

## INFLUENCE OF POTATO STARCH OXIDATION ON TEXTURE AND RHEOLOGICAL BEHAVIOUR OF SOME SWEET DESSERTS

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The aim of the work was to apply objective methods for texture evaluation of desserts of oxidised potato starch preparations using instrumental measurement of rheological properties and texture. Desserts were made from commercial starch preparations, *i.e.* “Skrobia budyniowa” and “Skrobia żelująca”, with a different degree of carboxyl groups substitution (0.03% and 0.11%, respectively). The starch with a higher degree of oxidation caused decreasing of texture parameters of desserts. Viscosity variability ( $\eta^*$ ) at the frequency range from 1 to 10 s<sup>-1</sup> was very well described by Bingham model of viscosity (for viscoplastic fluids with initial yield stress) for all the examined desserts. A lower degree of oxidation of starch preparation “Skrobia budyniowa” resulted in the highest values of storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of these desserts while higher oxidation of starch preparation “Skrobia żelująca” caused the lowest values of these rheological parameters. Thus, increasing the degree of carboxyl groups substitution resulted in more continuous microstructure of dessert gels.

### INTRODUCTION

Oxidised starches are very popular food thickening and texturing agents. They represent about 65% of five types of modified starches present on the Polish market. These preparations are produced by hypochlorite treatment and their physico-chemical properties as well as usability strongly depend on the quantity of the reagent used and, consequently, on the degree of substitution [Wurzburg, 1986]. The main applications of oxidised starches are production of puddings and jelly sweet desserts. According to the Polish Standards the quality of these types of products is evaluated by subjective, sensory methods. Participation of experienced experts in the evaluation reduces classification errors but objective, standardised instrumental methods should be developed.

Texture of food products is related to objective treatment (processing handling, storage) but, on the other hand, to social habits, *i.e.* consumer's acceptance of foods. Texture profile analysis (TPA) is an objective method of sensory analysis pioneered by Szcześniak [1963] who defined the textural parameters. The TPA is based on the recognition of texture as a multi-parameter attribute. Two groups of these parameters are distinguished: (i) primary parameters (hardness, cohesiveness, springiness/elasticity, and adhesiveness), (ii) secondary (derived) parameters (fracturability/brittleness, chewiness and gumminess) [Szcześniak, 1966].

Instrumental Texture Profile Analysis was developed constituting an interesting way of analysing a series of textural parameters in only one test [Pons & Fiszman, 1996;

Meullenet & Gross, 1999]. The penetration tests were found a useful method for investigations of gels [Edwards *et al.*, 1998; Gregson *et al.*, 1999]. Aguilera and Rojas [1996] regarded texture as a manifestation of the rheological properties of food. Eliasson and Kim [1992] found the relationship between rheological measurements and mechanical properties of potato starch pastes. Thus, a close relationship between rheological behaviour and texture of a product was confirmed and knowledge of the gel rheological character allowed explaining variability of instrumental TPA parameters.

The aim of this work was to evaluate texture and rheological properties of desserts obtained from commercial Polish oxidised potato starch preparations as well as to determine the influence of the degree of carboxyl groups substitution on these properties.

### MATERIAL AND METHODS

**Material.** Commercial potato starch preparations “Skrobia budyniowa” (SB) and “Skrobia żelująca” (SZ) as well as native potato starch (SN), produced by the Polish company WPPZ S.A., Luboń, were used in the study.

Puddings and jellies were made according to the Polish Standard PN-A-74723 and plant standard Zakładowa Norma ZN-84/MRiBŻ-I-09/89, respectively.

Preparation of puddings: The suspension of 17.6 g of starch preparation in 50 mL of cold milk was poured into the boiling milk, mixed with 20 g of sucrose and then boiled for 30 s. The pudding was poured into a cup and allowed to set at room temperature for 4 h.

Preparation of jellies: The mixture composed of 60 g of starch preparation, 100 g of sucrose and 500 mL of water was boiled under continuous agitation for 180 s, then acidified with 2 g of citric acid. The obtained dessert was poured into a cup and allowed to set at room temperature for 2 h.

**Methods.** The degree of substitution of carboxyl groups in oxidised potato starch preparations was determined according to the FAO committee (Joint Expert Committee on Food Additive) recommendations [FAO Food and Nutrition, 1997]. The method consists in the conversion of carboxyl groups into the acidic form with 0.1 N hydrochloric acid, washing with distilled water till complete removal of the chloride anion, and titration with 0.1 N sodium hydroxide.

Gelatinisation was monitored using a Brabender viscograph for 6% starch suspensions under the following conditions: measuring cartridge 0.07 Nm, heating/cooling rate 1.5°C/min, thermostating time 30 min.

Texture properties of the examined desserts were measured using a TA-XT2 texture analyser (Stable Micro System, UK). The sample was twice penetrated with cylindrical aluminium probe of 35 mm diameter with flat end until 25 mm was reached at the penetration speed of 1.0 mm/s. Five replicates were made for each probe.

To assess the texture of soft gels usually made using oxidised starches the following parameters were accepted: (i) hardness (or firmness) [N] – defined as the maximum peak force during the first penetration cycle; (ii) adhesiveness [Ns] – defined as the negative force area for the first bite. It represents the work required to overcome the attractive forces between the surface of food and the surface of other material which the food comes into contact with; (iii) cohesiveness [-] – defined as the ratio of the positive force area during the second compression to that during the first compression; (iv) springiness (or elasticity) [-] – is related to the height that the food recovers during the time that elapses between the end of the first bite and the start of the second bite. It is calculated as the ratio of the time of the second compression to the time of the first compression; (v) gumminess [N] – defined as the result of multiplication of hardness and cohesiveness.

Viscoelastic properties of the examined desserts were measured using a Rheostress 1 rheometer (Thermo Haake, Germany) in oscillation mode. Cone-plate device (diameter 35 mm, cone angle 2°, minimal gap 0.106 mm) was used for dynamic measurement. Frequency ranged from 1 to 10 s<sup>-1</sup> which corresponds to radial speed from 6.28 to 62.8 rad/s, respectively. Storage modulus (G'), loss modulus (G'') and phase angle ( $\delta/\text{tg}\delta$ ) were the measures of changes in viscoelastic properties. For traditional characteristics of apparent viscosity, complex values  $\eta^*$  were calculated.

Measurements were done in seven replications.

Dynamic oscillatory measurements should be conducted within linear viscoelastic range of the examined material. Stress amplitude sweep method, in which the applied stress was ramped from 1 to 100 Pa at an angular frequency of 6.28 rad/s (1 Hz), was used. Storage moduli were collected and plotted as a function of the applied stress (not shown). Central point on the curve plateau responded to  $\tau = 10$  Pa and this value was accepted as the applied stress in the oscillatory test for both: viscous fluids – puddings and pseudo-stable gels – jellies.

The fresh made desserts were rapidly frozen in liquid nitrogen and lyophilised. The dried samples were coated with gold and examined in a scanning electron microscope JSM 5200 (JEOL, Japan) at 10 kV.

Statistical analysis of results was carried out with a Statistica ver. 5 [1984–1995] program.

## RESULTS AND DISCUSSION

Starch preparations “Skrobia budyniowa” (SB) and “Skrobia żelużąca” (SZ) revealed a low degree of substitution of carboxyl groups (Table 1). These levels of carboxyl groups content are typical rather for bleached starches (E 1403) than for oxidised ones (E 1404) [FAO Food and Nutrition, 1997]. Higher oxidised starches (even above 1% carboxyl groups content) commonly used in the paper industry, are not applied in the food industry due to significant depolymerisation occurring during the oxidation process [Manelius *et al.*, 2000].

TABLE 1. Degree of substitution in potato starch preparations.

Preparation type	Content of carboxyl groups [%]	Degree of substitution
“Skrobia budyniowa”, SB	0.03	0.001
“Skrobia żelużąca”, SZ	0.11	0.004

Different pasting properties (Figure 1) as well as texture characteristics (Table 2) suggest various applications of the examined starch preparations. In spite of very slight oxidation applied for the production of SB, this preparation revealed threefold lower viscosity peak as well as a significant increase in viscosity at lower temperature, compared to native starch (Figure 1). The most important effect of this reaction, strongly influencing usability of SB preparation, is the increase in the final viscosity, which indicated an increase in gelling properties. Significant drop of the peak of the curve and final viscosity resulted from much stronger depolymerisation related to more intense oxidation applied during technological processing of SZ preparation (Table 1).

TABLE 2. Characteristics of texture properties of desserts.

Dessert	Starch type	Hardness [N]	Adhesiveness [Ns]	Springiness [-]	Cohesiveness [-]	Gumminess [N]
Pudding	SN	4.14±0.453	3.56±1.169	1.01±0.039	0.96±0.060	3.96±0.324
	SB	5.82±0.327	26.62±2.534	1.00±0.044	0.77±0.117	2.17±0.385
	SZ	1.68±0.198	7.02±1.312	1.00±0.010	0.69±0.019	1.16±0.105
Jelly	SN	4.77±0.948	11.73±1.169	1.02±0.021	0.79±0.183	3.68±0.125
	SB	7.14±0.042	24.61±5.629	1.03±0.038	0.65±0.035	4.67±0.223
	SZ	5.35±1.195	5.70±3.734	1.10±0.053	0.47±0.014	2.50±0.487

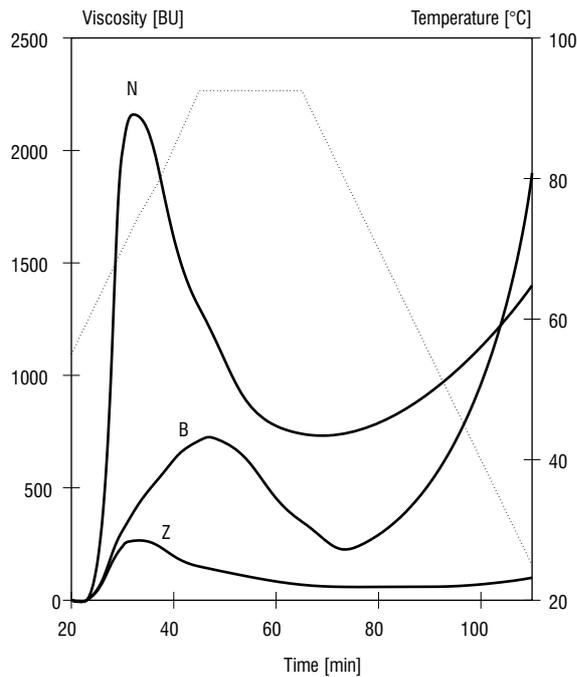


FIGURE 1. Brabender viscosity curves for 6% potato starch suspensions: N – native potato starch; B – potato starch preparation “Skrobia budyniowa”; Z – potato starch preparation “Skrobia żelująca”.

Morikawa and Nishinari [2000] informed that storage modulus ( $G'$ ) of potato starch pastes heated up to 95°C changed with starch concentration according to the following equation  $G' = C^{2.8}$  (where C means concentration ranging from 0.5% to 30%). Evangelidou *et al.* [2000] studied the influence of carbohydrates on the time-temperature course of structure formation from solutions of natural and oxidised starches and found a significant effect of oxidised starch:sucrose ratio on the course of storage and loss moduli changes during paste cooling, *i.e.* formation of gel structure. Considering these conclusions and different concentration of starch or sucrose in puddings and jellies (6 and 9%, or 7 and 15%, respectively), decision was made to compare changes of rheological properties for desserts separately.

Texture parameters revealed significant diversification caused by the oxidation process but constant tendency in parameter variability was not found (Table 2). Springiness of all the examined desserts was almost constant (values varying from 1.00 to 1.10). Maximum of texture properties in desserts obtained from SB preparation were observed. Especially high values of adhesiveness were found for both types of desserts using SB preparation. Hardness and guminess of SB preparation jellies were also higher than those of jellies obtained from SN and SZ preparations. Cohesiveness was the only texture parameter which revealed a decrease connected with an increased degree of oxidation. Guminess of pudding decreased regularly. These results indicate that the use of higher oxidised starch preparation, with lowered molecular mass caused by oxidation, decreased the values of texture parameters.

In contrary to texture parameters, values of rheological parameters of puddings and jellies (Figure 2–5) were gathered into two easily recognisable groups. Values of  $G'$  for jellies were about six times higher than those for puddings (Figure 2). The curves for  $G' = f(\omega)$  relationship

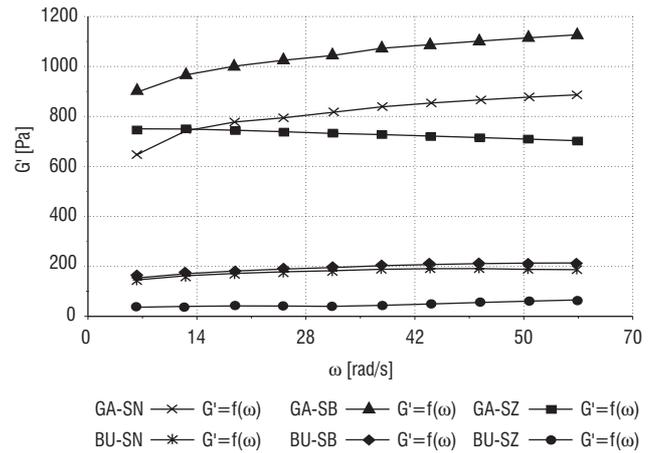


FIGURE 2. Storage modulus for desserts of potato starch preparations (GA – jelly; BU – pudding).

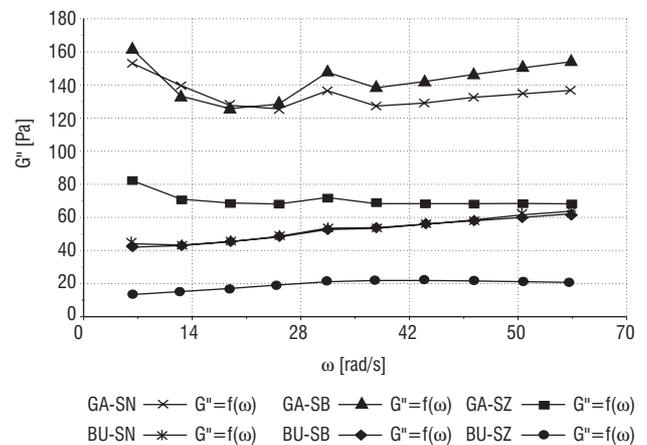


FIGURE 3. Loss modulus for desserts with addition of potato starch preparations (GA – jelly; BU – pudding).

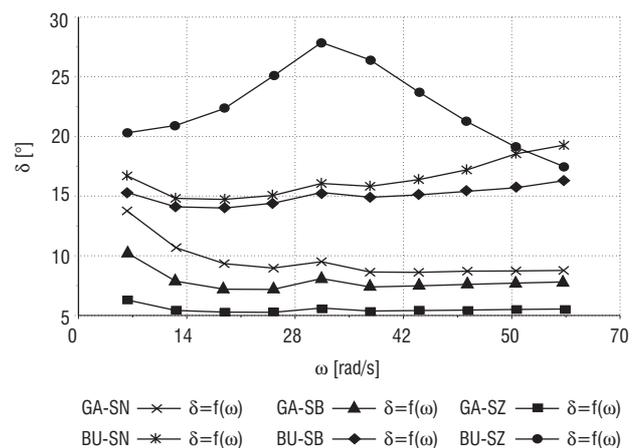


FIGURE 4. Phase angle for desserts with addition of potato starch preparations.

for jellies from SB and SN preparations were parallel and  $G'$  values increased with frequency increase (900–1100 Pa and 650–900 Pa, respectively). The shape of the curve for jelly from SZ preparation was different and  $G'$  values decreased with frequency increase (750–700 Pa). High  $G'$

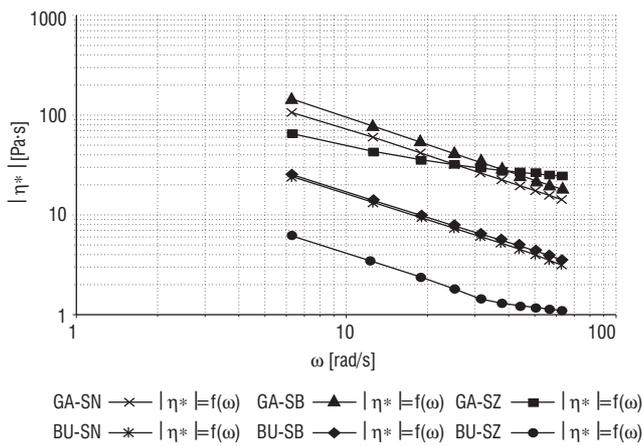


FIGURE 5. Viscosity curves for desserts with addition of potato starch preparations (GA – jelly; BU – pudding).

values for all jellies confirmed predominance of elastic properties in their rheological behaviour. Almost the same values and parallel course of the curves of the  $G' = f(\omega)$  relationship were characteristic for puddings obtained from SB and SN preparations. For SZ preparation pudding lower  $G'$  values than for the latter were obtained. It is worthy attention that for all puddings the  $G'$  values were practically constant during the frequency sweep. Thus, puddings should be classified as weak gels for which  $G'$  is constant in laminar flow region [Rosalina & Bhattacharya, 2002].

The difference between the curves of the  $G'' = f(\omega)$  relationship for puddings and jellies was also found (Figure 3). The curves for jellies from SB and SN preparations initially decreased and next they increased after they reached the shear rate of about 32 rad/s while the curves for puddings (with 3–4 times lower  $G''$  values) presented stable tendency to increase. The  $G''$  values for jelly from SZ preparation were also lower than those for jellies from SB and SN preparations and decreased with increasing shear rate. The course of the curve  $G'' = f(\omega)$  for puddings from SZ preparation was similar to this for jelly and the  $G''$  values were also on the lowest level. The analysis of variability of loss modulus,  $G''$ , which corresponds to the share of viscous properties in viscoelastic characteristics of materials, showed rheological character of puddings from SB and SN preparations to be more viscous than that for pudding from SZ preparation.

The curves of phase angle in function of shear rate shown in Figure 4 confirmed viscous character of puddings in order of increasing viscosity  $SB < SN < SZ$  and elastic character of jellies in order of increasing elasticity  $SN \leq SB < SZ$ . The lowest elasticity of pudding and the highest

elasticity of jelly from SZ preparation (despite the lowest values of  $G''$  and  $G'$ ) were sharply confirmed by phase angle or its tangent (Table 3).

It should be pointed out that the curves of the  $G' = f(\omega)$  and  $G'' = f(\omega)$  relationships for jellies and puddings from SB and SN preparations were similar which suggested that 0.03% oxidation (0.001 degree of substitution) resulted only in quantitative changes. Different course of the curves for desserts obtained from SZ preparation (0.11% oxidation, as well as 0.004 degree of substitution) and the lowest values of  $G'$  and  $G''$  suggested even qualitative changes in rheological behaviour. Probably, it could be caused by a drop in the molecular weight of SZ preparation as a result of alkaline hydrolysis accompanying oxidation reaction during sodium hypochlorite treatment applied in technological processing [Manelius et al., 2000].

The course of viscosity curves presented in Figure 5 was mathematically described using the software by Thermo Haake coupled with RheoStress. All presented curves were accurately described by the Bingham model of viscosity for oscillation mode of measurements [Schramm, 1998]. The form of this Bingham model is as follows:  $\eta = \eta_p + \tau_0/\omega$ , where:  $\eta$  = viscosity at particular oscillation,  $\eta_p$  = plastic viscosity,  $\tau_0$  = initial yield stress, and  $\omega$  = angular speed. The Bingham model of viscosity as well as Bingham flow curve described viscoplastic fluids with initial stress yield. This non-Newtonian fluid is characterised by shear thinning as a result of ordering or partial deformation of the inside structure. High coefficients of determination ( $R^2$  close to 1) calculated for modulus coefficients suggested that the examined desserts behaved like Bingham fluid in the frequency range from 1 to 10  $s^{-1}$  (Table 4). Different behaviour of desserts from SZ preparation was again confirmed. Stronger structure of these desserts can be a reason of a lower drop of viscosity during shearing.

The SEM analysis of microstructure of potato starch desserts (Figure 6 a–f) seemed to confirm the results of rheological measurements. Although, direct comparison of

TABLE 4. Coefficients of Bingham model of viscosity.

Dessert	Starch type	Plastic viscosity, $\eta_p$ [Pa·s]	Shear stress, $\tau_0$ [Pa]	$R^2$ [-]
Pudding	SN	1.487	152.0	0.999
	SB	1.226	146.9	0.999
	SZ	0.431	36.1	0.997
Jelly	SN	5.510	645.7	1.000
	SB	5.065	888.2	0.999
	SZ	20.28	284.9	0.998

TABLE 3. Mean values of rheological parameters of desserts in the examined frequency range.

Dessert	Starch type	Storage modulus, $G'$ [Pa]	Loss modulus, $G''$ [Pa]	$\text{tg } \delta (G'/G'')$ [-]	Phase angle, $\delta$ [°]
Pudding	SN	178.5	52.6	3.39	16.46
	SB	193.7	52.2	3.71	15.05
	SZ	47.4	19.3	2.46	22.43
Jelly	SN	810.0	134.2	6.03	9.57
	SB	1043.6	142.7	7.31	7.86
	SZ	729.3	70.3	10.37	5.52

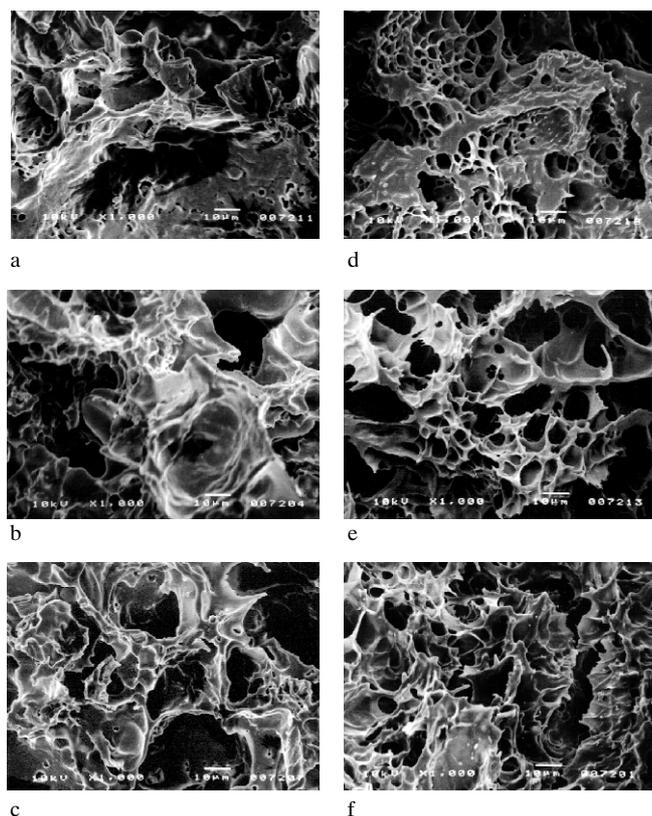


FIGURE 6. SEM photos of the microstructure: a – SN pudding, b – SB pudding, c – SZ pudding; d – SN jelly, e – SB jelly, f – SZ jelly.

structural differences was difficult due to different recipes for both desserts resulting in various: starch concentration, pH-acidity, sugar, protein and fat content (Figure 6 a–f). However, the most distinct differences between microstructure of pudding and jelly were observed in relation to the character of gel network. In the case of puddings, all the analysed samples of potato starch formed continuous network of gel with both amylopectin and amylose-rich phase. The microstructure of jellies can be described as a closely-packed system with molecularly dispersed starch where amylopectin phase was shown to be more continuous, and amylose appeared as dispersed droplets [Svergmärk & Hermansson, 1991]. However, constant trend of changes in the structure of starch desserts caused by oxidation could be observed. Both jellies and puddings made from native potato starch (Figure 6 a, d) were characterised by more discontinuous gel structure, compared to that obtained from modified starches. The structure of desserts made from oxidised starch preparations became gradually more continuous with an increased degree of substitution with carboxyl groups.

## CONCLUSIONS

1. “Skrobia budyniowa” and “Skrobia żelująca” preparations characterised by different degree of substitution of carboxyl groups revealed different pasting properties, significantly changed in comparison to native potato starch.

2. Texture parameters of desserts revealed significant diversification caused by application of different preparations of oxidised potato starch. Maximum hardness and adhesiveness were obtained for desserts made from slightly

oxidised starch preparation “Skrobia budyniowa”.

3. The highest values of storage and loss moduli were reported for low-oxidised “Skrobia budyniowa”, while the lowest ones for highly-oxidised “Skrobia żelująca” preparations.

4. Slightly oxidised preparation “Skrobia budyniowa” as well as native potato starch revealed similar values of rheological parameters that were found different from these of “Skrobia żelująca”, the preparation of significantly higher degree of substitution.

5. The structure of desserts made from oxidised potato starch preparations became gradually more continuous with increased degree of substitution of carboxyl groups.

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### WPLYW STOPNIA UTLENIEŃ SKROBI ZIEMNIACZANEJ NA TEKSTURĘ I WŁAŚCIWOŚCI REOLOGICZNE WYBRANYCH DESERÓW

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Celem pracy było zastosowanie obiektywnych metod oceny tekstury deserów z preparatów utlenionej skrobi ziemniaczanej w oparciu o instrumentalne pomiary właściwości reologicznych i tekstury. Do badań użyto handlowych preparatów skrobi wyprodukowanych z naturalnej skrobi ziemniaczanej o nazwach: “Skrobia budyniowa” i “Skrobia żelująca” o różnym stopniu substytucji grupami karboksylowymi (odpowiednio, 0.03 i 0.11%). Stwierdzono, że stosowanie skrobi o wyższym stopniu utlenienia powoduje obniżenie parametrów tekstury deserów (tab. 2). Zmienność lepkości zespolonej deserów,  $\eta^*$ , w zakresie częstotliwości od 1 do  $10^{-1}$ s najlepiej opisuje moduł lepkości Binghama charakteryzujący ciecz lepkoplastyczne z granicą płynięcia. Najwyższymi wartościami modułu sprężystości,  $G'$ , i modułu stratności,  $G''$ , charakteryzowały się desery z preparatu “Skrobia budyniowej” o niższym stopniu utlenienia, a najniższymi desery z preparatu “Skrobia żelującej” - o wyższym stopniu utlenienia (tab. 3, 4). Tak więc, wzrost stopnia podstawienia grupami karboksylowymi wiązał się z utworzeniem bardziej ciągłej struktury żelowej obydwu typów deserów (rys. 6).