Effect of thermal modifications of potato starch on its selected properties☆

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A B S T R A C T

Aqueous suspensions prepared from native potato starch (with the concentration 4 g/100 g) were heated to temperatures of 59, 64, 69, 74, 79, 84, 89 or 94 °C, under continuous stirring. The resultant solutions were cooled, frozen and defrosted, and subjected to analyses.

The heating and freezing of a potato starch suspension changed its properties, with the direction and extent of these changes depending on the temperature of pre-heating. The re-pasting of the produced starch preparations in a Brabender viscosimeter increased their viscosity to 50% compared to the pastes produced from native starch. The assayed viscosity of the pastes depended on the pre-heating temperature and was changing following the determined second degree polynomial function. The thermal characteristics (DSC) of the analyzed preparations revealed peaks that corresponded to transitions of native starch pasting and retrograded starch solubilization. The strength of the produced gels, determined with the use of an oscillatory-rotational rheometer, was greater than that of gels produced from native starch and depended on the pre-heating temperature, however these changes followed the determined second order polynomial function. Microscope preparations (SEM) of retrograded starch differed significantly in porosity that was also found to depend on the pre-heating temperature. Paste viscosity was positively correlated with the size of gel sacks determined with a laser particle size analyzer (LSA).

1. Introduction

Starch is one of the key energetic components in a man's diet. As a result of many thermal processes applied during food production and preparation, in food products starch occurs mainly in the form of paste. Pasting proceeds in a water environment at increased temperatures. It consists of several stages and depends on a variety of factors including, e.g., botanical origin of starch (Singh, Singh, Kaur, Sodhi, & Gill, 2003), content of amylose (Chen, Yu, Kealy, Chen, & Li, 2007), starch−water ratio in the solution (Fukuoka, Ohta, & Watanabe, 2002), temperature (Peng, Zhongdong, & Kennedy, 2007) and the heating rate (Patel & Seetharaman, 2006).

The first stage of pasting involves the swelling of starch granules. The swollen granules are insoluble, however their reversible swelling occurs in water with a temperature of up to 50 °C. In this process starch absorbs water, thereby increasing its volume even by 30% (Leszczyński, 2004). Along with further heating of a starch dispersion, hydrogen bonds responsible for the structural cohesiveness of granules break up, allowing water to penetrate inside the granules and enabling the hydration of linear fragments of amylopectin (Xie, Yu, Chen, & Li, 2008). This process leads to the irreversible swelling of starch granules, the volume of which increases several times (Wurzburg, 2000, pp. 1−17). These phenomena cause the loss of starch crystallinity and an increase in the viscosity of the paste formed. The viscosity reaches the maximum values when dissolved and depolymerized starch substance migrates from the most swollen granules to the solution (Sangeetha & Rai, 2006). These transformations do not proceed simultaneously in all starch granules. In the case of potato starch, pasting proceeds firstly in the largest granules characterized by a lower initial pasting temperature compared to the granules with smaller size (Kaur, Singh, McCarthy, & Singh, 2007). The differences observed in the initial pasting temperatures may be due to, e.g., a various ratio

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of amylose–amylopectin in granules of various sizes (Singh & Kaur, 2004).

At the final stage of starch pasting, when temperature exceeds 85 °C, the granules are subject to damage (they break up). It leads to depolymerization and dissolution of starch chains, which is accompanied by a decrease in viscosity of the paste being formed. Thus the produced starch paste contains dissolved carbohydrate substance and fragments of starch granules and displays traits typical of the non-Newtonian fluid (Leszczyński, 2004). Rheological properties of a paste produced from potato starch which — considering its chemical structure — is an amylophosphate acid, are determined by many factors, with the most significant ones including: starch granularity, content of amylose, content of phosphorus (Jayakody, Hoover, Liu, & Donner, 2007), types and concentrations of elements saturating starch (Singh, Kaur, & McCarthy, 2007), length of amylopectin chains (Jane et al., 1999), and starch modifications.

Cooling the starch paste reduces the motility of granules in a solution, which results in their approximation and agglomeration as well as in re-increase of paste viscosity. At an appropriate concentration, the paste is subject to gelling and forms compact, gelatinous mass, in which the starch substance absorbs significant quantities of water (Blazek & Copeland, 2008). The storage of starch gels, especially at a temperature approximating 0 °C, causes them to undergo changes called "pastes aging". The paste is becoming turbid and its viscosity decreases. The gel becomes rigid, its surface is thickening and some water appears on it, which indicates the ongoing phenomenon of syneresis (Charoenrien & Preechathammawong, 2012). These changes are due to starch retrogradation (Karim, Norziah, & Seow, 2000), that consists in the transition of part of dissolved starch into the insoluble fraction. In the course of the retrogradation process, the straight chains of starch dissolved in water (amylose in particular) are gradually stranding into helices and then bind into double helices that are strengthened with hydrogen bonds, with simultaneous dehydration. Within a few hours of gel storage, these helices are subject to aggregation. They form permanent, thermostable and insoluble in water crystalline structures (Zięba, 2009, pp. 67–71).

Hydrothermal modification of starch has been addressed in many works that were aimed at elucidating the impact of heat-moisture treatment on starches (Juansang, Puttanlek, Rungsardthong, Puncha-arnon, & Uttapap, 2012; Varatharajana, Hoovera, Liub, & Seetharamanc, 2010) and that of the temperature close to the pasting temperature on a water starch suspension (annealing) (Rocha, Felizardo, Jane, & Franco, 2012). Some other works have been focused on partial or incomplete gelatinization (Chung, Lim, & Lim, 2006), while others on the properties of starch paste that had been subjected to cyclic freezing and defrosting (Wang et al., 2013) and of spray-dried starch after partial gelatinization (Fua, Wang, Li, & Adhikaric, 2012; Fua, Wang, Li, Zhou, & Adhikari, 2013)

No investigations have been conducted so far that would involve the pre-heating of a water starch suspension followed by its freezing and defrosting. Such a combination of thermal modifications is an interesting issue contributing to the state of the art.

The aim of the present study was to determine the impact of heating a water dispersion of starch to various temperatures, followed by its freezing and defrosting on the selected properties of re-prepared starch paste.

2. Materials and methods

2.1. Materials

The initial study material was Superior Standard potato starch produced by PEPEES Łomża S.A. in the year 2010.

2.2. Modification procedure

A water suspension (450 mL) was prepared from native potato starch in a measuring vessel of a Brabender viscograph (Germany), in the concentration of 4 g/100 g. The suspension was heated with the rate of 1.5 °C/min to temperatures of 59, 64, 69, 74, 79, 84, 89 or 94 °C under continuous stirring. The resultant solution was cooled to 30 °C with the rate of 1.5 °C/min, frozen for two days at a temperature of −20 °C (Bosch, Poland), and defrosted for 2 h at a temperature of 40 °C. The native starch (not subjected to hydrothermal treatment) was denoted with a symbol NS, whereas the modified preparations were named: H59, H64, H69, H74, H79, H84, H89 or H94 (the number following "H" denotes temperature which the starch suspension was heated to before being frozen).

2.3. Determination of re-pasting characteristics

The re-pasting characteristics were determined according to the method of Kapelko, Zięba, Golachowski, and Gryszkin (2012) with modifications. The re-pasting characteristics of starch dispersions were determined with a Brabender viscograph (Germany), using a 700 cmg measuring can. The can with the defrosted solution was placed in the apparatus and kept for 10 min at 40 °C under continuous stirring at 75 rpm. Afterward, the mixture was heated with the rate of 1.5 °C/min until reaching a temperature of 94 °C. After the mixture had been kept at this temperature for 10 min, it was cooled to 30 °C with the rate of 1.5 °C/min and kept at this temperature for another 10 min. The characteristics of paste formation were then used to determine: the viscosity of paste once it has reached the temperature of 94 °C (η 94), paste viscosity after keeping it at 94 °C for 10 min (η 94/10), paste viscosity after it has reached the temperature of 30 °C (η 30), and paste viscosity after keeping it at 30 °C for 10 min (η 30/10).

2.4. Determination of mechanical spectrum

The mechanical spectrum was determined according to the method of Zięba, Juszczak, and Gryszkin (2011b) with modifications. The analysis was conducted with the use of an RS6000 Rheostress oscillatory-rotational rheometer by Haake (Germany). The paste was collected after completed paste characteristics in a Brabender viscograph and placed in a system of coaxial cylinders (Z38AL type — cylinder radius: 21.7 mm; rotor radius: 19.01; lower gap: 8.1 mm) of the rheometer. Next, the paste was cooled and relaxed for 15 min at a temperature of 25 °C. Measurements were conducted at a constant deformation amplitude (0.03) and in a frequency range of 0.1–10 Hz.

2.5. Determination of thermal characteristics of pasting

The thermal characteristics of pasting were determined according to the method of Zięba, Szumny, and Kapelko (2011a) with modifications. The resultant modified preparations (produced acc. to Section 2.2) were dried in an air flow dryer (Memmert, Germany) at a temperature of 30 °C for 24 h, ground and sieved through a screen with a mesh diameter of 400 μm. Determinations were carried out using a differential scanning calorimeter DSC 822E by Mettler Toledo (Germany). Before the measurement, the apparatus was calibrated using an indium sample and a zinc sample. The analyzed sample (ca. 10 mg on a dry matter basis) was placed on the bottom of a measuring vessel and then distilled water was added in the ratio of 3:1 (water:starch). The vessel was closed and thus prepared sample was conditioned for 30 min at a temperature of 25 °C. The analysis was conducted in a temperature range of 25–100 °C, with a heating rate of 4 °C/min. The thermal characteristics