SHORT COMMUNICATION

Physically modified starch preparations in gels and in dough – rheological properties

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Summary
Thermal and rheological properties of physically modified wheat, potato and pea starches were determined in comparison to those of the native ones. The enthalpy value of a pea starch preparation was higher compared to that of the native pea starch. Storage and loss moduli of 10% gels from native starches were higher than the values obtained for modified starches. The rheological properties of non-yeasted wheat doughs were changed under supplementation (10%) with modified starch preparations. Compared to the control sample, an increase in storage and loss moduli was noticed at temperatures from 30 °C to 60 °C, whilst at temperatures up to 90 °C, the values of both moduli were found to decrease.

Keywords
wheat; potato; pea starches; physical modification; rheology; dough; differential scanning calorimetry

A characteristic feature of the starch gelatinization process is the solubilization of amylose, accompanied by the irreversible swelling of starch granules. Cereal starches swell over a wider temperature range, compared to potato starch granules, which indicates a different distribution of amylose fraction in the granules of cereals and tubers [1, 2]. All these factors influence biological and technological applications of starch. Starch can play several distinct roles in the breadmaking process. It may be a substrate for amylases which produces fermentable saccharides for yeast fermentation and serves as a reservoir for water absorption. Further, it may also be a diluent for gluten, thereby contributing to the optimal viscoelastic properties of dough [3]. The nutritional properties of starch in food are to a large extent related to its susceptibility to digestion and/or absorption in the gastrointestinal tract. Our earlier research, concerning different functional and biological properties of starches of different origin and their modified preparations, showed that they could be functional ingredients of food indicating a health-promoting potential like lowering pH of caecal digesta and decreasing blood serum markers, e.g. glucose, triacylglycerols, total cholesterol and HDL fraction [4–6].

In this study, we analysed the effect of physical modification of wheat, potato and pea starch on their rheological properties in gels and in non-yeasted wheat dough.

MATERIAL AND METHODS

Material

Native industrially-isolated commercial starches, namely, wheat (WS; Przedsiębiorstwo Przemysłu Ziemniaczanego, Niechlów, Poland), potato (PS; Wielkopolskie Przedsiębiorstwo Przemysłu Ziemniaczanego, Luboń, Poland) and pea (PeaS; Cosucra, Warcoing, Belgium) were reference samples and constituted the starting material for experimental modification. The native starches were modified in a laboratory scale by means of some physical processes. Briefly, the suspension of starches in distilled water (1 : 3.5) was autoclaved (121 °C, 1 h) and then cooled at 4 °C during 12 h. The autoclaving/cooling cycles were performed three times. The retrograded gel was

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homogenized with distilled water and spray-dried at 130 °C inlet temperature and 50 °C outlet temperature [4]. The following abbreviations of starch preparations were used in the manuscript: WSP – wheat starch preparation, PSP – potato starch preparation and PeaSP – pea starch preparation. Commercial wheat flour from a local market was used for dough preparation.

Methods

Chemical components of native and modified starches were determined as follows: nitrogen by the Kjeldahl method and ash after mineralization in a muffle oven at 900 °C according to the ISO methods [7, 8]; amylose content was determined according to MORRISON and LAIGNELET [9]; and resistant starch (RS) content was determined according to CHAMP et al. [10].

The thermal properties of starches were investigated on a Mettler DSC-30/TC 15/STAR^e calorimeter (Mettler-Toledo, Greifensee, Switzerland), with heating and cooling cycles in a temperature range from 20 °C to 180 °C, with a heating rate of 3 °C·min^{-1}. The samples examined were mixed in a ratio of 30 mg of sample per 90 mg of water.

Rheological measurement of starch gels was carried out using heating 10% of native or modified starches at 90 °C for 10 min in a water bath with minimal stirring. The temperature of the sample was controlled by a thermocouple. The hot starch dispersion was transferred to a Bohlin VOR Rheometer (Bohlin Instruments, Lund, Sweden) with a concentric cylinder C-25 measuring system and cooled from 90 °C to 20 °C. The samples were measured with a small-amplitude oscillation test. The cooling rate was 1 °C·min^{-1}, the frequency 1 Hz and the strain 0.003. The storage modulus (G') and loss modulus (G'') were measured as a function of time and temperature.

Dough rheology was studied using dough prepared from commercial wheat flour with supplementation of 10% of native or modified starches at the optimal volume of water, without yeast. After mixing for 3 min in a laboratory mixer (MML25; ZBPP, Bydgoszcz, Poland), the dough was stored for 15 min in a plastic bag for stress relaxation. Viscoelastic properties of the dough were measured using a stress-controlled rheometer (Bohlin VOR Rheometer) using a parallel-plate device (diameter, 25 mm). The dough sample was formed to a small ball and placed between two plates. The gap was adjusted to 1.5 mm and silicon oil was applied around the plate edges to prevent the sample from drying. The temperature range was 30–100 °C with a heating rate of 2 °C·min^{-1}, the frequency was 1 Hz. The storage (G') and loss (G'') moduli were measured as a function of time and temperature.

RESULTS AND DISCUSSION

Chemical characteristics of the native and modified starches are presented in Tab. 1. The physical processes used for starch modification caused an increase in contents of ash and protein in comparison with the native starches. In turn, a decrease was noticed in amylose content of starch preparations. The wheat starch preparation was found to have a 2-times higher level of resistant starch than the native wheat starch, whereas potato and pea starch preparations to have 10 and 3-times lower contents of resistant starch, respectively, in comparison with the native starches.

Tab. 1. Chemical composition of native and modified starches.

Samples	Ash [%]	Protein [%]	Amylose [%]	Resistant starch [%]
Native starches				
WS	0.25 ± 0.02 b	0.14 ± 0.04 b	25.10 ± 0.95 e	3.06 ± 0.04 e
PS	0.27 ± 0.02 b	0.09 ± 0.001 bc	26.22 ± 1.06 e	60.82 ± 1.25 a
PeaS	0.11 ± 0.01 d	0.09 ± 0.001 c	36.11 ± 1.42 a	31.53 ± 0.84 b
Starch preparations				
WSP	0.44 ± 0.04 a	0.17 ± 0.02 a	22.46 ± 1.24 d	6.73 ± 0.04 d
PSP	0.36 ± 0.01 a	0.16 ± 0.06 b	25.13 ± 1.13 c	6.27 ± 0.08 d
PeaSP	0.21 ± 0.01 c	0.11 ± 0.06 ab	28.68 ± 1.15 b	10.64 ± 0.14 c

Values represent mean ± standard deviation, $n = 3$. Values are expressed in % of dry matter. Values followed by the same letter in the same column are not significantly different at 95% confidence level.
The native starches: WS – wheat, PS – potato, PeaS – pea. Preparations from starches: WSP – wheat, PSP – potato, PeaSP – pea.

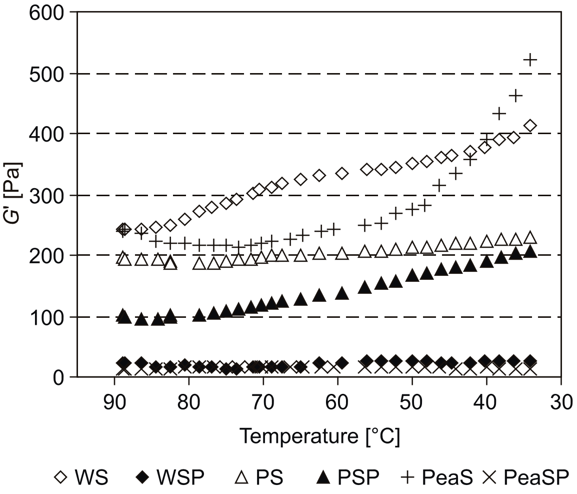

Fig. 1. Effect of cooling on the storage modulus (*G*') of 10% native and modified starches in dispersions pre-heated at 90 °C for 10 min.

The native starches: WS – wheat, PS – potato, PeaS – pea. Preparations from starches: WSP – wheat, PSP – potato, PeaSP – pea.

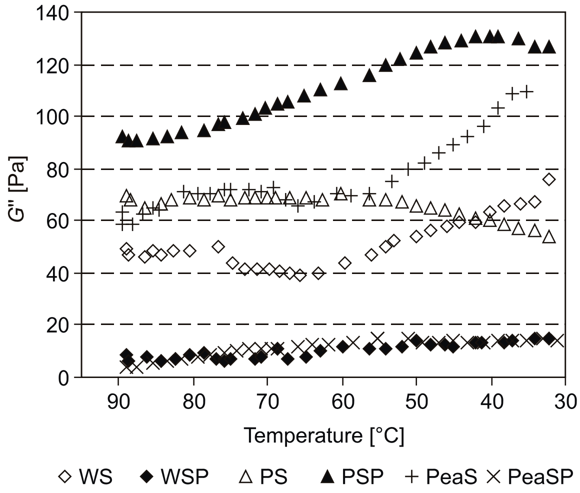

Fig. 2. Effect of cooling on the loss modulus (*G*") of 10% native and modified starches in dispersions pre-heated at 90 °C for 10 min.

The native starches: WS – wheat, PS – potato, PeaS – pea. Preparations from starches: WSP – wheat, PSP – potato, PeaSP – pea.

Peak temperatures determined for wheat, potato and pea native starches were similar – 61.7 °C, 64.3 °C and 63.3 °C, respectively. However, the enthalpy (ΔH) values were different, the highest being found for native potato starch (13 $J{\cdot}g^{-1}$), whereas in the case of wheat and pea starches, it was 9.0 $J{\cdot}g^{-1}$ and 9.3 $J{\cdot}g^{-1}$, respectively. The results obtained correspond with those reported for native starches of different botanical origin by other authors [11–13]. For modified wheat and potato starches, it was not possible to determine the peak temperatures or enthalpy values. Peak temperature recorded for the pea starch preparation accounted for 53 °C, which was lower compared to the native pea starch. However the enthalpy value recorded for that preparation (9.6 $J{\cdot}g^{-1}$) was higher compared to the native wheat and pea starches. Differential scanning calorimeter enabled investigating the order/disorder transition that occurs upon heating an aqueous suspension of starch granules. The ordered structure of starch was disrupted when native starches were modified by using some physical processes such as autoclaving or cooling. Starch retrogradation enthalpies are usually 60–70% smaller than the gelatinization enthalpies and transition temperatures are by 10–26 °C lower than those observed for gelatinization of starch granules. The amylose content has been reported to be one of the factors affecting starch retrogradation [13]. In the present study, the native and physically-modified pea starches had the highest amylose content as compared to the other samples (Tab. 1). The retrogradation of pea starch was likely to induce the formation of amylose complexes, which affected the lower temperatures (onset, peak, conclusion) and higher enthalpy than those of the native pea starch. The peak temperature between 128 °C and 140 °C was found by Wronkowska et al. [14] for starch preparations obtained upon physical and biochemical modifications. Morikawa and Nishinari [15] found the peak temperatures of chemically-modified potato starch (hydroxypropylated phosphate cross-linked) to reach around 45 °C and that of native potato starch to reach 60 °C.

Rheological changes in 10% gel dispersion of native or modified starches were measured with a small-amplitude oscillation test during cooling of a pre-heated dispersion from 90 °C to 20 °C. For all native starches, the storage modulus (*G*') was higher than for all modified preparations (Fig. 1). Special attention should be paid to a rapid increase in the *G*' value noted after cooling the native pea starch from 90 °C to 50 °C. This is likely to be due to a new hard "structure" of retrograded amylose, its remarkable amount being detected in this sample (Tab. 1). The lowest *G*' values were noticed for wheat and pea starch preparations (Fig. 1). The amorphous fraction of these samples formed a new network, which resulted in the retrogradation phenomenon. The preparation of potato starch was characterized by a higher *G*' value,

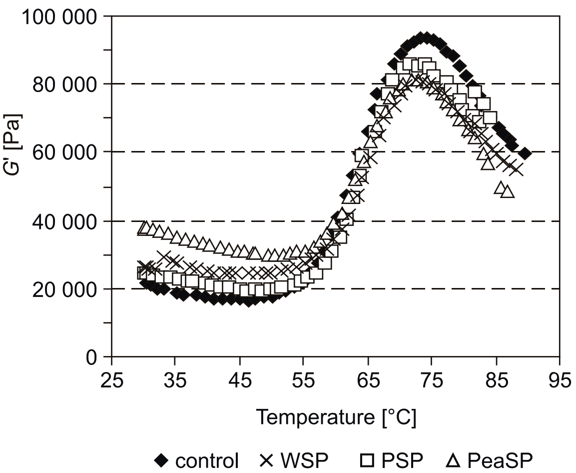

Fig. 3. Effect of modified starches on storage modulus (*G*') of non-yeasted wheat dough.

Preparations from starches: WSP – wheat, PSP – potato, PeaSP – pea.

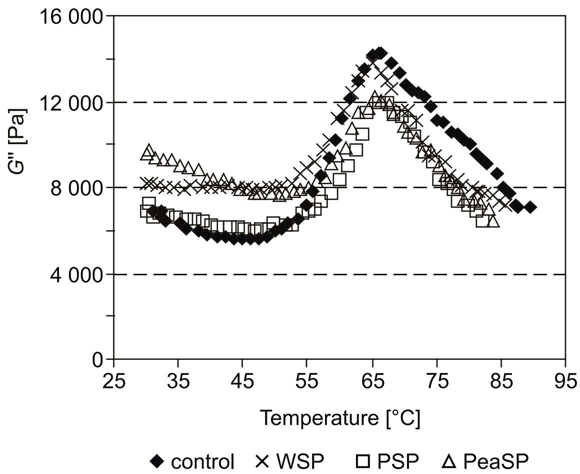

Fig. 4. Effect of modified starches on loss modulus (*G*") of non-yeasted wheat dough.

Preparations from starches: WSP – wheat, PSP – potato, PeaSP – pea.

which was probably affected by the presence of retrograded amylose particles in the gel structure. Compared to the native starches, the lowest *G*" values were determined for wheat and pea preparations, whereas the highest one was found for the potato preparation (Fig. 2).

The dynamic rheological properties of non-yeasted wheat dough with 10% supplementation of modified starches are shown in Figs. 3 and 4. All starch preparations added to the wheat dough significantly affected the heat-induced rheological properties of dough. The storage and loss moduli of doughs increased in a temperature range of 55 °C to 65 °C. This phenomenon could be connected with the transport of water between two biopolymers – from gluten to starch. Then, at temperatures from 60 °C to 90 °C, a decrease was noticed in *G*' and *G*" values as compared with the control wheat dough (Fig. 3, 4). It should be emphasized that the addition of wheat and pea starch preparations to wheat dough affected the measured rheological parameters and thus could have the disadvantageous effect on the structure of crumb bread.

A study of the heat-induced rheological changes of non-yeasted wheat dough made from commercial gluten suggested that the changes in the moduli between 55 °C and 75 °C were attributable to starch gelatinization [16]. The gluten matrix is a major determinant of the rheological characteristics of dough. IZYDORCZYK et al. [17] presented in general that the addition of starch to wheat flour reduced the strength of the respective flour-water dough, but this was not unexpected since the replacement of wheat flour with starch is likely to decrease the concentration of gluten. Also affinity of various starches to water could affect water distribution among dough components as well as different characteristics of starch granules (size, amylose content, swelling power) could influence the rheology of the dough system. As it was found in our previous study [5], the physical processes used for modification of native wheat, potato and pea starches elicited changes in water binding capacity. The affinity to water was much higher in the case of the wheat and potato preparations in comparison with the native starches.

CONCLUSION

Storage and loss moduli of 10% gels prepared from native starches were higher compared to those determined for the physically modified starch preparations. The rheological properties of non-yeasted wheat doughs were significantly affected after 10% supplementation with the investigated starch preparations. A decrease was noticed in *G*' and *G*" values of doughs in the temperature range of 60–90 °C, compared to the control sample. From the technological point of view, the results obtained in this study appear to be of importance in the technological process, when the components that have a good ability for water sorption take part in the homogenous mixture as well as in dough. Nevertheless, more extensive studies are needed to investigate the application of physically modified starch preparations in breadmaking.

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