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Effect of high pressure on thermal, structural and osmotic properties of waxy maize and Hylon VII starch blends

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Abstract

Hylon VII, waxy maize starch and their mixtures (1:1, 1:3, 3:1, w/w) were subjected to a high pressure treatment (650 MPa/9 min) in an excess of water (30%). High sensitivity differential scanning microcalorimetry (HSDSC), X-ray, Pulse ^{1}H-NMR spectroscopy, and scanning electron microscopy (SEM) were used to analyse changes in the physico–chemical properties and microstructure of modified starches.

High pressure-treated Hylon VII showed a slight degree of granules gelatinisation (GD = 10.8%). Whereas, "pressurised" waxy maize starch manifested complete disintegration of granules (GD = 85.9%) and formed a gel-like structure. The gelatinisation degree of "pressurised" starch mixtures decreased along with an increase in Hylon VII concentration. The starch preparations (650 MPa/9 min) after rehydration revealed low values of a swelling index and mobility of water molecules along with an increase in Hylon VII concentration. The high pressure-treated starches, with the exception of Hylon VII, manifested significant changes in their crystalline structure.
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Keywords: High pressure; Maize starches; DSC; Pulse ^{1}H-NMR; SEM

1. Introduction

It is a common knowledge that heating starch granules in an excess of water at gelatinisation temperature results in an endothermic disruption of the ordered structures within granules (Douzals, Perrier-Cornet, Gervais, & Coquille, 1998). The phenomenon of starch gelatinisation was defined by Hermansson and Svegmark, 1996 as phase transition of granules from an ordered state to the disordered one. The gelatinisation of starch granules evokes granule hydration, swelling and leakage of amylose, which in turn results in a loss of an anisotropic order, crystallinity as well as granular shape. Generally, the mechanism of starch gelatinisation is determined not only by the structure and chemical composition of starch granules (amount of amylose, degree of polymerisation, presence of non-starch compounds, type of polymorph), but is also closely linked with the amount of solvent and the level and kind of energy supplied. Starches obtained from mutant wheat varieties (up to 39.5% of amylose content) (Bocharnikova et al., 2003) or corn varieties ("amylose extender" up to 75% of amylose) (Gidley & Bociek, 1985), have been reported to require more energy to gelatinise than the waxy starches (trace amount of amylose) (Fornal, Błaszczak, & Lewandowicz, 1998). The gelatinisation of starch granules in a limited amount of water triggers a two-phase gelatinisation mechanism (Svensson & Eliasson, 1995). These authors pointed out that a minor reduction in the crystallinity of starch granules occurred after the hydration of the amorphous regions – as the first phase of the gelatinisation process.

Starch subjected to high pressure may gelatinise as early as at room temperature (Stolt, Stoforos, Taoukis, & Autio, 1999). The high pressure causes an irreversible distortion of

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the crystalline region in starch granules (French, 1984) prior to a reversible hydration of the amorphous phase, which in turn leads to the destruction of the granular structure (Rubens & Heremans, 2000). It was found that the effects of high pressure and heat-water treatment on the mechanism of starch gelatinisation and granule structure were not alike (Stute, Klingler, Boguslawski, Eshtiaghi, & Knorr, 1996). The mechanism of starch gelatinisation during the high pressure treatment as well as the structure and properties of starch gels obtained under high pressure conditions are still under investigation (Rubens et al., 2000; Bauer, Hartmann, Sommer, & Knorr, 2004; Błaszczak, Valverde, & Fornal, 2005a). The properties of starch pastes and gels obtained under high pressure differed from those of the heat-gelatinised ones (Stolt, Oinonen, & Autio, 2001). However, Stute et al. (1996) noticed that starches of different botanical origin (different type of polymorph) gelatinised at different pressure ranges. Wheat, maize, barley and potato starches treated with high pressure maintained their granular shape and demonstrated limited swelling (Błaszczak et al., 2005a; Stolt et al., 2001; Stute et al., 1996). The latter authors, when analysing (under SEM) the microstructure of potato starch treated with high pressure (600 MPa for 3 min), confirmed that also the "pressurised" granules maintained their granular shape. These authors found that the outer part of granules (surface) was formed by the unchanged structure ascribed to a more organised polymer structure, and the internal one was filled completely with a gel-like network. In contrast, according to Stute et al. (1996), high pressure-treated waxy maize starch (600 MPa) showed complete disintegration of granules. Stolt et al. (1999) found that, under high pressure, 10% dispersion of waxy maize starch formed a weak gel. The mode of starch polymer chains packing in the granule structure is regarded decisive for starch behaviour under high pressure (Rubens et al., 2000). These authors claimed also that the degree of the crystalline structure melting at high pressure might have depended on the type of starch (amylose–amylopectin ratio) being responsible for specific interactions which determine starch behaviour. Stolt et al. (2001) pointed out the role of the stabilising effect of amylose under high pressure.

The study addressed an analysis of changes in the physico–chemical properties and microstructure of Hylon VII (H), waxy maize starch (A) and their mixtures (H:A, 3:1, 1:1, 1:3, w/w) that were subjected to a high (hydrostatic) pressure treatment in an excess of water as a function of time. The physical properties of rehydrated gels obtained from the high pressure-treated starches were investigated as well.

2. Materials and methods

2.1. Materials

The experimental material was native food starch Hylon VII (68% of amylose), refined from high amylose maize that was a gift of the National Starch & Chemical, Food Starch, Poland. The waxy maize starch (trace amounts of amylose) – the second raw material, was purchased from Sigma (S-9679). The additional experimental samples were obtained by mixing both the above mentioned starches (Hylon VII and waxy maize starch) at different ratios, i.e., 1:1, 1:3, and 3:1 (w/w).

2.2. Sample preparation

The pressure treatment of starches and starch mixtures was performed in the excess of water, i.e., using a 30% (w/w) starch–water suspension. The suspension was closed into teflon tubs (10 mL), precisely mixed, deaerated, closely sealed and pressure-treated (Błaszczak et al., 2005a).

2.3. Pressure treatment

The pressure treatment of starch–water suspensions was performed in a high pressure device (high pressure press type LV30/16, produced by The Centre of High Pressure Analysis, Polish Academy of Sciences, Warsaw, Poland).

The teflon tubes were put into a high pressure chamber (with the capacity of approximately 25 mL) filled with pressure-transmitting medium which also minimised adiabatic heating. The samples were pressure-treated at 650 MPa for 9 min. The time for reaching the working pressure was 120 s. The temperature inside the pressure chamber averaged 20 ± 2 °C. The pressure treatment was performed in two repetitions for each combination.

After the pressure treatment, the starch pastes and gels were frozen in liquid nitrogen and freeze-dried. The starch preparations obtained were used for DSC, pulse NMR, X ray analysis and for determination of swelling index.

2.4. High sensitivity differential scanning microcalorimetry

The calorimetric investigations of 0.5% aqueous dispersions (sample volume of 0.5 mL) of native starches, their mixtures and swelling samples (for 24 h) of these starches treated with high pressure were performed with a high sensitive differential scanning microcalorimeter DASM-4 (Puschino, Russia). The measurements were carried out at a temperature range of 10–130 °C, excess pressure of 2.5 atm., and a heating rate of 2 °C min^{-1}. Each experiment was performed after calibration of the heat capacity scale. It was shown that under these conditions corrections for dynamic temperature lag and residence time of samples in a calorimetric cell were not necessary (Andreev, Kalistratova, Wasserman, & Yuryev, 1999; Danilenko, Shtikova, & Yuryev, 1994).

The thermodynamic properties of the samples were determined according to the methods published earlier (Andreev et al., 1999; Danilenko et al., 1994; Matveev et al., 2001). The baselines for symmetrical and unsymmetrical calorimetric peaks (Fig. 1) were determined according to the method of Matveev et al. (2001).

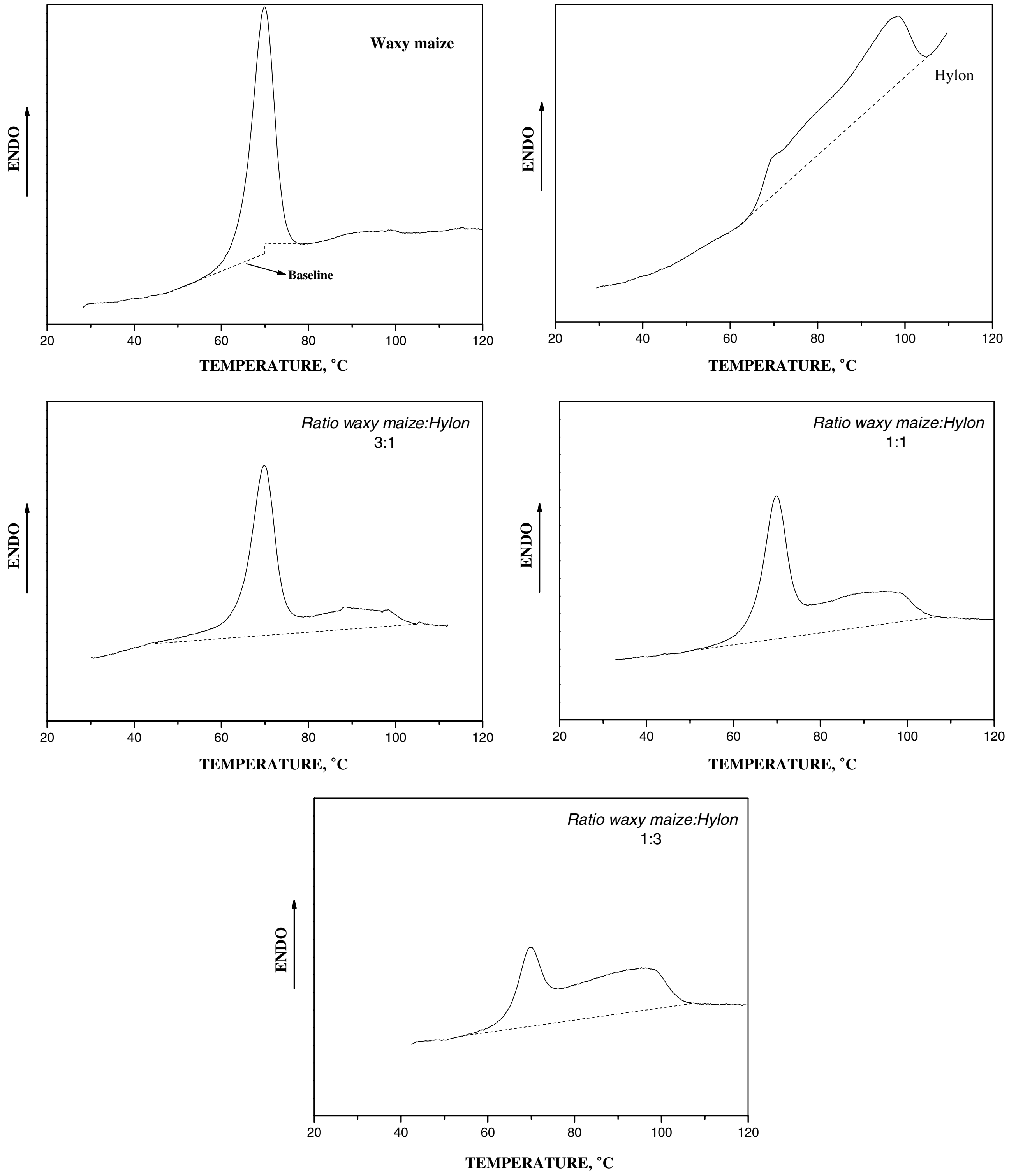


Fig. 1. DSC-thermographs of native waxy maize starch, Hylon VII and their mixtures (3:1, 1:1, 1:3, w/w).

The average values of thermodynamic parameters, at a 95% significance level, were determined from five measurements. The thermodynamic parameters were converted to a dimension per mole of anhydroglucose unit (162 gmol^{-1}). The measurement errors in melting temperature and melting enthalpy were ±0.1 K and ±0.3 kJmol^{-1}, respectively.

The values of the gelatinisation degree (GD) were calculated using the following equation:

$$\mathrm{GD} = \{(\varDelta H_{\mathrm{ns}} - \varDelta H_{\mathrm{ts}})\varDelta H_{\mathrm{ns}}^{-1}\} \times 100\%$$

where $\varDelta H_{\mathrm{ns}}$ and $\varDelta H_{\mathrm{ts}}$ are the melting enthalpies of native and pressure-treated starches, respectively.

2.5. Determination of the swelling index

Preparations of starch (20 mg, d.w.) obtained after “pressurisation” and freeze-drying (moisture, 8%) were put into a fine, wire screens (commercially available product) that were inserted into a glass flask (250 mL) completely filled with distilled water. After 24 h, the wire screens with swollen starch preparations were taken out from the flask and the excess of water was precisely filtered off using filter paper. The wire screens with the swollen starch preparations were weighed.

The values of the swelling index (SWI) were calculated using the following equation:

$$\mathrm{SWI} = \{(P_{\mathrm{sws}} - P_{\mathrm{o}})P_{\mathrm{o}}^{-1}\} \times 100\%$$

where P_{sws} and P_{o} are the weight of swollen and absolutely dry samples, respectively.

2.6. Pulse ^{1}H-NMR spectroscopy

The spin–spin relaxation time of water molecules (T_2) was determined by using pulse ^{1}H-NMR (Minispec, PC-120, Bruker, Germany), the operational frequency being 20 MHz. The measurements were carried out at 25 °C. The values of T_2 were determined by using a Carr–Purcell–Meibom–Gill (CPMG) pulse sequence (Carr & Purcell, 1954; Meibom & Gill, 1958).

Since, a high deviation from the exponential function was obtained, PC numerical simulation was used to decompose the experimentally obtained echo envelope into single exponentials (T_{2a} and T_{2b}). The experimental error in the estimation of T_2 did not exceed 6%.

2.7. X-ray

The X-ray analysis was performed using a TUR 62 diffractometer (Carl Zeiss, Germany) under the following conditions: X-ray tube CuKa (Ni filter), 30 kV, current 15 mA, scanning from $\theta = 2$–18°.

To avoid the influence of relative humidity on relative crystallinity, the starch samples were placed in a desiccator and conditioned in the atmosphere of relative humidity of 92% for 48 h. To this end, the desiccator was filled with sodium carbonate saturated aqueous solution.

2.8. Microscopic analysis

For scanning electron microscopy (SEM), the starch gels/suspension (0.5 mL) were rapidly frozen in liquid nitrogen and freeze-dried. The fractures of dried gels were stuck on a specimen holder using a silver plate, and then coated with gold in a vacuum evaporator (JEE 400, Jeol). The specimens obtained were viewed in a Jeol JSM 5200 scanning electron microscope at an accelerating voltage of 10 kV.

3. Results and discussion

The thermodynamic melting parameters obtained for the native waxy maize starch and Hylon VII (Fig. 1, Table 1) are consistent with the earlier published data (Friedman, Mauro, Hauber, & Katz, 1993; Matveev et al., 2001; Yuryev, Wasserman, Andreev, & Tolstoguzov, 2002). A symmetrical thermogram, obtained in the case of waxy maize starch, was attributed to the melting of the A-type crystallites, while the unsymmetrical thermogram of Hylon VII describes the melting of two B-type crystallites (B- and B*-types) with different thickness as well as V-type crystallites (Matveev et al., 2001; Yuryev et al., 2002). It was shown that an increase in the Hylon VII concentration in the starch mixtures resulted in a distinct peak’s asymmetry in the DSC profiles of analysed mixtures (Fig. 1). The melting temperature of starch depends on structural organization of the amylopectin clusters. Thickness of crystals, their polymorphous structure and free energy of surface of face side significantly affect the melting temperature of starch granules. Unlike the crystalline form of waxy maize starch, which consists of amylopectin (A-type crystals), the high amylose starches showed a complex crystalline structure. The crystalline lamellae of high amylose starches consist of B- and B*-type crystals with different thickness and thermostability (Yuryev et al., 2002). Thus, the broad DSC curves obtained for Hylon VII may be considered as the sum of three curves (peak) from melting B-, B*- and V-type crystals (Błaszczak, Fornal, Valverde, & Garrido, 2005b). Bershtein and Egorov (1994) found that thickness of the crystalline lamellae affects the melting temperature of semi-crystalline synthetic polymers. An increase in the thickness of crystals leads to an increase in their melting temperature. The smaller the differences between the melting and crystallisation temperatures the bigger (perfect) the crystals formed. The above mentioned relationship was confirmed by the study of Yuryev et al. (2002) on the melting temperatures of B-type crystallites obtained at different crystallisation temperatures.

Treatment of waxy maize starch with high pressure (650 MPa/9 min) resulted in significant changes in the crystalline structure of granules, which in turn resulted in their complete gelatinisation (Fig. 2, Table 1). On the contrary, the crystalline structure of modified Hylon VII remained practically unchanged, although some changes in its DSC

Table 1
The values of the melting enthalpies of native and high pressure-treated starches and degree of gelatinisation (GD)

Waxy maize:Hylon VII ratio	ΔH, (kJ mol^{-1})		GD (%)
	Native	High pressure-treated	
1:0	5.0	0.7	85.9
3:1	4.3	0.7	83.7
1:1	5.7	1.3	77.2
1:3	5.1	2.9	43.1
0:1	3.7	3.3	10.8

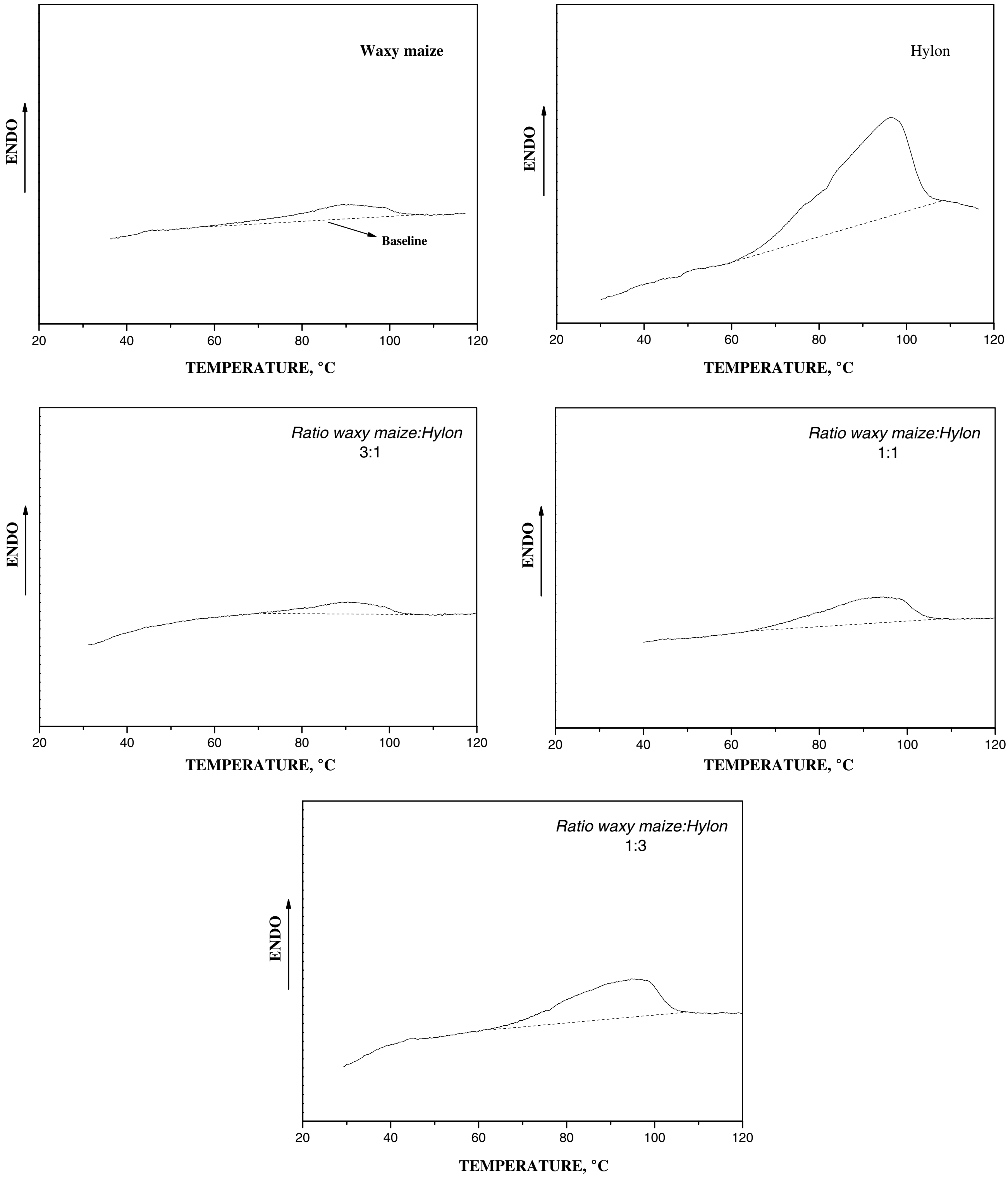


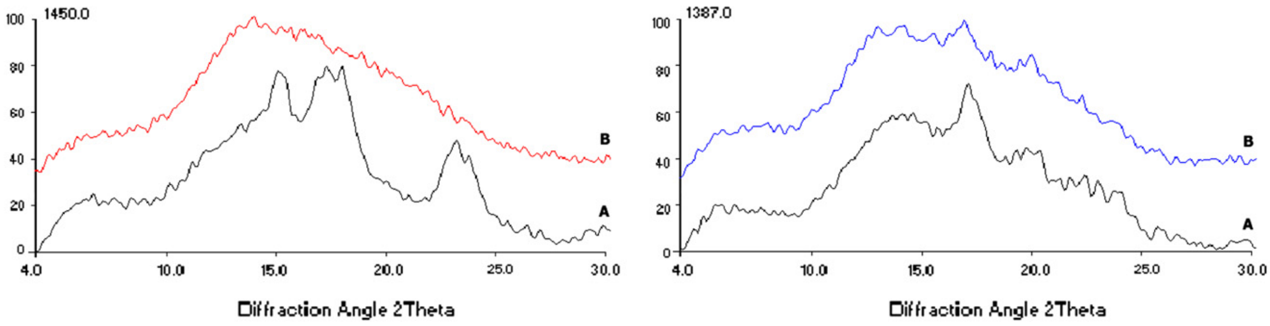
Fig. 2. DSC-thermographs of high pressure-treated (650 MPa/9 min) waxy maize starch, Hylon VII and their mixtures (3:1, 1:1, 1:3, w/w).

profile were observed. The profile of DSC-thermograms and values of melting temperatures obtained for "pressurised" starch mixtures, with 50% and 75% concentration of Hylon VII, revealed similar character with that of the treated Hylon VII (Fig. 2, Table 1). It is worth mentioning that no temperatures typical of melting of the waxy maize starch were observed in these thermograms. It can be assumed that, in contrast to waxy maize starch, the high pressure treatment of Hylon VII led to a slight disruption of its crystalline structure. The values characterising the gelatinisation degree (GD) of the waxy maize starch and Hylon VII (Table 1) treated with high pressure confirmed the above-presented suggestion. The data obtained showed that the high pressure treatment affected granules structure of waxy maize starch (GD = 85.9%) to a greater extent than those of Hylon VII (GD = 10.8%). It is worth emphasising that the GD values of other starch preparations were intermediate between those for waxy maize starch and Hylon VII, depending on their ratio in the mixture.

The results obtained from the X-ray analysis of ‘‘pressurised’’ starch preparations (Fig. 3) confirmed the above described DSC results.

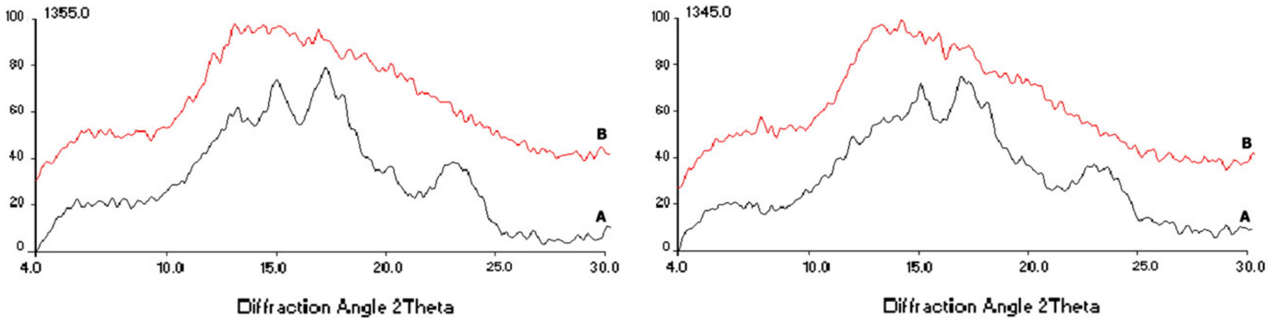
Taking into consideration the results of DSC and X-ray studies of waxy maize starch treated at 650 MPa for 9 min as well as suggestions of Rubens et al. (2000), it can be stated that the tangible changes in granule structure resulted from the hydration of amorphous phase and irreversible distortion of the crystalline structure in starch structure. This phenomenon was probably responsible for completely amorphous character of the high pressure-treated waxy maize starch (Fig. 3) (Błaszczak et al., 2005b). In contrast, the ‘‘pressurized’’ Hylon VII retained the granular character as well as the type of crystallinity (B- and V-type polymorph), however some decrease in the intensity of crystalline reflexes was reported by Błaszczak et al. (2005b). Consequently, the concentration of the waxy maize starch in the ‘‘pressurized’’ starch mixtures, already at 50%, affected its higher susceptibility to pressure, which in turn resulted in a distinct disruption of the crystalline structure of the polymorph (Fig. 3).

The swelling characteristics of the modified starch preparations (Fig. 4) indicated that in the presence of water, all the preparations formed a gel-like structure with a limited swelling index. Whereas, modified Hylon VII was only able to form starch–water dispersion. The limited swelling of such systems may be ascribed to the presence of the gel-like



Waxy maize

Hylon VII



Waxy maize : Hylon VII (3:1)

Waxy maize : Hylon VII (1:1)

Waxy maize : Hylon VII (1:3)

Fig. 3. X-ray diffraction patterns of native (A) and high pressure-treated (B) (650 MPa/9 min) waxy maize starch, Hylon VII and their mixtures (3:1, 1:1, 1:3, w/w).

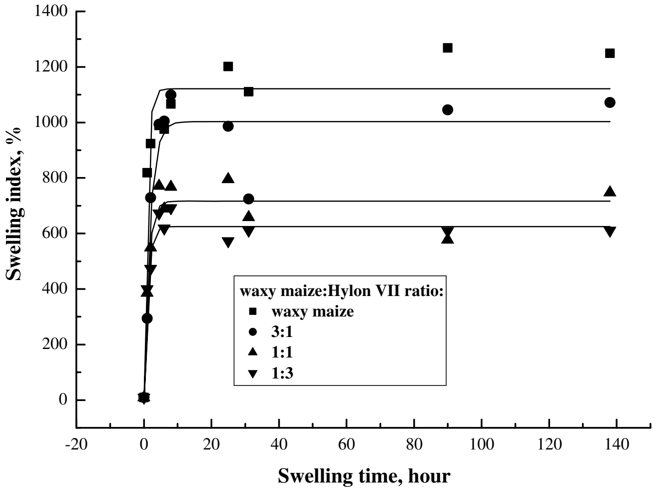


Fig. 4. Swelling curves of high pressure-treated (650 MPa/9 min) waxy maize starch and starch mixtures (waxy maize:Hylon VII, 3:1, 1:1, 1:3, w/w).

network that was formed already during high pressure treatment. It follows that the high pressure treatment of native amylopectin starch as well as its mixtures is accompanied by the formation of a three-dimensional gel network. For the investigated starch systems the maximal values of SWI (SWI_{max}) (Fig. 5) appeared to depend on the ratio of waxy maize/Hylon VII in the initial mixtures. An increase in Hylon VII concentration in the mixture led to a decrease in SWI_{max} values. A mathematical analysis of the data indicates that the changes observed in the SWI_{max} values could be described by a linear regression (Fig. 5) with a sufficiently high correlation coefficient ($R = 0.98$). Taking into consideration that: (i) properties of gels depend on their structure (Clark, Gidley, Richardson, & Ross-Murphy, 1989), (ii) treatment of Hylon VII with high pressure resulted in slight disruption of granules (Błaszczak et al., 2005b), (iii) the granules of Hylon VII after the treatment were dispersed in water but not swollen, and (iv) the high pressure-treated Hylon VII demonstrated a low gelatinisation degree (Table 1), it can be stated that waxy maize starch forms a three-dimensional gel network, whereas Hylon VII serves as a filler (Fig. 6). The presence of Hylon VII in modified starch mixtures led to a decrease in SWI_{max} values in the gels analysed (Fig. 5).

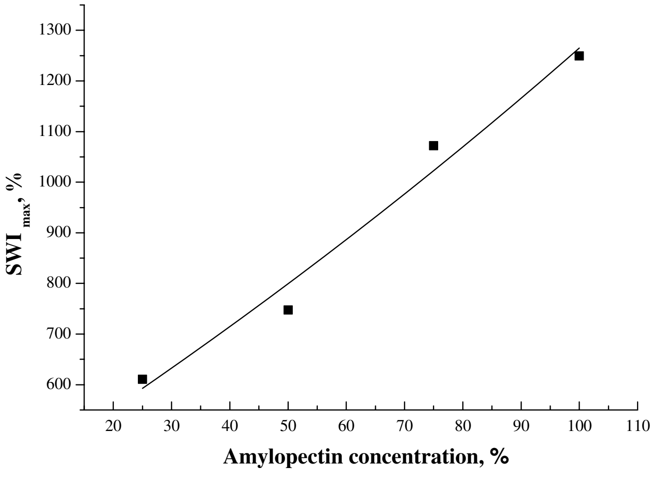
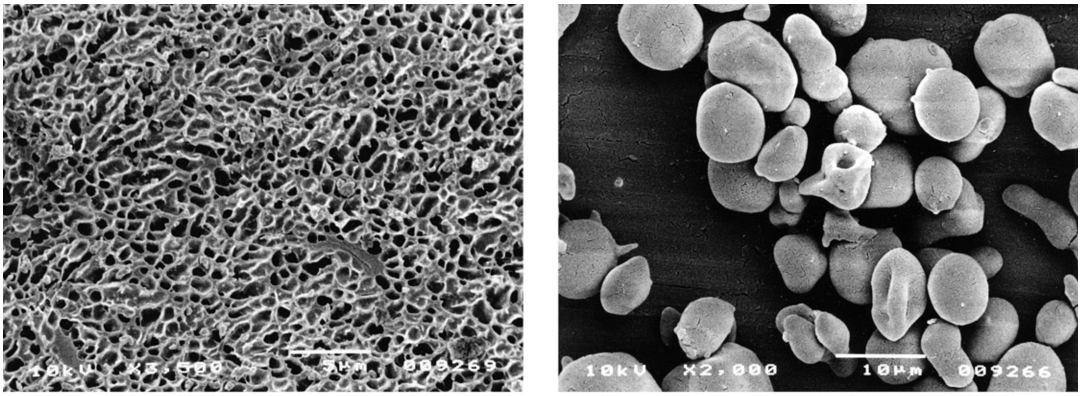


Fig. 5. Changes of the SWI_{max} versus amylopectin concentration in starch mixtures treated with high pressure (650 MPa/9 min).

The microscopic observations of starches treated with high pressure seem to confirm the above-presented suggestion. As it was shown in Fig. 6, the "pure" waxy maize starch treated with high pressure (650 MPa/9 min) formed continuous and homogenous microstructure of a gel-like network. In the case of gels obtained from pressurised starch mixtures (waxy maize:Hylon VII, 1:1, 3:1), their microstructure was formed by an amylopectin network filled with the granules of Hylon VII that appeared almost intact. The microstructure of gel obtained from the pressurised mixture with 75% of Hylon VII addition differed from the microstructure of the above described ones. In that case, the slightly swollen granules formed a network with solubilized amylopectin outside the granules. Taking into account the fact that after the high pressure treatment the majority of Hylon VII granules retained their granular shape (Fig. 6) and crystalline structure (Figs. 2 and 3; Table 1), it may be assumed that the Hylon VII granules may be considered as a filler with ordered structure. The SEM studies of "pressurized" potato starch, conducted by Błaszczak et al. (2005a), showed that the outer part of starch granules remained unchanged, however the inner structure of granules was filled with a gel-like structure.

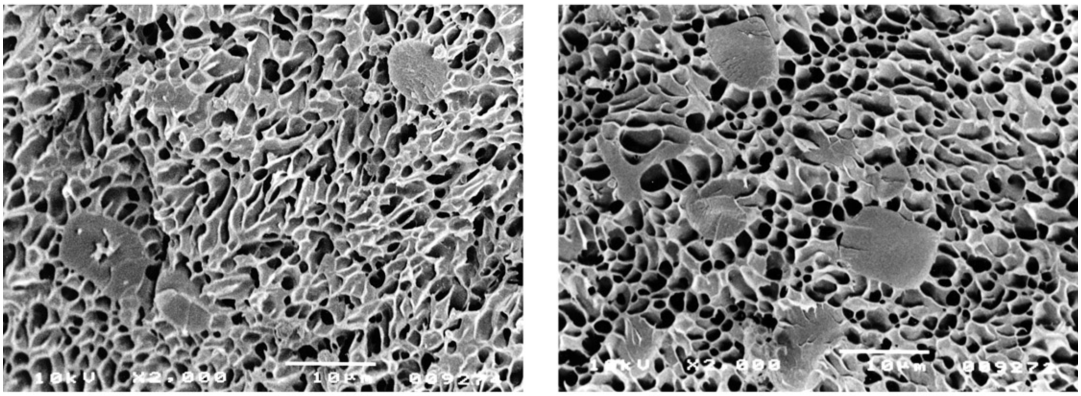
It is generally believed that microscopy analysis confirms or is confirmed by other analytical methods. The effect of a such combination may provide complete and valuable information about structure - functional properties relationship of the material analysed. Since it is assumed that microscopy is the sum of artefacts, that may appear during sample preparation, the below-presented thesis was also based on the results obtained from DSC and X-ray studies. The differences observed in the microstructure of starch preparations, changed proportionally to the share of Hylon VII/waxy maize starch in the mixtures, and were evoked rather by the pressurisation than the method of sample preparation. It is worth stressing that the idea was not to analyse the polymer network formation (i.e., size of pores or thickness of pore walls) but to visualize that the high pressure treatment of amylopectin starches resulted in complete granule disruption and that these changes were triggered by significant physico–chemical changes in granule structure (melting of crystalline lamella, irreversible hydration of the amorphous region) (Błaszczak et al., 2005b) than by freezing.

The ability of gel network formation by amylopectin macromolecules was found to be unexpected since it conflicts with generally accepted conception about the mechanism of starch gelation. It was suggested that the chemical structure (polymerisation degree ⩾110) and physico–chemical properties of amylose enable its macromolecules to form a gel network on cooling, whereas amylopectin



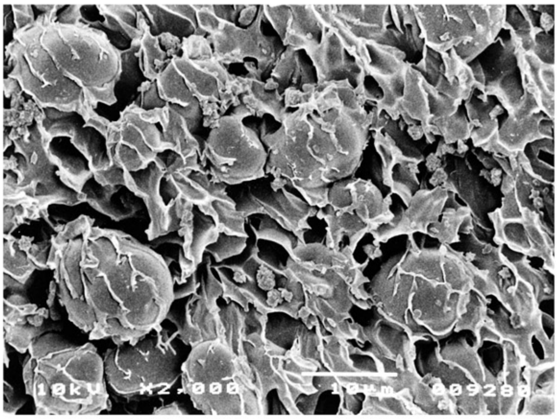
Waxy maize

Hylon VII



Waxy maize : Hylon VII (3:1)

Waxy maize : Hylon VII (1:1)



Waxy maize : Hylon VII (1:3)

Fig. 6. SEM micrograph of high pressure-treated (650 MPa/9 min.) waxy maize starch, Hylon VII and their mixtures (3:1, 1:1, 1:3, w/w).

as granule remnants and/or ghost structure forms dispersion medium in a gel system (Clark et al., 1989; German, Blumenfeld, Guenin, Yuryev, & Tolstoguzov, 1992; Gidley & Bulpin, 1989; Hoover, 1995; Kalichevsky & Ring, 1987; Morris, 1990). Nevertheless, studies on mixed amylose–amylopectin model systems indicated that under some conditions amylopectin may form the continuos phase (a relative ratio of amylose <22%) (Doublier & Llamas, 1993; Leloup, Colona, & Buleon, 1991). Hermansson and Svegmark (1996) observed under light microscopy the microstructure of a macromolecular solution of potato starch paste (8%) and potato amylopectin (12%). These authors found that microstructure of such pastes was formed by completely gelatinized and continuous phase of amylopectin, and amylose that was dispersed as a droplets. From the data, presented by these authors, indicate that such a structure may be formed under following conditions: cooking to temperatures higher than that of gelatinisation (90–95 °C), autoclaving, jet cooking (120 °C) and/or heavily shearing until no remnants of swollen granules remained.

A similar gel-like structure was observed under SEM (Fig. 6) after the high pressure treatment of 30%waxy maize starch dispersion (650 MPa/9 min). It is worthy stressing that such a structure was obtained at room temperature without using shear forces.

Taking into consideration the above-presented results and suggestions that: (i) the ability of macromolecules to form gel depends, particularly, on their degree of polymerisation (DP) (Gidley and Bulpin, 1989; Clark et al., 1989; Gidley, 1989), (ii) DP of amylopectin maize macromolecules is about 2×10^6 (Swinkels, 1985), and (iii) treatment of waxy maize starch with high pressure significantly affects the physical and chemical structure of amylopectin (Błaszczak et al., 2005b), it can be supposed that under high pressure conditions (650 MPa/9 min) at room temperature amylopectin macromolecules are capable of forming the three-dimensional gel network. Our results confirmed a very high potential of new technologies for obtaining starches with specific physico–chemical properties that are necessary in the processing of desired food products.

The measurements of spin–spin relaxation time of water molecules in starch preparations (650 MPa/9 min) after rehydration demonstrated two distinct regions of T_2 values; one with T_2 between 138 and 720 ms, and the other with values between 31 and 120 ms (Table 2). The relaxation data obtained indicate that T_2 values significantly depended on waxy maize concentration in the starch blends. The peak maxima of the 138–720 ms region were denoted by T_{2a}, whereas the peak at a shorter relaxation time was assigned to T_{2b}. The rehydrated gel of waxy maize starch preparation (650 MPa/9 min) demonstrated the highest T_2 values. The relaxation times of other rehydrated gels significantly decreased along with an increase in Hylon VII concentration (Fig. 7). According to the literature data, the two T_2 values imply that there are two types of water molecules, differing in their mobility (Choi & Kerr, 2003; German et al., 1988; German et al., 1992; Wang, Choi, & Kerr, 2004). These authors suggest that an enhancement of the spin–spin relaxation is connected with hindering rotation of the water molecules and due to that the proton spins can exchange energy. According to this, the peak obtained at a longer relaxation time (T_{2a}) may be associated with more mobile water, whereas the one obtained at a shorter time (T_{2b}) was assigned to less mobile water. Choi and Kerr (2003) analysing water mobility in the native and chemically modified wheat starch gels, using ^{1}H-NMR, suggested that the longer T_2 region could be related to the continuous amylose-rich gel and the intergranular amylopectin-rich gel, whereas the shorter one was connected with granule remnants. It was also demonstrated that the water mobility of the maltodextrin gels (containing no granules) was characterized by two relaxation times (German, Blumenfeld, Yuriev, & Tolstoguzov, 1989; German et al., 1992). According to Lilford, Clark, and Jones (1980), the complex relaxation of water molecules in biopolymer gels is due to an inhomogeneous distribution of water. That kind of distribution probably resulted from the formation of different structural elements in the pressurised and then in the rehydrated starch gels. The relaxation data obtained for pressurised and rehydrated starch preparations seemed to be in close relation to those presented-above. The relaxation data and the values of SWI (swelling index determination) (Fig. 5) point to a significant influence of amylopectin concentration (waxy maze starch) on the osmotic properties of the pressurised starches. The results presented indicate that amylopectin affected both the populations of water existing in the pressurised starch system. However, it should be emphasized that far less is known about the nature of such a phenomenon, hence it needs further, detailed investigation.

Table 2
T_2 values measured (^{1}H-NMR) for pressurized (650 MPa/9 min) and rehydrated starch gels

Waxy maize:Hylon VII ratio	T_{2a}, ms	T_{2b}, ms
1:0	720	120
3:1	451	115
1:1	314	63
1:3	138	31

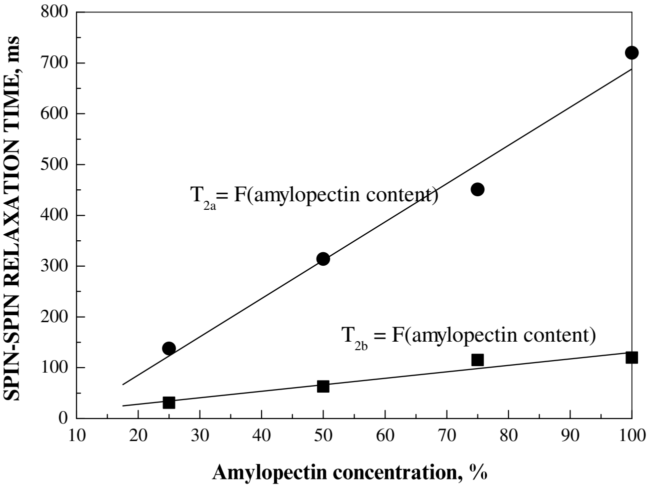


Fig. 7. Spin–spin relaxation time of water molecules in starch preparations (650 MPa/9 min) after rehydration versus amylopectin concentration.

4. Conclusions

The high pressure treatment of waxy maize starch resulted in its complete gelatinisation and the formation of a gel-like network. An increase in the concentration of Hylon VII in starch mixtures subjected to high pressure led to a decrease in the gelatinization degree of the starch preparations obtained. The lowest value of the gelatinization degree was found for Hylon VII. As a result of high pressure effect, the formation of the three-dimensional gel network was observed for all investigated systems, except for Hylon VII that formed dispersion with water. The gels may be considered as multicomponent gel mixtures where amylopectin forms continuous phase of gel, while Hylon VII plays the role of a filler with ordered structures. An increase in Hylon VII concentration in the starch mixtures (waxy maize starch:Hylon VII) resulted in a decrease in the swelling index and a decrease in the mobility of "free" and "bound" water molecules in the gels.

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