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EVALUATION OF THE USABILITY OF SORPTION ISOTHERMS FOR SPECIFICATION OF WEIGHT GROWTH FACTOR IN NOODLE PRODUCTS

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Abstract. The studied noodles were characterized by a homogenous chemical composition. The sorption isotherms were specified with the static-desiccator method at a temperature of 20°C. The equilibrium water content essentially depended on the type of product. Significant growth of the water content was noted in both studied noodles at a_w of about 0.75. Above $a_w = 0.75$ some capillary condensation probably occurred. Based of the BET equation, the monolayer capacity was determined for the two types of noodles (noodle I – 6.34 and noodle II – 5.78 g (100 g d.m.)$^{-1}$) and – on its basis - their proper sorption area (MI – 222.9 and MII – 202.9 m^2 g^{-1}). The general capillary capacity was also determined in the range of capillary condensation, showing a higher value of this parameter in the MI noodle. Based on the Kelvin equation, the most probable capillary radius was determined, and the radius of capillaries undergoing fulfilment in the initial stage of condensation. However, sorption isotherms proved to be inadequate for the prediction of weight growth in noodle products.

Keywords: sorption isotherms, monolayer, sorption surface, water activity

INTRODUCTION

Weight growth factor is a parameter whose value is a resultant of material quality and technology and indicates the behaviour of the product during culinary processing.

The weight growth factor is an indicator determining the proportion of cooked noodle mass with relation to raw noodle mass. Its value indicates the ability of a product to bind water and it is a reflection of the state of water bonding substances, first of all proteins and starches. Additionally, the value of the weight growth factor can be a determinant of product usability in the economic sense. It indicates how much of the cooked product can be achieved from a specified amount of raw product (Obuchowski 1997).

OBJECTIVE

The objective of the research reported was to determine the connection between the character of noodle surface determined by the type of die used during the drawing and the ability to absorb water during culinary processing that is shown in the value of the weight growth factor.

MATERIAL

The materials studied were "egg-free" noodle-type spaghetti (MI and MII) produced on the basis of semolina from hard wheat *Triticum durum* Desf., modified by Navigator. Both types of noodles were produced in industrial conditions by one of the Polish producers. Noodle MI was drawn using a phosphorus-bronze die, as a result of which its surface is matt and rough. Noodle MII was drawn using a Teflon die, as a result of which its surface was shiny and smooth. Both types of noodles were dried at high temperatures (80-120°C) for 4-5 hours.

The noodles were stored in hermetically sealed polypropylene foil packages, under normal conditions, and unpacked directly before the determinations.

All reagents used for analysis and preparation of saturated saline solutions were pure reagents for analysis.

METHODS

The course of sorption isotherms of the studied noodles was determined with the static-desiccation method using saturated saline solutions. The scope of testing included water activity from 0.07 to 0.98 (Świtka 1992, Tyszkiewicz 1987). The temperature was 20°C. The time of system equilibrium settlement was 80 days. Achieved results were presented using the EXCEL program.

The BET equation was determined on the basis of empirical data with the method of the least squares. Adjustment of the empirical data to the BET equation was made on the basis of average value of the calculation error (Se), determination factor (R^2) and the correlation index (R) (Makać *et al.* 2000, Łomnicki 2006).

In order to determine the parameters of the sorption process, such as monomolecular layer capacity with corresponding water activity and energy constant, the BET equation was used as follows:

$$a = \frac{\nu_m c \frac{p}{p_s}}{(1 - \frac{p}{p_s})[1 + (c-1)\frac{p}{p_s}]} \qquad (1)$$

where: a – adsorption (kg kg^{-1}), v_m – maximum adsorption magnitude corresponding to complete surface coverage in monolayer of adsorbate (kg kg^{-1}), c – constant related in an exponential way to the difference between the heat of adsorption between the first and following layers, accepted to be constant and equal to the heat of condensation, p – vapour pressure of the adsorbed chemical compound in its gas phase (Pa), p_s – adsorbed chemical compound vapour pressure over the liquid in balance with adsorption temperature (Pa) (Atkins 2003, Ościk 1979, Paderewski 1999).

Knowing the volume of water vapour adsorbed at a temperature lower than the boiling temperature and the so-called surface of sitting water, the specific surface of the adsorbent was calculated based on the following equation:

$$a_{sp} = \omega \frac{v_m}{M} N \tag{2}$$

where: a_{sp} – specific surface sorption area (m^2 g^{-1}), N – Avogadro number ($6.023 \cdot 10^{23}$ molecules mol^{-1}), M – water molecular mass (18 g mol^{-1}), ω – surface of water sitting ($1.05 \cdot 10^{-19}$ m^2 molecule^{-1}) (Paderewski 1999).

The size and capacity of capillaries of the tested material were determined on the basis of the run of the isotherms of adsorption within the range of capillary condensation. Calculations were made on the basis of Kelvin equation:

$$\ln \frac{p}{p_s} = \frac{2\sigma v}{r_k RT} \tag{3}$$

where: v – molar volume of adsorbed water (kg kg^{-1}), σ – surface tension of liquid at temperature T (N m^{-1}), r_k – radius of the capillary (m), R – gas constant (8.314 J (mol K)$^{-1}$), T – temperature of the process (K) (Ościk 1979, Świtka 1992).

The graphical interpretation of the obtained pairs of numbers (*V-r*), called the structural curve, formed the basis for the determination of capillary radius (*dV/dr-r*) with the use of the method of graphical differentiation of distribution curves. The maximum values for the distribution curves corresponded to the most frequently occurring pore radii (Świtka 1992).

Weight growth factor (A) was calculated according to the equation:

$$A = \frac{M_u}{M_s} \tag{4}$$

where: M_u – cooked noodle mass (kg), M_s – raw noodle mass (kg) (Obuchowski 1997).

DISCUSSION OF RESULTS

The comparison of the sorption features was based on the evaluation of:

- mutual positions of adsorption isotherms determined at the temperature of 20°C (Tab. 1, Fig. 1),
- adsorption isotherms parameters determined on the basis of the BET model (Tab. 2),
- structural characteristics of studied products determined on the basis of Kelvin equation (Tab 3),
- weight growth factor (Tab. 4).

Table 1. Results of the t-Student tests concerning the difference between average values at different experimental variants

a_w	MI			MII			$t_{e.}$	$t_{c.}$
	X $_{śr}$.	SD	V (%)	X $_{śr}$.	SD	V (%)		
0.070	4.974	0.043	0.870	4.456	0.074	1.655	10.47	4.303
0.111	5.881	0.019	0.325	5.256	0.031	0.588	29.45	4.303
0.231	7.898	0.016	0.202	7.123	0.061	0.859	21.23	4.303
0.330	9.317	0.017	0.185	8.492	0.044	0.513	30.45	4.303
0.440	10.27	0.009	0.092	9.639	0.003	0.027	112.8	4.303
0.548	11.18	0.004	0.037	10.49	0.006	0.058	162.4	4.303
0.699	12.94	0.030	0.233	12.06	0.024	0.199	39.21	4.303
0.754	13.74	0.019	0.142	12.88	0.047	0.367	983.7	4.303
0.851	17.40	0.026	0.149	16.37	0.062	0.381	26.35	4.303
0.932	26.19	0.153	0.584	25.23	0.155	0.614	7.605	4.303
0.979	31.61	0.087	2.554	30.78	0.948	3.080	1.161	4.303

Source: Own research.

Analysis of the significance of differences ($p<0.05$) using the t-Student test for bonded pairs showed that achieved statistic $t = 16.18$ is greater than the critical value $t_{0.05} = 2.228$, which was the basis for rejection of the zero theory assuming a lack of differences between average water contents in examined noodles at specified levels of a_w. Similar results were achieved using the t-Student test for the difference between average values at different variations. Analysis of the differences significance ($p<0.05$) showed that in the range of a_w from 0.07 to 0.93 there is a difference between average water contents in researched noodles. Only at $a_w = 0.98$ was there a lack of significant difference in average water contents in the noodles (Tab. 1). Taking into account the material composition of the studied products and technological process parameters, it was assumed that differences in sorption features of studied noodles resulted from differences in the structure of their surfaces.

A resultant of the studied noodles sorption features was the sorption isotherm describing the mechanisms of water bonding during its absorption (Zeller *et al.* 1999). The determined isotherms (Fig. 1) reflected the physical adsorption process proceeding on porous substances. The result of this process was characteristic for the form of type II curve isotherm. Sigmoid sorption curves indicated the creation of multi-molecular water layers on the surface of both researched noodles. Other authors also achieved the same results (Erbas 2005, Ocieczek 2007).

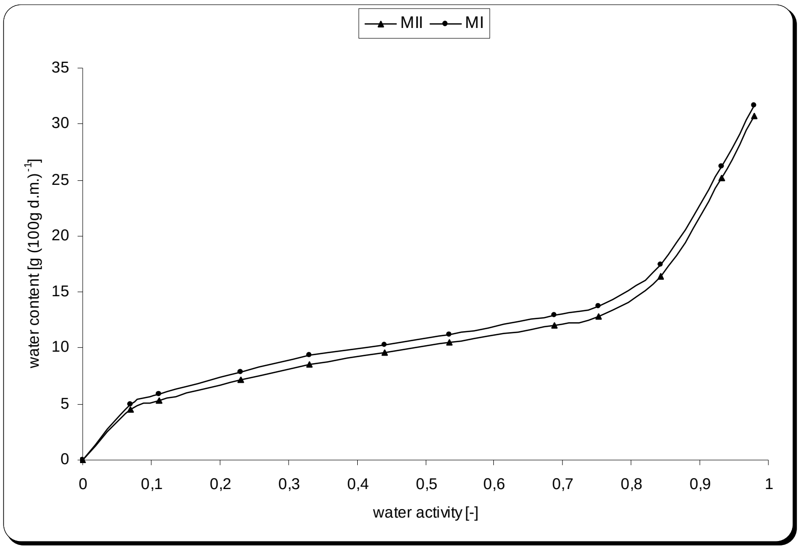

Fig. 1. Sorption isotherms of pasta products

Humidity adsorption by both studied noodles increased with increase of a_w. Humidity absorption from the environment was conditioned by the presence of protein and starch in the noodles. These components, being macromolecules rich in polar places (groups –OH or –H), enable significant humidity adsorption (Hebrard *et al.* 2003, Troccoli *et al.* 2000). The process of water absorption by proteins was revealed after exceeding the a_w value of 0.6, which resulted in swelling of the amino acid chains and structural changes in the protein molecules. Water absorption by starch is not only determined by the amount of water in the environment, but also by the temperature of this environment. Development of starch granules (wheat) can be observed only after exceeding the temperature of 57°C, at which starch processing occurs (Obuchowski 1997).

The MII noodle was characterized by a lower sorption capacity than the MI noodle in the scope of a_w. Shape and location of steam sorption isotherms can be different depending on the product type, its components, water affinity and active surface (Roman-Gutierrez *et al.* 2003). In the analysed case, we can presume that the higher location of the MI noodle isotherm resulted from the differences in superficial structure of the noodle dough determined by the type of die used in the forming process. The surface roughness of the MI noodle was a result of using a phosphorus-bronze die with higher adhesion than the Teflon die (Obuchowski 1997).

After exceeding the level of 0.75 a_w the absorption effect became particularly significant. It can be presumed that above 0.75 a_w in both of the studied noodles capillary condensation occurred.

On the basis of the course of sorption isotherms in the range of 0.07-0.33 a_w the BET equation was determined, defining the rate of its adjustment (R^2, R, Se) to empirical data, and the parameters (V_m, c, a_w) of the BET equation were also determined. The achieved results are presented in Table 2.

Table 2. Parameters of the BET equation of the studied pasta products

Product	R^2	R	Se	V_m	c	a_w
MI	0.993	0.996	0.002	6.34	64.95	0.226
MII	0.991	0.996	0.002	5.78	59.54	0.225

Source: Own research.

Values of the coefficient of determination (R^2) indicated that about 99% of the water content variability in both tests was determined by the water activity. Very high values of the correlation index (R~99%) indicated significant strength of the relation between the studied variables. Values of the average error estimation (Se) indicated that empirically determined water contents were different from the ones determined with the BET function by an average of 0.002g $(100 \text{ g d.m.})^{-1}$.

The monolayer capacity (V_m), which can be determined on the basis of BET equation, concerns the adsorbents sorption capacity and serves as an indicator of polar site availability for water vapour. By defining the monolayer, it is possible to analyse different physical and chemical aspects of food product spoilage (Mathlouthi *et al.* 2001).

In the analysed experiment variation, the MI noodle monolayer capacity was greater than the MII noodle capacity. The capacity V_m determines not only the amount of particular component occurrence in polar sites, but also their physical state. Mechanical damage by which starch granules are endangered during crops milling and during noodle drawing can make a contribution to the changes in their physical state, which affects site availability (Erbas *et al.*2005, Hebrard *et al.* 2003, Roman-Gutierrez *et al.* 2003).

In both of the studied noodles, the water activity corresponding to the monolayer assumed similar values. However, at specific levels (11-12%) recommended for the storage of food, the water content and water activity of the MI noodle was lower than that of the MII noodle. This can indicate greater storage durability of the MI noodle.

The energy constant c reflects the difference between desorption enthalpy from monolayer and fluid adsorbent evaporation enthalpy. The value of the physical adsorption process enthalpy is estimated at about 20 kJ mol^{-1}. Such a small change in the enthalpy most often does not influence the identity of physically adsorbed molecules. However, it should be considered that the presence of surface can cause their deformation. In the chemical adsorption process, molecules form a chemical bond with the surface. Chemisorption enthalpy is much greater than the physi-sorption. Their typical values are estimated at about 200 kJ mol^{-1} (Atkins 2003, Ościk 1970, Paderewski 1999).

The achieved results indicate that, in the researched case, it was rather a physical adsorption process that was taking place. However, to achieve complete certainty about the character of the proceeding phenomena, spectroscope research should be performed.

On the basis of V_m, the proper sorption surface was determined. The achieved results (Tab. 3) showed that the MI noodle had a larger specific surface. At the same time, development of the specific surface of sorption of the researched noodles indicates that in both cases the dominating capillary form was meso-capillaries.

On the basis of the Kelvin equation from the adsorption isotherms, describing the field of capillary condensation, characteristic capillary parameters were determined (Tab. 3). This equation enables calculation of the equilibrium relative pressures to corresponding capillary radii (Paderewski 1999).

Table 3. Structural characteristics of the studied pasta products

Product	Specific surface of sorption ($m^2\ g^{-1}$)	General capacity of capillaries (mm^3 (100 g d.m.))$^{-1}$	Radius of capillaries at $a_w = 0.75$ (nm)	Most probable radius of capillaries (nm)
MI	222.9	88.94	2.888	6.079
MII	202.9	85.26	2.708	5.720

Source: Own research.

The MI noodle had a greater general capillary capacity in comparison to the MII noodle. At $a_w = 0.75$, when the capillary condensation process presumably began, the MI noodle capillaries with a radius of about 2.89 nm were subject to fulfilment, whereas in the MII noodle there were capillaries with radii of about 2.71 nm. Additionally, the most probable radius of capillaries in the MI noodle was about 6.08 nm, while in the MII noodle it was about 5.72 nm. Thus, it can be assumed that differences in the noodles surface structure are conditioned by the type of die used during the drawing and influences the noodles sorption features determined on the basis of the course of sorption isotherms.

The repeated hydration process, called re-hydration, precedes the consumption of most available dried products. The course of the re-hydration and its final effect depend on such factors as: material type and chemical composition, type of initial processing and drying method used, storage conditions, process temperature and the rate of the material dryness (Krokida *et al.* 2003, Kuek *et al.* 2006, Nowak *et al*. 2001). In dried products exposed to re-hydration, there is simultaneous water absorption into the dried material, increase in the re-hydrated product and elution of some of the dry mass components. The result of these phenomena is the weight growth factor (Tab. 4).

Table 4. Values of weight growth factors in the studied noodles

Product	Average value of the weight growth factor	SD	V(%)
Noodle I	2.69	0.048	1.773
Noodle II	2.80	0.031	1.089

Source: Own research.

An analysis of the significance of differences ($p<0.05$) showed that there is a difference ($t = 2.96 > t_{0.05} = 2.92$) between the average weight growth factor values in the researched noodles.

Absorption and maintenance of the water in the product structure depends on the amount and quality of protein and starch. Despite the almost six times lower protein content than starch content, there was a significant factor determining the product weight growth after the cooking process. Hebrard's studies have shown that wheat protein has a five times greater sorption ability than starch (Hebrard *et al.* 2003). Starch ability to bond water molecules in its structure increases with increase in temperature (Troccoli *et al.* 2000). The phenomenon of gluing, manifesting itself with a loosening of the starch granules and a transition from a relatively packed crystal form into a disordered amorphous form, accompanies the increase in temperature with a surplus of water in the product environment (Obuchowski 1997).

In addition to the amounts of particular components in the product composition, their state is also very important. Both the material quality and technological process parameters influence the structure of ready product. The noodle can be significantly influenced by dynamic forces during its formation and can cause the creation of a product with a micro-capillary structure.

It can be presumed that the relatively low value of the weight growth factor in the MI noodle was a result of mechanical denaturation of gluten proteins and mechanical damage to starch during drawing. Significant changes in the protein and starch structure can occur during the formation of noodle dough on the phosphorus-bronze die used in the production of MI noodle. The noodle dough shows greater adhesion in proportion to the phosphorus-bronze die than the Teflon one used for the production of the MII noodle. Under the influence of denaturation, there is a breach of the internal protein molecule structure related to disruption of weak, non-covalent bonds. It is considered that there are amount and quality changes in the mutual relations of disulfide and sulfhydryl groups bonds. As a result of this process, new, unusual features are created for native protein, such as the creation of a pseudo-fibrillar structure, increase in adhesiveness and decrease in hydration, adhesiveness and solubility rates. Products from such denaturated material are rough. Intensive mechanical processing of the dough during drawing also involves the release of a significant amount of heat, causing an increase in temperature (Obuchowski 1997).

Thus, it can be assumed that differences in the state of the noodle components are conditioned by the type of die used during drawing, which influences the noodles re-hydration features, as determined on the basis of the weight growth factor.

To sum up, it should be stated that the type of die used during the drawing process conditions the sorption and re-hydration features of noodle products. However, there is a lack of correlation between these features. The roughness of the noodle surface is a result of using a phosphorus-bronze die which caused the formation of larger values in the product, such as: monolayer, specific surface of sorption and general capillary capacity. At the same time, use of a phosphorus-bronze die caused a decrease in the hydration rate expressed in the weight growth factor. This phenomenon was most probably a result of the mechanical denaturation of proteins and mechanical damage to starches during drawing on the phosphorus-bronze die.

CONCLUSIONS

1. Sorption isotherms of the studied noodles had a sigmoid shape characteristic of high-starch products. The shape of the sorption curves indicated a course of multi-layer adsorption and porous structure of researched products.

2. The humidity adsorption by both researched noodles increased with the increase of a_w. The MII noodle had lower humidity equilibrium values than the MI noodle in the whole range of a_w.

3. The monomolecular layer capacity calculated on the basis of the BET equation was greater in the case of MI noodle. The consequence of this was also higher values of the proper sorption surface for the MI noodle.

4. The water activity corresponding to the optimum moisture of noodles during storage suggests greater storage durability of the MI noodle.

5. The value of BET equation energy constant indicates a typical physical (~60-65) character of the studied process.

6. The MI noodle had a greater noodle capillary capacity than the MII noodle. At the beginning of the capillary condensation process in the MI noodle, there is fulfilment of capillaries with a larger radius than in the MII noodle. Additionally, in the MI noodle, capillaries with larger radii than in the MII noodle were dominant.

To sum up, it should be stated that the researched noodles were distinguished by sorption and re-hydration features. However, isotherms of sorption describing sorption features are inadequate for specification of weight growth in noodle products by describing their re-hydration features.

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OCENA PRZYDATNOŚCI IZOTERM SORPCJI DO OKREŚLANIA WSPÓŁCZYNNIKA PRZYROSTU WAGOWEGO W WYROBACH MAKARONOWYCH

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Streszczenie. Badane makarony charakteryzowały się jednorodnym składem chemicznym. Izotermy sorpcji zostały wyznaczone metodą statyczno-eksykatorową w temperaturze 20°C. Równowagowa zawartość wody była istotnie zależna od typu produktu. Wyraźny wzrost zawartości wody stwierdzono w obu badanych makaronach przy a_w około 0.75. Prawdopodobnie powyżej $a_w = 0{,}75$ następowało zjawisko kondensacji kapilarnej. W oparciu o równanie BET wyznaczono pojemność monowarstwy (makaron I – 6,34 i makaron II – 5,78 $g \cdot (100\ g\ s.s.)^{-1}$) i na jej podstawie powierzchnię właściwą sorpcji (MI – 222,9 i MII – 202,9 $m^2 \cdot g^{-1}$). Określono również ogólną objętość kapilar w obszarze kondensacji kapilarnej stwierdzając wyższe wartości tego parametru w makaronie MI. W oparciu o równanie Kelvina określono najbardziej prawdopodobny promień kapilar oraz wskazano promień kapilar ulegających wypełnieniu w początkowej fazie zjawiska kondensacji. Jednakże izotermy sorpcji są niewystarczające do prognozowania współczynnika przyrostu masy w wyrobach makaronowych.

Słowa kluczowe: izotermy sorpcji, monowarstwa, powierzchnia właściwa sorpcji, aktywność wody