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Pasting and rheological properties of oat starch and its derivatives

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ABSTRACT

Modification of starch led to new product with new desirable properties. Oat starch was subjected to different chemical modifications (acetylation, oxidation and phosphorylation). These processes greatly influenced physico-chemical properties of starch. There were observed shifts in molecular mass, as well as in amylose, lipid and phosphorus content. Also some changes were observed in gelatinization characteristics of starches, the most visible in case of acetylated starch. Introduction of functional groups greatly increased such starch properties, in comparison to native one, like water binding capacity (WBC) and aqueous solubility (AS). Also the influence of chemical modifications on rheological properties of oat starch pastes were investigated. Pasting characteristics of 5.00% starch suspensions were performed. For acetylated and starch phosphate pasting curves had a similar course. The other group of pasting curves was created by viscosity profiles obtained for oxidized and native starches. Rheological properties of 4.00%, w/w starch pastes were evaluated based on flow curves and results of equilibrium tests. Power law rheological models were fitted to the obtained data. All pastes were classified as shear thickened fluids. Flow index values were practically temperature independent, with exception for native starch paste. Yield stress values were calculated for pastes at 20 °C, but were impossible to determine for acetylated starch due to sample gelling. Rheological properties of starch pastes and pasting characteristics were compared. The viscosity oscillations of native and oat starch phosphate pastes were observed. Possible reasons of thixotropy behavior occurrence at 20 °C, and its vanishing at 50 °C were discussed.

1. Introduction

Quite often native starch is not a best product in a particular process or application, due to its shortcomings like low shear resistance and thermal stability, thermal decomposition and high tendency towards retrogradation. In order to improve such properties, starch could be subjected into modification process. Modifications allow starch to maintain desirable appearance and texture despite stress occurring during industrial processing of starch. There are various ways of starch modifications (physical, chemical, enzymatic and combined), designated to change one or more of its properties. The physiochemical properties of starch can be drastically altered by chemical modifications and lead to new product with desired properties, suitable for specific goal (BeMiller & Whistler, 2009; Swinkels, 1990).

Differences among rheological properties of starch water solutions depend on amylose and amylopectin content, the presence of functional groups, i.e. phosphate, and also granularity. As a consequence it could be observed that each starch has a distinguished pasting temperature, and also pasting profile. Starch pasting characteristics and rheological properties of pastes depend on starch botanical origin. Starch is mainly obtained from cereal grains, mostly maize, and other plant sources including potatoes. The most often used, and also investigated, is maize starch and its derivatives (Sandhu & Singh, 2007; Singh, Inouchi, & Nishinari, 2006). A lot of interest arouse about starches of different origins (Srichuwong, Sunatri, Mishima, Isono, & Hisamatsu, 2005) such as wheat (Blazek & Copeland, 2008), rice (Li, Shoemaker, Maa, Shen, & Zhong, 2008; Wang et al., 2010; Yu, Ma, Menager, & Sun, 2010) and potatoes (Singh, Isono, Srichuwong, Noda, & Nishinari, 2008; Zaidul et al., 2007).

Rheological properties of starch pastes determine their possible application as thickeners or as gelling agents. The most basic rheological characteristic of starch paste is viscosity, which changes in broad range upon applied shearing. Starch paste may contain unswollen granules, partially swollen granules, fragments of swollen granules, swollen starch aggregates, dissolved starch molecules and retrogradated starch precipitates. Properties of starch pastes like viscosity, texture, the paste transparency and resistance to shear and tendency to retrogradate play very important role in commercial application of starch (BeMiller & Whistler, 2009; Swinkels, 1990).

The possibility of describing these changes as function of shear rate requires the knowledge of parameters of the basic rheological power law state equations like Herschel–Bulkley or Ostwald–de Waele. From technological point of view the knowledge of yield

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Nomenclature

Symbols

t	time (s)
η	viscosity (Pa s)
$\dot{\gamma}$	shear rate (s^{-1})
τ_0	yield stress (Pa)

stress is very important. In many cases viscosity of food products depends not only on shear rate, but is also changing in time. Such behavior classifies mentioned above systems into group of time-dependent materials. Thixotropy phenomenon is observed when many foodstuffs are subjected to shear (Abu-Jdayil, 2003; Campbell, Leong, & Yeow, 2005; O'Donnell & Butler, 2002). One of the methods used to detect this phenomenon is hysteresis loop test. Such behavior is caused by complicated structure of a material subjected to shear. Interactions among macromolecules could imply the mechanism of retarded structure adaptation to current shear conditions. As a result, viscosity of investigated system is changing in time evolving to equilibrium in given shear conditions.

In spite of a low level of its manufacture, oat starch attracts most attention among cereal starches. It offers untypical properties such as small size of granules, well developed granule surface, and high lipid content (Hoover, Smith, Zhou, & Ratnayake, 2003; Mirmoghtadaie, Kadivar, & Shahedi, 2009; Zhou, Robards, Glennie-Holmes, & Helliwell, 1998). Some papers related to mechanical and durability properties of thin layer made of (acetylated) oat starch and plasticizers were recently published (Galdeano, Grossmann, et al., 2009; Galdeano, Mali, et al., 2009). But there is no comprehensive analysis of rheological properties, including pasting profile, of native and modified oat starches. In this paper, interactions between oat starch gels and gels of its derivatives such as acetylated, oxidized, and phosphorylated into mono- and di-starch phosphate starches are described.

2. Materials and methods

2.1. Materials

Oat starch was isolated according to Paton (1977) on a laboratory scale from oat grains of the naked Polar variety harvested in 2005 in the Breeding Station in Strzelce Krajenskie in Poland. This starch was subjected to the following modifications.

- Acetylation method described by Phillips, Huijum, Duohai, and Harold (1999) was used to prepare acetylated starches. Starch (100 g) was dispersed in distilled water (225 mL) and stirred for 1 h at 25 °C. NaOH (3%) solution was used to adjust the suspension pH to 8.0. Acetic anhydride (10 g) was added drop-wise to the stirred slurry, while maintaining the pH within the range of 8.0–8.4 using 3% NaOH solution. The reaction was allowed to proceed for 10 min after the completion of acetic anhydride addition. The slurry was then adjusted to pH 4.5 with 0.5 N HCl. After sedimentation, it was washed free of acid, twice with distilled water and once with 95% ethanol, and then oven-dried at 40 °C.
- Oxidation according to Forsell, Hamunen, Autio, Suorti, and Poutanen (1995) using sodium hypochlorite as oxidizing reagent.
- Phosphorylation in order to obtain mono starch phosphates according to Lim and Seib (1993) using sodium tripolyphosphate (STPP) and sodium phosphate (STMP).

3. Methods

Chemical composition of the investigated starches was analyzed: apparent amylose content according to Morrison and Laignelet (1983), lipids (ISO 3947:1977), total phosphorus (ISO 3946:1982). Acetyl groups according to Wurzburg and Whistler (1964), carboxyl groups according to ISO 11214:1996, carbonyl groups according to Potze & Hiemstra (1963), water binding capacity (WBC) and aqueous solubility (AS) according to Richter, Augustat, and Schierbaum (1969). Granularity profile was measured with Fritsch Analysette 22 laser analyzer (Idar-Oberstein, Germany).

3.1. Molecular mass determination

For determination of weight and number average molecular mass HP-SEC experiments were performed on the system consisting of pump (Knauer K-501), precolumn OHpak SB-G, column OHpak SB-805 HQ (Shodex) and refractive index detector (Knauer K-2001). 20 microliters of starch dissolved in DMSO (1.25 wt.%) were eluted with deionized water at the flow rate 1 mL/min.

3.2. Differential scanning calorimetry (DSC)

A DSC measurements were performed according to procedure described by Hoover et al. (2003) A Shimadzu DSC-60 instrument (Kyoto, Japan) was used. The heating was performed in the range of 20–115 °C with the 10 °C/min rate of the temperature increase. Empty pan was used as a standard. Experiments were triplicated.

4. Rheology

4.1. Pasting characteristic of aqueous starch suspensions

Characteristics of pasting were performed for 5.00 wt.% suspensions with the RS 150, (Haake, Karlsruhe, Germany) rheometer with a Vane rotor FL40 measuring system (volume 75 mL, 75 rpm). The samples were heated from 25 °C to 96 °C with the rate of 1.5 °C/min, followed by 10 min storage at 96 °C and return to 25 °C with the same rate. The samples were then stored for subsequent 5 min. Experiments were triplicated.

4.2. Pastes preparation

Known amount of starch (4.00%, w/w) suspended in relevant volume of either redistilled water was 30 min agitated at ambient temperature. The container with that suspension was transferred into water bath and 30 min stirred at 98 °C. Then the paste was poured into measuring system of the rheometer.

4.3. Apparent viscosity measurements

The first stage of the rheological studies included a hysteresis loop test which demonstrated that the pastes exhibited thixotropy when sheared. The rheological properties of all starch pastes were manifesting in different course of flow curves, because the viscosity of thixotropic material is a function of shear rate and the time of shear. The results of hysteresis loop test are strongly depend on the time and volume of the sample and were not used. Instead, a conventional method of studying fluids with time-dependent behavior was employed, i.e. apparent viscosity changes with time were measured at a fixed shear rate (De Kee, Turcotte, & Chan Man Fong, 1996; Kembłowski & Petera, 1979). The operational system provided recording lasting 600 s changes of the apparent viscosity at a constant shear rate selected from the range of 0–1000 s^{-1}. The time-dependent changes in viscosity at a fixed shear rate are due

to the fact that the structure of paste is preserved and the system is able to adjust to the existing shear conditions. The moment at which the value of shear rate became fixed was taken as a start of the measurement, $t = 0$ (since the time during which the shear rate stabilized was incomparably shorter than the duration of the experiment). It is a moment when the system has a fully developed structure. When $\dot{\gamma}$ is raised, this structure begins to change. This phenomenon is detecting in viscosity decreasing. As data for developing flow curve the first apparent viscosity value η^{δ} was used from the time line, i.e. viscosity for $t = 0$ s. Accordingly, the term $\eta(\dot{\gamma})$ should be expressed as an appropriate equation describing viscosity as a function of shear rate. In this work was used the Herschel–Bulkley model:

$$\eta(\dot{\gamma}) = \tau_0 \cdot \dot{\gamma}^{-1} + \kappa \cdot \dot{\gamma}^{n-1}$$

The parameters of Herschel–Bulkley equation were estimated minimizing the following objective function by the Marquardt–Levenberg method:

$$\sum_{j=1}^{N} \left(\eta_j^{\delta} - \hat{\eta}_j\right)^2 \underset{\tau_0,\kappa,n\geq 0}{\longrightarrow} \min$$

where $\hat{\eta}_j = \eta(\dot{\gamma}_j) = \tau_0 \cdot \dot{\gamma}_j^{-1} + \kappa \cdot \dot{\gamma}_j^{n-1}$

Measurements of apparent viscosity were carried out with the RS 150, Haake (Karlsruhe, Germany) rheometer with the two co-axial Z40 cylinders system with 75 cm^3 volume ($d_{in} = 0$ mm). Investigated 4.00%, w/w paste was cooled down with 30 min and relaxated at measuring temperature in the sensor system. A co-axial cylinders system has been successfully applied in investigating the rheological properties of food systems (De Kee et al., 1996). Basing on author previous experience, both cone-plate and co-axial cylinders, concerning investigated systems, gave results within accuracy of measuring error. The authors decided to use co-axial tool, due to lower evaporation rate and better thermal stability. Executed preliminary tests proved, that pastes sedimentation constant rate was far greater than time needed to complete the experiment. The measurements of rheological properties were performed at two temperatures: 20 °C and 50 °C. Measurements temperature was controlled by means of an ultrathermostat F-6 (Haake, Germany) with 0.1 °C accuracy. Experiments were run in triplicate.

5. Results and discussion

5.1. Physico-chemical properties of starches

The results of analysis of oat starch and its derivates are presented in Table 1. Modifications of oat starches changed its properties. Apparent amylose content in oat starch is reported to vary from 19% to 33% (Hoover et al., 2003; Zhou et al., 1998), so results obtained in this research are below this broad limit. Some discrepancies might be due to varietal differences and method of analysis. On other hand, similar results were published for starch extracted from polish varieties of oat (Gibiński & Berski, 2006).

The amount of amylose decreased after modifications, with exception for oxidation process. Such apparent increase was observed (Fortuna, Juszczak, Pietrzyk, & Wróbel, 2002) and could be explained by partial depolymerization of amylopectin and liberation of enough long chains to create color complex with iodine reagent. Acetylation could lead to depolymerization of amylose chains. Amylose is located mostly in amorphic regions and only in external lamellas of crystalline regions (Chen, Schols, & Voragen, 2004). It could indicate, that acetylation occurs in these areas. But other authors (Betancur-Ancona, Chel-Guerrero, & Canizares-Hernandez, 1997; Singh, Chawla, Singh, 2004; Sodhi & Singh, 2005) observed elevated levels of amylose in starch after acetylation. Starch phosphate was characterized by smaller amounts of amylose that could be due to degradation effect of both process temperature and alkali conditions on amylose molecules (Fortuna et al., 2001).

In comparison to other starches, oat starch contains substantial amounts of lipids (Hoover et al., 2003; Zhou et al., 1998). Lipids content in this study was within range given by some authors (Gibiński, Pałasiński, & Tomasik, 1993; Hoover et al., 2003), higher amounts ranging 1.8–2.5% were also noted (Hartunian-Sowa & White 1992). Such broad variation could be ascribed to differences among oat varieties, environmental factor or method of analysis (Tester & Karkalas, 1996). Chemical modifications led to decrease in starch lipid content, probably due to elevated pH during modification process. Lipids could be saponified, and next washed up during purification process. Decreased lipid level after oxidation was also observed by Forsell et al. (1995).

Phosphorus is very important constituent of starch. In cereal starches it is mostly present in form of phospholipids, which is responsible for lowered paste viscosity and transparency (Morrison, 1988). Phosphorus content in oat starch lies within range 60–190 mg% (Gibiński & Berski, 2006; Zhou et al., 1998), so

Table 1
Molecular masses, chemical composition and some other properties of oat starches.

	Native	Acetylated	Oxidized	Mono
M_w (g mol^{-1})	9.02×10^7	5.57×10^7	4.42×10^7	5.08×10^7
M_n (g mol^{-1})	8.80×104	3.51×104	9.02×10^4	9.02×105
Amylose[a] (%)	14.46	5.65	15.44	8.32
Lipids (%)	1.61	1.29	1.25	1.27
Phosphorus (bound) (mg%)	37.3	21.8	29.2	121.7 (86.1)
Acetyl gropus (%)	–	5.86	–	–
Carboxyl group (%)	–	–	0.25	–
Carbonyl groups (g/100 g)	–	–	0.125	–
WBC (AS)[b] (g/g (%))				
60 °C	2.51 (0.95)	5.34 (5.63)	6.23 (11.21)	16.79 (11.67)
80 °C	4.95 (1.04)	12.83 (12.83)	11.97 (20.91)	23.75 (18.13)
90 °C	5.94 (2.07)	33.06 (43.62)	18.03 (29.38)	101.65 (27.99)
95 °C	6.38 (3.08)	37.69 (47.83)	28.59 (39.33)	95.57 (12.27)
Granularity profile[c]				
d_{10} (μm)	4.0	3.3	2.9	2.9
d_{50} (μm)	6.0	4.8	4.1	4.2
d_{90} (μm)	8.5	6.9	5.9	6.3

[a] Apparent amylose content.
[b] WBC, water binding capacity; AS, aqueous solubility.
[c] d_{10}, d_{50} and d_{90} denote size of granules (μm) below of which was less than 10% of the sample volume, average size of granules (μm) and size of granules below of which was 90% of the sample volume, respectively.

result obtained in this research was below lower limit. This difference could be due to different analytical method and environmental and varietal factors. Phosphorylation process led to substantial increase of incorporated phosphorus content that greatly influenced preparation properties (Table 1). Although the reaction conditions were the same as in work Lim and Seib (1993), the total phosphorus content was lower than the values reported earlier for wheat and maize starches (Lim & Seib, 1993). This smaller ability to incorporate phosphorus could be attributed to difference of starch origin, its granular size and fragility. It could be also caused by lack of granular pore or enough large inner channels which facilitate physical access of phosphorylation agent to the interior of granule (Juszczak, Fortuna, & Wodnicka, 2002).

Acetyl groups content in oat starch was 5.86%, that is equivalent to DS 0.23 and these values are higher than reported by Mirmoghtadaie et al. (2009), but higher amount of acetic anhydrite was used in this experiment (10.21 g in place of 6 or 8 g). Our results are in accordance with Chen et al. (2004), where substitution degree was higher in case of small granules starches.

Oxidation leads to creation of carbonyl and carboxylic groups, and their presence could be used as indicator of process effectives. First carbonyl groups are created, later on carboxylic ones, at C2, C3 and C6 carbon atoms (Kuakpetoon & Wang, 2001). Starch oxidation by means of sodium hypochlorite favors creation of carboxylic groups. According to Wing (1994) hypochlorite oxidation at pH 10–12 favors creation of greater numbers of hydrophilic carboxylic groups, and process at lower pH favors creation of cross-linking carbonyl groups. In our study modification took place in alkali condition (pH = 9.5), in contrast to process with hydrogen peroxide or sodium chlorite (Fortuna et al., 2002; Wang & Wang, 2003).

Data related to water binding capacity (WBC) and aqueous solubility (AS) are given in Table 1. Values for native starch were lower than previously reported (Doublier, Paton, & Llamas, 1987; Gibiński, Pałasiński, & Tomasik, 1993; Wang & White, 1994) both for WBC and AS, especially when measured at 95 °C, but when compared to newer research (Gibiński & Berski, 2006). WBC at 90 °C value was within range, although slightly higher than average value, and AS was also within the range, but lower when compared to average value.

As it is clearly seen both WBC and AS were increased after modification processes. In most cases AS of acetylated and oxidized starches was higher than for native starch, which is similar to other authors observations (Wang & Wang, 2002, 2003). Also Khalil, Hashem, and Hebeish (1995) proved that introduction of acetyl groups to starch molecules opens their structure and, combined with polymer degradation, increases its solubility. Starch phosphate solubility was higher than for native starch. It seems that some polymer degradation occurred during processing.

In case of starch phosphate amounts of bounded water increased in comparison to native starch and is also higher than in case of acetylated and oxidized starch. Introduction of phosphorus caused increased water absorption (Lim & Seib, 1993)

5.2. Pasting and rheological properties of investigated starches

Viscosity of cereal starch pastes is determined by lipids, mostly lysophospholipids, creating complexes with amylose, slowing down or even hindering granules swelling. Other effects are related to decreased amylose solubility, retarded pasting and limited gel creation. Such complexes require higher temperatures to be subjected into dissociation (Singh, Singh, Kaur, Sodhi, & Gill, 2003; Wang & White, 1994).

Oat starch, among other starches, is characterized by high pasting temperature (Fig. 1) due to presence of high amounts of lipids (Hoover et al., 2003; Zhou et al., 1998). Results obtained for native starch were similar to those presented by Hoover et al. (2003).

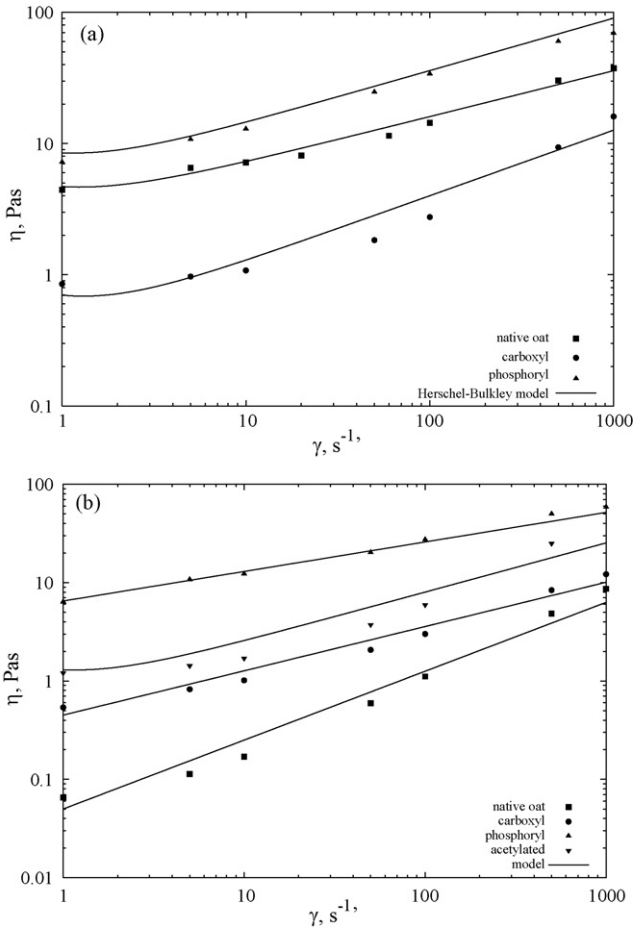

Fig. 1. The $\eta_0(\dot{\gamma})$ functions for oat starch and its derivatives at 20 °C (a) and 50 °C (b).

Applied modifications caused a decrease in pasting temperature, most visible in case of phosphorylated starch.

Oxidation caused a decrease in viscosity of pastes. It is due to degradation of polymer (partial depolymerization, partial cleavage of glycosic bonds, lowered molecular mass) (Kuakpetoon & Wang, 2001). Also in case of acetylated starch lowered viscosity was observed. (Wang & Wang, 2002; Lawal, 2004). On the contrary some authors observed increased viscosity in case of acetyl starches (Liu et al., 1999; Sodhi & Singh, 2005). Acetylated starch was characterized by lower pasting temperature, in comparison to native one, lower viscosity at high temperature, and rapid development of viscosity on cooling, which is well described in literature (Wang & Wang, 2002). Starch phosphates was characterized by high viscosity of paste, a well known phenomena (Lim & Seib, 1993)

Table 2 summarizes results of the differential scanning calorimetric studies. One could see that except acetylation other modifications only slightly decreased onset (T_o) and peak (T_p) temperatures. High enthalpy of melting for original starch can

Table 2
Results of the differential scanning calorimetric measurements.

	Transition temperature		Enthalpy of gelatinization ΔH (J/g)
	T_0	T_p	
Original	60.5	65.2	9.53
Acetylated	47.6	54.5	3.15
Carboxyl	58.0	63.4	9.53
Monostarch phosphate	56.6	64.3	7.42

Table 3
Pasting characteristics of oat starches.

Starch	PT (°C)	$\eta^{A}_{96\,^{\circ}C}$(Pa s)	$\eta^{A}_{96\,^{\circ}C}$(Pa s)	η^{A}_{max}(Pa s)	T_{max} (°C)	η^{A}_{min}(Pa s)	T_{min} (°C)	$\eta^{A}_{25\,^{\circ}C}$Pa s	$\eta^{A}_{25\,^{\circ}C/5}$Pa s
Native	94.4	0.05	1.00	1.58	87.4	0.68	63.8	0.87	0.90
Acetylated	79.5	1.12	0.86	1.30	91.0	0.85	90.3	4.30	4.40
Oxidized	86.0	0.10	0.84	0.98	94.3	0.51	74.0	0.71	0.80
Monostarch phosphate	71.0	1.50	2.28	2.29	96.0	2.11	80.6	4.50	4.67

PT, pasting temperature; $\eta^{A}_{96\,^{\circ}C}$, apparent viscosity at 96 °C; $\eta^{A}_{96\,^{\circ}C/10}$, apparent viscosity after 10 min at 96 °C; η^{A}_{min}, maximum of apparent viscosity (peak viscosity); T_{max}, temperature at apparent maximum viscosity; η^{A}_{min}, minimum of apparent viscosity; T_{min}, temperature at apparent minimum viscosity; $\eta^{A}_{25\,^{\circ}C}$, apparent viscosity at 25 °C; $\eta^{A}_{25\,^{\circ}C/5}$, apparent viscosity after 5 min at 25 °C.

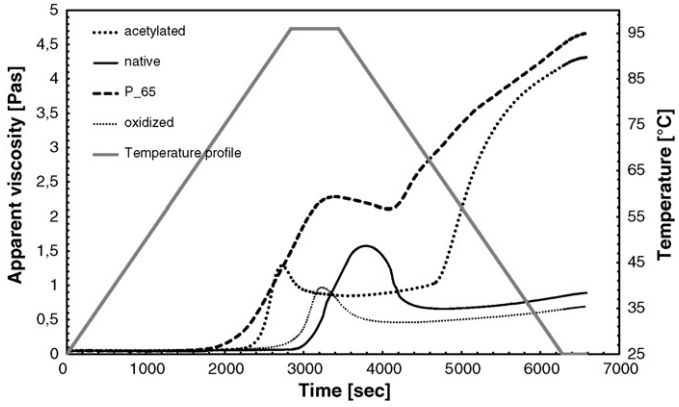

Fig. 2. Pasting characteristic of oat starch and its derivatives.

be interpreted in terms of a native complex in which that starch existed. Although oxidation reduced molecular weight of the starch substance, the oxidized material had similar enthalpy of the phase transition. This might be rationalized in terms of inter- and intramolecular interactions involving introduced carboxylic groups. Also phosphorylation into monostarch phosphate turned original non-ionic starch into anionic starch and the same kind of interactions provided relatively only slightly decreased enthalpy of melting. Acetyl moiety in starch produced essential disorder in the starch matrix and, hence, enthalpy of melting was the lowest.

Viscosity changes as function of shear of 4.00% (w/w) native and modified starch pastes indicate on complex rheological behavior. All investigated systems behave like shear-thickening, both at 20 °C and 50 °C (Fig. 1). In all cases lines $\eta(\dot{\gamma})$ are increasing relations in function of shear rate, but these functions are slowly growing. For shear rate in range 1–1000 s^{-1} at 20 °C viscosity of the investigated pastes is within 1–100 Pa s range. The lowest viscosity was observed for oxidized starch paste. Starch chains degradation occurring during modifications is reflected both in pasting profile parameters (Table 3, Fig. 2) as well as in shearing of its paste (Fig. 1). Although oxidized starch is not characterized by the lowest pasting temperature, but has the lowest apparent viscosity, that is revealed during pasting profile test (Fig. 2). Moreover during final stage of pasting (temperature decreasing) apparent viscosity of paste does not exceed η^{A}_{max} value (Table 3). Such behavior indicates on definitely viscous character. Starch indeed does not create 3D network (as not gelling), but the presence of highly polar carboxylic and carbonyl groups is manifested by stable viscosity behavior during shear flow (Fig. 1). This is observed by a lack of rapid viscosity changes caused by temperature increase and shear. Similar rheological behavior was observed in case of native oat starch paste. Viscosity of these pastes at 20 °C and 50 °C is slightly higher than for oxidized starch pastes, and its changing in the range 5–20 Pa s for lower temperature, and 1–10 Pa s for higher ones (Fig. 1). Analysis of pasting profile results is consistent with these findings (Fig. 2). Temperature at which the viscosity begins to rise is termed pasting temperature. After pasting of starch at 94.4 °C paste apparent viscosity ($\eta^{A}_{max} = 1.58$ Pa s) is lowering to 0.68 Pa s, and next is consequently increasing, not exceeding 1 Pa s at 25 °C. Starch modification relying on introduction of acetyl or phosphate groups caused changes in rheological behavior of pastes. They were the most visible during starch pasting (Fig. 2). Both starches pasted below 80 °C. Maximum viscosity (peak viscosity) of acetylated starch was lower than for native one, but for phosphorylated it was the highest, and reached 2.29 Pa s. Temperature decrease during measurement caused dramatic increase in viscosity of the discussed starches (Fig. 2): apparent viscosities at 25 °C exceeded 4 Pa s. Viscosity changes as function of shear (Fig. 1) indicate slight decrease of starch phosphate paste viscosity at 50 °C, which was changed for both temperatures in range 10–100 Pa s. Acetylated starch paste shearing at 20 °C caused gelling, which was manifested by rapid viscosity increase (results not presented). Viscosity of acetylated starch paste at 50 °C was similar to native one.

Power type rheological models were fitted to experimental data (Table 4). For native starch paste values of consistency coefficient decreased with temperature, in contrast to rising flow index. Oxidized starch pastes were characterized by the lowest value of consistency coefficient at 20 °C. In the case of acetylated starch estimation was made for rheological data obtained at 50 °C $\tau_0 = 0.50$ Pa and value of flow index $n = 1.5$. Temperature changes caused no variation in rheological index values for starch phosphate and oxidized starch paste, which indicated on high thermal stability

Complex rheological behavior of the investigated starches is based on interaction among glucan's chains. Detailed measurements of viscosity changes in time for given shear rates revealed thixotropy phenomenon (Fig. 3a and b). During shearing of native oat starch paste (20 °C) it was observed that $\dot{\gamma}$ increase deepened relationship of viscosity vs time. Paste shearing at increasing shear rate is related to supply of mechanical energy, which is

Table 4
Values of rheological model for investigated starch pastes.

Oat starch	τ_0, (Pa)		k, (Pa s^n)		n	
	20 °C	50 °C	20 °C	50 °C	20 °C	50 °C
Native	1.50 ± 0.05	0.00	3.20 ± 0.10	0.05 ± 0.01	1.35 ± 0.05	1.70 ± 0.05
Acetylated	–	0.50 ± 0.05	–	0.80 ± 0.05	–	1.50 ± 0.05
Phosphate	2.80 ± 0.05	0.00	5.70 ± 0.10	6.50 ± 0.05	1.40 ± 0.05	1.30 ± 0.05
Carboxyl	0.30 ± 0.05	0.00	0.45 ± 0.10	0.40 ± 0.05	1.50 ± 0.05	1.45 ± 0.05

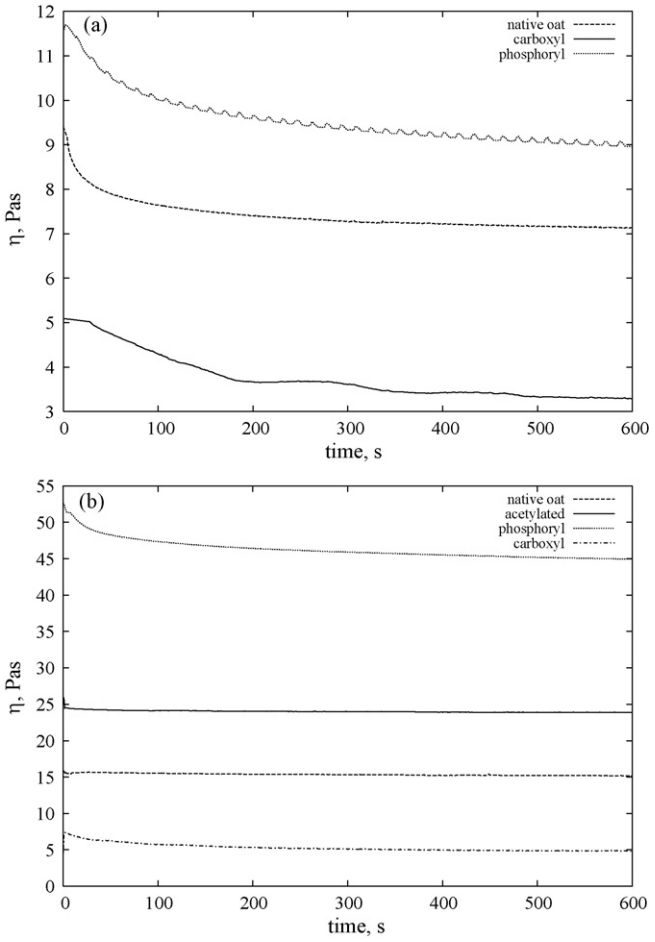

Fig. 3. Change of the apparent viscosity for 4.00% starch pastes at $\dot{\gamma} = 100\ s^{-1}$ at 20 °C (a) and 50 °C and $\dot{\gamma} = 500\ s^{-1}$ (b).

stored by polysaccharide chains present in paste. Systems do not follow changes with shear conditions, which would otherwise reveal a viscosity shift. Moreover, it was discovered, that this phenomenon vanishes for extremely high values $\dot{\gamma}$. Increasing temperature up to 50 °C is changing oat paste behavior causing chaotic reaction on increase of shear rate, up to vanishing of phenomenon of viscosity vs time relation. At higher temperature native oat starch paste shearing is causing irreversible changes in paste structure: it is destructed. Chemical starch modification changes rheological behavior, especially at higher temperature (Fig. 3a and b). In case of starch phosphate at 20 °C it is worth to notice untypical behavior (Fig. 3a). Energy supplied during shearing is creating paste structure, resulting in viscosity increase. Starch paste stores some amount of energy, then it is dissipated and resulting in decrease of viscosity. This phenomenon is repeated, and paste viscosity is going to equilibrium value. Discussed equilibrium curve depicts stress relaxation phenomenon. Similar, but for smaller scale, the phenomenon is observed for oxidized starch paste. Increase in temperature causes weakening of thixotropy phenomenon: mobility of chains is growing resulting in weaker interaction. As result of shear, the pastes are not able to accumulate important amounts of energy, which is manifested by equilibrium state reached in shorter time. Temperature rise causes the weakening of thixotropy phenomenon: mobility of chains is growing leading to reduced interactions among them. As a result of shearing pastes are not able to accumulate large amounts of energy. This is displayed by attaining equilibrium state in short period of time.

6. Conclusions

Introduction of phosphate and acetyl groups into oat starch changed rheological behavior of modified starches pastes when compared to native one. For acetylated and starch phosphate pasting curves had a similar course. It was observed a decreased pasting temperature (when compare to native one). These starches were gelling, and it was manifested by the highest values of viscosity: η^{A}_{min} and $\eta^{A}_{25\,^{\circ}C}$. Temperature independent flow index was a consequence of stable rheological behavior of starch phosphate paste. Based on its value, discussed pastes could be classified as shear thickened fluids. At 20 °C acetylated oat starch paste created strong gel, and flow curve interpretation was possible only at 50 °C. At such temperature (conditions) discussed paste as the sole, revealed the yield stress. The other group of pasting curves was created by viscosity profiles obtained for oxidized and native starches. During programmed temperature decrease their viscosity was growing, but not exceeding 1 Pa s. Native and oxidized starch pastes revealed yield stress, and for oxidized starch paste its value was the lowest reaching 0.30 Pa s. Flow index values proved that nature of pastes rheological properties were temperature independent. Also these pastes were recognized as shear thickened. The investigation of viscosity changes in function of time for given/specific shear rates disclosed thixotropy phenomenon. The most interesting behavior was observed in case of oat starch phosphate paste: its viscosity oscillated in time, which could be due to stress relaxation occurrence. Similar phenomenon (in nature), but not for such scale, was observed for native starch paste. Temperature increase resulted in diminishing thixotropy intensity. At higher temperature equilibrium viscosity was reached at shorter time.

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