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THE INFLUENCE OF THE EXTRUSION ON SOME PROPERTIES OF THE PRODUCTS FROM POTATO STARCH

Abstract

Potato starch was processed in a Polish 2S 9/5 industrial twin screw extruder to study the physical and structural modifications which occur of during exstrusion. The relations betwen the physical properties and structural modifications of starch biopolymers are reported. The study of the structure of potato extrudates by the small angle X-ray scattering was developed.

Introduction

Extrusion processing of starchy raw materials is known to cause macromolecular changes in the physical constitution of the starch granule [5, 12]. Several authors have studied the changes to define the extent of modification at a molecular level necessary understand and control the extrusion process [7, 19]. The barrel temperature and moisture content in the native provide the most versatile control expansion ratio of the extrudate [3, 4, 17].

Increased process intensity, which occurs at higher temperature, higher screw speed and lower moisture content – lead to a deeper modification. The partial or complete destruction of crystalline structure of the raw starch granule in the extruder has been demonstrated by X-ray diffraction patterns and scanning electron micrographs [2, 5, 13, 15]. The extrusion produced starches of lower pastes viscosities than the unprocesed material, and the gel permeation chromatography showed that starch biopolymers were degraded into macromolecular components [8, 19].

The formation of linear oligosaccharides has been observed on the extrusion cooking of the potato starch [14].

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Also the wide X-ray diffraction and small angle X-ray scattering methods can be used to observe the changes in the long and short range ordering in a starch granules [1, 6, 11]. Especially a reflection due to long range ordering in starch (corresponding to the distance d = 10 nm) was observed by means of the SAXS method for many native materials and for products which were differently processed. The SAXS method also allows to investigate quite amorphous materials and to obtain many parameters which can be characterized in these materials.

The relations between the extent of molecular degradation starch biopolymers and the changes in physical properties of extrudate has been studied. However, the main aim of this study was to investigate the effects of extrusion processes on potato starch products by the small angle X-ray scattering.

Materials and Methods

Samples

The samples of commercial potato starch (PN-93/A-74710) were used. Approximate analysis indicated that it contained 0.26 % of ash, 0.02 % of protein /N·6.25/, 0.03 % of fat and 19.5 % of moisture.

Extrusion

Extrusion was carried out in a Polish 2S 9/5 industrial twin srew extruder (16). Barrel temperature varied over the length of the barrel from feed to die as follows: 80-120-150-170-100, 80-110-140-160-100. Feed moisture content was adjusted to 10.5% 19.5% (d.b.). The moisture 10.5% was achieved by airdrying of native starch.

Expansion

The expansion ratio was defined as the ratio between the diameter of the extrudate and the diameter of the die (expansion ratio = diameter of product/diameter of the opening). An average of 10 estimations was utilized. The diameters of airdried extrudates from each sample were measured with verrnier caliper to the nearest 0.05 mm.

Density

Ten measurements of the extrudate stick were made per extrusion duplicate. Density of extrudate was estimated as kg/m^3 according to Eq. (1);

$$\xi = m/(\Pi r^2 l) \tag{1}$$

where: r - radius, l - length, m - weight.

Shearing stress

A shear test was carred out with Instron type 4302 to determine the texture of starch extrudates. Shearing stress (N/cm^2) was calculated by dividing shear by the cross-sectional area of extrudate (averages of 10 readings).

Macromolecular degradation of starch components was estimated by means of the gel permeation chromatography of solutions in 0.1 M K0H on Sepharose CL-2B [8].

The polysaccharide concentrations in the column fractions were determined with anthron [10].

SAXS measurements

Measurements were performed on a slit-collimated Kratky camera using a Cu anode tube as the radiation source. A scintillation counter with a nickel filter and a pulse-height analyser were used to measure the scattered intensity. The samples for the SAXS experiments were prepared as follows:

– the extrudates were ground in a coffee mill to pass through a 0.2 mm screen, then, dried in an electric dryer and placed in special 1 mm capillares. The scattering curve of a given sample was available from several subsequent runs to eliminate the background scattering (scattering of the air, empty capillary, parasitic scattering of the slits, etc.). The measurements were carried out in the range of 2Θ from 0.076 to 6.52° in 0.0076 to 0.038° intervals and counting time of 100 s. Scattering curves were presented in the intensity versus q, manner as follows:

$$q = (4\Pi/\lambda)\sin(\Theta/2) \qquad (2)$$

Geometry of SAXS camera used and other measurement conditions allowed to consider these scattering curves as slit-smeared data for a beam of infinite length. The scattering curves were polished twice i.e. prior and after subtracting the background. The calculations were carried out using modified Vonk's program [21].

Results and Discussion

The investigations of the different starch samples by means of the SAXS method were focused on measurements of the long-range ordering in starch granules (ordered distribution of polysaccharide macromolecules).

It was shown in many papers [1, 6, 11] that starch slurries of different raw materials are characterized by a distinct peak in SAXS range, which may dissapear after processing. This peak may be accompanied by a number of diffraction peaks in classical diffraction range. It is illustrated in Fig. 1 and 2, which show SAXS scattering curves for slurry of raw potato starch (curve 1) and of the potato extrudate (curve 2)

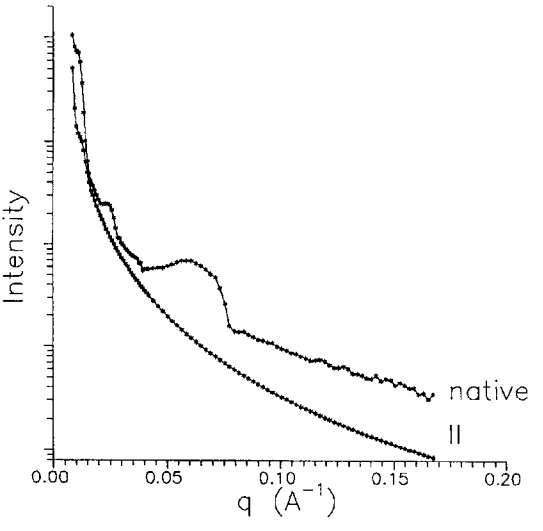

Fig. 1. SAX scattering curves for water suspension of potato starch (curve native) and potato extrudate II (curve II).

and the X-ray diffraction pattern for these materials obtained after drying the suspension, respectively. Diffraction peaks therein are due to semi-crystalline areas in starch (the peaks in the of wide angle diffraction range) and lamellar structure of semi-crystalline and amorphic areas (peak in the SAXS range).

Frequently, this semi-crystalline organization completely vanished, but SAXS method, provides to investigation of fully amorphous material. In such cases the scattered intensity is proportional to square difference betweeen electronic density of the scattered inhomogeneities and its surroudings. It depends on size and amount of these inhomogeneities. Therefore, the SAXS method is suitable for the study of inhomogeneities in condensed materials.

The characteristic of samples completed the study of starch elution (Fig. 3).

Table 1 shows treatment conditions of the extrusion process and properties of potato starch extrudates.

Results presented in Table 1 show that these samples have entirely different properties (expansion ratio, density, shearig stress) due to different extrusion conditions.

Table 1

Effect of extrusion parameters on physical and textural properties of potato starch extrudates

Sample	Barrel temp.* [°C]	Feed moisture [%]	Expansion ratio	Density [kg/m^3]	Shearing stress [N/cm^2]
I	80–170	10.50	6.10	51.94	4.03
II	80–160	19.50	1.86	365.14	301.93

* see in the text

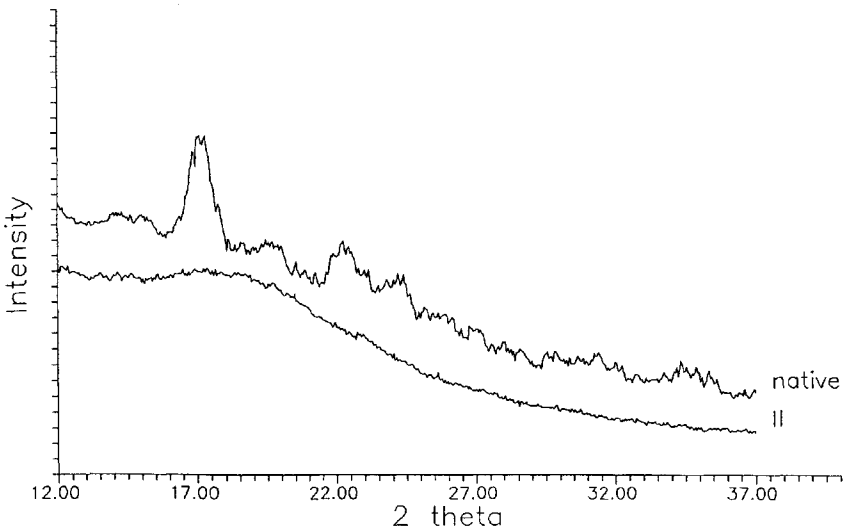

Fig. 2. X-ray diffraction pattern for native potato starch (curve native) and for potato extrudate II (curve II).

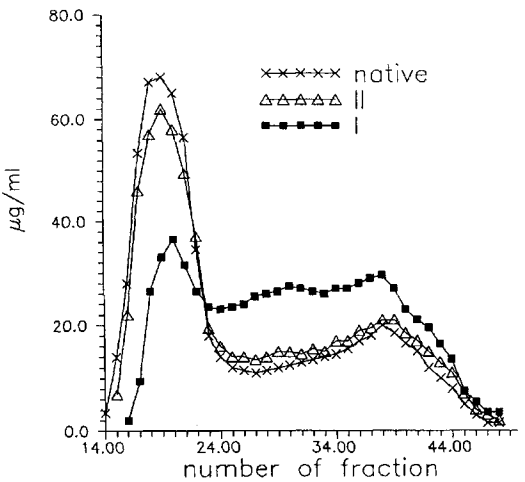

Fig. 3. Elution profiles from Sepharose CL-2B of native and extruded I (80–170°C, 10.5 % feed moisture) and II (80–160°C, 19.50 % feed moisture) potato starches.

It is generally accepted that the molecules of starch undergo degradation on extrusion [7, 9, 20]. The material eluted at the void volume from the gel permeation chromatography (Fig. 3), was amylopectin (Λ_{max}= 540–550), as identified by its reaction with iodine. On extrusion (curve 1 and 2) the contents of fraction I (amylopectin) was reduced and fraction II (amylose) was increased (tube numbers 25 and higher).

Degraded molecular products of amylopectin were eluted along with amylose forming one broad peak. The extent of this molecular transformation in extruded starch, would explain the variation of the physical properties with extrusion parameters (Tab. 1).

Fig. 1. compares the SAXS scattering curves of two samples of potato starch extrudates, properties of which are presented in Table 1. In Fig. 4. only the final part of the scattering curves are presented but sequence of the scattering curves is the same for the full measured range.

For potato starch extrudates a very interesting correlation of SAX scattering and the extrusion conditions was found (Table 1 and Fig. 4).

The expansion ratio gradually decreased from the first sample extruded more expansively to the second extruded at milder conditions.

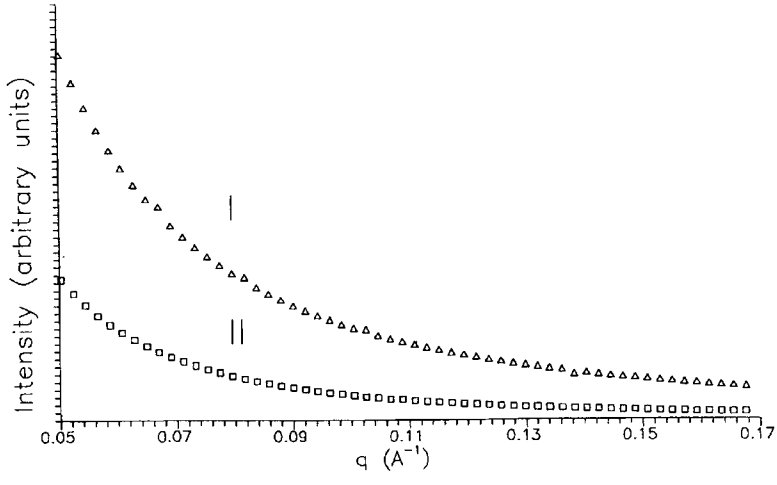

Fig. 4. The final part of the SAX scattering curves for I–II potato extrudates samples.

Investigations carried out by means of the SAXS method are presented in Fig. 4. The results show a correlation between physical properties of potato starch extrudates and intensity of the SAX scattering. The SAX scattering is the most profound for the Ip sample. This sample has the highest expansion ratio, because extrusion of the potato starch caused the formation of electronic density inhomogenieties and the more intensive process produced more inhomogeneities.

In Figs. 5, 6, the full X-ray small angle scattering curves in log-log axis are presented. The SAXS curves have very interesting pattern. In the long range of the final portion the scattering curves are almost linear. The slopes (tg α) of these parts are -2.0 and -2.6 for I and IIp lines, respectively.

Hence, question about the origin of these inhomogeneities appears.

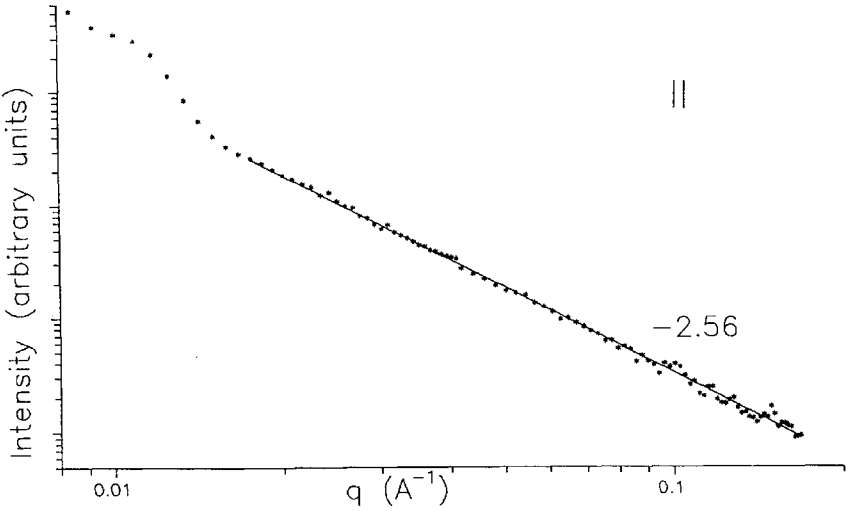

Fig. 5. SAX scattering curve (in log-log axes) for the I sample.

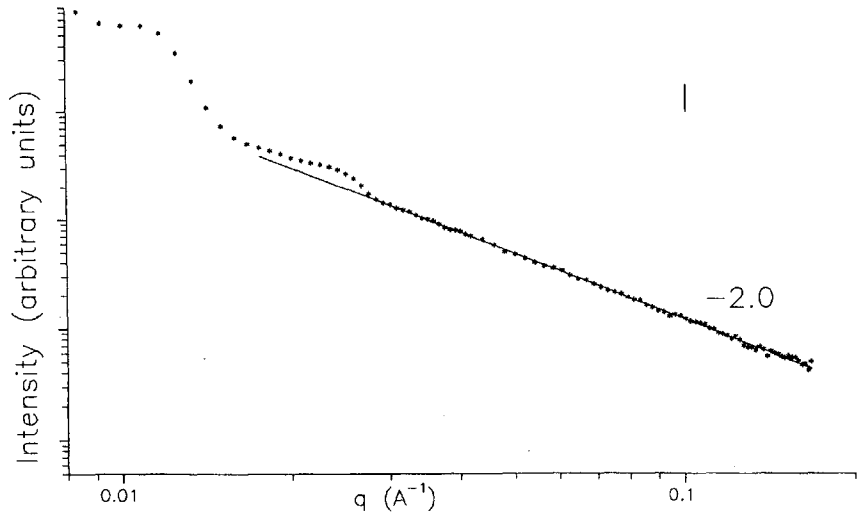

Fig. 6. SAX scattering curve (in log-log axes) for the II sample.

The SAX scattering intensity depends on the size and amount of inhomogeneities as well as on difference between eletronic density of the inhomogeneities and the surrouding. Observed intensity of the SAX scattering for four samples of potato starch is rather low. The extrusion produced the pores in the starch material but it is difficult to assume that these pores have diameter the size of which fits the range available for the

SAXS measurements (1–80 nm). When pores in a material are present and their size is within the range of SAXS measurements, the intensity of the SAX scattering is fairly high, because the electronic density of the air is very small; for example the intensity of the SAX scattering of the porous glass (with value of the specific surface about 16 m^2/g) is about 10–20 times higher than that observed for our samples. Thus, we can assume that observed SAX scattering does not originate from pores existing in the extrudates.

In the SAX scattering curves presented in Figs. 5 and 6 in the log-log system show a linearity in their long, final portions. It follows the rules for the SAXS method for a two phase system (inhomogeneities and surrounding), but for smooth-surfaced inhomogeneities slit-smeared data the slope should reach -3.

The lower slope suggests fractally rough surface of inhomogeneities [18].

Therefore, one might suggest that the inhomogeneities which were formed on extrusion originated from fluctuations and modulations of electronic density of a small part of the starch granules. **This conclusion correspond with the elution profile of extrudates; the extrusion at lower moisture levels led to an extended degradation of starch.** These fluctuations could result from a destruction of the crystalline and amorphous lamellae as well as mixing of these fragments. This suggestion needs a further proof.

Conclusions

The results obtained by the SAXS method show a link between intensity of the SAX scattering and extrudate characteristic parameters (kind of extrudate, expansion ratio, density, shearing stress) **as well as with the level of the degradation of starch biopolymers.**

The SAXS method demostrated that after the extrusion electronic density inhomogeneities are formed in the extrudates. The intensity of the SAX in the extrudate increased with the expansion ratio.

Extrudates were made in Department of Food Enginering of Agriculture University, Lublin, Poland

REFERENCES

[1] Cameron R.E., Donald A.M.: Polymer, **33**(12), 1992, 2628.
[2] Charbonniere R., Duprat P., Guilbot A., (Abstr.): Cereal Sci. Today, **18**, 1973, 286.
[3] Chinnaswamy R., Hanna M.A.: J. Food Sci., **53**, 1988, 834- 840.
[4] Chinnaswamy R., Hanna M.A.: Cereal Chem., **67**, 1990.
[5] Chinnaswamy R., Hanna M.A., Zobel H.F.: Cereal Foods World., **34**, 1989, 415-422.

[6] Cieśla K., Żółtowski T., Diduszko R.: Food Structure, **12**, 1993, 175-180.
[7] Colonna P., Doublier J.L., Melcion J.P. Monredon F., Mercier C.: Cereal Chem., **61**, 1984, 538-543.
[8] Colonna P. and Mercier C.: Carbohydr. Polym., **3**, 1983, 87-108.
[9] Davidson V.J., Paton D., Diosady L.L., Rubin L.J.: J. Food Sci., **49**, 1984, 1154-1157.
[10] Homolka J.: Diagnostyka biochemiczna. PZWL, Warszawa 1961, p. 297.
[11] Jenkins P.J., Cameron R.E., Donald A.M.: Starch, **12**, 1993, 417-420.
[12] Kaletunc G., Breslauer K.: Cereal Chem., **70**, 1993, 548-552.
[13] Kim J.C., Rottier W.: Cereal Foods World, **25**, 1980, 62-64, 66.
[14] Mercier C.: Staerke, **29**, 1977, **48**-52.
[15] Mercier C., Charbonniere R., Grebaut J., Gueriviere J.F.: Cereal Chem., **57**, 1980, 4-9.
[16] Mościcki L.: Postępy techniki przetwórstwa spożywczego, **1**, 1994, p. 46.
[17] Owusu-Ansach J., Voort F.R., Stanley D.W.: Can. Inst. Food Technol. J., **17**, 1984, 65-70.
[18] Schmidt P.W.: J. Appl. Cryst., **24**, 1991, 413-435.
[19] Tang J., Ding X.L.: Cereal Chem., **71**, 1994, 364-369
[20] Vergnes B., Villemarie J.P., Colonna P., Tayeb J.: J. Cereal Sci. **5**, 1987, 189-202.
[21] Vonk C.G.: J. Appl. Cryst., **8**, 1975, 340.

WPŁYW PROCESÓW EKSTRUZJI NA NIEKTÓRE WŁAŚCIWOŚCI SKROBIOWYCH PRODUKTÓW ZIEMNIACZANYCH

Streszczenie

W skrobi ziemniaczanej, poddanej obróbce w przemysłowym dwuślimakowym Polskim ekstruderze 2S 9/5, badano fizyczne i strukturalne modyfikacje występujące w czasie procesów ekstruzji. Omówiono relacje pomiędzy fizycznymi właściwościami i strukturalną modyfikacją biopolimerów skrobi. Rozwinięto badania struktury ekstrudatów oparte na zjawisku mało kątowego rozpraszania promieni rentgenowskich (SAXS). Wpływ gotowania ekstruzyjnego, na ekspansję, gęstość i siły ścinania produktów zostały omówione w stosunku do transformacji skrobi mierzonej metodą SAXS. Wykazano bliską zależność pomiędzy intensywnością rozpraszania SAXS a charakterystyką parametrów (wskaźnika ekspansji, gęstości, sił ścinania i makromolekularnej degradacji skrobi) ekstrudatów. Wyniki otrzymane metodą SAXS wskazywały, że po procesach ekstruzji w ekstrudatach są tworzone wiele elektronowych gęstości niejednorodności; jeśli wskaźnik ekspansji jest większy wtedy intensywność rozpraszania SAXS jest również większa. Oprócz tego, metoda SAXS pozwala wnioskować o charakterze tych niejednorodności; nachylenie końcowej części krzywej rozpraszania SAXS sugeruje, że formowane niejednorodności mają fraktalną powierzchnię.

Rezultaty wskazują nowe możliwości użycia metody SAXS do badań fizycznych i teksturalnych zmian skrobiowych ekstrudatów ziemniaczanych.