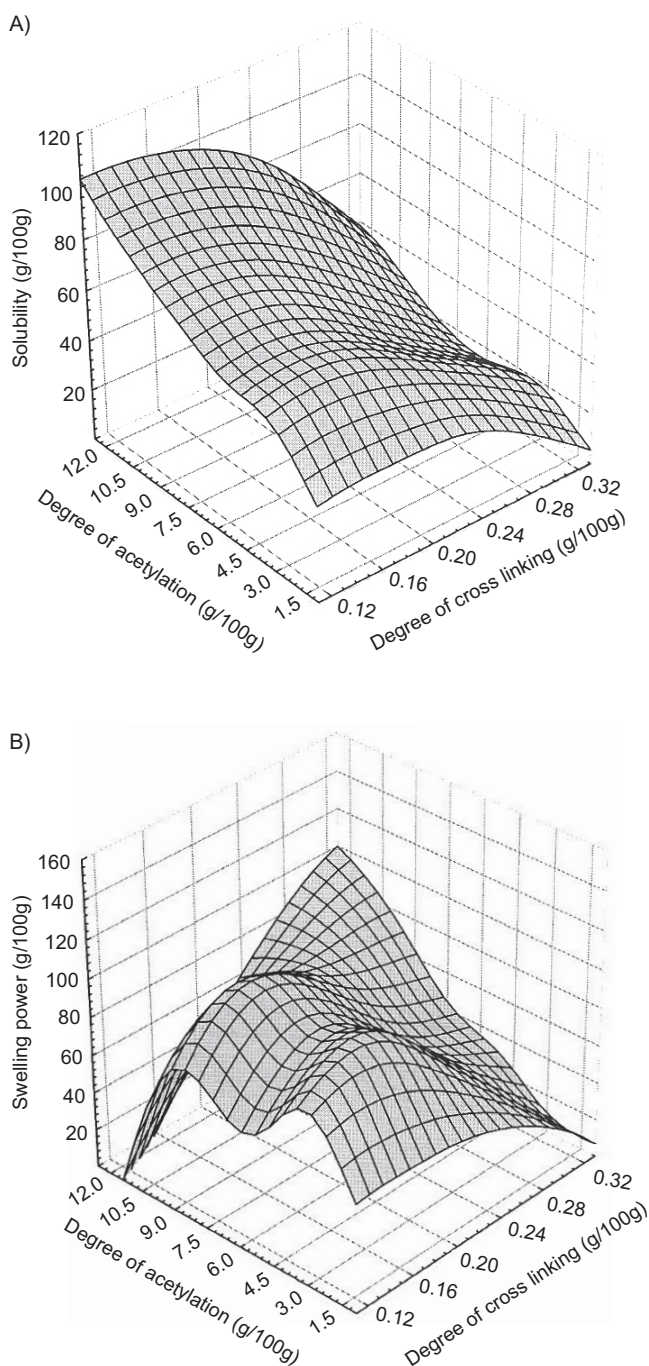


FIGURE 2. Effect of an esterification degree of the produced acetylated adipate of retrograded starch on its solubility in water (A) and swelling power (B).

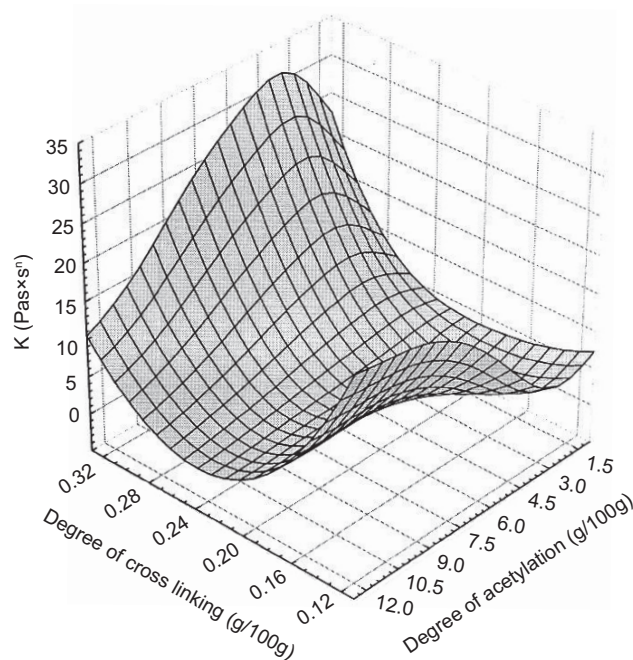


FIGURE 3. Effect of an esterification degree of the produced acetylated adipate of retrograded starch on the value of consistency coefficient (K).

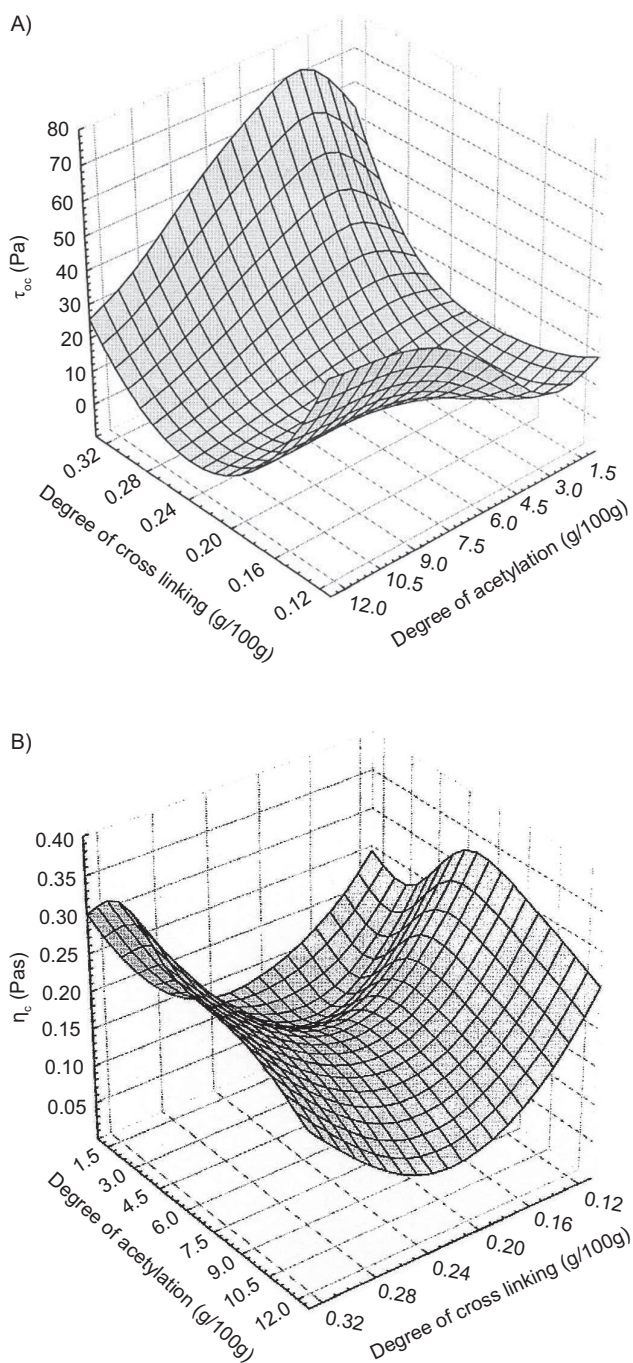


FIGURE 4. Effect of an esterification degree of the produced acetylated adipate of retrograded starch on yield stress τ_{oc} (A) and plastic viscosity η_c (B).

of esterification with acetic and adipic acids, the discussed coefficients reached relatively low values. Changes in the values of coefficients τ_{oc} and K proceeding upon the influence of single modifications (acetylation or crosslinking with adipic acid) of retrograded starch were presented in previous works [Zięba *et al.*, 2011; Kapelko *et al.*, 2012a, 2015]. Changes in the discussed rheological coefficients along with a changing degree of acetylation are described by second order equations possessing maxima [Kapelko *et al.*, 2012a]. In turn, the value of the consistency coefficient K of the paste prepared from retrograded starch adipate decreases along with a lower degree of starch crosslinking [Kapelko *et al.*, 2015]. It may,

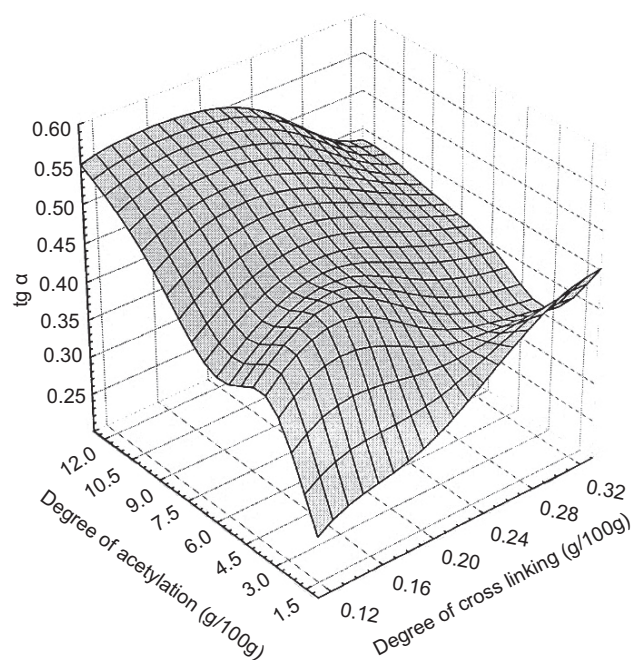


FIGURE 5. Effect of an esterification degree of the produced acetylated adipate of retrograded starch on the tangent of phase angle shift ($\text{tg } \alpha$).

therefore, be concluded that the changes induced by double chemical modification were not the sum of changes proceeding as a result of single modifications. Instead, interaction of both factors was observed.

A measure of paste viscosity at the end of the shearing process is the η_c coefficient determined from the Casson's equation. Changes upon the influence of crosslinking, in a wide range of variability, had a parabolic character with the minimal value, whereas changes induced by acetylation had a parabolic character and possessed the maximum value (Figure 4b). For this reason, the highest values of η_c coefficient were achieved at the highest and the lowest crosslinking with adipic acid residues and the medium degree of acetylation. Analogous character of changes of η_c coefficient was observed in the case of acetylated retrograde starch [Kapelko *et al.*, 2012a].

Figure 5 depicts changes in $\text{tg } \alpha$ being a measure of the strength of the formed gels. The tangent α expresses the relative contribution of viscous and elastic traits in modeling the viscoelastic properties of the material. The values $\text{tg } \alpha > 0.1$ are typical of weak gels, whereas the values $\text{tg } \alpha < 0.1$ characterize strong gels [Schramm, 1994]. All gels produced from preparations of acetylated adipate of retrograded starch formed weak gels ($0.26 < \text{tg } \alpha < 0.57$), and changes evoked by one modification were significantly determined by the esterification degree of the second modification. At low values of acetylation degrees, the increasing crosslinking was inducing an increase in $\text{tg } \alpha$ value. An opposite tendency occurred at high substitution with acetic acid residues. At the low crosslinking of starch, the $\text{tg } \alpha$ value was increasing in a wide variability range along with an increasing acetylation degree. This correlation was, however, not observed at higher starch crosslinking with adipic

acid residues. As in the case of earlier discussed rheological coefficients, here we may also speak of the interaction of both modifying factors. The use of single chemical modifications of retrograded starch enable explicit determination of the character of changes in $tg\ \alpha$ coefficient upon the influence of a varying degree of esterification. Its value decreases along with increasing crosslinking of retrograded starch adipate [Kapelko *et al.*, 2015], and in the case of acetylated retrograded starch the changes have a character of the polynomial second degree function possessing the minimal value [Kapelko *et al.*, 2012a].

CONCLUSIONS

The conducted esterification of retrograded starch allowed obtaining preparations with a various degree of substitution with acetic and adipic acids, which determined their properties. The total increase in esterification degree caused a decrease in amylose content. In a wide range of variability, the solubility of the analyzed preparations in water was increasing along with an increasing degree of acetylation and a decreasing degree of crosslinking with adipic acid residues. Viscosity of the formed pastes was increasing, in a wide range, along with increasing crosslinking of starch. The conducted modifications afford the possibility of modelling both the solubility and viscosity of pastes produced from acetylated adipate of retrograded starch.

RESEARCH FUNDING

Publication supported by Wrocław Centre of Biotechnology, programme The Leading National Research Centre (KNOW) for years 2014–2018.

CONFLICT OF INTEREST

Authors declare no conflict of interest.

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Submitted: 31 December 2015. Revised: 27 July and 8 August 2016. Accepted: 21 September 2016. Published on-line: 19 January 2017.

