Physicochemical, thermal and rheological properties of starches isolated from malting barley varieties

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Abstract The aim of this work was to characterize physicochemical, thermal and rheological properties of starches isolated from malting barley varieties. The analyzed starches contained 19.6–25.2 g of amylose, 42.47–70.67 mg of phosphorus, 0.50–1.26 g of protein and 0.10–0.61 g of fat per 100 g of starch dry mass. The clarity of the 1 % (w/w) starch pastes ranged from 5.4 to 9.8 %. Values of the characteristic gelatinization temperatures were in the ranges of 56.5–58.5 °C, 61.2–63.0 °C and 66.7–68.7 °C, respectively for T_O , T_P and T_E , whereas values of gelatinization enthalpy were from 6.49 to 9.61 J/g. The barley starches showed various tendency to retrogradation, from 24.52 to 44.22 %, measured as $R = \Delta H_R / \Delta H_G$ value. The pasting curves showed differences in pasting characteristics of the barley starches, where values of peak (PV) and final (FV) viscosities were 133–230 mPa·s and 224–411 mPa·s, respectively. The barley starch pastes exhibited non-Newtonian, shear thinning flow behaviour and thixotropy phenomenon. After cooling the starch gels showed different viscoelastic properties, however, most of them behaved like weak gels ($\tan \delta = G''/G' > 0.1$). Significant linear correlations between the parameters of pasting characteristic and some rheological parameters were found.

Keywords Starch · Malting barley · Physicochemical properties

Introduction

Barley (*Hordeum Vulgare* L.) is cultivated as a commercial crop in about hundred countries all over the world (Mahdi et al. 2008). At present it is on the fifth place, of world crops, after the rice, wheat, corn and soya ones (Baik and Ullrich 2008; Bello-Perez et al. 2010). Comparing with other cereals, barley cultivation gives good effects even on low fertility soils. This results from the fact that barley is able to develop at variable soil-climatic conditions (Mahdi et al. 2008). In a past centuries barley was an important source of food, especially in East West, Africa and North Europe. At present only 2 % of world barley crops are intended for food. The remaining part of these crops is used by breweries and also is intended for animal feeding (Baik and Ullrich 2008). Starch is the main component of barley grain, where it occupies about 65 % of its total mass (You and Izydorczyk 2007). There are barley varieties that contain low (2 %), medium (25 %) and high (40 %) amounts of amylose. Apart from starch, barley grain contains proteins (10–17 %), β -glucans (4–9 %), free lipids (2–3 %) and mineral compounds (about 2 %) (Oscarsson et al. 1997). Contrary to other cereal starches, the functional properties of barley starch have not been well examined yet. The reason is probably the fact that barley grains are mainly utilized for feeding, as well as for production of malt. Moreover, the industrial process for isolation of starch from barley grains is very complicated due to many isolation stages, time consuming operations and very large water consumption resulting from the presence of β -glucans which absorb water and thus make the process difficult (Czuchajowska et al. 1997; Soares et al. 2007). Beside the traditional hulled (covered) barley varieties, there are also hull-less (naked) barley varieties, which are characterized by higher amylose, protein and β -glucans contents as compared to the first ones. However, the hulled barley varieties are more

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preferred in brewing industry due to filtering properties of the hulls that are used for filtering the wort (Bhatty 1999).

An ideal malting barley variety should fulfil numerous agronomical, malting and brewery criteria. At present there are no global requirements for quality of the malting barley. For example, in Europe barley varieties with high starch content are desired (Munoz-Amatriain et al. 2010). Starch isolated from malting barley varieties should be easily hydrolyzed into carbohydrates during mashing. This can be achieved when a starch is pasting at low temperatures, because high pasting temperatures are destructive for the starch hydrolyzing enzymes. Therefore, barley starches that are characterized by great starch granules and thus low pasting temperatures are preferred in brewery industry (Mac Gregor 1996).

Malting barley is widely used in fermentation industry as the raw material for malt production. The physicochemical properties of the barley starch are not well known due to many difficulties connected with an industrial process of starch isolation from the barley grains. Therefore, the aim of this work was to characterize the starches isolated from malting barley varieties in respect of their physicochemical, thermal and rheological properties.

Material and methods

The starches were isolated from malting barley varieties registered in 2008–2011 by the Research Centre for Cultivar Testing (COBORU) in Słupia Wielka (Poland). The malting barley samples originated from five individual Polish plant breeding units: (1) KWS Lochow Polska, (2) Hodowla Roślin Smolice Sp. z o.o. Grupa IHAR, (3) RAGT Semences Polska Sp. z o.o., (4) Hodowla Roślin Strzelce Sp. z o.o. Grupa IHAR and (5) Saaten-Union Polska Sp. z o.o. The individual barley varieties originated from the plant breeding units given in parentheses were abbreviated here as follows: BS1 – Alciana (1), BS4 – Conchita (1), BS9 – Victoriana (1), BS2 – Basza (2), BS3 – Bordo (2), BS5 – GoodLuck (3), BS8 – Signora (3), BS6 – Kormoran (4), BS7 – Marthe (5). The starches were isolated from the barley seeds by laboratory method recommended for isolation of cereal starches (Richter et al. 1968). The isolated starches were dried at room temperature (about 25 °C), then ground in a laboratory mill and sieved through a sieve with 0.125 mm mesh.

Physicochemical properties

Apparent amylose content was determined by spectrophotometric method described by Morrison and Laignelet (1983) using UV/Vis spectrophotometer (V-530, Jasco, Japan). Total phosphorus content was determined according to ISO standard (ISO 3946:2000). The total protein content (N x 6.00) were determined according to Kjeldahl method. Total lipid

content was determined according to Soxhlet method. Swelling power and solubility were determined at 75 °C. Paste (1/100 g) clarity as transmittance at $\lambda=640$ nm was measured by spectrophotometric method.

Thermal characteristic

Thermodynamic gelatinization characteristics were determined using differential scanning calorimeter (DSC F204 Phoenix, Netzsch, Germany). Water–starch dispersion (3:1) was heated in the DSC aluminum pan in the temperature range of 25–110 °C with heating rate of 10 °C/min. The empty aluminum pan was used as a reference. An onset (T_O), peak (T_P), and endset (T_E) gelatinization temperatures and enthalpy of gelatinization (ΔH_G) were determined from the thermograms. After cooling the sample was stored in refrigerator at 4 ± 1 °C for 7 days. Then the sample was reheated at the same conditions as for gelatinization. The onset (T_O), peak (T_P), endset (T_E) temperatures and enthalpy of retrogradation (ΔH_R) were calculated. The percentage of retrogradation (%R) was calculated from the ratio of ΔH_R to ΔH_G .

Rheological properties

The pasting characteristic was determined using Rapid Visco Analyser (TecMaster, Perten Instruments AB, Sweden). The starch–water suspension (5/100 g) underwent a controlled heating and cooling cycle under constant shear (160 rpm), where it was held at 50 °C for 1 min., heated from 50 to 95 °C at 12 °C/min. and held at 95 °C for 2.5 min., cooled to 50 °C at 12 °C/min. and held at 50 °C for 2 min. The following pasting parameters were recorded: pasting temperature (PT), peak viscosity (PV), hot paste viscosity (HPV), breakdown (BD=PV-HPV), final viscosity (FV) and setback (SB=FV-HPV).

For the rheometric experiments (flow curves and sweep frequency tests) starch-in-water dispersion (5/100 g) was heated at 95 °C for 30 min. Hot starch paste was put into the measuring system of rheometer, allowed to relax and cooled to temperature of measurement.

The rotary viscometer Rheolab MC1 (Physica, Germany) with a system of coaxial cylinders (cup diameter: 27.12 mm, bob diameter: 25.00 mm) was used for determination of flow curves at temperature of 50 °C in the shear rate range from 1 to 500 s⁻¹. The experimental curves were described by power law equation:

$$\tau = K\dot{\gamma}^n \quad (1)$$

where: τ - shear stress [Pa]; K - consistency coefficient [Pa·sⁿ]; $\dot{\gamma}$ - shear rate [s⁻¹], n - flow behaviour index.

The sweep frequency test at 25 °C was done using Mars II (Thermo-Haake, Germany) rheometer with cone/plate geometry (cone diameter: 60 mm, angle: 1°, gap size: 0.052 mm). The test was performed at constant strain of 0.01 in the linear viscoelastic region and at angular frequency range of 1–100 rad/s. The power law equations were used to describe the experimental curves:

$$G' = K' \cdot \omega^{n'} \quad (2)$$

$$G'' = K'' \cdot \omega^{n''} \quad (3)$$

where: G' – storage modulus [Pa]; G'' – loss modulus [Pa]; ω – angular frequency [rad/s]; K' , K'' , n' , n'' – constants.

Textural properties

Textural properties of starch gels were evaluated by penetration test using EZTest Texture Analyzer (Shimadzu, Japan) equipped with a 20 N load cell. Starch dispersion at concentration of 5/100 g was heated at 95 °C for 30 min. Hot starch paste was poured into cylindrical container (diameter: 60 mm, height: 50 mm), cooled down at room temperature, covered with a screw tap and stored for 20 h at 6 °C. After conditioning at room temperature, the sample container was placed under penetration probe (20 mm diameter) and the test was started. The probe penetrated into the gel to a depth of 20 mm, at speed of 1 mm/s. The maximum force at the rupture point of the gel was taken as rupture strength (F_R). The distance that the probe penetrated before the gel break occurred (d^*) gave an indication of the gel brittleness. The shorter was that distance, the more brittle was the gel. An index of the gel strength was taken as the force at a point in the initial stage of penetration (5 mm), where little deformation occurred (Genovese et al. 2010). Adhesiveness of the analyzed starch gels represented an energy needed to separate the gel sample from the apparatus probe.

Statistical analysis

For statistical evaluation of the results the one-way analysis of variance at the significance level of 0.05 was used. Significance of differences between the means was determined by Duncan test at significance level of 0.05. Coefficients of Pearson's linear correlations between selected determined parameters were also calculated at significance level of 0.05. Additionally Principal Component Analysis (PCA) was used to provide a ready means of visualizing the differences and similarities among the barley starches. All the calculations were performed using Statistica v. 9.0 software.

Results and discussion

Physicochemical properties

In Table 1 values of physicochemical parameters of starches isolated from malting barley varieties are summarized. Linear starch fraction content of the samples ranged between 19.6 and 25.2/100 g of starch dry mass, for BS2 and BS7 starch, respectively. These values were comparable with literature data concerning various kinds of barley starches (Bello-Perez et al. 2010; Czuchajowska et al. 1998; Gao et al. 2009; Tang et al. 2004; Yoshimoto et al. 2002), however, much higher amylose content of the starch isolated from Brazilian malting barley variety was reported by Soares et al. (2007). These authors claim that amylose content of starch is dependent on the conditions of the plant growing. Amylose content significantly affects functional properties of barley starch: starch with high amylose content shows greater susceptibility to retrogradation and its pastes are more elastic (Bello-Perez et al. 2010). This parameter also significantly affects starch pasting characteristic. Yanagisawa et al. (2006) observed positive correlations between amylose content and final viscosity (FV), setback (SB) and hot paste stability. Apart this, Tang et al. (2001) found correlation between size of starch granules and their amylose content. Moreover, amylose content is determined by botanical source of starch and climatic and soil conditions during the plant growing (Singh et al. 2003). Phosphorus content of the analyzed barley starches ranged between 42.47 (for BS7 starch) and 70.67 (for BS6 starch) mg per 100 g of starch dry mass. These values were closed to these presented by others (Gao et al. 2009; Goering et al. 1973; Suh et al. 2004; Tester 1997). Phosphorus is one of non-carbohydrate compounds of endosperm of grain, which has an essential effect on functional properties of starch (Singh et al. 2003). Phosphorus content of cereal starches significantly affects their pasting characteristics and susceptibility to retrogradation (Suh et al. 2004). Protein content of the analyzed starches isolated from malting barley varieties amounted from 0.50 (for BS8 sample) to 1.26 (for BS3 sample) g per 100 g of starch dry mass. These values were similar to these reported by Czuchajowska et al. (1998) and Soares et al. (2007). Slightly lower values of protein content of the barley starches were reported by Goering et al. (1973) and Gao et al. (2009). Lipids content of the analyzed starches ranged between 0.21 (for BS8 starch) and 0.61 (for BS9 starch) g per 100 g of starch dry mass (Table 1). According to Kaukovirta-Norja et al. (1997) starch lipids significantly affect water holding capacity of starch and its solubility in water, as well as its pasting temperature. Moreover, Tester (1997) found that lipids content of waxy, normal and high-amylose barley starches increased with increase in

Table 1 Physicochemical properties of barley starches

Sample	Amylose content [g/100 g d.m.]	Phosphorus content [mg/100 g d.m.]	Protein content [g/100 g d.m.]	Fat content [g/100 g d.m.]	Swelling power [g/g d.m.]	Solubility [g/100 g d.m.]	Paste clarity [%]
BS1	20.7±0.7 ^{ab}	49.17±1.0 ^a	0.64±0.04 ^c	0.41±0.0 ^c	6.69±0.20 ^{ac}	4.52±0.04 ^a	6.8±0.4 ^{ab}
BS2	19.6±0.4 ^c	54.63±1.0 ^b	0.75±0.02 ^d	0.10±0.0 ^d	6.88±0.11 ^{ab}	3.79±0.08 ^b	6.5±0.2 ^a
BS3	20.6±0.2 ^{ab}	61.13±1.7 ^c	1.26±0.06 ^f	0.33±0.0 ^{ab}	6.43±0.14 ^c	5.00±0.28 ^d	7.2±0.1 ^{bd}
BS4	21.1±0.2 ^b	45.73±0.5 ^d	0.51±0.00 ^a	0.47±0.0 ^f	6.91±0.18 ^{ab}	4.42±0.04 ^a	7.3±0.4 ^d
BS5	20.1±0.3 ^{ac}	50.70±1.9 ^a	1.17±0.01 ^e	0.41±0.0 ^c	7.35±0.14 ^d	5.20±0.08 ^d	6.5±0.2 ^a
BS6	21.0±0.6 ^{ab}	70.67±2.1 ^f	0.75±0.02 ^d	0.30±0.0 ^a	7.16±0.33 ^{bd}	4.64±0.21 ^{ac}	5.9±0.2 ^c
BS7	25.2±0.4 ^d	42.47±1.7 ^c	0.59±0.02 ^{bc}	0.35±0.0 ^b	8.73±0.06 ^e	3.35±0.06 ^e	6.8±0.4 ^{ab}
BS8	20.8±0.3 ^{ab}	48.97±0.9 ^a	0.50±0.00 ^a	0.21±0.0 ^e	6.85±0.17 ^{ab}	4.08±0.06 ^b	9.8±0.1 ^e
BS9	20.6±1.0 ^{ab}	53.90±15 ^b	0.57±0.02 ^{ab}	0.61±0.0 ^g	6.89±0.01 ^{ab}	4.89±0.08 ^{ce}	5.4±0.0 ^c

Mean values from three repetitions±SD

Values in columns followed by the same superscript letters do not significantly differ at significance level of 0.05

temperature at which the plant was growing. In our study, the statistical differentiation between the water holding capacity and solubility in water at 75 °C of the starch samples was small, however, the highest water holding capacity was determined for BS7 starch, whilst the highest solubility in water was showed by BS5 starch. Slightly higher values of these parameters for starches from various barley varieties were reported by Subaric et al. (2011), whilst similar values of solubility in water of starch from malting barley variety were given by Soares et al. (2007). According to Hoover (2001) water holding capacity and solubility of starch in water is strongly affected by interactions between starch polymer chains within amorphous and crystalline structures of starch. The range of these interactions is dependent on amylose to amylopectin ratio, branching degree of starch and length of side chains in amylopectin. Li et al. (2001) found that differences in water holding capacity and solubility in water between starches isolated from various botanical sources resulted mainly from differences between total amylose content, presence of amylose-lipids complexes, and amylopectin chains with DP of 6–24 content. In our study, significant linear correlation between water holding capacity and amylose content ($r=0.86$, $p<0.05$) was found. The clarity of all the starch pastes was in a wide range of values, however, it did not exceed the value of 10 %. The highest value of transmittance was determined for BS8 starch, whilst the lowest one for BS9 starch. The clarity of the starch paste depends on many factors, such as amylose to amylopectin ratio and non-starch compounds content, mainly proteins and lipids. Moreover, according to Singh and Singh (2001) the way of starch paste preparation, i.e. temperature, time and the rate of heating of the starch suspension, is the factor that affects clarity of the starch paste after storage, because it determines the interactions between the polymer chains in starch.

Gelatinization properties

The parameters of gelatinization and retrogradation characteristics are summarized in Table 2. Values of onset temperature ranged from 56.5 °C (for BS9 starch) to 58.5 °C (for BS1 starch), peak temperature - from 61.2 °C (for BS8) to 63.0 °C (for BS5), while endset temperature - from 66.7 °C (for BS8) to 68.7 °C (for BS3). All these temperatures are similar to these reported by other authors (Gao et al. 2009; Li et al. 2001; Suh et al. 2004; Tang et al. 2001, 2002). Slightly higher values of endset temperature are presented in the work by Yoshimoto et al. (2002), whilst Tester and Morrison (1990) and Yasui et al. (2002) found lower values of temperatures of thermal transitions for starches isolated from normal and waxy barley varieties. Moreover, Yasui et al. (2002) reported that starch from waxy barley was characterized by higher gelatinization temperatures and higher gelatinization enthalpy as compared to normal barley starch. According to Suh et al. (2004) low onset and endset gelatinization temperatures result from high ratio of short to long starch polymer chains. Moreover, the differences in temperatures of the thermal transition of starch result from differences in shape and size of particular starch granules (Suh et al. 2004). Gelatinization is very important functional property of starch, which mainly depends on starch composition (amylose to amylopectin ratio, proteins, phosphorus, lipids and enzymes contents) and molecular structure of amylopectin (the main chain length, degree of branching, molecular mass) (Singh et al. 2007). The In the present study the endset temperatures of gelatinization significantly correlated with protein content ($r=0.70$, $p<0.05$) and with peak temperatures ($r=0.84$, $p<0.05$). Values of gelatinization enthalpy of the starches from malting barley varieties ranged from 6.49 J/g (for BS9 starch) to 9.61 J/g (for BS7 starch). Similar values of gelatinization enthalpies were reported by Bello-Perez et al. (2010) and Subaric et al. (2011), whilst slightly lower values of that parameter were determined by

Table 2 Parameters of thermodynamic gelatinization and retrogradation characteristics of barley starches

Sample	Gelatinization				Retrogradation				
	T_O [°C]	T_P [°C]	T_E [°C]	ΔH_G [J/g]	T_O [°C]	T_P [°C]	T_E [°C]	ΔH_R [J/g]	R [%]
BS1	58.5±0.1 ^g	62.7±0.1 ^c	68.2±0.2 ^d	9.49±0.39 ^{ab}	44.4±0.1 ^c	54.0±0.2 ^a	61.0±0.3 ^{ab}	3.17±0.16 ^a	33.40
BS2	57.2±0.0 ^d	61.9±0.1 ^a	67.5±0.1 ^{ab}	9.50±0.23 ^{ab}	45.2±0.2 ^f	54.3±0.3 ^{ab}	61.7±0.1 ^{cd}	3.11±0.05 ^{ac}	32.73
BS3	57.6±0.1 ^{abc}	62.3±0.1 ^b	68.7±0.1 ^g	9.58±0.22 ^a	46.8±0.2 ^g	55.0±0.4 ^b	61.6±0.1 ^c	3.27±0.14 ^a	34.13
BS4	57.6±0.3 ^{ab}	62.2±0.1 ^{ab}	67.7±0.2 ^{bc}	8.89±0.17 ^{cd}	40.8±0.3 ^b	51.4±0.6 ^d	59.6±0.1 ^f	2.81±0.18 ^b	24.52
BS5	57.7±0.2 ^{bc}	63.0±0.2 ^f	68.4±0.2 ^d	7.85±0.05 ^f	45.8±0.3 ^a	54.7±0.2 ^{ab}	62.1±0.2 ^{de}	2.88±0.09 ^b	36.68
BS6	57.4±0.2 ^{ad}	61.5±0.1 ^e	67.1±0.1 ^f	8.79±0.05 ^c	42.2±0.2 ^c	52.6±0.9 ^c	60.7±0.1 ^a	2.92±0.07 ^{bc}	33.21
BS7	57.9±0.1 ^c	62.2±0.1 ^{ab}	67.4±0.2 ^a	9.61±0.07 ^a	45.7±0.1 ^a	54.5±0.3 ^{ab}	62.2±0.4 ^e	3.26±0.12 ^a	33.92
BS8	56.8±0.0 ^f	61.2±0.1 ^d	66.7±0.1 ^e	9.20±0.07 ^{bd}	45.8±0.2 ^a	54.3±0.3 ^{ab}	61.1±0.3 ^b	3.15±0.09 ^a	34.23
BS9	56.5±0.3 ^e	62.7±0.3 ^c	67.9±0.1 ^c	6.49±0.15 ^e	43.1±0.3 ^d	53.1±0.2 ^c	61.0±0.3 ^{ab}	2.87±0.09 ^b	44.22

T_O onset temperature, T_P peak temperature, T_E endset temperature, ΔH_G enthalpy of gelatinization, ΔH_R enthalpy of retrogradation

$R = \Delta H_R / \Delta H_G \times 100 \%$

Mean values from three repetitions±SD

Values in columns followed by the same superscript letters do not significantly differ at significance level of 0.05

Song and Jane (2000). Higher values of ΔH_g for normal and waxy barley starches are reported by Tester and Morrison (1990), Li et al. (2001) and Suh et al. (2004). Gelatinization enthalpy is general measure of starch crystallinity, and it is an indicator of losses of crystalline structure of starch due to gelatinization process, as well (Singh et al. 2003, 2007). Thermal properties of starch are affected by many factors, such as: size and shape of starch granules, phosphorus content, degree of starch crystallinity, length of amylopectin chains (Singh et al. 2003, 2007). According to Yasui et al. (2002) quantity and structure of amylopectin are main factors which affect the value of gelatinization enthalpy. Li et al. (2001) reported that gelatinization enthalpy of waxy barley starch decreased with decrease in starch granule size. In our study a negative linear correlation was observed between gelatinization enthalpy and lipids content ($r = -0.69$, $p < 0.05$). Retrogradation is a characteristic phenomenon that involves forming hydrogen bonds between starch polymer chains when cooked starch paste is cooled (Subaric et al. 2011). During this process amylose forms double helices composed of 40–70 glucose units, whilst amylopectin undergoes crystallization due to re-association of the outermost short branches. According to Singh et al. (2003) and Subaric et al. (2011) the value of retrogradation enthalpy for a given starch is usually about 60–80 % lower than that of gelatinization enthalpy. Similarly, the temperatures of thermal transition of the crystallized starch are about 10–26 °C lower than these determined during gelatinization of starch. Lower temperatures of thermal transition of the retrograded amylopectin result from the fact that during storage of the starch paste the small crystalline regions are formed, which disintegration involves much less energy (Bello-Perez et al. 2010). In Table 2

experimentally determined characteristic temperatures and enthalpies of thermal transitions of the retrograded malting barley starches are summarized. Values of peak temperature ranged between 40.8 and 46.8 °C, for BS4 and BS3 starches, respectively. The starches differed only little among each other in the values of endset temperature, which ranged from 59.6 to 62.2 °C, for BS4 and BS7 samples, respectively. Values of the phase transition temperatures of the retrograded starches were similar to these presented by Subaric et al. (2011), however, they were slightly higher than these reported by Suh et al. (2004) and Song and Jane (2000). Values of the retrogradation enthalpy were in the range from 2.81 J/g (BS4 sample) to 3.27 J/g (BS3 sample) and they were comparable to the literature data (Song and Jane 2000; Suh et al. 2004; Subaric et al. 2011). The rate of retrogradation calculated from the values of gelatinization and retrogradation enthalpies amounted from 24.52 to 44.22 %, for BS4 and BS9 starches, respectively. These values are in agreement with these presented by Song and Jane (2000) and Suh et al. (2004), however, lower degree of retrogradation of barley starch samples were reported by Bello-Perez et al. (2010).

Pasting behaviour

When starch-in-water suspension is heated the starch granules swell, rupture and as a result amylose is leached from their interior and colloidal solution is formed. If starch system is cooled down its viscosity increases due to forming a three-dimensional network structure, which is composed of amylose and amylopectin chains linked together by hydrogen bonds. That network is able to holding water (Bello-Perez et al. 2010). Both physical and chemical properties of starch, such

as mean granule size, size distribution, amylose to amylopectin ratio or mineral elements content, affect its behaviour during pasting in water (Singh et al. 2003). After exceeding the characteristic pasting temperature the viscosity of the starch-water mixture strongly increases. Subsequent heating the system leads to a decrease in viscosity, however, at the cooling stage its viscosity increases again, up to a given final viscosity. Examples of pasting curves of the analyzed barley starches are presented in Fig. 1a. In the case of BS1 starch the highest value of peak viscosity and the highest final viscosity, which was greater than the peak viscosity, were found. The lowest value of peak viscosity and smooth decrease in viscosity during heating cycle were observed for BS5 sample. Peak viscosity is a measure of an ability of starch granules to hold water (Bello-Perez et al. 2010). Parameters of pasting characteristics of barley starches are summarized in Table 3. All the analyzed starches showed high values of pasting temperature, which ranged from 86.5 to 91.3 °C. This is in accordance with pasting temperature reported by Song and Jane (2000) and Suh et al. (2004). Slightly lower values of pasting

temperatures were determined by Bello-Perez et al. (2010) and Subaric et al. (2011). According to Sandhu and Singh (2007) high pasting temperature results from great resistance of starch granules to swelling. Moreover, phospholipids present in the starch can form helical complexes with amylose and thus restrict swelling power of starch granules, that can result in an increase in pasting temperature (Song and Jane 2000). Increased pasting temperature of cereal starches is due to greater lipids and protein contents. These compounds form complexes with amylose and thus restrict starch swelling (Singh et al. 2003). According to Tester and Morrison (1990), amylopectin is responsible for the ability of starch granules to swelling, while the linear starch fraction and lipids can restrict water absorption by starch granules. In the present study the barley starches were characterized by wide range of values of peak viscosity (Table 3), which amounted from 133 mPa·s to 230 mPa·s, for BS5 and BS6, respectively. High values of peak viscosity were also determined for BS1 and BS7 samples. The breakdown (BD) is the parameter of pasting characteristic that is a measure of a decrease in viscosity

Fig 1 Pasting (a) and flow (b) curves of barley starch pastes

Table 3 Parameters of pasting characteristics of barley starches

	Sample	PT [°C]	PV [mPa·s]	HPV [mPa·s]	BD [mPa·s]	FV [mPa·s]	SB [mPa·s]
<i>PT</i> pasting temperature, <i>PV</i> peak viscosity, <i>HPV</i> hot paste viscosity, <i>BD</i> = <i>PV</i> - <i>HPV</i> breakdown, <i>FV</i> final viscosity, <i>SB</i> = <i>FV</i> - <i>HPV</i> setback	BS1	86.9±1.0 ^a	229±3 ^b	153±2 ^d	77±1 ^a	411±8 ^g	259±6 ^g
	BS2	91.3±0.0 ^b	203±1 ^c	130±1 ^{ab}	73±2 ^a	316±7 ^b	186±6 ^c
	BS3	90.9±0.4 ^b	188±3 ^a	150±3 ^d	38±1 ^d	224±8 ^c	74±6 ^d
	BS4	87.7±0.6 ^a	193±4 ^a	126±3 ^a	67±2 ^g	285±7 ^e	159±5 ^e
	BS5	87.3±1.0 ^a	133±4 ^c	101±3 ^c	32±1 ^c	271±7 ^a	170±4 ^b
Mean values from three repetitions±SD	BS6	86.8±0.8 ^a	230±6 ^b	145±3 ^c	85±5 ^b	348±10 ^f	202±8 ^f
Values in columns followed by the same superscript letters do not significantly differ at significance level of 0.05	BS7	86.5±1.4 ^a	229±6 ^b	144±3 ^c	85±3 ^b	323±7 ^b	179±4 ^{bc}
	BS8	87.6±0.4 ^a	188±1 ^a	133±1 ^b	55±2 ^e	269±5 ^a	136±6 ^a
	BS9	86.9±1.0 ^a	181±3 ^d	119±2 ^f	62±3 ^f	251±9 ^d	131±8 ^a

during subsequent heating of starch paste. Values of this parameter were the highest for BS6 and BS7 samples, which also showed the highest peak viscosities. The lowest value of BD was determined for BS5 sample, which also exhibited the lowest value of peak viscosity (Table 3). Significant negative correlation between protein content and BD ($r=-0.69$, $p<0.05$) and positive correlation between gelatinization enthalpy and HPV ($r=0.69$, $p<0.05$) were found. Subsequent cooling of starch paste results in significant increase in its viscosity, which is indicated as setback (SB). Values of SB ranged between 74 and 259 mPa·s, for BS3 and BS1 starches, respectively. Final viscosities of all the barley starches were significantly higher than their peak viscosities. The higher value of final viscosity was found for BS1 starch, while the lowest one for BS3 starch.

Flow and viscoelastic properties

The increase in viscosity of the starch system which is observed during starch pasting results from many structural changes of starch, such as non-reversible starch granule swelling and amylose leaching from starch granules. Typical starch paste exhibits properties of non-Newtonian, shear thinning fluid. The rheological properties of starch paste strongly depend on time of shearing and shear rates. Examples of flow curves of the barley starches are presented in Fig. 1b. The parameters of the power law model used to describe the experimental curves are summarized in Table 4. The highest values of shear stress within the shear rate range used were recorded for BS7 starch, while the lowest ones for starch isolated from BS3 barley. Moreover, all the starch pastes exhibited thixotropy phenomenon, that was demonstrated in hysteresis loops representing dependence of shear stress on increasing and decreasing shear rates (Fig. 1b). The thixotropy phenomenon results from retarded in time reconstitution of the structure of starch under shear stress. In the present study, the power law model is well fitted to the experimental data, that is confirmed by high values of determination coefficient (R^2)

(Table 4). Values of consistency coefficient (K) ranged between 1.97 Pa·sⁿ, for BS3 starch, and 4.67 Pa·sⁿ, for BS7 starch. Values of flow behaviour index (n) were from 0.29, for BS9 starch, to 0.38, for BS4 and BS8 starches. These values confirm the non-Newtonian, shear thinning flow behaviour of the starch pastes. According to Lagarrigue and Alvarez (2001) values of flow behaviour index decrease with increase in starch concentration in the system. Significant linear correlation ($r=0.68$, $p<0.05$) between consistency coefficient and water holding capacity of the starches was found.

Viscoelastic properties of material result from the occurrence of certain structures that are able to absorb energy which is partially stored and partially dissipated after releasing the applied stress. The ratio of the energy dissipated to the energy stored per each cycle is defined as $\tan \delta$ and gives information about physical behaviour of the system (Singh and Singh 2001; Singh et al. 2003, 2007). During cooling of the starch paste values of $\tan \delta$ decrease due to formation of the gel structure. Decrease in values of $\tan \delta$ can result from retrogradation of starch and interactions between leached amylose and starch granules giving increase in gel strength during cooling of starch paste (Singh et al. 2007). Values of G' and G'' moduli depend on amylose content, swelling and crystallinity of starch. Examples of mechanical spectra of selected barley starch gels are presented in Fig. 2a. It was found that in each analyzed gel the values of G' were greater than these of G'' , that depicts a domination of elastic properties over the viscous ones. Figure 2b shows changes in values of loss tangent with angular frequency. Values of K' parameter representing initial value of G' ranged from 19.53 (BS6 sample) to 41.81 (BS9 sample), while values of K'' parameter indicating initial value of G'' were from 1.77 to 2.76, for BS3 and BS1 samples, respectively (Table 4). All the analyzed starch gels only slightly differed among each other in values of n' and n'' parameters, which reflect susceptibility of storage and loss modulus, respectively, to changes in angular frequency. Significant linear correlations between K'' parameter and pasting characteristic parameters: BD, FV and SB were found, with

Table 4 Parameters of power law models describing flow curves and mechanical spectra of barley starches

Sample	K [Pa·s ⁿ]	n	R ²	K'	n'	R ²	K''	n''	R ²
BS1	3.50±0.00 ^c	0.34±0.00 ^{bcd}	0.9638	24.54±0.95 ^{ab}	0.14±0.01 ^{ab}	0.9870	2.76±0.26 ^d	0.45±0.02 ^{dc}	0.9988
BS2	3.44±0.25 ^c	0.32±0.01 ^d	0.9597	22.90±3.24 ^a	0.14±0.00 ^{ab}	0.9600	2.41±0.23 ^{ad}	0.46±0.02 ^{abe}	0.9984
BS3	1.97±0.20 ^a	0.37±0.01 ^{ab}	0.9846	28.80±1.12 ^b	0.10±0.02 ^d	0.9752	1.77±0.25 ^{bc}	0.50±0.01 ^{cf}	0.9964
BS4	2.64±0.11 ^b	0.38±0.01 ^a	0.9644	22.87±1.74 ^a	0.15±0.01 ^a	0.9746	2.13±0.15 ^{ac}	0.48±0.02 ^{abc}	0.9935
BS5	2.54±0.21 ^b	0.35±0.01 ^{abc}	0.9644	20.23±2.27 ^a	0.15±0.01 ^a	0.9794	2.07±0.19 ^{abc}	0.49±0.01 ^{bc}	0.9978
BS6	2.55±0.12 ^b	0.36±0.00 ^{abc}	0.9609	19.53±1.70 ^a	0.14±0.01 ^{ab}	0.9636	2.45±0.30 ^{ad}	0.43±0.02 ^d	0.9986
BS7	4.67±0.25 ^d	0.33±0.02 ^{cd}	0.9640	22.06±2.07 ^a	0.14±0.02 ^{ab}	0.9735	2.37±0.21 ^{ad}	0.46±0.02 ^{ade}	0.9963
BS8	2.19±0.15 ^{ab}	0.38±0.01 ^a	0.9674	22.19±0.98 ^a	0.12±0.01 ^b	0.9549	1.67±0.22 ^b	0.52±0.02 ^f	0.9988
BS9	3.59±0.14 ^c	0.29±0.00 ^c	0.9689	41.81±6.46 ^c	0.08±0.00 ^c	0.9707	2.06±0.25 ^{abc}	0.48±0.00 ^{abc}	0.9980

Mean values from three repetitions±SD

Values in columns followed by the same superscript letters do not significantly differ at significance level of 0.05

values of Pearson's linear correlation coefficient (r) amounting 0.72, 0.90 and 0.89, respectively ($p<0.05$). Moreover, n'' parameter was strongly negatively correlated with BD, FV and SB parameters ($r=-0.78$, $r=-0.78$, $r=-0.75$, respectively ($p<0.05$)).

Textural properties

Texture characteristics of the barley starch gels (5 %) was performed by penetration test, which is recommended for weak gels (Genovese et al. 2010). Values of the determined

Fig 2 Mechanical spectra (a) (G' empty markers, G'' filled markers) and dependence of phase angle on angular frequency (b) of barley starches gels

Table 5 Texture parameters of barley starch gels

Sample	Gel strength [N]	Rupture strength [N]	Brittleness [mm]	Adhesiveness [N·mm]
SB1	0.44±0.03 ^a	1.14±0.05 ^a	9.12±0.42 ^b	−1.50±0.10 ^d
SB2	0.47±0.09 ^{ac}	0.95±0.06 ^a	11.43±0.84 ^c	−0.68±0.14 ^{ab}
SB3	0.13±0.01 ^d	0.15±0.00 ^b	5.94±0.11 ^a	−0.26±0.07 ^c
SB4	0.77±0.11 ^f	1.08±0.22 ^a	6.22±0.36 ^a	−0.73±0.19 ^a
SB5	0.63±0.03 ^b	1.00±0.19 ^a	6.57±0.70 ^a	−0.33±0.07 ^{bc}
SB6	0.55±0.07 ^{bc}	1.05±0.07 ^a	8.13±1.17 ^b	−0.46±0.23 ^{abc}
SB7	0.44±0.03 ^a	1.77±0.08 ^d	10.42±0.13 ^c	−1.36±0.45 ^{de}
SB8	0.65±0.04 ^b	0.93±0.06 ^a	6.53±0.10 ^a	−0.57±0.16 ^{abc}
SB9	0.33±0.06 ^c	0.72±0.02 ^c	9.19±0.67 ^b	−1.12±0.07 ^c

Mean values from three repetitions±SD

Values in columns followed by the same superscript letters do not significantly differ at significance level of 0.05

parameters are collected in Table 5. The BS4 gel represented the highest value of elasticity of all the gels tested, while BS3 gel showed the lowest value of this parameter. High values of elasticity were also recorded for BS5 and BS8 gels. Elasticity of starch gel is connected with the force that causes reversible deformation of the gel structure. An essential role in the elasticity of the starch gel play interactions between swollen starch granules and the continuous phase of the system, which consists of solubilised amylose molecules (Gałkowska and Fortuna 2008). The highest rupture force was showed by BS7 gel, while the lowest one by BS3 gel (Table 5). Significant linear correlations between rupture force and amylose content ($r=0.68$, $p<0.05$), water holding capacity ($r=0.88$, $p<0.05$) and flow behaviour index ($r=0.79$, $p<0.05$) were found. Values of brittleness recorded for barley starch gels ranged from 5.94 to 11.43 mm, for BS3 and BS2 gels, respectively. Adhesiveness represents the surface properties of the starch gel. The main factor that affects adhesiveness of the starch gel is structure of the starch polymers. Decrease in molecular weight of amylose and decrease in the amount of branch chains in amylopectin cause increase in adhesive forces existing in the starch gel. Moreover, adhesiveness of the starch gel depends on cohesive and adhesive forces and viscous and viscoelastic properties of the gel (Gałkowska and Fortuna 2008). In the present study the BS1 starch gel was the most adhesive, while the least adhesive was the BS3 sample. Significant linear correlations between values of consistency coefficient (K) and selected texture parameters of the starch gels, i.e. rupture force, brittleness and adhesiveness were found ($r=0.70$, $r=0.83$, $r=-0.83$, respectively, at $p<0.05$). Moreover, a negative linear correlation between flow behaviour index (n) and brittleness of the starch gels was stated ($r=-0.77$, $p<0.05$).

Principal component analysis

Figure 3a and b show results of principal component analysis (PCA) on the basis of the selected parameters of rheological

Fig 3 Principal component analysis: **a** distribution of analysed parameters, ΔH_G gelatinization enthalpy, ΔH_R retrogradation enthalpy, PV peak viscosity, FV final viscosity, K consistency coefficient, n consistency coefficient, K' , K'' , n' , n'' parameters of power law equations, GS gel strength, RS rupture strength; **b** distribution of barley starch varieties

characteristics of the starch pastes and gels. The first two factors explain 67.03 % of the overall variation (with eigenvalues of 4.93 and 3.12, respectively). Figure 3a shows distribution of the variables on the plot of factors. The strongest correlations were found between values of factor 1 and final viscosity and rupture strength, as well as between factor 2 and flow behaviour index. Almost all the analysed parameters play an important role for the first factor, while for the second factor this is mainly for parameters of the rheological characteristics. In Figure 3b distribution of the analysed starches on the plot of factors 1 and 2 are presented. Factor 1 shows that there are similarities between the following starches: BS3 and BS9, BS5 and BS8, and BS1 and BS7. On the other hand, factor 2 clearly separates BS9 starch from the other ones, and it groups these latter into three groups: BS1, BS2 and BS7, BS6 and BS3, and BS4, BS5 and BS8.

Conclusions

Starches isolated from malting barley varieties were characterized by different amylose, phosphorus and protein contents, as well as by different thermal and rheological properties. The barley starch pastes exhibited non-Newtonian, shear thinning flow behaviour and thixotropy phenomenon. The starch gels showed properties of weak gels, that manifested in the shape of the mechanical spectra and in the values of texture parameters. Significant linear correlations between pasting and rheological parameters were found. Results of the Principal Component Analysis revealed statistical differentiation between the starches isolated from various malting barley varieties.

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