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EFFECTS OF OPERATIVE CONDITIONS ON PRODUCTS OBTAINED OF STARCH-OIL MIXTURES BY SINGLE-SCREW EXTRUSION

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ABSTRACT

Background. The aim of the study was to evaluate the fat binding and physicochemical properties of the products under conditions of potato starch extrusion containing rapeseed or linseed oil and rapeseed oil with glycerol.

Material and methods. The study dealt with the extrudates of potato starch produced with the addition of rape seed or linseed oil and rapeseed oil and glycerol at 22% humidity. The extrudates were obtained at two screw speeds: 80 rpm and 100 rpm. Extrudates containing rapeseed oil and glycerol (R6G) were obtained at a temperature distribution of 115/130/150°C, while those with the participation of rapeseed oil and linseed oil were obtained at 120/135/128°C. Water solubility index (*WSI*), water absorption index (*WAI*), specific surface area (S_{BET}) and quantity of fat permanently bound were determined for the products obtained.

Results. When oils were added, the solubility of extrudates decreased as compared to the control samples (starch without oil; *S*). Rapeseed oil added to the starch mixture at the levels of 3 g and 6 g in had no significant effect on the solubility of the product and amounted to: 80.3–82.6% and 78–79.6%. The largest decrease in solubility (*WSI*, 55.4–57.1%) was demonstrated for samples with 6% addition of rapeseed oil and 10 g glycerol. For these samples (R6G), a significant increase in the index *WAI* (376–397%) was recorded. Extrudates obtained with the addition of 3 g of rapeseed oil absorbed slightly more water than those with 6 g of oil added. The specific surface area (S_{BET} 230–256 m^2/g) determined from the water vapor adsorption isotherm indicates no statistically significant difference at $\alpha = 0.05$ for products with rapeseed oil, linseed oil, and controls. A significant increase in the specific surface area (S_{BET} 284–347 m^2/g) was observed for samples with 6g rapeseed oil and 10 g glycerol added. For samples with 3 g of rapeseed oil, the amount of bound fat was 1.9–2.1 g/100 g of starch and for 6% the starch percentage was 2.96–3.5 g/100 g.

Conclusion. The water solubility of starch extrudates with the addition of oils decreases with an increase in screw speed. Starch extrudates with linseed oil and rapeseed oil plus added glycerol are characterized by an increase in water-absorption capacity with respect to the control extrudates. The products obtained with the addition of rapeseed oil and glycerol exhibit a significant increase in their specific surface area. The quantity of fat permanently bound during extrusion depended on: the oil type, its percentage in the mixture and the screw speed. The linseed oil was the least absorbed in the starch structure, but rapeseed oil binding increased with the increase in its level in the mixture.

Keywords: oil-potato starch extrudates, oil binding

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INTRODUCTION

Extrusion is used in the production of supplements, analogues of meat products, snacks, confection bakery, and functional foods. During extrusion, modifications in the plant and animal-origin proteins as well as refinement of the feed raw materials can be possible (Rzedzicki, 1998; Szpendowski et al., 1990; Śmietana et al., 1997). Raw materials subjected to extrusion can be divided into structural materials (mainly starch), fillers (protein fraction, cereal grain and oilseed, milk proteins, components abundant in dietary fiber such as wheat bran), plasticizers (water, vegetable oils), and additives (salt, sugar) (Cichoń et al., 1993; Fornal, 1998; Guy, 2001; Mościcki, 2003).

Starch is the main structure-forming material. Its physicochemical properties are dependent on the botanical origin of a plant and determine the formation of structures in the product which is obtained or formed. When assessing the suitability of starch for processing, it is necessary to analyze the degree of its polymerization, amylose to amylopectin ratio, particle size, and lipid content (Fornal, 1998). These may all affect the product's quality, taste and nutritional values. Extrusion may reduce the energy value of the final product due to the formation of complexes that are more resistant to the action of digestion enzymes (Jamroz and Rogalski, 1994; Fornal, 1998; Kiczorowska and Lipiec, 2002). In the extrusion technology, fats also play an important role in the transport of a mass with low humidity – they prevent the outer layer of the material from overheating and sticking to the cylinder or extruder screw (Fornal, 1998; Mościcki, 2003; Rzedzicki, 1998). During extrusion, high temperatures mean that fats are readily absorbed; they may limit the starch degradation. The addition of lipids into the mixtures for extrusion is in the range from 0.5% to 5% and depends on the raw material composition and process parameters, which are aimed at optimizing the final product. Adding too much fat may reduce the degree to which the product expands. Adding just 3% oil causes the formation of compacted starch-protein structures that do not contain any air chambers (Colonna and Mercier, 1983; Fornal, 1998; Rzedzicki, 1998). With the addition of fat to the extruded mixtures, an increase in the value of the expansion factor of the product is observed. After exceeding an oil concentration of 5%, a further increase in the amount of oil resulted in a dramatic reduction (Abu-hardan et al., 2011).

The selection of extrusion parameters and composition of the raw material affects the direction and intensity of changes in the starch material (Mercier and Feillet, 1975; Linko et al., 1981). The most important changes in starch during extrusion are related to the gelatinization, melting, dextrinization, and formation of fat-starch complexes, which all affect the quality of the final product associated with changes in water absorption, solubility, and susceptibility (sensitivity) to the amylolytic enzymes action (Anderson et al., 1969; Cichoń et al., 1993; Fornal et al., 1993).

The aim of the study was to evaluate the fat binding and physicochemical properties of the products under conditions of potato starch extrusion containing rapeseed or linseed oil and rapeseed oil with glycerol. The analysis included an assessment of solubility, water absorption, specific surface area, and the amount of bound fat in a starch matrix.

MATERIAL AND METHODS

Material

The commercial potato starch used in this study was made by ZPZ Łomża. Native potato starch contains: 0.26% ash, 0.03% fat, 19.01% moisture, 0.02% protein. The rapeseed oil produced by ZT "Kruszwica" S.A., Poland, linseed oil produced by Goccia Doro, Italy, glycerol obtained from TechlandLab and the starch-oil blends were moistured to 22% DM.

The samples were extruded at varied temperatures and/or extruder screw speeds (Table 1). In order to bind fats, a catalyzer in the form of K_2CO_3 was applied. The process was conducted in a single-screw modified extruder TS-45 (Metalchem Gliwice, Polish design) with a yield of 20 kg/h, with L/D = 16:1, die diameter 4 mm, compression screw 3:1. The fragmented extrudates were screened through a sieve to isolate the fractions of grain with a diameter below 0.2 mm for the analysis included in the study.

Table 1. Characteristics of samples and extrusion parameters

Name samples	The qualitative and quantitative characteristics of starch-oil blends g in sample					Extrusion parameters	
	starch potato	oil		glycerol	K_2CO_3	screw speed rpm	temperature °C
		rapeseed	linseed				
S	100	–	–	–	–	80	120/135/128
		–	–	–	–	100	
R3		3	–	–	3	80	
		3	–	–		100	
R6		6	–	–		80	
		6	–	–		100	
L6		–	6	–		80	
		–	6	–		100	
R6G		6	–	10		80	115/130/150
		6	–	10		100	

Methods

Water solubility index (*WSI*) and water absorption index (*WAI*)

Determination of the water absorption index, WAI, and water solubility index, WSI was performed according to Anderson, Conway, Pfeifer, and Griffin (1969). Samples (1 g) were suspended in 30 ml of distilled water at a temperature of 20°C, homogenized at *RCF* = 112 g, for 5 min. After homogenization, material was centrifuged at *RCF* = 1790 g, for 20 min. Unbound water, the test tube with the material was set upside down on filter paper for drying. After 30 min the amount of absorbed water was determined from the Eq. (1):

$$WAI, \% = \frac{\text{weight gain of gel}}{\text{dry weight of extrudate}} \cdot 100 \qquad (1)$$

The test tube with the material was dried for 24 h at 105°C, the amount of water solubility was determined from the Eq. (2):

$$WSI, \% = \frac{\text{weight of dry solids in supernatant}}{\text{dry weight of extrudate}} \cdot 100 \qquad (2)$$

Specific surface area (S_{BET}) calculated on water vapor isotherm

The specific surface area was calculated on the basis of monomolecular adsorption of water vapour within a water activity (*aw*) range of 0.01–0.35. The specific surface area was determined from the Eq. 3 (Labuza, 1968; Włodarczyk-Stasiak and Jamoroz 2008).

The material was dried for 24 h, at 105°C. Water vapour adsorption on the extrudates (2 g) studied was made at a temperature of 20ºC. Air humidity control was effected by means of a water solution of sulphuric acid. The amount of adsorbed water vapour was determined from the difference between the dry weight and the weight of the sample after the final measurements of adsorption. Analysis of water vapour adsorption was conducted in three replications.

$$S_{BET},\ m^2/g = \frac{\text{monolayer value} \times \text{Avogadro number} \times \text{settlement area of a molecule of water}}{\text{molecular weight of water}} \qquad (3)$$

Fat binding

The percentage of oil binding was calculated as the difference between oil content (added) in mixtures, before extrusion, and oil content in extrudates, and expressed as g oil/100 g sample. Before extraction, extrudates were finely ground. The extraction time (hours) was chosen after preliminary tests to obtain the maximum yield in the oil. Oil was extracted using n-hexane by Model 1043 HT apparatus Soxtec Systems (De Pilli et al., 2007).

The ANOVA was used to calculate significant differences in treatment means and LSD ($p < 0.05$). The data reported in all the results are an average of triplicate observations. In the study, the mean values (x) and the standard deviation (σ) were calculated from the range ($x–2\sigma$; $x+2\sigma$).

RESULTS AND DISCUSSION

Water solubility index (*WSI*)

Analysis of starch extrudates solubility with selected oils indicates a wide variation (Fig. 1). The highest solubility was noted for the starch extrudate without oil added, which was obtained by applying a slow screw speed (80 rpm). No significant differences ($\alpha = 0.05$) for extrudates with a 3 g and 6 g addition of rapeseed oil extruded at 80 rpm and 100 rpm were reported. A slower screw speed (80 rpm) and the addition of 6 g of linseed oil decreased the solubility of the product from 61% to 71%. The lowest solubility was noted for extrudates with the addition of 6 g of rapeseed oil and 10% glycerol (R6G). The screw speed parameter during the preparation of extrudates R6G did not significantly affect the *WSI* ($\alpha = 0.05$).

The decrease in the solubility of extrudates made of rice flour with 3% monoglyceride was demonstrated by Pan et al. (1992). Lowering the solubility of products during extrusion of cereal blends containing fats was also studied by Singh et al. (1998), Dextrumaux et al. (1999) and Galloway et al. (1989).

Water absorption index (*WAI*)

The addition of oil to the majority of extrudates resulted in a decrease in *WAI* index with reference to the control samples (Fig. 2). The largest decrease in water absorption was recorded for extrudates with 3 g and 6 g of rapeseed oil added. For these products, both the amount of added rapeseed oil and screw speed did not affect the statistically significant differences at $\alpha = 0.05$. The highest value of the index *WAI* was reported for samples with the addition of 6g rapeseed oil and 10 g glycerol (R6G). For these extrudates (R6G), screw speed did not affect the change in the statistically significant *WAI* value.

The increase in the fat fraction in durum flour, hazelnut flour, and rice grit blends contributed to a decrease in the *WAI* index (Yağcı and Göğüş, 2008). The authors explain that the presence of fat fractions may

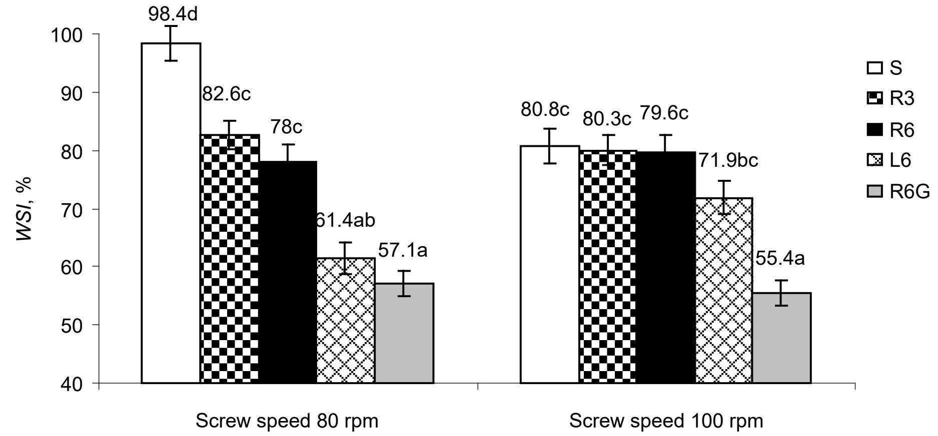

Fig. 1. Water solubility starch-oil extrudates: S – starch, R3 – starch + 3 g oil rapeseed, R6 – starch + 6 g oil rapeseed, L6 – starch + 6 g oil linseed, R6G – starch + starch + 6 g oil rapeseed + 10 g glycerol. The same letters indicate values that are not significantly different at α = 0.05

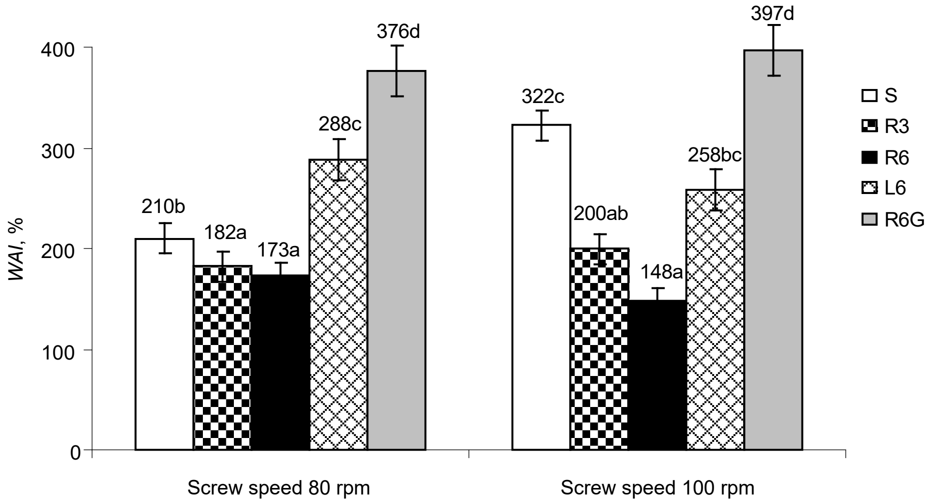

Fig. 2. Water absorption starch-oil extrudates: S – starch, R3 – starch + 3 g oil rapeseed, R6 – starch + 6 g oil rapeseed, L6 – starch + 6 g oil linseed, R6G – starch + starch + 6 g oil rapeseed + 10 g glycerol. The same letters indicate values that are not significantly different at α = 0.05

decrease the degradation of starch and the degree of its gelatinization, which contributes to reducing the water absorption. Researchers have also shown that increasing the extrusion temperature may affect the growth of *WAI*, which decreases along with an increase in the screw speed. According to Mercier and Feillet, (1975), in general the *WAI* index is elevated with a temperature increase. The authors indicate that the temperature range 180–200°C during extrusion is optimal to achieve a high index of *WAI* values, whereas exceeding them will decrease the water absorption of the product, probably due to the higher starch dextrinization.

Specific surface area

The specific surface area of products obtained during the extrusion of starch with oil added was determined using steam in the range *aw* of 0.01–0.35. The projected extrusion conditions and the quality of the raw material did not cause a large diversity in specific surface area (Fig. 3). The specific surface area of starch extrudates (control) ranged from 240 m^2/g (80 rpm) to 242 m^2/g (100 rpm). The addition of 3 g or 6 g of rapeseed oil or 6 g of linseed oil did not result in statistically significant differences (α = 0.05). Extrusion of starch containing rapeseed oil and glycerol (R6G) contributed significantly to the development of surface area. The process conducted at a slower screw speed (80 rpm) had an impact on the worse development of the surface area of the sample R6G (S_{BET} 284 m^2/g) than at higher speed (100 rpm), S_{BET} 347 m^2/g.

Bhatnagar and Hanna (1997) tested the influence of selected lipids and monoglyceride addition on porosity, density, and shear strength of maize extrudates. The authors showed that a lipid share of up to 4% in the mixture subjected to extrusion shapes lower porosity and increased density. Dextrumaux et al. (1999) studied the effect of adding fatty acids on the structure and textural properties of extrudates produced from corn grits. With an increase in the fatty acid content, the average size of the extrudate “cell” was remarkably reduced.

Extrusion of starch material with glycerol can lead to the thermoplastic starch being obtained. Glycerol is an additive that weakens the molecular degradation of starch during extrusion (Carvalho et al., 2003; Chinnaswamy and Hanna, 1990; Pan et al., 1998).

According to Raphaelides et al. (2011), as a result of extrusion of starch-fatty acids with the addition of glycerol, helical complexes of amylose and fatty acids are formed, which have a hydrophobic helix interior

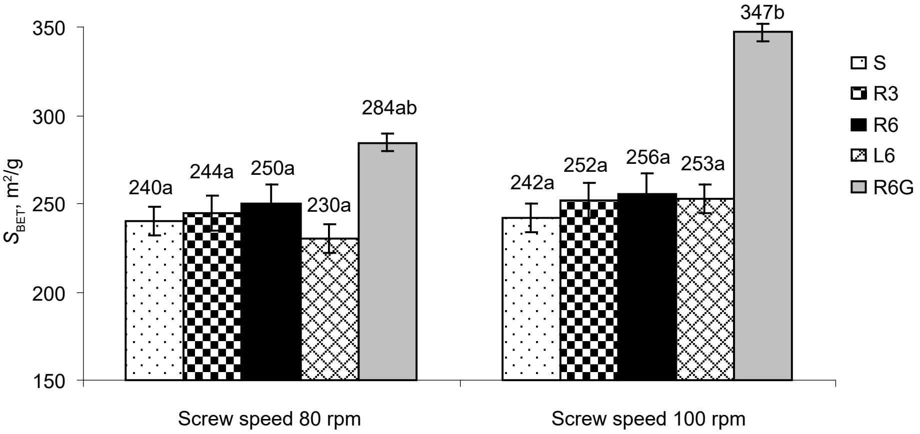

Fig. 3. Specific surface area starch-oil extrudates: S – starch, R3 – starch + 3 g oil rapeseed, R6 – starch + 6 g oil rapeseed, L6 – starch + 6 g oil linseed, R6G – starch + starch + 6 g oil rapeseed + 10 g glycerol. The same letters indicate values that are not significantly different at α = 0.05

and outer hydroxyl amyl groups that can attach the glycerol molecules by means of hydrogen bonding.

It is therefore likely that in starch extrudates with added glycerol, low starch degradation and availability of hydroxyl groups increases the hydrophilicity of the starch matrix, which is observed for sample L6G.

Fat binding

The influence of selected extrusion parameters and participation of oils in the blend on their incorporation into the structure of starch extrudates was analyzed (Fig. 4). A screw speed of 80 rpm affected permanent fat binding in the structure of the starch. Regardless of the screw speed, the R3 products obtained with the addition of 3g rapeseed oil permanently bind more than 63% of the fat added before the test. Extrudates containing 6g of rapeseed oil (R6) stably bind about half of the added oil. It can be concluded that the amount of bound oil affects the screw speed: the speed is slower, the retention time of the material in the extruder is

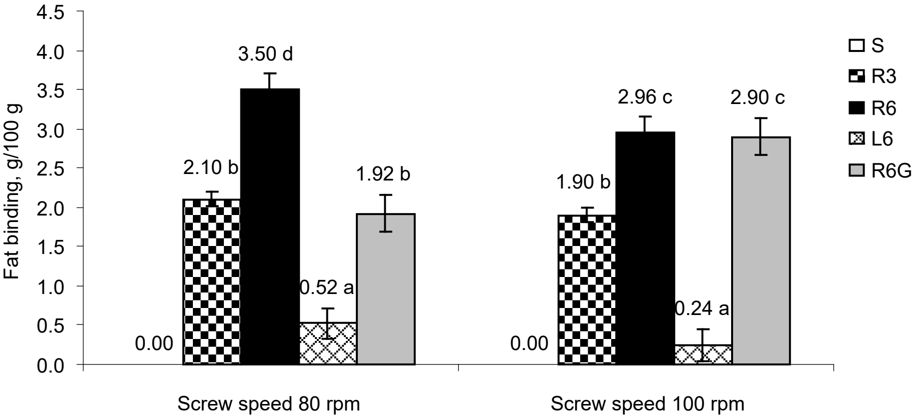

Fig. 4. Fat binding extrudates: S – starch, R3 – starch + 3 g oil rapeseed, R6 – starch + 6 g oil rapeseed, L6 – starch + 6 g oil linseed, R6G – starch + starch + 6 g oil rapeseed + 10 g glycerol. The same letters indicate values that are not significantly different at α = 0.05

lengthened, resulting in stronger fat binding. It is also likely that starch, as a hydrophilic material, has limited ability with regard to permanent oil binding.

Potassium carbonate used in a concentration of 2% or 3% results in high yields of alkyl esters of fatty acids and reduces the formation of soaps. The use of K_2CO_3 as a catalyst in the synthesis of starch esters of fatty acid influences the high degree of their substitution (Filip et al., 1992).

Extrusion of starch blends with selected vegetable oils, in the presence of a catalyst (K_2CO_3), may allow the esterification of potato starch with fatty acids. The degree of substitution of the product is a function of the fatty acid ester chain length and the type of catalyst (Junistiaa et al., 2008)

De Pilli et al. (2005; 2007; 2008) analyzed the formation of starch–lipid complexes during extrusion-cooking of almond flour (58% fat). The authors indicate that moisture and temperature are the main factors affecting the formation of starch-fat complexes. They proved a dependence between fat loss increase [%] at the highest values of barrel temperature and feed moisture. Loss of part of the lipid fraction may be associated with "melting" of previously formed starch-lipid complexes.

CONCLUSIONS

Water solubility of starch extrudates with the ddition of oils decreases with an increase in screw speed. Starch extrudates with linseed oil and rapeseed oil plus glycerol are characterized by an increase in water-absorption capacity with respect to the control extrudates. The products obtained with the addition of rapeseed oil and glycerol exhibit a significant increase in their specific surface area. The oil retention in the extruder barrel mainly depends on the screw speed. A lower speed of the screw during extrusion and the type of oil in the mixture determines the stronger binding of fat in the starch structure.

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