

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Extrusion-Cooking of Starch

L. Moscicki, M. Mitrus, A. Wojtowicz,
T. Oniszczyk and A. Rejak

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/52323>

1. Introduction

The extrusion technology, well-known in the plastic industry, has recently become widely used in food industry, where it is referred to as extrusion-cooking. It has been employed for the production of so called engineered food and special feed.

Generally speaking, extrusion-cooking of vegetable raw materials consists in the extrusion of grinded material at baro-thermal conditions. With the help of shear energy, exerted by the rotating screw, and additional heating by the barrel, the food material is heated to its melting point, than is conveyed under high pressure through a series of dies and the product expands to its final shape. That results in much different physical and chemical properties of the extrudates in comparison to raw materials used.

Food extruders – processing machines (see fig. 1), belong to the family of HTST (High Temperature Short Time) equipment, with a capability to perform cooking tasks under high pressure. This aspect may be explained for vulnerable food and feed as an advantageous process since small time span exposures to high temperatures will restrict unwanted denaturation effects on e.g. proteins, amino acids, vitamins, starches and enzymes. Physical technological aspects like heat transfer, mass transfer, momentum transfer, residence time and residence time distribution have a strong impact on the food and feed properties during extrusion-cooking and can drastically influence the final product quality (Mościcki et al., 2009, Moscicki, 2011, Mościcki, 2011).

Nowadays, extrusion-cooking as a method is used for the production of different food staff, ranging from the simplest expanded snacks to the highly-processed meat analogues. The most popular extrusion-cooked products are following:

- direct extrusion snacks, RTE (ready-to-eat) cereal flakes and diverse breakfast foods produced from cereal material and differing in shape, colour and taste and easiest to implement in terms of production;
- snack pellets - half products suitable for fried or hot air expanded snacks, pre-cooked pasta;
- baby food, pre-cooked flours, instant concentrates, functional components;
- pet food, aquafeed, feed concentrates and calf-milk replacers;
- textured vegetable protein (mainly from soybeans, though not always) used in the production of meat analogues;
- crispy bread, bread crumbs, emulsions and pastes;
- baro-thermally processed vegetable components for the pharmaceutical, chemical, paper and brewing industry;
- confectionery: different kinds of sweets, chewing gum, and many others.

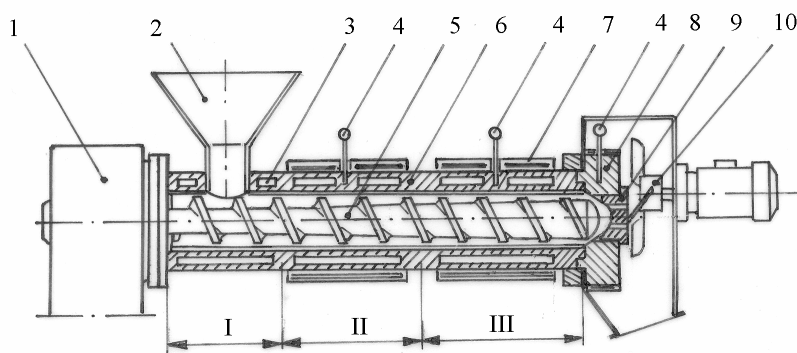


Figure 1. A cross-section of a single-screw extrusion-cooker: 1 - engine, 2 - feeder, 3 - cooling jacket, 4 - thermocouple, 5 – screw, 6 - barrel, 7 - heating jacket, 8 - head, 9 - net, 10 -cutter, I - transport section, II – compression section, III – melting and plasticization section (Mościcki et al., 2009).



Figure 2. Different type of extrusion-cooked food and feed products (Mościcki et al., 2009).

2. Starch and starchy products

Extrusion-cooking is accompanied by the process of starch gelatinization, involving the cleavage of intermolecular hydrogen bonds. It causes a significant increase in water absorption, including the breakage of starch granules. Gelatinized starch increases the dough viscosity, and high protein content in the processed material facilitates higher flexibility and dough aeration. After leaving the die hot material rapidly expands as a result of immediate vaporisation and takes on a porous structure. In the extruded dough protein membranes closing occur creating cell-like spaces, and starch, owing to dehydration, loses its plasticity and fixes the porous nature of the material. Rapid cooling causes the stiffening of the mass, which is typical for carbohydrate complexes embedded in a protein matrix and their total enclosure by the membrane of hydrated protein. The resulting product is structurally similar to a honeycomb shaped by the clusters of molten protein fibres.

Starch occurs primarily in cereal grains and potatoes. It takes the form of granules of different and characteristic shape, depending on the origin as well as on the variety and type of fertilization. As commonly known, two main components of starch are amylose and amylopectin displaying different physical and chemical properties, for example, chemical structure. The technological assessment of extrudates takes two factors into account: the water solubility index (WSI) and the water absorption index (WAI). These properties were studied in many laboratories and the conclusions were that WAI of many starch products increases together with the temperature rising in the extruder's barrel. It has been assumed that the maximum value is obtained around the temperature ranges from 180 to 200 °C. When these temperatures are exceeded, WAI drops and causes the WSI increase. The lower material initial moisture content used in extrusion, the higher extrudate's WSI rate can be obtained. A noticeable influence on the product properties has the percentage of amylose and amylopectin and its ratio in the processed material.

The extrusion processing of starchy materials certainly impacts the changes in product viscosity (pasting characteristic) after dissolving in water. This feature is very important for the technological point of view. Using Brabender viscometer we can see that the characteristic viscosity curve for starch is clearly reduced through extrusion; at the same time, the decrease of viscosity is greater if higher temperatures were applied during the extrusion-cooking. The application of higher pressure during the extrusion (compression changing) does not affect the extrudate viscosity; however, it affects on viscosity stability of products retained at a temperature of 95 °C. In some cases, the properties of extrudate may be arranged by amylose bounding with fatty acids or monoglycerides.

Another factor determining changes in the starch molecules during the extrusion-cooking process is the pressure and the values of existing shearing forces. In order to obtain certain technological properties of extrudates, which are often semi-finished products intended for further processing, it is necessary to set proper parameters of the extrusion process. This is achieved by the use of screws with varying compression degrees, relevant rpm of the working screw, appropriate die size, SME input, etc.

3. Starch transformation by thermo-mechanical treatment

Starch can be modifying by enzymatic, chemical or physical methods depend on processing and application fields of final products. Different types of processing, based on disruption and melting the semi-crystalline structure of starch may be used to transformation of native starch to form a thermoplastic starch (TPS) starch. Thermo-mechanical treatment that combines temperature and shear stress, like extrusion or injection moulding, is useful to transform granular starch into TPS. TPS modify by these methods may be applied as basic raw material or partial replacement of plastics for packaging materials applications in selected areas of food industry, horticulture, agriculture, but also for biomedical and cosmetic industries as gels, foams, films or in the form of a membrane with defined properties or biodegradability (Yimlaz, 2003).

Starch modification with thermomechanical treatment is difficult because of important increase of starch viscosity during heating and shearing, what may be the reason of uncontrolled dextrin's formation and browning reaction, especially when temperature above 100 °C is used. Some kind of plasticizers may improve intensity of starch transformations, i.e. water is most commonly used and the minimum moisture content required for starch gelatinization is around 33%. There are many studies about the different transformations of starchy material to thermoplastic forms with intermediate and high water level. High water content in the mixture also influences the onset temperature, glass transition temperature and rheological properties of molten materials (Della Valle et al., 1995, Igura et al, 2001, Nashed et al., 2003, van Soest et al., 1996a). In many scientific publications also other plasticizers were examined i.e. monoglycerides or glycerol, as flexibility improvers (Schogren, 1993). Addition of glycerol is of influenced on the onset of gelatinization and results in an increase in the activation energy for the melting of the starch crystallites and results in higher glass transition temperatures and higher interactions forces between glycerol and starch polymers (Della Valle et al., 1995, van Soest & Knooren, 1997, van Soest et al., 1996b, You et al., 2003). During the extrusion process high shear stresses and high values of energy input take place and under these conditions the melting process may be enhanced (Della Valle et al., 1995). Specific mechanical energy (SME) values necessary to transformations decrease with increasing water level in raw material. Corn or waxy corn and wheat or barley starch were most often investigated as basic thermoplastic raw materials (Nashed et al., 2003, Barron et al., 2000).

Modifications in the presence of plasticizers can be done by thermomechanical processing techniques like heating, kneading, injection, compression or vacuum moulding or extrusion below 150 °C (Yimlaz, 2003). Depending on the starch origin some specific differences are observed. Wheat, corn or potato starches behave different for different plasticisers or lubricants content and different processing conditions.

Test results achieved with different types of rheometers used to simulate the thermomechanical conditions differ and depend on the equipment used. The influence of the intensity of the treatment can be tested with a batch mixer, a cone and plate rheometer, a Shear Cell device with well defined shear rate, a Couette-type device with variable eccentricity or a

compression moulding device. All these devices can simulate to a certain extent different temperature and treating time processes i.e. mixing-kneading, extrusion-cooking or injection moulding (Yimlaz, 2003, Peighambardoust et al., 2004, Peighambardoust et al., 2007, van den Einde et al., 2004, van den Veen, 2005). The shear rate, temperature profile, residence time during treatment influence simultaneously the starch behaviour and properties. Also in these research results the changes in properties in excess of water were observed. Most studies on the influence of water on the properties were carried out at high water content, but it is well known that extrusion-cooking or injection moulding processes are done with a limited (10-30%) water content. Properties of products can be measured by WAXS or intrinsic viscosity (Barron et al., 2000). Product behaviour and properties after extrusion with a high level of water content are not always acceptable because of crystallinity, retrogradation and stress-strain profiles of the materials expressed by the tensile strength or elongation (van Soest & Knooren, 1997). Depending on the amount of glycerol in TPS the product may be in its glassy or rubbery state at ambient temperature (Yimlaz, 2003). In the presence of sufficient water or glycerol under gelatinization conditions native starch becomes gel-like in appearance or properties but during the thermoplastic processing behaves like a polymer melt. The tests with different starch origins can be found in literature (Yimlaz, 2003, Peighambardoust et al., 2004, van den Einde et al., 2004).

Tests of starch melting usually are performed in a two-bladed counter rotating batch mixer Brabender Mixograph simulating mixing-kneading conditions interfaced with a computer and control unit. Wójtowicz (2009) tested various starches with water and glycerol according to following procedure: mixer temperature was set to 85 °C and heating was started directly after chamber closing and rotation of screws was increased from 5 to 100 rpm during 3 minutes. Comparison of starches origins were performed at the same temperature-time but screw rotation increased from 5 to 80 rpm. Samples were treated during 10 minutes in total. During mixing the torque was recorded continuously.

In the study presented by Wójtowicz & van der Goot (2005) investigations results on similar starch-glycerol mixtures with limited water addition (below 30%) subjected on the heating and shearing behaviour are presented. The purpose of the treatment was to use special designed shearing device - Shear Cell for obtains a starchy molten phase under thermo-mechanical processing similar to extrusion. This new equipment is based on the cone and plate rheometer ideology on a pilot scale (Figure 3). There is possibility to isolate singular parameters during processing like temperature, rotation speed or shear stress in this equipment (van den Einde et al., 2003). The details of this shearing device can be found elsewhere (Peighambardoust et al., 2004, van den Einde et al., 2004, van den Veen et al., 2004). The based material was potato starch with addition of glycerol 20-25% and with 5-20% amount of added water (w/w). Treatment temperature was selected on 85 °C for samples with 15 and 20% of water added, 88 °C for samples with 5 and 10% of water added and 115 °C for starch - glycerol mixtures. The rotation speed was 10 rpm during first 2 minutes and increased simultaneously to 100 rpm during 3 minutes. The torque changes during the treatment were recorded.

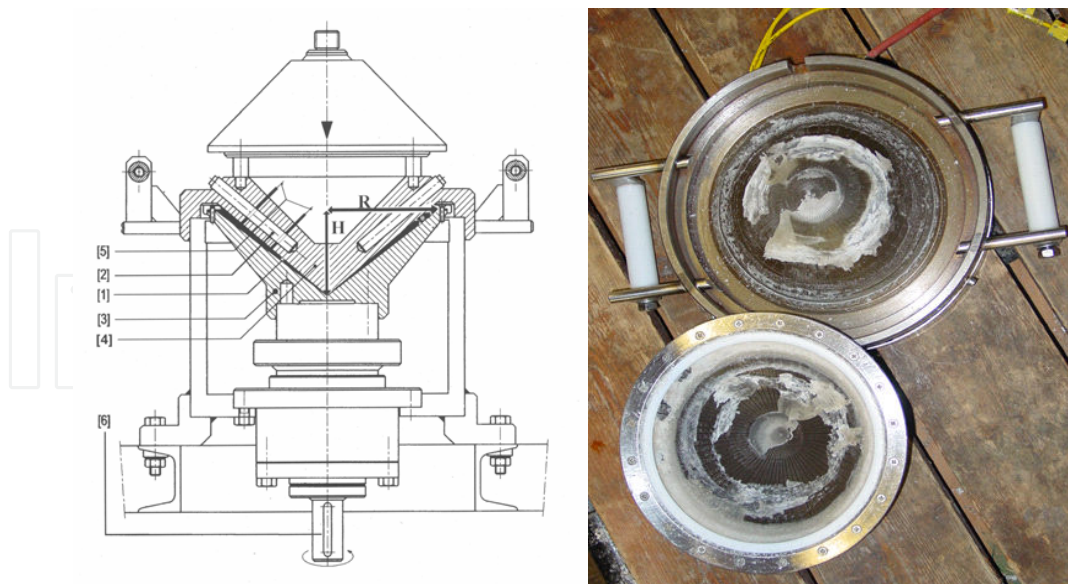


Figure 3. Shear Cell equipment scheme and after starch processing: 1- shearing zone, 2 – heating elements, 3 – rotating plate, 4 – non-rotating cone, 5 – thermocouple, 6 – torque measurement point. Cone angle = 100° , shear zone angle = $2,5^\circ$, $r = 0,1$ m, $h = 0,082$ m (Wójtowicz & van der Goot, 2005)

Research results showed that the addition of water in amount from 5 to 20% influenced on almost every recorded parameter during treatment in Brabender Mixograph. During treatment starch-glycerol-water mixtures it was observed decreasing start melting temperature from 80°C for mixtures with limited water addition (5%) to $65\text{--}70^\circ\text{C}$ for samples with 20% of added water. Also the time needed to start melting of samples decreased with increasing of water addition. It seems to be that water becomes a plasticizer for starch and this is in accordance with previous reports (van Soest et al., 1996a). Also the effect of water addition on torque values and decrease of torque with increasing water content in mixtures was observed.

It was also found that potato starch required lower melting temperature than wheat and corn starch with glycerol and water addition but simultaneously higher maximum torque values were reported during the melting tests. The lowest torque values were reached for corn starch samples independent on water addition. The temperature range needed to melting beginning was $80\text{--}95^\circ\text{C}$ for corn starch-glycerol mixtures, $78\text{--}91^\circ\text{C}$ for wheat starch-glycerol mixtures and $78\text{--}88^\circ\text{C}$ for potato starch-glycerol mixtures mixed under 80 rpm used, depend on water content in the treated sample. Higher water level influences on lower temperature reached and lower max torque values during tests (Fig. 4).

During the tests the effect of water addition on torque values and decrease of torque with increasing water content in mixtures was observed. Torque values reported for mixing-kneading were quite low comparing the extrusion process and Shear Cell treatment. On the Figure 5 and 6 there are shown potato starch-glycerol (80-20) mixtures behaviours during treatment with different water addition in similar condition (85°C heating temperature and 100 rpm) in Brabender Mixograph and Shear Cell, respectively. Unfortunately mixtures with

low amount 5% of water added showed the highest values of torque and increasing the water content influence on lower torque in both types of treatment.

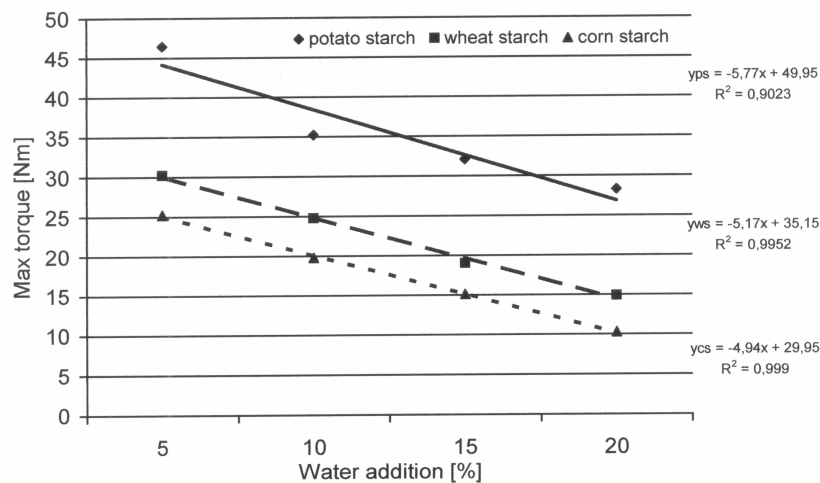


Figure 4. Torque values during mixing-kneading of various starch origins with 20% of glycerol addition and different level of water added (Wójtowicz, 2009)

Differences between curves in Fig. 5 and 6 may be important for definition of shearing influence on samples behaviour and properties. Also time of the beginning of rheological changes is similar except sample with 5% of added water. During intensive thermomechanical treatment in the Shear Cell shorter time required to starting changes inside the structure is observed. It may be explained much higher shear stress during shearing-heating in Shear Cell (Wójtowicz, 2009). It was not possible to start the melting process in potato starch-glycerol mixture without water addition because of to low temperature of heating in Brabender device equipped with water heating system and maximum temperature which can be achieved is 98 °C during heating. After tests in Shear Cell it is known now that start-melting temperature for these recipes is about 115 °C (Wójtowicz & van der Goot, 2005).

It is also important that increasing of total amount of plasticizers (water and glycerol) influenced on lower torque values during measurements, as showed on the Figure 7 and 8. Increased glycerol addition also has a strong effect on torque results. Nashed et al. (2003) reported through DSC that glycerol behaves as an anti-plasticizer because of hindering the gelatinization process and linear increase of onset temperature with increasing glycerol content was observed during treatment of wheat starch-water-glycerol mixtures. During thermo-mechanical treatment of starch-glycerol mixtures it was clear that higher glycerol addition influenced on decreasing melting or gelatinization time and temperature and also torque during treatment decreased (Wójtowicz & van der Goot, 2005).

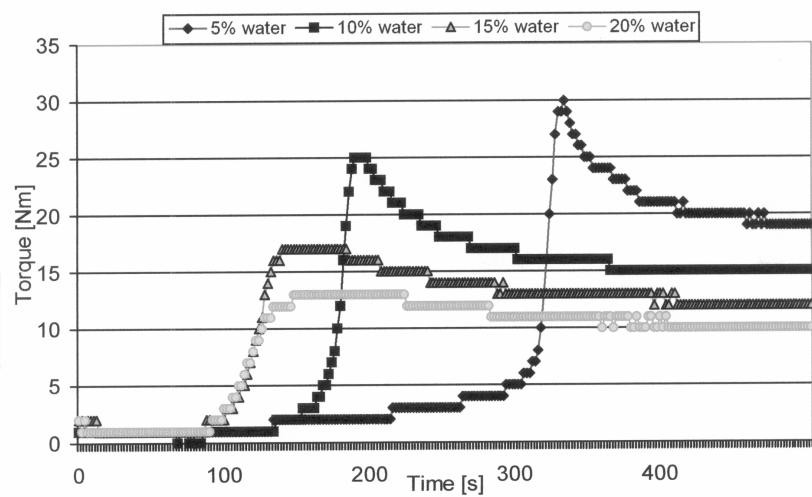


Figure 5. Torque values during treatment in the Brabender Mixograph of potato starch-glycerol (80-20) mixtures with different water addition (Wójtowicz, 2009)

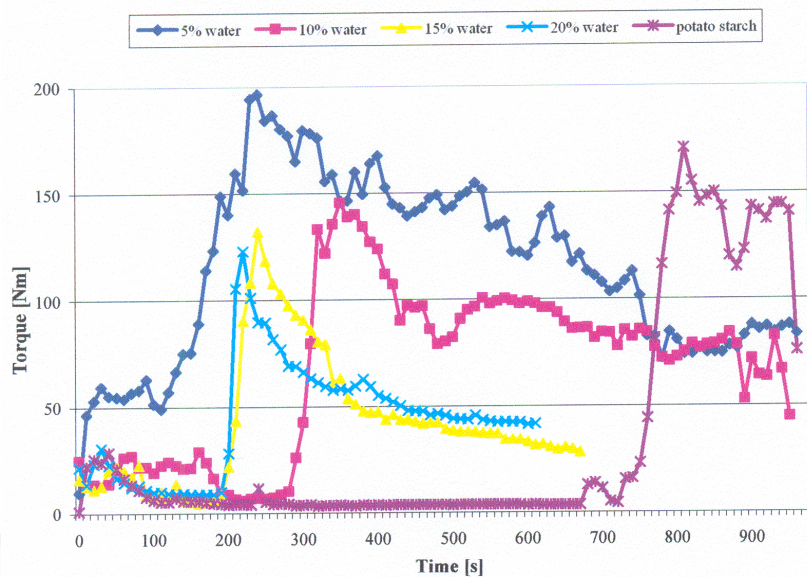


Figure 6. Torque values during treatment in the Shear Cell of potato starch-glycerol (80-20) mixtures with different water addition (Wójtowicz & van der Goot, 2005)

Wójtowicz and van der Goot (2005) noted that there were also visible differences in transparency and flexibility of achieved samples after different treatment type (Fig. 9). After mixing-kneading in Brabender equipment samples became elastic, with foam consistency and non-transparent, milky white colour. Only for samples of potato starch with small amount of water added material became a little brittle and partially transparent with 5% added water and completely transparent, glassy look like with higher level of water added. But these last samples were much stickier after treatment then the others. When they were warm be-

has flexible and easy undergo elongation and formation different shapes. After cooling at room temperature material became hard to formulation, and no more flexible. All the samples with addition of glycerol and heated-sheared in the Shear Cell had visibly transparent glassy-like appearance and smooth surface, directly after processing in worm stage they were easily to elongation, showed rubbery properties and they were longer elastic after cooling to room temperature (Wójtowicz & van der Goot, 2005). This phenomenon may be the result of pressure differences between both types of equipment during processing, in Shear Cell the pressure was much higher than in mixer and air bubbles or steam formed in transformed material disappeared pushed out through silicone seal by pressure inside the apparatus. Mixing-kneading equipment had lower pressure in testing chamber and it was not possible venting processed material, it may be the reasons of foamy structure of modify starch.

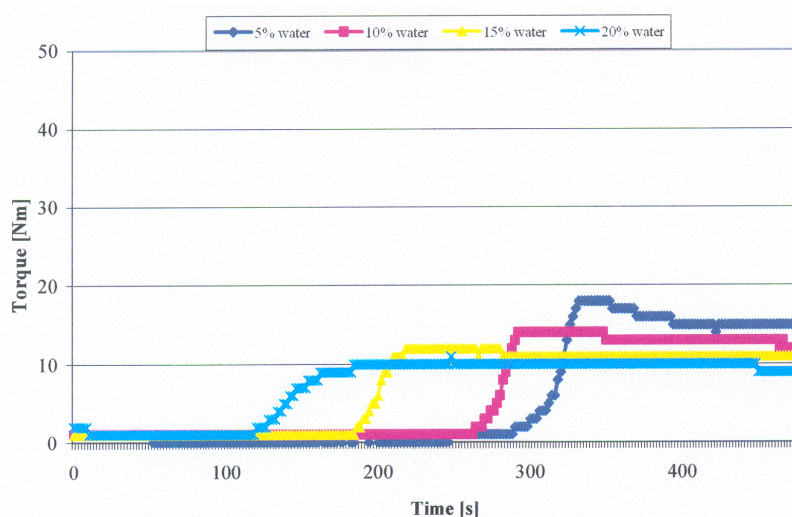


Figure 7. Torque values during treatment in the Brabender Mixograph of potato starch-glycerol (75-25) mixtures with different water addition

The intrinsic viscosity of starch (η) is very sensitive for thermomechanical treatment and the degradation of molecular weight compounds in starch, therefore it can be used as a method to molecular weight measurement. The authors (Wójtowicz & van der Goot, 2005) report an intrinsic viscosity of native starch and sheared-heated samples measured according the Ubbelohde viscometer method (Cunningham, 1996) at 25 °C.

Intrinsic viscosity of native potato starch was 369,8 ml/g. Intrinsic viscosity of samples treated in Brabender Mixograph varied from 174 ml/g for starch-glycerol (80:20) mixtures with 5% water added to 202 ml/g for starch-glycerol (75:25) with 20% water added. These values compare to native starch were much lower and it may suggest breakdown of starch granules during Brabender treatment. But differences between samples were smaller than observed after shearing-heating process in Shear Cell. Results for samples processed in Shear Cell also were lower than for native starch and values variation was between 108 for samples of starch-glycerol (80:20) mixtures with 10% water added and 215 ml/g for starch-glycerol

(75:25) without water added (Wójtowicz & van der Goot, 2005). It means that during shear-heating treatment in Shear Cell high macromolecular degradation takes place. Intrinsic viscosity values were slightly dependent on glycerol content in mixtures and with increasing glycerol content decrease of intrinsic viscosity were observed in potato starch-glycerol-water mixtures treated in the Shear Cell under similar conditions.

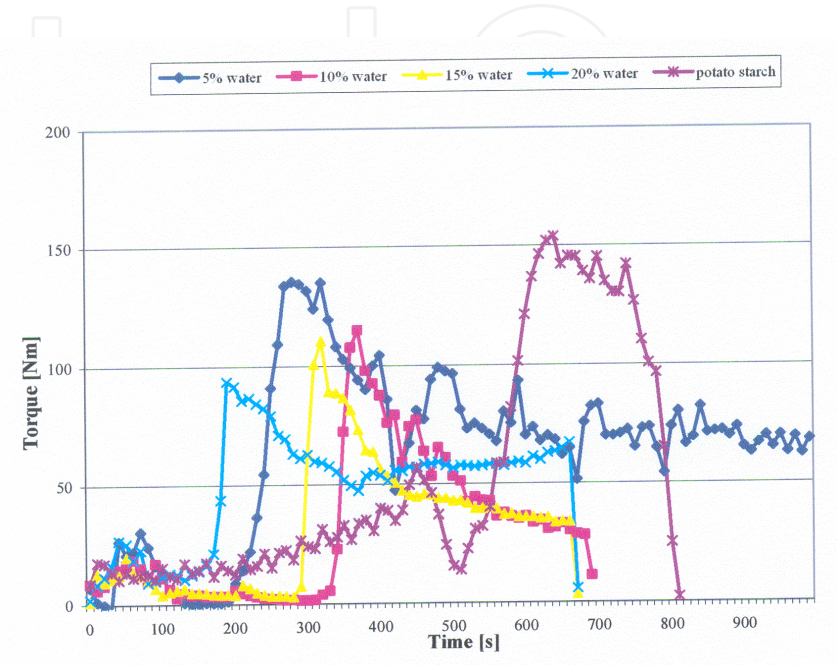


Figure 8. Torque values during treatment in the Shear Cell of potato starch-glycerol (75-25) mixtures with different water addition



Figure 9. Overview of samples after treatment in: a) BrabenderMixograph, b) Shear Cell

These results are in accordance with Fujio et al. (1995) for potato, corn and wheat starches, van den Einde et al. (2003) for cornstarch and also Rushing & Hester (2003) for polymers. Intrinsic viscosity is very sensitive especially on thermomechanical degradation. Low values of shear stress influenced on lower intrinsic viscosity of treated starch-glycerol mixtures. But in all cases variations between intrinsic viscosity's values are quite small and it can be concluded that almost the same degree of starch molecules degradation was noted. In comparing with native starch intrinsic viscosity values reduced over 50%, so residue starch molecules was broken by thermomechanical treatment. By comparing those data with data generated by van den Einde et al. (2003), it can be concluded that potato starch was less thermostable than corn starch.

4. Starch modification by extrusion-cooking

Native starch is not always suitable for practical use. Therefore, various starch modification techniques have been developed for food and non-food applications. Generally there are chemical methods. In many cases, especially in the food sector, chemically modified starch can be replaced by that extrusion-cooked. During the extrusion-cooking physical and chemical transformation of starch takes place and no chemicals are needed. Baro-thermal treatment causes gelatinisation of starch, accompanied by rupture of intermolecular bonds, resulting in rupture of starch grains and significantly increase of water absorption.

The degree of changes in starch depends on properly selected process parameters and the residence time of raw material in the extruder. That allows us to create the expected properties of the obtained modified starches, including the degree of gelatinization and viscosity of the gels. These products may find wide application in food industry as food additives, very often by replacing chemically modified starchy products. Extrusion-cooked starch may find its use as a component of food products in the manufacture of instant products, different kinds of fillings in the confectionery industry, as a gelling agent, structure stabilizer and water- or fat-absorbent fillers. That may be very attractive from the consumer point of view. Application extrusion-cooking is a relatively cheap alternative in the production of modified starches.

4.1. Materials and methods

Potato starch Superior type was purchased from PEPEES Company (Lomza, Poland). Its moisture content was 17%. During the extrusion-cooking process the 4 levels of moisture content of raw material (17, 20, 25 and 30%) were used.

Extrusion-cooking of potato starch was carried out using a modified single screw extrusion-cooker TS-45 (Polish design) with $L / D = 16$, and the die with one opening with a diameter of 3 mm was used. During the study three temperature of extrusion process (100, 120 and 140 °C) and a variable screw's speed (1.00, 1.33, 1.66 and 2.00 s⁻¹) were used. The process energy consumption was measured with a wattmeter connected to the extruder and the specif-

ic mechanical energy (SME) input was calculated (Janssen et al, 2002, Mitrus, 2005a, Mitrus & Moscicki, 2009, Wolf, 2010).

Degree of starch gelatinization was measured by enzymatic method in accordance with Polish standard PN-A-79011-11:1998.

Cross-sectional expansion index was determined as the diameter of extrudates divided by the diameter of the matrix opening (Moscicki, 2011). Measurements were done in 10 repetitions.

Water absorption index was determined according to the method of Anderson et al. (1970) with own modification. The extrudates were crushed using a laboratory mill to particles with a diameter less than 0.3 mm. A 0.7 g ground sample was suspended in 7 ml of distilled water at 20 °C in a tared centrifuge tube, stirred intermittently over a 10 min period. The resulting suspension was centrifuged at speeds 250 s^{-1} for 10 minutes in T24D type centrifuge. The supernatant liquid was poured into a tared evaporating dish. The remaining gel was weighted and the WAI was calculated as $\text{WAI} = w_g/w_s(\%)$, where w_g is a weight of gel and w_s is the weight of dry sample. Measurements were performed in 6 replications.

Water solubility index was determined from the amount of dried solids recovered during evaporation of supernatant obtained from the WAI analysis according to the method of Harper (1981). Results were calculated from formula $\text{WSI} = w_{ds}/w_s(\%)$, where w_{ds} is the weight of dry solids of supernatant and w_s is the weight of dry sample. Measurements were performed in 6 replications.

The data reported was subjected to analysis of variance (ANOVA) by Duncan's test ($P < 0.05$) using SAS 9.1 software.

4.2. Results and discussion

Specific mechanical energy during potato starch extrusion-cooking depends on the process parameters. The research revealed that the values of SME were within a range $298.8\text{--}990\text{ kJkg}^{-1}$ ($0.083\text{--}0.275\text{ kWhkg}^{-1}$). These values were lower than the values obtained by Della Valle et al. (1995). The lowest energy consumption was observed during the extrusion-cooking process of potato starch at 140 °C. The highest energy consumption was recorded during the extrusion-cooking process at a temperature of 100 °C (at moisture content of 17 and 20%) and at 120 °C (moisture content 25 and 30%).

Studies have shown the energy consumption dependence from extruder screw speed (Fig. 10). Effect of moisture content on the SME was inconclusive. When carrying out the process at 100 °C, little change was observed (decrease) in specific mechanical energy. At higher temperature of extrusion it was observed that an increase in moisture content of starch increases the rate of the SME. It was most likely caused by increasing viscosity of processed slurry. Due to the presence of water the starch melts and underwent liquefaction, resulting in lower glass transition temperature.

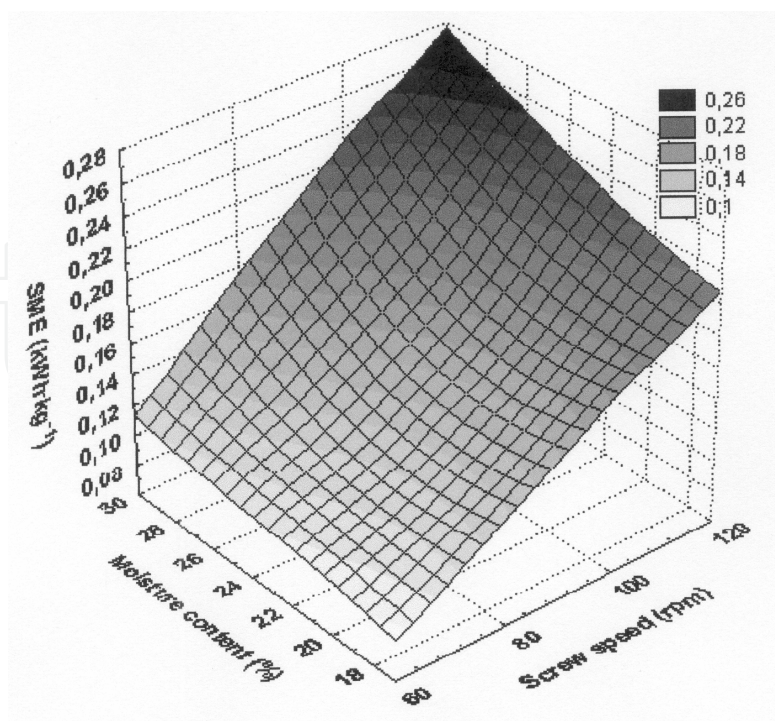


Figure 10. SME changes during potato starch extrusion-cooking at 120 °C

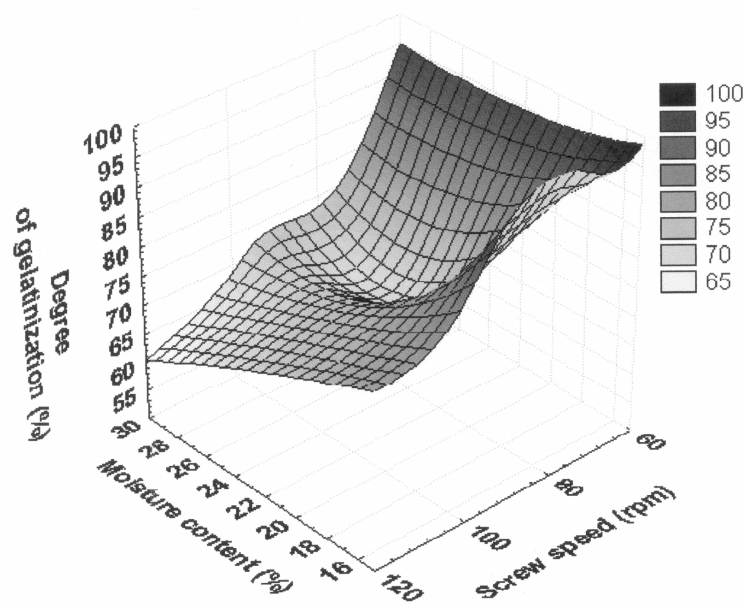


Figure 11. Degree of gelatinization of the potato starch extrusion-cooked at 100 °C

During our research has been noticed that the degree of potato starch gelatinization decreased with increase of extrusion-cooking temperature and when processed starch contained more water (Fig. 11). That was evident especially when high rpm of the screw was

used. The highest degree of gelatinization (96.5%) was recorded for starch extruded at 100 and 120 °C at the moisture content of 17%. The lowest degree of gelatinization (41%) was recorded for starch extruded at 140 °C at the moisture content of 30%. Such relatively low degree of gelatinization may happen due to relative short residence time of the dough in the extruder, which could stimulate the process. Nevertheless that has to be proved in more detailed measurements. Extrudates obtained under these conditions had properties of thermo-plastic starch.

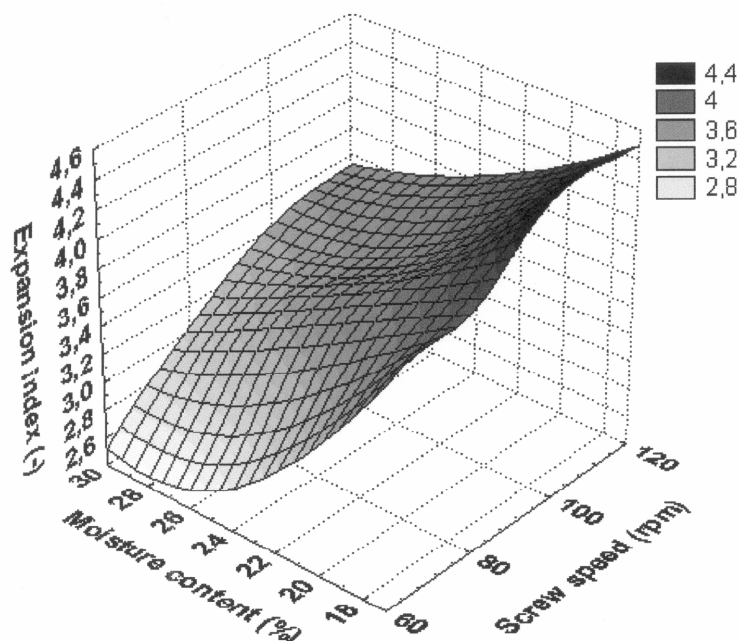


Figure 12. Expansion index of the potato starch extrusion-cooked at 100 °C

Measurements of the expansion index of extruded potato starch showed that its value decreases with moisture content increase (Fig. 12). Extruder screw speed increase caused increase of expansion index. This is a common phenomenon for the most of the extrudates. Extrudates were characterized by a typical structure, resembling a honeycomb structure. At high moisture contents of raw material (25 and 30%) the formation of "glassy" extrudates with a low degree of expansion was observed. This effect was particularly visible for extrusion temperatures of 120 and 140 °C. Extrudates obtained under these conditions had homogeneous, amorphous structure without pores and steam bubbles. Such behavior of the processed material is related to the glass transition temperature (T_g) of starch and temperature of steam bubbles formation (T_p) (Della Valle et al., 1997, van Soest et al., 1996c). When the product temperature is higher than T_g and close to T_p , bubbles growth stops and the extrudate obtained its structure. At high moisture contents of raw material T_g and T_p may be lower than the temperature at which extrudate shrinkage begins as a result of condensation (about 100 °C). At low moisture con-

tents T_p is much higher than 100 °C and, therefore, an increase of steam bubbles before they end up collapsing, resulting in a high degree of expansion.

Native potato starch has WAI approximately 97% and WSI approximately 0.25%. The study showed that the baro-thermal modification of starch significantly affects on its water absorption and solubility in cold water.

The research revealed that the value of WAI initially increased with increasing screw speed, and decreased at high speeds of extruder screw. With the increase in moisture content of processed potato starch the increase of water absorption was observed (Fig. 13). WAI values of the extruded potato starch ranged from 282 to 569% and generally did not deviate from the values obtained for a typical starch extrudates (Mercier et al., 1998).

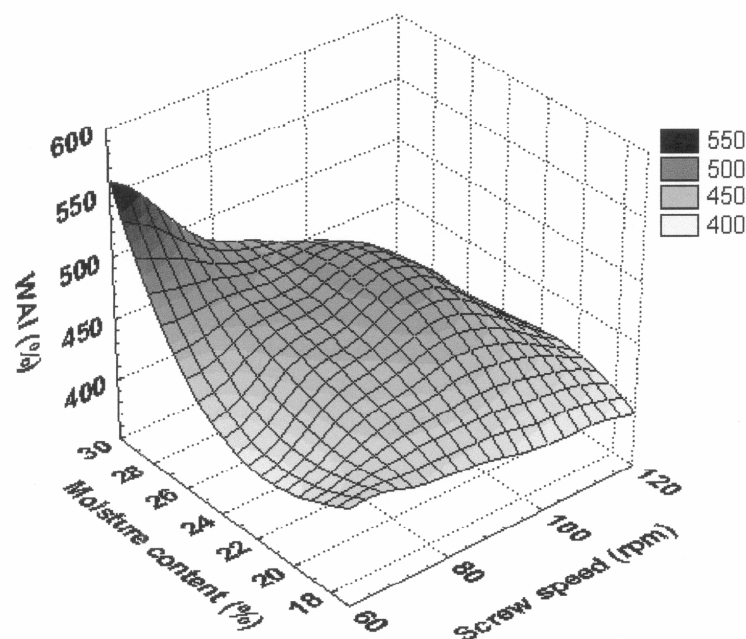


Figure 13. WAI of the potato starch extrusion-cooked at 100 °C

The highest values of water absorption were observed for starch extruded at 100 °C, the lowest for starch processed at 120 °C. It was connected with the progress of the degree of gelatinization. The increase in extrusion temperature to 140 °C caused a re-appreciation of WAI. Most likely due to lower glass transition temperature, the starch was more rapid melting, and liquefaction, which could limit the degree of its degradation. Analysis of variance of the WAI, depending on the moisture content and screw speed, showed statistically significant differences, with significance level of 0.05. Only for extrudates obtained at 140 °C there were no significant statistical differences in the relationship between water absorption and the screw speed.

The research showed that the value of the WSI increased with screw speed increase. The starch moisture content increase caused reduction of extruded starch solubility (Fig. 14). The

highest values of solubility (40%) were obtained for the modified starch at 120 °C. Process temperature growth caused an initial increase (120 °C) and then decrease (140 °C) in starch WSI. The changes of the solubility of starch were related with changes in the process of gelatinization and starch degradation due to starch moisture content increase. At low to intermediate moisture content and high temperature, the water contained in starch might behave like a lubricant (Igura et al., 2001). Degradation of starch progressed by increasing extruder screw speed at low moisture content because less lubricant (water) was available. Analysis of variance of the WSI, depending on the moisture content and screw speed, showed statistically significant differences, with significance level of 0.05.

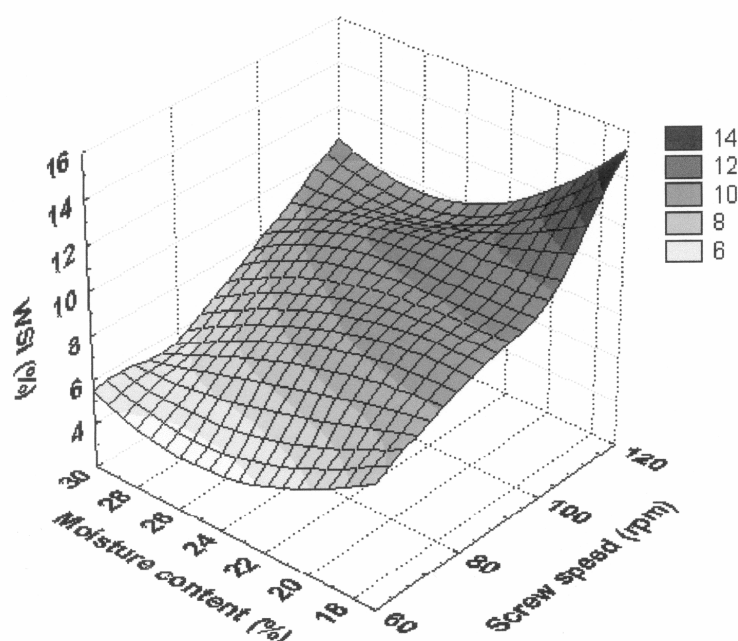


Figure 14. WSI of the potato starch extrusion-cooked at 100 °C

5. Thermoplastic starch

The interest to use starch as a basis for packaging material originates to the 1970's when environmental awareness increased drastically. Since then a steady development of new products can be seen. The possibility to compete in price with traditional materials, like plastics, has always been indispensable for the general acceptance of these new materials.

Starch biodegrades to carbon dioxide and water in a relatively short time compared with most synthetic polymers. Considering some drawbacks of the existing technologies of biodegradable materials manufacture, in the recent years there have been started large-

scale researches to increase amount of starch in starch-plastic composites to the highest possible level. The final objective of these investigations is to obtain commercial items for one-time use, produced from pure starch and to exclude synthetic polymers from the formulation. Thermoplastic starch (TPS) seems to be a perfect solution because it can be processed with conventional technologies used in synthetic plastic manufacture (extrusion, injection moulding).

To obtain thermoplastic starch, thermal and mechanical processing should disrupt semi crystalline starch granules. As the melting temperature of pure starch is substantially higher than its decomposition temperature there is a necessity to use plasticizers, for example water. Under the influence of temperature and shear forces, disruption of the natural crystalline structure of starch granules and polysaccharides form a continuous polymer phase is reported. TPS produced from starch plastified only with water becomes very brittle at room temperature. To increase material flexibility and improve processing other plasticizers are also used, e.g. glycerol, propylene glycol, glucose, sorbitol and others. To improve the mechanical properties of TPS based materials also other additives can be applied, like emulsifiers, cellulose, plant fibres, bark, kaolin, pectin and others.

5.1. Materials and methods

5.1.1. Injecting moulding

The blends of a potato starch Superior type, produced by AVEBE Company (NL), a glycerol (98,5% purity) produced by Polfa Odczynniki (PL) and cut flax fibres supplied by Polish producer BELKO Ltd Co., were used as a basic material during processing. The raw materials were mixed in a ribbon blender; a glycerol content varied from 18 to 30 wt % blend mass, and the fibres from 5% to 10% at the selected blends. After mixing the blend samples were packed in airtight plastic bags and stored for 24 hrs to intensify glycerol penetration into starch grains. Immediately before the extrusion the blends were remixed.

Production of thermoplastic starch (TPS) was made in two steps. In first step starch, glycerol and flax fibre blends were extruded in a twin-screw extruder PASQUETTI, an Italian design, characterized by $L/D = 5$, and the screws diameter - 45mm. The extruder's die was fitted with a bronze matrix having one hole of the diameter $\phi = 3$ mm. Thermoplastic starch was made with the screw's speed of $1,5 \text{ s}^{-1}$. The temperature of extrusion in particular barrel parts and a die were between 80°C and 140°C ; pressure in the die fluctuated between 10 MPa and 18 MPa. The product was cut by high-speed knife, which helped obtain pellets of previously set small size (Oniszczyk, 2006).

In the second step, the TPS pellets were processed on the injection moulding machine ARBURG 220H90-350, $L/D = 20,5$. The injection speed was maintained at the level of $0,07\text{--}0,09 \text{ ms}^{-1}$, injection time - 3s, and the temperature of the processes reached from 100°C to 180°C . The samples of injection mouldings (Fig. 15) were used during further examination of mechanical properties of mouldings (Oniszczyk, 2006).

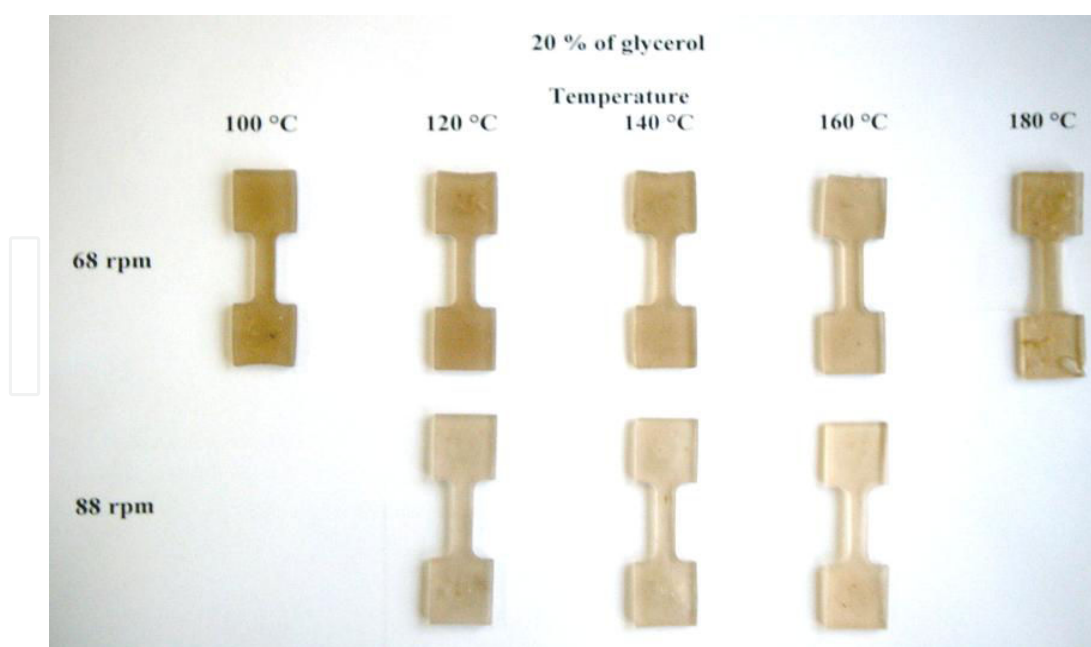


Figure 15. Samples of TPS mouldings

5.1.2. Film blowing

Similar procedure of the TPS granulates production was used to obtain half product for the film blowing. The basic materials were the blends of 2 main components: potato starch and a glycerol. Selected blends were enriched with the addition of the emulsifiers: polyoxyethylene sorbitan monolaurate (Tween 20) and glycerol monostearate at the amount up to 2%.

The process of film extrusion with film blowing method was conducted on a line specially designed for film manufacture in the Department of Food Process Engineering, Lublin University of Life Science (PL), based on a single screw plastic extruder of $L/D=35$ (see Fig. 16). That line was produced by SAVO Ltd Co., Poland. TPS film was produced using 2 screws of varied geometry (a compression ratio: 2,0 and 3,5), and the screw rotational speed ranged from 50 till 90 rpm. The film was extruded at the barrel and crossdie temperature ranging 70 – 155 °C.

5.1.3. Measurement of physical properties

The measurements of glass transition temperature T_g of thermoplastic starch were done with the use of the Differential Scanning Calorimetry on the Perkin Elmer DSC 7. The samples of thermoplastic starch 7 – 10 mg mass were heated from the temperature of 25 °C to 180 °C at 10 °Cmin⁻¹ speed, and next cooled at the same rate down to 25 °C and finally heated up to 180 °C. The thermal transitions were calculated from the second heating cycle. To confirm the obtained results the tests were repeated in a DSC 2920 modulated DSC TA Instruments. The samples were heated from 0 °C up to 150 °C at the rate 1 °Cmin⁻¹ and then cooled at the same rate to 0 °C (Mitrus, 2005b).



Figure 16. TPS film blowing

The examination of the mechanical properties of TPS mouldings was performed on a universal texture appliance Zwick type BDO-FBO0, 5TH equipped in the head 0,5kN. The travel speed of the head was 3 mmmin^{-1} . The test focused on the maximum stress and maximum elongation during stretching (Oniszczyk, 2006).

The assessment of the original shrinkage of the biopolymer mouldings was done by means of the micrometer screw initiating the measurement 24 hours after producing the samples.

The tensile testing of film proceeded at the tester Zwick type Z2.5/TN1S using the standard tensile test ISO 527. There was applied the crosshead 1 kN, sample length 100 mm, sample width 17 mm, each sample thickness was measured with micrometer. The crosshead speed for initial stress was 10 mmmin^{-1} , speed up to flexibility limit – 50 mmmin^{-1} , test speed – 200 mmmin^{-1} . The measurements were made on maximum strength, tensile strength, elongation at the maximum strength and tensile.

5.2. Results and discussion

DSC technique has been used often to study the glass transition temperature of thermoplastic starch. The results differ from one another significantly (Shi et al., 2007, van Soest, 1996, Talja et al., 2007). In accordance to Yu & Christi (2001) some key factors, such as sample

preparation, type of pan and measurements conditions, have an affect on the results of thermal behavior of starch as measured by DSC. The tests show that both, amylose and amylopectin had a higher T_g 's in absence of glycerol. The estimates demonstrated that the T_g of dry amylose and amylopctin is 227 °C, while Bizot et al. (1997) assessed the dry starch T_g – 332 °C. What's more, to lower the T_g of potato starch closer to the ambient temperature 0,21 g of water should be used for 1g of starch (Bizot et al., 1997, Myllarinen et al., 2002). Myllarinen et al. (2002) confirmed that the T_g of amylose and amylopectin can be equal to the ambient temperature when the water content is 21%, however at the same glycerol level the T_g can be still as high as 93 °C. It can be concluded that glycerol is a less effective plasticizer than water. On the basis of computations they claim that in order to lower a T_g value to the ambient temperature 35% glycerol should be applied.

The glass temperature measurements revealed that with glycerol content growth in material blend, the T_g of the obtained material decreases almost linearly. The highest observed T_g was 132 °C for 15% glycerol, the lowest was 18 °C at a glycerol level of 30%. Figure 17 shows the changes of the glass transition temperature with changing glycerol content. The moisture content of all the mixtures was 15%. This results are similar to this obtained by Graff et al. (2003).

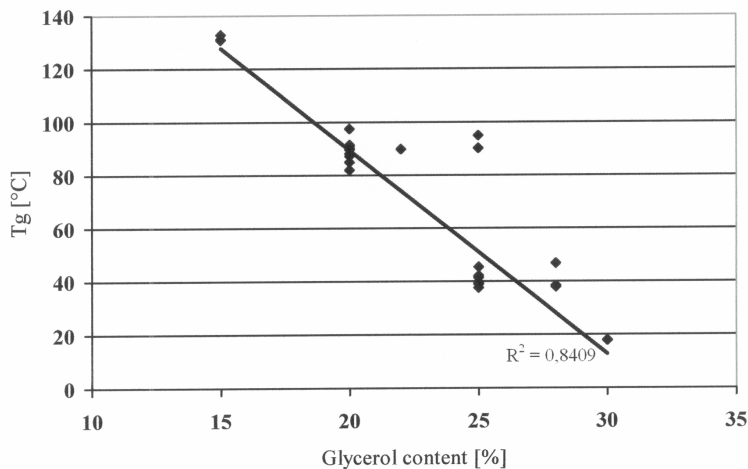


Figure 17. Influence of the glycerol content on the T_g of thermoplastic starch

The mechanical properties of biocomposites depend on a number of factors. These are the quantity and type of fibre added to the material, but also type and amount of plasticizers, finally - the production temperature plays also important role. A predominant influence on the mechanical properties of biocomposites have both: natural fibres and plasticizer. During our investigations it has been observed that the addition of fibres enhances the mechanical strength of mouldings samples. The addition of extra plasticizer causes the decline in its maximum stress.

Figure 18 shows the relationship between the maximal stress and the content of flax fibres in the samples containing 20, 22 and 25% of glycerol and produced at the material injection

temperature of 120 °C. On the basis of the performed examination, it can be stated that the addition of flax fibres positively influenced the mechanical properties of biopolymer mouldings. It was noted that together with the percentage growth of the fibres content the mechanical strength of samples was improved. The samples with 20% of glycerol content and 10 % of flax fibres were of the highest strength (26,5 MPa). In the case of mouldings obtained from granulate containing 22% of glycerol, the addition of 5% and 10% of fibres slightly influenced the improvement in strength. It was noted that together with the growth of the glycerol content in mouldings containing flax fibres their mechanical strength dropped. Glycerol acts like diluent and weakens the intermolecular bonds between flax fibres and starch. The lowest mechanical strength was observed with mouldings produced from granulates containing 25% of glycerol. The same tendency was registered in the case of samples obtained at different production temperatures the highest mechanical strength was displayed by mouldings produced at the material injection temperature of 140 °C (maximal stress 27,8 MPa), and the the lowest mechanical strength was noticed for mouldings obtained at the temperature of 180 °C (10,8 MPa).

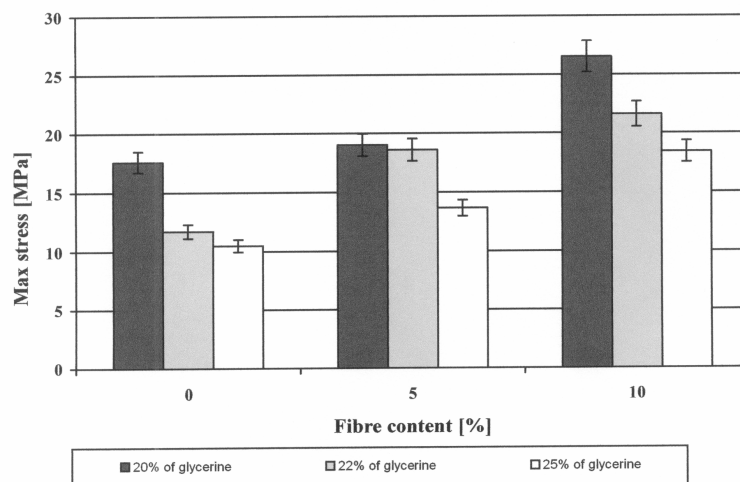


Figure 18. Relationship between the maximal stress and the fibre content in samples (sample injection temperature 120 °C)

Another important parameter is the maximal elongation of the samples during stretching. For TPS without fibres added, it can be stated that for the full spectrum of injection temperatures and for all glycerol concentrations investigated the maximal elongation coincides with increasing injection temperature and with the increase of the glycerol content of the sample. The addition of fibres affected the elongational behaviour of the material considerably.

During the research it was noticed that the maximal elongation values coincided with the growing temperature of material injection and with the increase of the glycerol content in the sample. The largest maximal elongation (58,5%) was recorded at the level of 25% of glycerol content in mouldings and the material injection temperature of 180 °C. The lowest maximal elongation of 10% was recorded with mouldings having 20% of

glycerol. To conclude, it corroborates the positive influence of plasticizer on the improvement of moulding flexibility.

Addition of flax fibres influenced the drop of the maximal elongation of biopolymer mouldings. The growth of the percentage share of fibres in the mixture worked upon the decrease of the flexibility of samples during the tension test (Fig. 19).

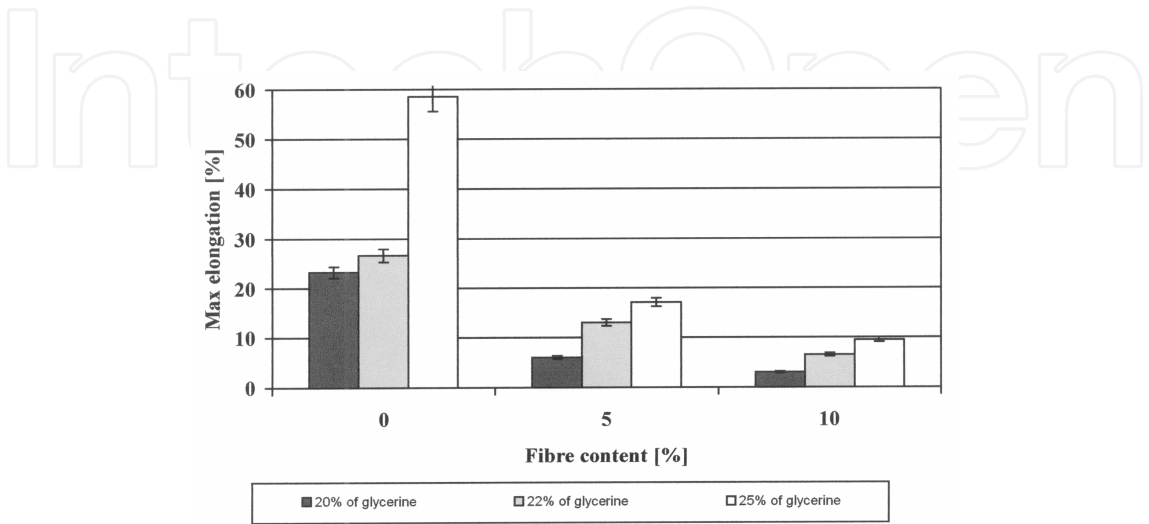


Figure 19. Relationship between the maximal elongation and the flax fibre content in samples (injection temperature 180 °C).

With the application of the production temperature of 180 °C, the largest maximal elongation (17,1%) was observed with the samples containing 25% of glycerol and 5% of flax fibres. The lowest maximal elongation (3%) was observed with mouldings produced from granulate containing 20% of glycerol and 10% of flax fibres. In the case of mouldings produced at the injection temperature of 120 °C, the addition of fibres barely influenced the reduction of the maximum elongation and amounted to 10,5% for mouldings containing 5% of flax fibres and 9,7% for mouldings of double fibre content. It proves the negative impact of fibres on the flexibility of biopolymer mouldings containing such material.

Besides the improvement of durability, the fibres used for the mouldings manufacture stabilize the shape and decrease the original shrinkage of ready products. Oniszczyk & Janssen (2009) describes that an increased linen fibre content is decreased the values for original shrink. The addition of plasticizer (glycerol) had an adverse effect on the original shrinkage.

The examination of original shrinkage of biopolymer mouldings showed that in the whole range of temperatures of sample production (100 °C, 120 °C, 140 °C, 160 °C and 180 °C) and after the time of shrinkage measurement (measured after 24 h) a similar tendency was observed. Together with the increase of the share of flax fibres, the value of the original shrinkage was dropping, regardless of the time when measurement of the shrinkage was made. However, together with the growth of the share of glycerol, the value of the original shrinkage of mouldings slightly increased (Fig. 20).

When examining the shrinkage of mouldings produced with 25% of glycerol share, considerable differences. After 24 h from producing mouldings, the shrinkage level was almost 11,7% in samples without fibres, 1,75% when applying 5% of flax fibres and 0,67% when 10% of fibres were added. For mouldings obtained with 20% of glycerol content, the shrinkage values were lower and least dependent on the addition of fibres. The shrinkage values for these trials did not exceed 1,5%, which indicates a significant stability of the material obtained in specific production conditions. The original shrinkage of mouldings without the addition of fibres was high and amounted to about 6% when using 22% of glycerol and about 12% with 25% of plasticizer. This indicates a stabilizing role of fibres, which maintained the original moulding structure in an almost unchanged shape. It is a very desirable feature when it comes to keeping the shape of ready packaging if produced from such biopolymers.

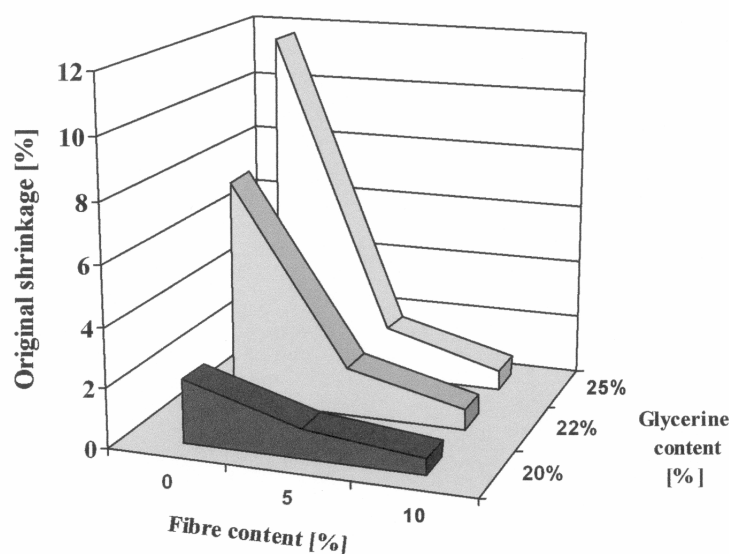


Figure 20. Influence of flax fibres content and glycerol content on the size of original shrinkage of (measured after 24 h); injection temperature 120 °C

The tests of the film extrusion showed that the best results were recorded for the starch mixtures with 20-25% glycerol. At processing temperature below 120 °C the material was not fully processed and some granulate residuals appeared at the film surface. The obtained films were thick, opaque and semi-transparent, that after some time lost flexibility and got brittle due to their drying up. When the higher pressing temperatures were applied as well as a screw with a mixer arm, films of good quality were obtained. They were flexible semi-transparent films readily put to the blow moulding. Unfortunately because of the crosshead

with 1mm slit application and a low powered compressor the resulting film had minimum thickness 120 μ m, yet the production of much more thinner ones is possible.

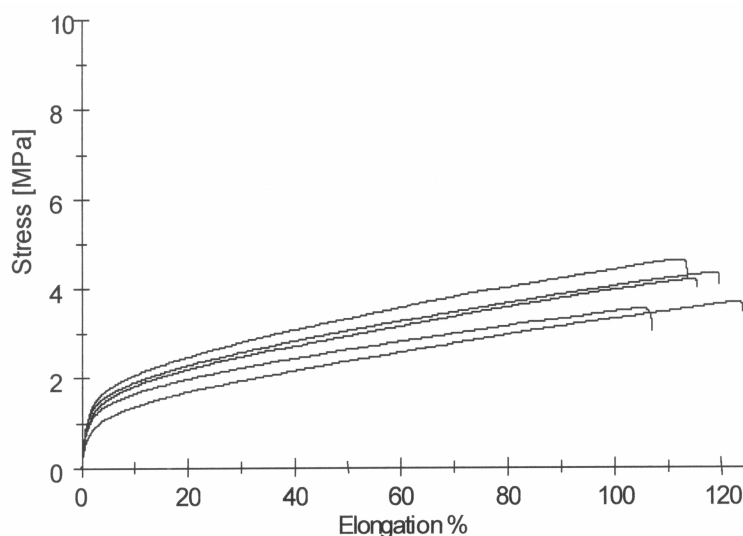


Figure 21. Example of the tests results of the TPS film strength

The addition of the emulsifiers: polyoxyethylene sorbitan monolaurate (Tween 20) and glycerol monostearate at the amount up to 2% has considerably improved film flexibility. Moreover, it was found that mixture damped up with only some water (2-5%) induced an increase of film flexibility and strength. Example of the tests results of the TPS film strength is shown on figure 21.

The analysis of the mechanical properties measurements of TPS films proved that the extrusion processing parameters, emulsifier presence and water content in the material exert a vital impact on film strength and its elongation. The use of the screw of 3,5 compression ratio, equipped with an extra mixing section affected film strength more, while a screw of 2,0 compression ratio influenced the film elongation in a greater measure. According to the expectations, the application of the screw of 3,5c.r. resulted in higher energy-consumption during extrusion processing.

6. Conclusive remarks

Extrusion-cooking technique allows creating the degree of gelatinization of processed starch. It is possible to achieve low or high level of gelatinization depending on the process parameters. This is especially important for food and feed applications.

Expansion index of starchy extrudates largely depends on the parameters of the extrusion process. Its value decreased with moisture content increase while increased with screw speed increase.

The extrusion process of starch increased the water absorption and cold water solubility. These changes are closely related to the course of the process of starch gelatinization; degradation and their extent depends on the extrusion parameters used

Modification of starch by extrusion-cooking technique is characterized by relatively low specific mechanical energy consumption. SME values were within a range from 298.8 to 990 kJkg⁻¹. Significant impact on the values of the SME had a screw speed, very little impact had a moisture content of raw material.

When the glycerol content in TPS increases from 15 to 30% the glass transition temperature decreases almost linearly from 132 to 18 °C at moisture contents 15%.

The performed examination of TPS injection moulding showed that it's possible to produce shaped biodegradable packaging materials. The addition of flax fibres to raw material mixture positively influenced the improvement of the mechanical strength of mouldings in the entire range of glycerol addition to mixtures (mouldings produced from the granulate containing 10% of flax fibres exhibited the greatest mechanical strength).

The increased glycerol content in the material and the growth of injection temperature resulted in better elasticity of mouldings. Its drop was caused by the presence of fibres in granulate.

The increase of the percentage share of glycerol in the mixture visibly contributed to the growth of the value of the original shrinkage of mouldings. The lowest values of the original shrinkage of samples were observed at the material injection temperature of 180 °C. The addition of flax fibres to mouldings in the entire range of their production temperatures positively influences the stability of shape and the reduction of shrinkage.

The most advantageous strength properties were recorded for the films with 20 – 25% glycerol. Polyoxyethylene sorbitan monolaurate (Tween 20) and glycerol monostearate in amount up to 2% have substantially improved (even by over 50%) film tensile susceptibility. The analysis of the mechanical properties measurements of TPS films proved that the extrusion processing parameters, emulsifier presence and water content in material exert a vital impact on film strength and elongation. The use of screw of 3,5 compression ratio equipped with extra mixing section affected film strength more, while a screw of 2,0 compression ratio influenced film elongation in a greater measure. According to the expectations, the application of the screw of higher compression ratio increases energy-consumption during extrusion processing.

Author details

L. Moscicki, M. Mitrus, A. Wojtowicz, T. Oniszczyk and A. Rejak

*Address all correspondence to: leszek.moscicki@up.lublin.pl

Department of Food Process Engineering, Lublin University of Life Sciences, Lublin, Poland

References

- [1] Anderson RA., Conway HF., Peplinski AK.: Gelatinization of corn grits by roll cooking, extrusion cooking and steaming. *Starch* 1970;22 130-134.
- [2] Barron C., Buleon A., Colonna P., Della Valle G.: Structural modifications of low hydrated pea starch subjected to high thermomechanical processing, *Carbohydrate Polymers* 2000;43 171-181.
- [3] Bizot H., Le Bail P., Leroux B., Davy J., Roger P., Buleon A.: Calorimetric evaluation of the glass transition in hydrated, linear and branched polyanhydroglucose compounds. *Carbohydrate Polymers* 1997;32 33 – 50.
- [4] Cunningham R.: Effect of processing conditions on intrinsic viscosity of extruded cornstarch, *Journal of Applied Polymer Science* 1996;60 181-186.
- [5] Della Valle G., Boche Y., Colonna P., Vergnes B. The extrusion behaviour of potato starch, *Carbohydrate Polymers* 1995;28 255-264.
- [6] Della Valle G., Vergnes B., Colonna P., Patria A.: Relations between rheological properties of molten starches and their expansion behaviour in extrusion. *Journal of Food Engineering* 1997;31 277-296.
- [7] Fujio Y., Igura N., Hayakawa I.: Depolymerization of molten-moisturized-starch molecules by shearing-force under high temperature, *Starch/Stärke* 1995;47 143-145.
- [8] Graaf RA., De Karman AP., JanssenLPBM.: Material properties and glass transition temperatures of different thermoplastic starches after extrusion processing. *Starch* 2003;55 80-86.
- [9] Harper JM.: *Extrusion of Foods*. Boca Raton: CRC Press; 1981.
- [10] Igura N., Katoh T., Hayakawa I., Fujio Y.: Degradation profiles of potato starch melts through a capillary tube viscometer, *Starch/Stärke* 2001;53 623-628.
- [11] Janssen LPBM., Moscicki L., Mitrus M.: Energy aspects in food extrusion-cooking. *International Agrophysics* 2002;16 191-195.
- [12] Mercier C., Linko P., Harper JM. *Extrusion cooking*. (2nd ed.). St. Paul: American Association of Cereal Chemists, Inc.; 1998.
- [13] Mitrus M.: Changes of specific mechanical energy during extrusion cooking of thermoplastic starch. *TEKA Kom. Mot. Energ. Roln.* 2005a;5 152-157.
- [14] Mitrus M.: Glass transition temperature of thermoplastic starches. *International Agrophysics* 2005b;19(3) 237-241.
- [15] Mitrus M., Moscicki L.: Extrusion-Cooking of TPS. In: Janssen LPBM, Moscicki L. (eds.) *Thermoplastic Starch. A Green Material for Various Industries*. Weinheim: Wiley-VCH.; 2009. p149-157.

- [16] Moscicki L., editor. Extrusion-Cooking Techniques. Weinheim: Wiley-VCH Verlag GmbH; 2011.
- [17] Mościcki L., Extrusion, effect on physical and chemical properties. In Gliński J., Horabik J., Lipiec J. (eds.) Encyclopedia of Agrophysics. Dordrecht: Springer; 2011. p284-287.
- [18] Mościcki L., Mitrus M., Wójtowicz A. Technika ekstruzji w przemyśle spożywczym. PWRiL: Warszawa; 2009 (in Polish).
- [19] Myllärinen P., Partanen R., Seppälä J., Forsella P.: Effect of glycerol on behaviour of amylose and amylopectin films. Carbohydrate Polymers 2002;50 355 – 361.
- [20] Nashed G., Rutgers R., Sopade P.: The plasticization effect of glycerol and water on the gelatinisation of wheat starch, Starch/Stärke 2003;55 131-137.
- [21] Oniszczyk T.: Effect of parameters of injection moulding process on the structural properties of thermoplastic starch packaging materials. PhD Thesis. Agriculture University in Lublinie; 2006 (in Polish).
- [22] Oniszczyk T., Janssen LPBM.: Influence of addition of fiber on the Mechanical properties of TPS moldings. In: Janssen LPBM, Moscicki L. (eds.) Thermoplastic Starch. A Green Material for Various Industries. Weinheim: Wiley-VCH.; 2009. p197-208.
- [23] Peighambardoust H., van Brenk S., van der Goot A., Hamer R., Boom R.: Dough processing in a Couette-type device with varying eccentricity: effect on glutenin macro polymer properties and dough micro-structure, Journal of Cereal Science 2007;45(1) 34-48.
- [24] Peighambardoust H., van der Goot A., Hamer R., Boom R.: A new method to study simple shear processing of wheat gluten-starch mixtures, Cereal Chemistry 2004;81(6) 714-721.
- [25] PN-A-79011-11:1998, Food concentrates – Test methods – Determination of degree of starch gelatinization (in Polish).
- [26] Rushing T., Hester R.: Intrinsic viscosity dependence on polymer molecular weight and fluid temperature, Journal of Applied Polymer Science 2003;89 2831-2835.
- [27] Schogren R.L.: Effect of moisture and various plasticizers on the mechanical properties of extruded starch. In: Ching C., Kaplan D., Thomas E. Biodegradable Polymers and Packaging. Lancaster, USA; Technomic Publishing Co.; 1993. p141-150.
- [28] Shi R., Zhang Z., Liu Q., Han Y., Zhang L., Chen D. Tian W.: Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending. Carbohydrate Polymers 2007;69 748-755.
- [29] Talja RA., Helén H., Roos YH. Jouppila K.: Effect of various polyols and polyol contents on physical and mechanical properties of potato starch-based films. Carbohydrate Polymers 2007;69 288-295.

- [30] van den Einde R., Bolsius A., van Soest J., Janssen L., van der Goot A., Boom R.: The effect of thermomechanical treatment on starch breakdown and the consequences for process design, *Carbohydrate Polymers* 2004;55(1) 57-63.
- [31] van den Einde R., van der Goot A., Boom R.: Understanding molecular weight reduction of starch during heating-shearing processes, *Journal of Food Science* 2003;68(8) 2396-2404.
- [32] van den Veen M.: Towards intensification of starch processing, PhD Thesis, Wageningen University, the Netherlands; 2005.
- [33] van den Veen M., van Iersel D., van der Goot A., Boom R.: Shear induced inactivation of α -amylase in a plain shear field, *Biotechnology Progress* 2004;20(4) 1140-1145.
- [34] vanSoest JJG.: Starch plastics: structure – property relationships. Phd Thesis. Utrecht University; 1996.
- [35] vanSoest J., Benes K., de Wit D., Vliegthart J.: The influence of starch molecular mass on properties of extruded thermoplastic starch, *Polymer* 1996a;37(16) 3543-3552.
- [36] vanSoest J., Bezemer R., de Wit D., Vliegthart J.: Influence of glycerol on the melting of potato starch, *Industrial Crops and Products* 1996b;5 1-9.
- [37] vanSoest JJG., Bezemer RC., De Wit D., Vliegthart JFG.: Influence of glycerol on the melting of potato starch. *Industrial Crops and Products* 1996c;5 1-9.
- [38] vanSoest J., Knooren N.: Influence of glycerol and water content on the structure and properties of extruded starch plastic sheets during aging, *Journal of Applied Polymer Science* 1997;64 1411-1422,.
- [39] Wolf B.: Polysaccharide functionality through extrusion processing. *Current Opinion in Colloid & Interface Science* 2010;15 50-54.
- [40] Wójtowicz A.: The melting process in thermoplastic starches. In: Janssen L., Moscicki L. (eds.) *Thermoplastic Starch. A green material for various industries*, Weinheim, Germany; Wiley-VCH Verlag GmbH & Co. KGaA; 2009. p105-117.
- [41] Wójtowicz A., van der Goot AJ.: The influence of water and glycerol addition on thermal processing rheology and microstructure changes of potato starch, *Electronic Journal of Polish Agricultural Universities, seria Agricultural Engineering*, 2005;8(4) #51.
- [42] Yimlaz G.: Thermoplastic starch matrices for encapsulation and controlled release of volatile compounds, PhD Thesis, Utrecht University, the Netherlands; 2003.
- [43] You X., Li L., Gao J., Yu J., Zhao Z.: Biodegradable extruded starch blends, *Journal of Applied Polymer Science* 2003;88 627-635.
- [44] Yu L., Christie G.: Measurement of starch thermal transitions using differential scanning calorimetry. *Carbohydrate Polymers* 2001;46 179-184.