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THE USE OF THE MERCURY POROSIMETER FOR THE EVALUATION OF MICROPORE SIZE DISTRIBUTION IN POTATO EXTRUDATES

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A b s t r a c t. Several samples of potato flour extrudates were obtained by simple and screw extruder. The effects of process variables (moisture, temperature) were related to the following extrudates features: expansion, density, and shearing stress. The microstructure of the extruded products was examined by mercury porosimeter. Total porosity and changes of the average pore radius were stated in relation to physical properties of the extrudates. Total porosity decreased when the expansion of the products increased. Feed moisture was the principal determinante of physical strength, and affected changes in the number, size and distribution of the pores.

K e y w o r d s: potato extrudates, internal porosity, mercury porosimeter

INTRODUCTION

The structure of extrusion expanded products depends on starch gelatinization and the starch melt at the die of the extruder. The puffing of direct expanded products is created by heating the feed material to temperatures over 100°C. Inside the extruder the water in the dough mass remains liquid because the dough is under a pressure varying from 3 to 11 MPa. Once the molten starch exits the extruder through the die openings, super-heated water is exposed to atmospheric pressure. The vaporization of water into steam during this rapid pressure loss causes stretching and expansion of the product. The water vapor pressure, which nucleated to form bubbles in the molten extrudate, is a positive factor, it gives these products a low density and light texture [19].

The larger bubbles tend to grow at the expense of smaller ones and a small number of bubbles grow into the large cells created in the final product. A fine crumb structure is obtained with low viscosity fluids [9]. As the temperature decreases below Tg (glass transition), the product solidifies and retains its expanded shape. The shape and size of these products are determined by the die design, the viscoelastic properties of the extrudate and the manner in which they are cut. The physical characteristics of the amorphous phase depends on the chemical composition.

For example, the presence of fiber rupturs the cell walls and prevents the gas bubbles from expanding to their full potential. Expansion reduceses with fiber addition [9,14].

An increase in protein (gluten) final moisture and possibly hydrogen ion concentration toughens the extrudate [7]. High-amylose products are denser and harder. Matz [15], recomends a 5-20% amylose level in starch to give adequate crispness and acceptable texture. The resistance of corn extrudates to crushing is less than that of wheat starch or flour [10], irrespective of density or pore characteristics.

Cooling rate after extrusion could be responsible for the wall properties. Hutchinson *et al.* [11] notes that the force required to break the surface of an extrudate is larger than that needed to break an internal pore wall.

It is well known that characteristics of extrudates such as texture, structure, expansion and sensory properties are affected by the many variables in the extrusion processes. Owusu-Ansah *et al.* [17] revealed the textural and microstructural changes in corn starch as a function of specific extrusion variables.

The porosity of the extrudates increases with decreased feed moisture, parallel to an increase in expansion and a decrease in breaking strength. Texture and sensory properties of extruded products are related to their degree of expansion [5,9,20]. Extrudates with various expansion ratios differ in the size, number and distribution of the air pockets [6,14]. Scanning electron microscope and image analysis have been used to examine the microstructure of extrudates [2,6,22].

The quantitative characteristic of various pores of extrudates is difficult to perform by most common laboratory methods. According to earlier works it is possible to determine internal porosity in an extrudate with a mercury porosimeter [8,21]. Therefore, in this work the mercury porosimeter to study the microstructure of extrudates was used. Some relations of physical properties of potato flour extrudates and their microstructure were found.

MATERIALS AND METHODS

Samples

Samples of commercial potato starch were used (PN-93/A-74710). Approximate analysis indicated that they 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 the Polish S45 and S 9/5 twin screw extruder, described by Mościcki [16]. Extrudates were made in the Departament of Food Engineering of the Agriculture University, Lublin, Poland.

The barrel temperature was differentiated over the length of the barrel from feed to die as follows: 1) 80-120-150-170-100, 2) 80-120-150-170-100, 3) 145-165-120, 4) 100-140-180-200-120, 5) 80-110-140-160-100 °C. The feed moisture content was adjusted to 10.5%, 13.5%, 14%, or 19.5% (d.b.). The moisture of 10.5%, 13.5% and 14% (d.b.) was achieved by air-drying of native starch.

Expansion

The expansion ratio was defined as the ratio of the diameter of the extrudate and the diameter of the die (expansion ratio = diameter of product/diameter of the opening). An average of 10 determinations was obtained. The diameters of air-dried extrudates from each sample were measured with a vernier caliper to the nearest 0.05 mm.

Density

Ten measurements of the extrudate stick were made per extrusion duplicate. Density of extrudate was recorded as kg/m^3 with pattern:

$$\zeta = \frac{m}{\Pi r^2 l}$$

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

Shearing stress

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

Mercury porosimetry

A Carlo Erba 2000 Hg intrusion porosimeter, linked to a Carlo Erba CUT/HEC 960 computer (Carlo Erba Strumentazione, Rodano, Italy), was used to determine the distribution of pore radii. One gram of <0.2 mm air-dried extrudate or whole samples were used; outgassing for 24 h was performed before measurements.

To find a correspondence between intrusion pressure and pore radius values, we assumed that pores were cylindrical in the calculations, and a surface tension value for Hg of 0.48 N/m extrudate contact angle of 141° were used in the Laplace equation. The pressure varied from 100 kPa to 200 MPa, and corresponded to a pore radius range of 3.6 to 7.5 μm.

RESULTS AND DISCUSSION

The porosity affected by the extrusion processes

The structure of potato extrudates obtained under different condition processes were analysed.

The physical aspects of 1-5 samples of extruded potato starch are shown in Table 1 and on Fig. 1. Feed moisture and temperature are the most significant of the extrusion variables. The increase in the expansion ratio of potato flour extrudates is clearly related to the decreasing moisture. The density and shearing stress of extrudates is reflected the change in expansion ratio. Expansion ratio, density and shearing stress depend on the coupling temperature and feed moisture in the barrel.

It is possible that this response is related to the specific properties (elastic, plastic) of the extrudates [9,13]. Optimization of the extrusion conditions resulted in maximum expansion of corn starch [4]. In the extrusion

Table 1. Effect of extrussion variables on physical and textural properties of potato starch products

Sample	Barrel temp. (°C)	Feed moisture (%)	Expansion ratio	Density (kg/m^3)	Shearing stress (N/cm^2)
1	80-170	10.50	6.10	51.94	4.03
2	80-170	14.00	4.78	87.49	13.30
3	145-165-120	13.50	3.77	108.94	14.24
4	100-200	14.00	3.34	196.57	51.24
5	80-160	19.50	1.86	365.14	301.93

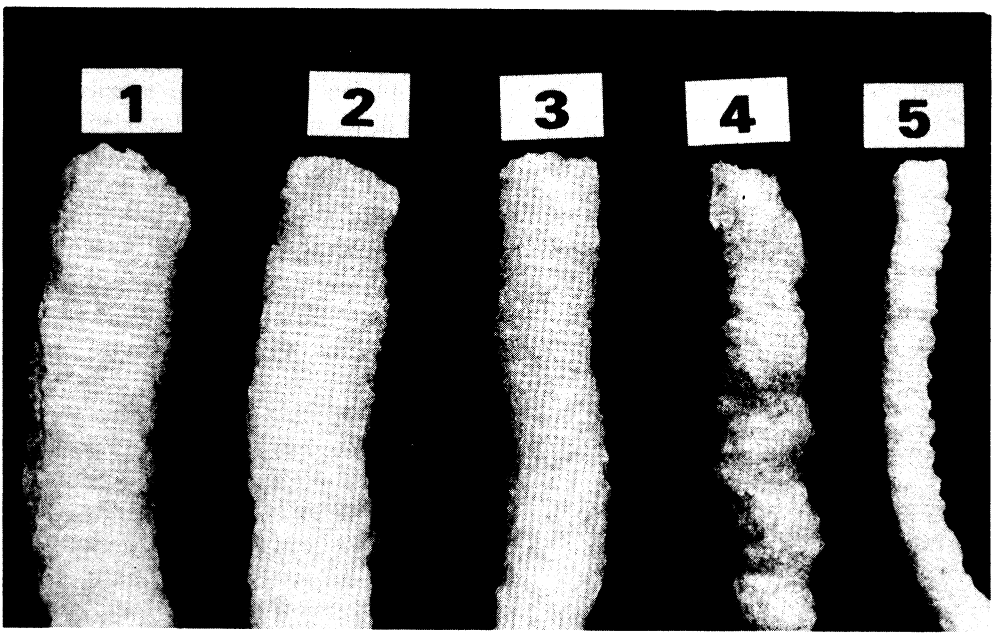

Fig. 1. Effect of extrussion processes on expansion ratio of potato starch products

processes, it was shown that starch gelatinization leads to an expanded texture [3,18]. Highly expanded products showed very porous structures with large numbers of air pockets. In such products moisture decrease leads to the development of structure. The porosity increases with the increase in expansion and decrease in shearing stress [14,17].

In recent works, the microstructure of extrudates has been analysed by the SEM method. The pictures usually show the size and distribution of air cells, their shape, and the thickness of their walls.

Such air pockets contain from several hundred to several thousand microns and they are visible to naked-eye. The value of the breaking the force and the amount of peaks received during the process of destroying such products inform us about their porosity and can be an attribute of some of the sensor features [17].

Internal porosity (TP) of extrudates evaluated by the mercury porosimeter

Not much attention was paid to the analysis of the micropores. However, we known that they appear in air cell walls and their sizes range from tenth parts of a micron to several microns. Their size and distribution depend on the extrusion variables and feed composite. Increased fiber content in corn feed increased the number of apertures in cell walls and reduced big air cells. Thus, the expansion ratio reduced with the fiber addition [12,14].

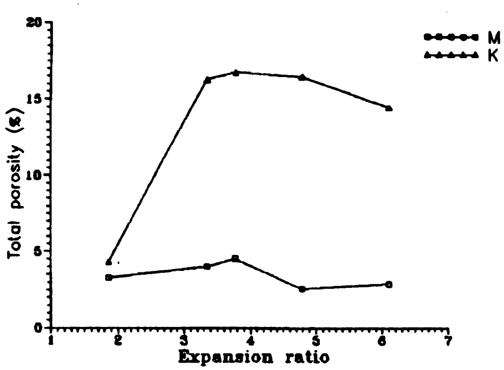

Fig. 2. Relationship between total porosity and expansion ratio on potato extrudates. K - natural extrudate, M - ground extrudate.

In corn meal extrudates with 10-30% of wheat bran addition, an abundance of spherical particles was observed in air cell walls [14]. According to Abdel-Aal E.-S.M. *et al.* [1], after coarse grinding the extrudates become micro-flakes which have distinguishable differences in size, thickness, and appearance.

The microstructure of natural and ground potato extrudates was analysed with the mercury porosimeter. The extrudates porosity (TP), calculated with the assumption of cylindrical pore model, depended on the expansion ratio.

This dependence was clearer for the natural extrudate samples (Fig. 2). Grinding of the samples visibly decreased their porosity, causing a significant averaging of the TP value and its practical independence from the expansion ratio. The TP values of the natural samples ranged from about 4% to 15%, and the values of the ground samples ranged from about 2.5% to 4.5%.

The comparison of the porosity values with the TP values for the initial material - potato flour (about 26%) indicates a significant decrease of the TP values in potato extrudates and allows us to state that the technological conditions of the process cause changes in the properties and microstructure of potato flour. This assertion is also supported by the absence of the dependency of TP on the expansion ratio for the ground samples.

A similar dependency was observed for the investigated samples between the size of the average radius of pores and the expansion ratio (Fig. 3).

Grinding the samples causes averaging of the value of the mean radius and its practical independence from the expansion ratio. Its comparison with the initial material (3 μm) indicates the decrease in the average pore radius. In the ground samples (Figs 2 and 3), small TP values were found (from 2.54% to 4.51%), with the pore radius from 1.62 μm to 2.20 μm. The lowest TP values were observed in the

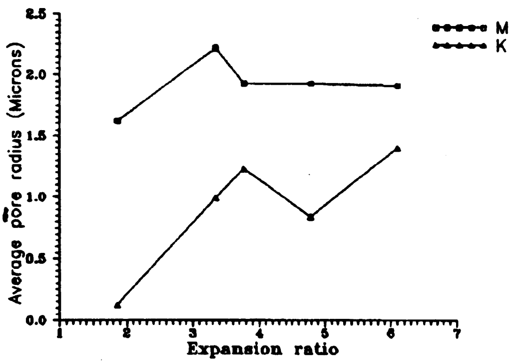

Fig. 3. Relationship between average pore radius and expansion ratio on potato extrudates K - natural extrudate, M - ground extrudate.

samples with the greatest expansion degree (Tabele 1, samples 1 and 2). It should be concluded that in those samples, the walls were very smooth and were of small internal porosity. Generally, in the ground samples, a greater number of pores with a radius bigger than 1 μm were observed.

However, the samples with the high expansion ratio showed a significant decrease in the number of pores with radius smaller than 1 μm.

The relation between the number of pores and their radius is illustrated by the cumulation curve (integral) and the differential curve. The differential curve is called a distribution curve (PSD). Figure 4 ABCDE shows the PSD curves for the chosen extrudate samples and for the native material (Fig. 4N), instead Fig. 4 A'B'C'D'E'N' shows cumulative curves for the same samples. As we can see, their character is similar and they indicate the weak porosity of the material despite the value of the expansion ratio. The PSD of the natural extrudate samples show differentiated character and indicate their porous structure; in samples 1 and 3 the pores are of the same size but their number is different.

In sample 1, a small number of pores with a radius ranging from 0.01 μm to 5.5×10^{-2} μm was observed, while in this range of the radius, in sample 3, greater numbers appeared (Fig. 4A, A' and C, C').

It seems that grinding of the highly expanded product may cause a significant disappearance of pores in the range below 1 μm.

In the sample of high density (sample 5, Fig. 4E and E') the appearance of pores with a radius below 0.01 mm was observed, which to some degree, could constitute the reflection of the micropores from the native material.

It seems that the extrusion conditions may have an important influence on the changes of microporosity in the range from 3.6 nm to 7.5 μm. Feed moisture (about 14% d.b.) influenced the maximum growth of microporosity in both natural and ground products.

Relatively high TP values were noted in the samples of investigated natural extrudates (14.42% to 16.76%), and in the most dense sample, the TP (4.30%) was close to the value of the ground sample (3.29%). In the sample with a high expansion (1), usually containing big air pockets, relatively low internal porosity values were observed, which can confirm the smooth surface of the puffed extrudates.

In the analysed sample the higher number of pores with a radius of over 1 mm, as well as a small number of pores with the radius of 5.5 x 10^{-3} μm to 5.5 x 10^{-1} μm were stated.

In the samples with a decreased expansion ratio, the number of pores with a radius below 1 μm up to 0.1 μm was the highest.

In the extrudates with great shearing forces, very compacted, the pore distribution was from 0.01 μm to about 7 μm; and great number of the pores were below 0.1 μm to 0.01 μm. The comparison between the PSD of extrudates with the PSD of the native material indicates a significant decrease in the pores with the radius from 1 μm to 10 μm in the product.

The transsectional surface of potato extrudates was examined by SEM. The micrographs obtained showed good agreement between the internal structure determined with the SEM method and mercury porosimeter (data not shown).

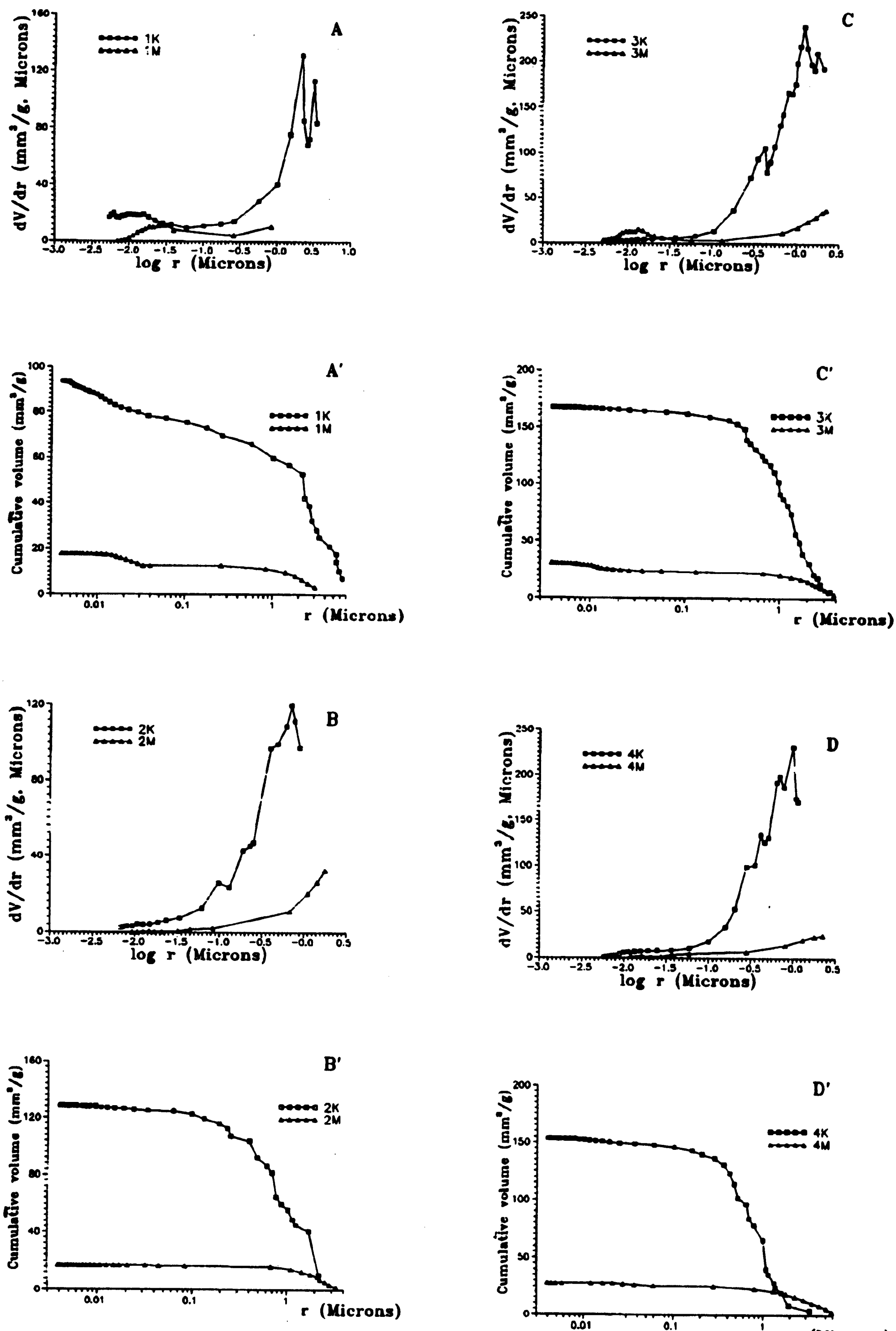

Fig. 4. Pore size distribution (ABCDE) and cumulative pore size distribution (A'B'C'D'E') for potato extrudates and for native material (N and N', respectively). K - natural extrudate, M - ground extrudate.

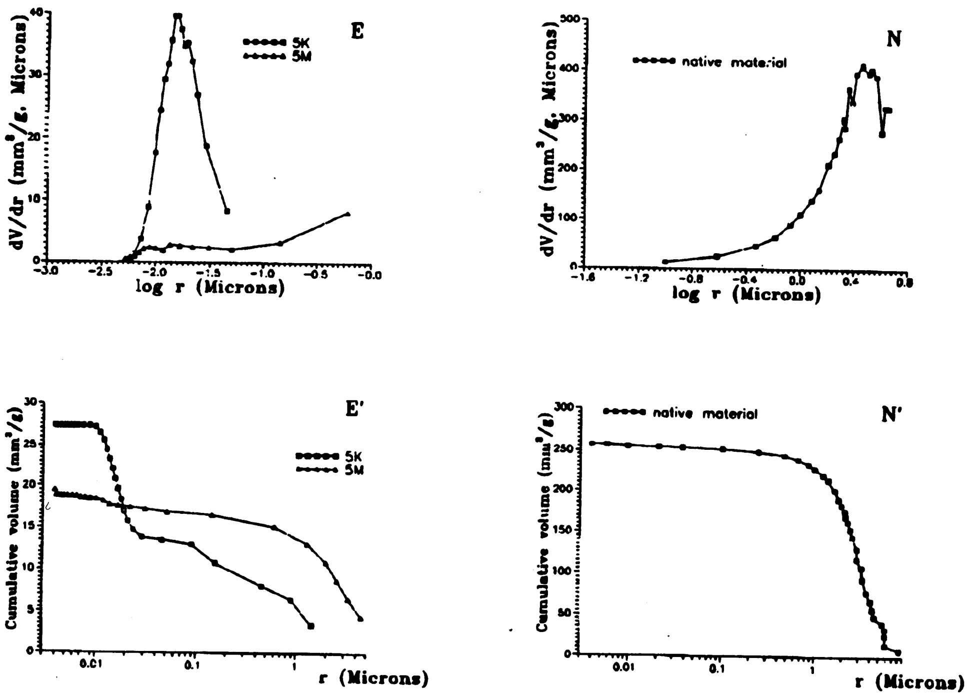

Fig. 4. Continuation.

CONCLUSION

It may be concluded from this study, that feed moisture is the most significant variable related to the expansion of flour potato extrudates. The microstructure of the extrudate is reflected in both the expansion and the physical strength of products. The shear stress of the extruded starch products was inversely proportional to the expansion volume.

The technological conditions of the extrusion process changed the properties and the structure of the native material. Total porosity average pore radius, pore size distribution, and cumulative curve were significantly lower for the natural and ground extrudates as compared to the native material.

Highly expanded samples showed lower internal porosity, from which we can conclude that after the radial expansion, the cell walls remain smoother. In extrudates with increasing density, the appearance of greater number of micropores was noted.

The crisp texture and total porosity volume of starch structure can reflect its rheological properties which need to be controlled in the extrusion process to produce the desired and uniform puffing.

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