MOISTURE SORPTION HYSTERESIS IN POTATO STARCH EXTRUDATES

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A b s t r a c t. Moisture sorption hysteresis loops of potato starch as native material and their extrudates were investigated to help understand the nature of the sorption process. The hysteresis loop for potato starch extrudate was greater than that for native potato starch. This was explained as a difference in internal porosity volume and changes in the structure of the absorbent. Some qualitative relationship between cumulative volume and the sorption dates calculated on the basis BET parameters were observed.

K e y w o r d s: sorption hysteresis, cumulative volume, potato extrudates

INTRODUCTION

The isothermal equilibrium relationship between moisture content and water activity of the food is represented by the moisture sorption isotherm, which has an important theoretical and practical implications [9]. Water affects the texture of dry food materials by plasticizing and softening biopolymers. These changes in starch and protein matrix alter the mechanical strength of the products. Katz and Labuza [10] proved the crispness intensity and overall hedonic texture of dry snack food is a function of water activity. Extruded dry foods loose crispness, when they adsorb moisture. Thus, they should be protected against environmental water vapour. Water activity is important for describing product-process interactions in many unit operations in food manufacturing, e.g.: drying, wetting, agglomerating, packaging, storing.

However, information on the texture of snack food and water activity is scarce in literature. The effect of water activity of 0.23 -0.84 range on the textural characteristics of puffed rice cake was shown [7]. Fornal *et al.* [5] assessed the quality and stability of extruded corn products. Świtka and Fornal [15] evaluated the suitability of selected mathematical equations to describe sorption isotherms of extruded corn derivatives.

The purpose of the present investigation was to obtain moisture sorption equilibrium data to characterize water sorption properties of extruded potato starch products.

MATERIALS AND METHODS

Materials

In the study, the samples of commercial potato starch (PN-93/A-74710) and their extrudates were used. Native potato starch contained 0.26% of ash, 0.02% of protein (Nx6.25), 0.03% of lipids and 19.5% of moisture. Starch products were presented earlier in the evaluation of pore size distribution, in our work [8].

Adsorption-desorption isotherm

The adsorption-desorption isotherms were measured using a vacuum chamber thermostat

system. Approximately 3 g of the ground extrudate samples were placed in glass vessels over water saturated sulfuric acid solution. Sixteen levels of relative water vapour pressures were selected in the range between 0.01 to 0.96. After 2 days of equilibration the mass of the samples with the adsorbed water was measured by weighing. The relative water vapour pressure, p/p_0, was estimated from the density levels of the sulfuric acid solutions measured after completing each equilibration step. The amount of adsorbed water was calcu- lated on the basis of the dry mass of the samples after finishing the adsorption measurements. All the samples were dried to a constant weight in an oven at $378^\circ K$. During the measurements the temperature was kept constant at $293^\circ K \pm 1$ and all the adsorption measurements were replicated three times.

The experimental adsorption-desorption isotherms were approximated using the B.E.T. equation [3]. The surface areas were determined from monolayer capacities assuming that the area occupied by water molecule is equal to $1.08 \ 10^{-19} m^2$ [11].

RESULTS AND DISCUSSION

Moisture sorption hysteresis and water activity

The adsorption and desorption isotherms of five extruded potato starches, Z1, Z2, Z3, Z4, Z5 and one native starch, Z0, are determined at $293^\circ K$, and selected samples are plotted in Figs 1 to 3. According to the classification of Brunauer *et al.* [3], the adsorption and desorption isotherms for the starches were of a typical sigmoid shapes of II type. The moisture sorption hysteresis loops for these potato starches were typical of sweet potato and kudzu starches as reported by Boki and Ohno [2]. The adsorption and desorption isotherms showed the effect of some physical properties of these products for, e.g. density and expansion ratio (Fig. 4) on the sorptive capacity of the material. At water activities of 0.01-0.80 range, the amounts of moisture sorbed by native and extruded starch were similar. At water activity above 0.80, greater
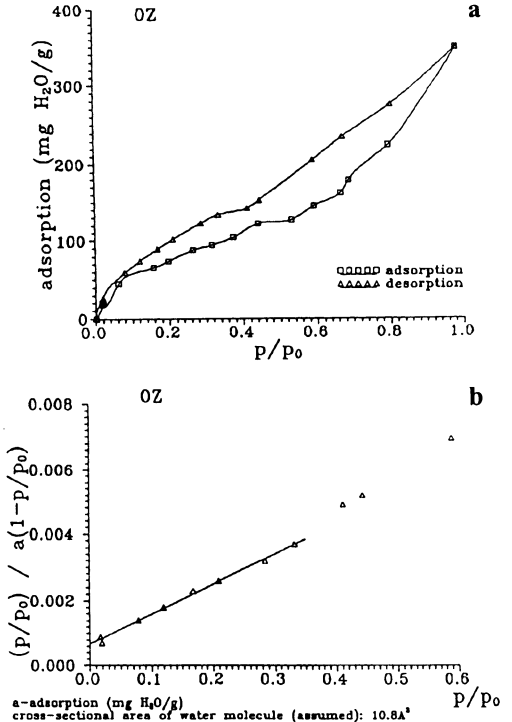
Fig. 1. Water vapour isotherm: hysteresis loop for the native potato starch (0Z) (a), desorption branch in B.E.T. coordinates (R=0.997, linearity ranges, p/p₀: 0.01-0.35) (b).

moisture increase in the extrudates was noted (Figs 1-3). According to Van den Berg and Bruin [16], a general sigmoid sorption isotherm is divided into three different parts; at different water activity ranges: I (0~0.22), II (0.22~0.73), III (0.73~1.0). Ranges II and III are characterised by sorption or penetration of water molecules into newly created pores of the already swollen structure and following mechanical entrapment in the void spaces of starch. Therefore, water uptake particularly at higher water activity seems to be easier in earlier deformed (during extrusion cooking) starch matrix than in the starch with granular structure. The experimental data have been approximated using the B.E.T. equation. An example of the linear form of the B.E.T. plot, determined, at p/p₀ from 0.01 to 0.35, for the samples Z0 and Z1 from desorption branch is shown in Figs 1b and 2b. The values of the corelation coefficient, R,
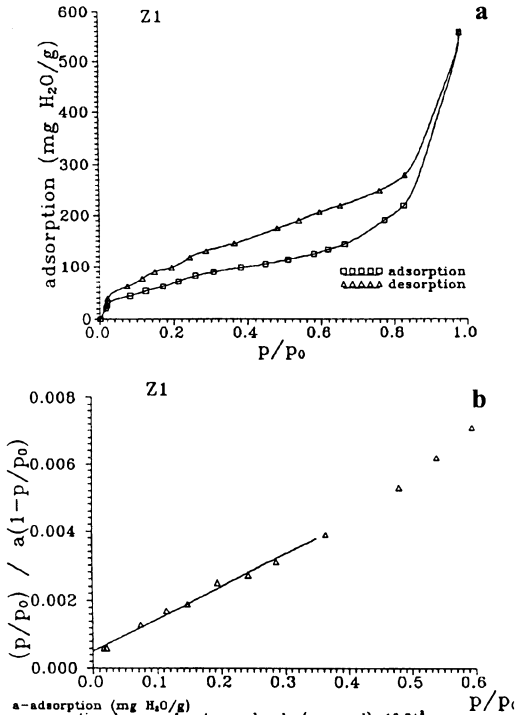
Fig. 2. Water vapour isotherm: hysteresis loop for the starch extrudate (Z1) (a), desorption branch in B.E.T. coordinates (R=0.993, linearity ranges, p/p₀: 0.01-0.35) (b).
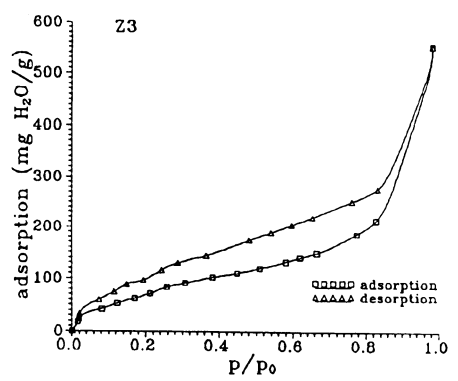

Fig. 3. Hysteresis loop for the starch extrudate (Z3).

indicate that the B.E.T. equation provides a good fit to the measured sorption data.

Characteristic features of type II isotherms are its hysteresis loop which is usually associated with the capillary condensation in the mesopore structures. In our case, the hysteresis loop corresponds to type H4 of the JUPAC [13]. The knee of the isotherms are rounded and is associated with the low value of C_{BET} constant, C, or the low net heat of adsorption [6].
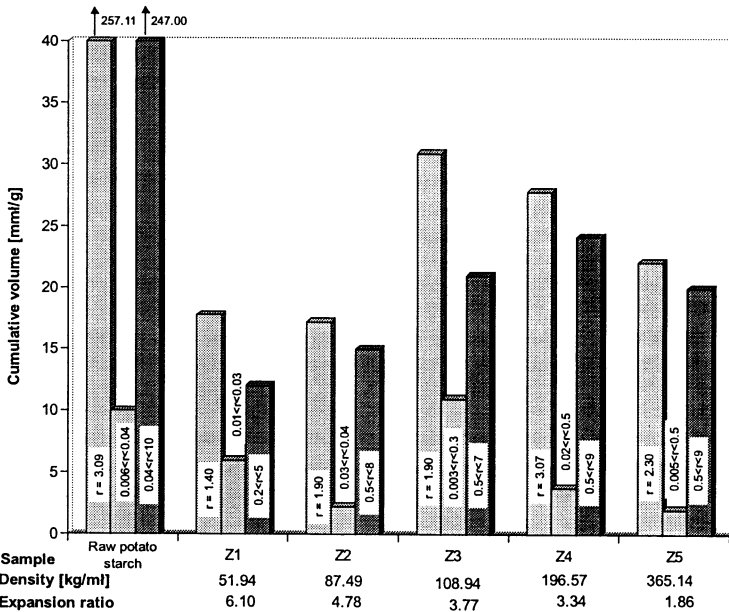

Fig. 4. Changes in the cumulative volumes of pores in different ranges of radius size in relation to the density and expansion ratio.

Low values of the B.E.T. constant, C (Table 1), indicate that starch extrudates are not a micropore adsorbents. The constant C, is often used to calculate the net heat of adsorption [12]. In the case of the investigated potato starch products the value of the net heat of adsorption or adsorption energy is up to 50.9-51.4 kJ mol^{-1} and 50.4-51.4 kJ mol^{-1} of the desorption processes, respectively. Evaluated energies are rather close to the heat of water condensation (43.9 kJ mol^{-1}), which proves that all the samples posses low energy surface.

example a vapor condensation in the small pores and irreversible swelling [14].

Relation: surface area - monolayer capacity and internal porosity

Extrusion cooking processes have been investigated mainly for the functional properties of the extruded products. The evaluation of expansion ratio and density can be the measures of the physical nature of the extrudate. The internal structure of the extrudates determines their textural properties. The difference in

T a b l e 1. Values of monolayer moisture capacity and sorption area of starch materials calculated by the B.E.T. equations

Sample	Adsorption isotherm			Desorption isotherm		
	Surface area (mg^2g^{-1})	Monolayer capacity $(mg\ g^{-1})$	BET constant C	Surface area $(m^2\ g^{-1})$	Monolayer capacity $(mg\ g^{-1})$	BET constant C
raw potato starch	259.7	71.9	20.4	368.7	102.0	14.5
Z1	241.1	66.7	21.3	327.2	90.6	25.8
Z2	248.4	68.7	18.6	347.2	96.1	17.7
Z3	294.2	69.0	17.7	347.2	96.1	17.7
Z4	341.3	66.8	18.2	344.2	95.2	17.6
Z5	214.4	59.3	21.3	328.1	90.8	21.8

Table 1 shows the effect of physical properties of the extrudates (see Fig. 4) on their monolayer moisture capacity and surface area. Application of native and extruded materials resulted in higher (71.9 mg g^{-1}, for adsorption and 102.0 mg g^{-1} for desorption isotherm) and lower (59.3-66.7 mg g^{-1} for adsorption and 90.6-96.1 mg g^{-1} for desorption isotherm) monolayer capacity, respectively. For all the examined starches, the B.E.T. surface area, S, estimated from the adsorption isotherms was of the range from 214.4 to 341.3 m^2 g^{-1} for the extrudates and of 259.7 for the native starch. The valeus evaluated from the desorption isotherms from 327.3 to 347.2 for the extrudates was equal to 368.7 for the raw material.

Higher values of the monolayer capacity and surface area (obtained from the desorption branch) could result from the change in surface structure of the adsorbent at dehydration, for

monolayer values and sorption areas could be attributed to the changes in the porous structure of the extrudate wall. High mechanical pressure used in pasta extrusion has been found to reduce the porosity and moisture diffusivity of wheat flour [1]. Porosity and pore size distribution may affect the physical structure and texture of extruded foods [4]. Thus, structure depends on the organization of cells in the extrudate, in particular on the shape and size of the cells. In the earlier study we found the relationship between porosity of the cell wall of potato starch extrudates and their expansion ratio [8]. Table 1 shows moisture sorption capacity and sorption area of the potato starch material. The small difference in the monolayer values and sorption area could explain some slight changes in the porous structure of the products.

On the basis of the cumulative volume curves determined by the mercury porosimeter,

in Fig. 4, the total cumulative volume (of the average pore radius) and the volume of pores with smaller as well as bigger radius was shown. According to the earlier study on Gregg and Sing [6], capillary condensation takes place in the mesopores and influences the characteristic hysteresis loop. Thus, mesopores do not play any significant role in the changes of the surface area and monolayer capacity of the extrudates. It seems that the proportion of pores with small radius (in the range of a hundredth part of a micron or less) in the cumulative volume may have a significant effect on both the surface area and monolayer capacity. From the adsorption data it follows, that samples Z3 and Z4 have the biggest surface area which corresponds to the biggest values of cumulative volumes of these samples. Samples Z1 and Z2 with the highest expansion ratios are characterised by the lowest total cumulative volume, and small proportion of pores with 0.01-0.04 μm radius, as well as a slight difference in the surface areas (241.1- 248.4 $m^2 g^{-1}$). Sample Z5 does not fit to the pre- sented analysis. It has the highest density and a very low volume of pores (about 2 $mm^3 g^{-1}$) with the radius in the range of 0.005-0.5 μm. On the other hand, it has the smallest surface area with a relatively high cumulative volume made up of mainly the pores with the radius in the range of 0.5-9 μm. Supposedly this kind of pore structure (with an excess of big pores) determines the small surface area of examined extrudates.

Highly expanded sample (Z1) showed lower internal porosity. Probably, after the radial expansion, the cell wall remained smoother. In the extrudate with increased density (sample Z5), greater number of micropores [8] in which capilary condensation take place was noted [6].

CONCLUSIONS

The moisture sorption isotherms of extruded potato starch products resemble the sigmoid shape of type II B.E.T. classification with small values of monolayer moisture capacity and a large hysteresis loop.

Only small differences in the B.E.T. parameters were observed in the samples Z1 and Z5 despite the significant changes in the density and expansion ratio.

The main differences of between the native potato starch and extrudated products were observed for the water activities above 0.8.

The porous structure of the absorbent affected mainly the values of the monolayer moisture capacity and surface area.

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