

## SORPTION FEATURES OF CORN AND RICE CRISPS

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**Abstract.** The aim of the study was to determine sorption features of extruded products on the example of plant food concentrates, rice and corn crisps. Measurements of sorption in disintegrated and non-disintegrated material were made with a static method on the basis of isotherms analysis, and with a dynamic method by determination of kinetics and rate of the vapour adsorption process of disintegrated products, in an environment with a water activity  $a_w = 0.07, 0.55, 0.69, 0.75, 0.85, 0.98$ , within 24 h of measurement. Sorption isotherms were determined in the range of water activity of  $a_w = 0.07-0.98$ . The monomolecular layer capacity  $V_m$  and corresponding water activity and adsorption specific surface area were calculated from the BET equation. Vapour adsorption isotherms of studied crisps corresponded with type II in the Brunauer classification, and differences observed in sorption of disintegrated and non-disintegrated material were probably a result of disintegration, causing development of surface in the studied products. Higher monolayer capacity and sorption specific surface area in the adsorption process were achieved in disintegrated products. Course of curves of vapour adsorption kinetics and rate was conditioned by the environment water activity and the initial water content in the studied products. Results of the Smirnow-Kołmogorow conformity test at the significance level of  $\alpha = 0.05$  showed that differences between the equilibrium water content calculated from the adsorption kinetics and the one achieved from vapour adsorption process were not statistically significant.

**Key words:** sorption isotherms, specific surface area, sorption kinetics

### INTRODUCTION

Plant food concentrates present on the Polish market, produced as a result of thermoplastic forming, are really popular among consumers. The group of food concentrates obtained in this way includes such products as so-called snack products which are dry snack products. To this group we can also add, among other things, cornflakes and corn crisps.

From the chemical point of view, plant food concentrates are comparatively durable due to their specific chemical composition, and mainly to their low water content. The principal reason for disqualification of those products by consumers is loss of crispness, determined by the amount of water absorbed by the main component of the products, i.e. carbohydrates (Katz and Labuza 1981, Labuza and Katz 1981).

One of the hypotheses (Labuza and Katz 1981) concerning the loss of crispness assumes that water absorbed by the product softens it and dissolves intermolecular substances gathered on cell walls. Another hypothesis concerning loss of crispness assumes that the product is crispy when its water content is lower than or equal to the value of monolayer capacity determined with the BET or GAB methods (Katz and Labuza 1981).

The quality and storage durability of extruded products are determined mainly by physicochemical changes related with the water activity and level of humidity of the products. Observation of those changes is necessary to elaborate recommendations which would allow maintenance of relative stability of products during the storage time. That is why the aim of the performed research was to determine sorption features of extruded plant food concentrates. Characterisation of sorption features was based on evaluation of mutual positions of adsorption isotherms determined in the temperature of 20°C and isotherm parameters on the basis of the BET model, and evaluation of the kinetics and rate of vapour sorption process curves.

#### MATERIAL AND METHODS

The research materials were plant food concentrates: corn and rice crisps. Initial water content in the products was determined with the drying method at the temperature of 105°C (PN-A-79011-3). Disintegrated and non-disintegrated crisps were used for the study of sorption features. Samples were put into hygrostats with a water activity  $a_w = 0.07-0.98$  and stored for a period of 25 days at the temperature of 20°C. For the purpose for mathematical description of empirically determined sorption isotherms and performance of sorption feature characterisation of researched crisps, sorption isotherms rearrangements were made using the BET equation (1), in the scope of water activity  $a_w = 0.07-0.44$ .

$$\frac{\frac{p}{p_0}}{a \left( 1 - \frac{p}{p_0} \right)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \cdot \frac{p}{p_0} \quad (1)$$

where:

$a$  – adsorption ( $\text{g g}^{-1}$ );

$V_m$  – maximal adsorption value corresponding to total surface coverage with mono-molecular adsorbate layer ( $\text{g g}^{-1}$ );

$C$  – constant, related in an exponential way with the difference between adsorption heat on the first and following layers, accepted as stable and equal to the condensation heat;

$p$  – vapour pressure of adsorbed chemical compound in the gas phase (Pa);

$p_0$  – vapour pressure of adsorbed chemical compound over the liquid in a state of equilibrium at the adsorption temperature (Pa).

The structure of the studied concentrates was defined by determination of the monomolecular layer capacity with corresponding water activity and sorption specific surface area on the basis of equation (2):

$$PS = \frac{V_m \cdot L \cdot N}{M} \quad (2)$$

where:  $PS$  – sorption specific surface area ( $\text{m}^2 \text{g}^{-1}$ )

$V_m$  – monolayer capacity ( $\text{g g}^{-1}$ );

$M$  – water molecular mass ( $18 \text{ g mol}^{-1}$ );

$N$  – Avogadro number ( $6.023 \cdot 10^{23} \text{ molecules mol}^{-1}$ );

$L$  – surface area covered by water molecule ( $1.05 \cdot 10^{-19} \text{ m}^2 \text{ molecule}^{-1}$ ).

Kinetics and rate of the sorption process were determined only in the non-disintegrated products. Kinetics of steam sorption in researched samples was defined with a dynamic method, using the measurement stand allowing for maintenance of permanent measurement temperature  $20^\circ\text{C} \pm 1^\circ\text{C}$  and permanent water activity in the environment at the level of  $a_w = 0.07, 0.55, 0.69, 0.75, 0.85, 0.98$ . The kinetics of steam sorption was determined within 24 hours. A change in the mass during adsorption was recorded every 1 min using a computer program POMIAR WIN.

Kinetic curves and rate curves were the sorption kinetics interpretation. Kinetic curves were a graphical record of the amount of adsorbed water changes ( $\text{g H}_2\text{O (100 g d. m.)}^{-1}$ ) in time. Whereas, rate curves reflected vapour adsorption rate changes in time ( $\text{g (100 g d.m. min)}^{-1}$ ) and they were obtained by differentiation of kinetics curves with a calculation method.

The Smirnow-Kołmogorow conformity test was used for the evaluation of sorption phenomenon by comparison of water content calculated on the basis of vapour adsorption kinetics and determined from adsorption isotherms for researched products. The testing statistics had the form of (3):

$$D_{0.05} = 1.36 \sqrt{\frac{N_1 + N_2}{N_1 N_2}} \quad (3)$$

where:  $D_{0.05}$  – critical value;

1.36 – coefficient for significance level  $\alpha = 0.05$ ;

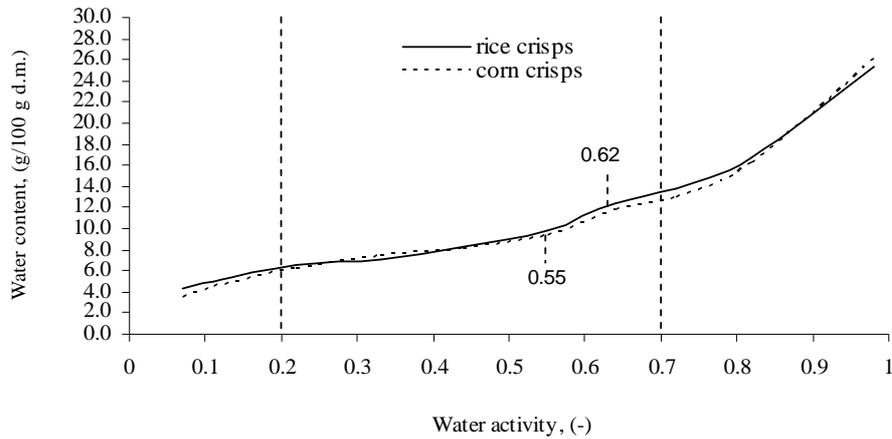
$N_1, N_2$  – size of researched samples.

## RESULTS

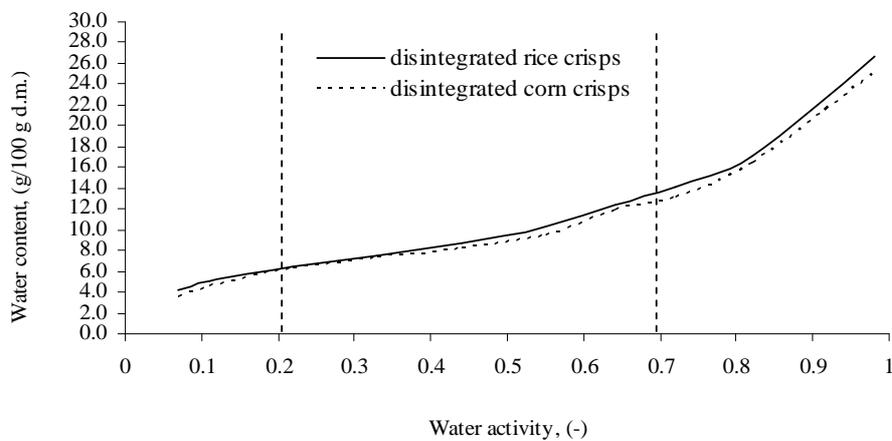
Corn crisps were characterized by higher water content (8.19 g (100 g d.m.)<sup>-1</sup>). Water content in rice crisps was at the level of 7.03 (g (100 g d. m.)<sup>-1</sup>).

Obtained adsorption isotherms of the studied crisps were characterized with a sigmoid shape, indicating a similarity to isotherms type II according to the Brunauer and partners classification (Brunauer *et al.* 1940). The type II is characteristic for products containing significant amounts of starch (Fig. 1 and 2).

Adsorption isotherms of the studied extruded products showed similar course and reflected product sensitivity to the influence of environments with varied water activity. An intensive growth of water content was found in non-disintegrated rice crisps at water activity equal to 0.62 and in corn crisps at the activity at about 0.55 (Fig. 1). Adsorption isotherms of disintegrated rice crisps were characterized by a lack of area with a noticeable change of intensity of water absorption from the environment. However in disintegrated corn crisps a growth of water content at the water activity at about 0.60 (Fig. 2) was noted. Probably the sorption difference observed on the basis of comparison of shape and localization of sorption isotherms of disintegrated and non-disintegrated material was an effect of the disintegration process causing a development of surface of the studied products and loosening of their structure (Ocieczek 2007). As a result of products disintegration new adsorption centres could be discovered (Lewicki 2000). The extrusion process causes fixation of carbohydrates in the amorphous state. However, increase of the environment humidity and, in consequence, adsorption of water causes transition of the product to a viscoelastic state. Additionally there can be structural transformations of defined components of researched products. Those processes proceed both in a disintegrated product and in a non-disintegrated product. However, increase of surface area, loosening of structure and discovery of additional sorption centres causes that processes proceed more intensively. As a result we can observe intensity of the adsorption process (Marzec and Lewicki 2004).



**Fig. 1.** Adsorption isotherms of products extruded in integrated form, determined at the temperature of 20°C



**Fig. 2.** Adsorption isotherms of products extruded in disintegrated form, determined at the temperature of 20°C

On the basis of the sorption isotherms course in the co-ordinate system  $(p/p_0)/a(1-p/p_0)$  and  $p/p_0$ , the BET equation parameters, monomolecular layer capacity  $V_m$  and corresponding water activity, energy constant and sorption specific surface PS were determined in the range of  $a_w = 0.07-0.44$  (Tab.1).

In the adsorption process higher monolayer capacities were achieved for the disintegrated products. For rice crisps the monolayer capacity was estimated at 5.10 (g g<sup>-1</sup>) and for corn crisps at 4.93 (g g<sup>-1</sup>). In disintegrated products the monolayer capacity determined for corn crisps was estimated at 4.89 (g g<sup>-1</sup>). In the adsorption process the lowest monolayer capacity was achieved for rice crisps in reference to the studied extruded products (Tab.1).

It can be assumed that the disintegration process contributed in a higher degree to the discovery of new function groups able to adsorb water molecules in rice crisps than in corn crisps. Most likely such a state was a consequence of differences in the structure of rice and corn starch, its flexibility to changes taking place in the process of extrusion and disintegration (Ociecek 2007).

**Table 1.** The BET equation parameters of studied concentrates in the vapour adsorption process

| Product                   | Capacity of monolayer (g g <sup>-1</sup> ) | Water activity (-) | C <sub>energ.</sub> | Specific surface of sorption (m <sup>2</sup> g <sup>-1</sup> ) |
|---------------------------|--|--------------------|---------------------|--|
| Rice crisps               | 4.76                                       | 0.18               | 171.9               | 167.7  |
| Disintegrated rice crisps | 5.10                                       | 0.19               | 68.54               | 179.7  |
| Corn crisps               | 4.89                                       | 0.21               | 40.98               | 172.3  |
| Disintegrated corn crisps | 4.93                                       | 0.20               | 42.42               | 173.7  |

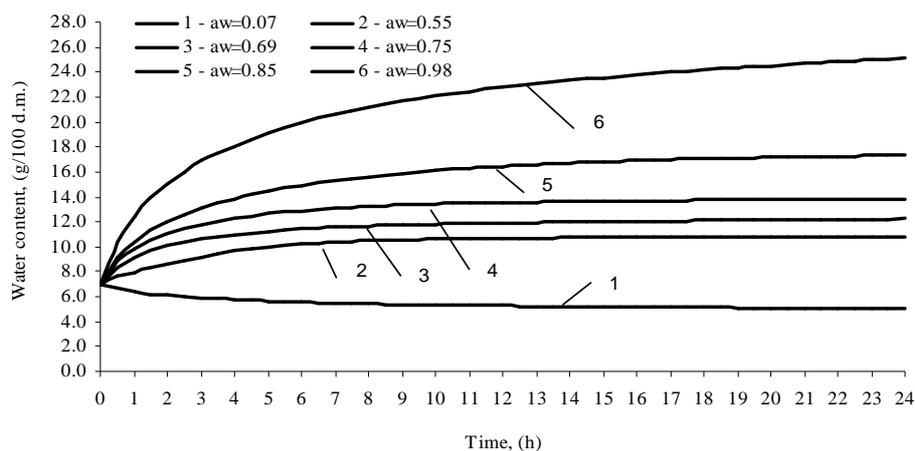
Source: Own correlation.

The water activity corresponding to the monolayer assumed lower values in rice crisps, both in non-disintegrated and disintegrated crisps. On the basis of achieved water activity values it can be assumed that in those products changes related with growth of water amount in the product during its storage will proceed less intensively than in corn crisps.

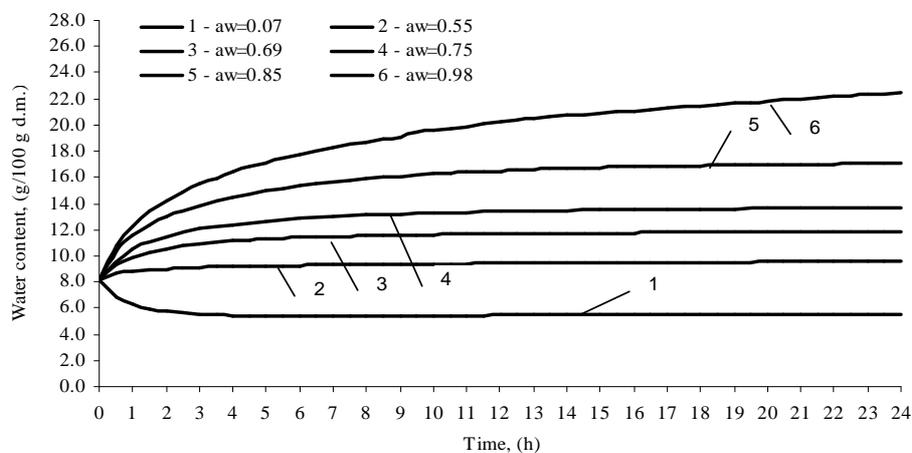
Values of the energy constant C were lower in the corn product (Tab.1) and allowed the assumption that the researched process had the character of physical sorption. In the case of rice crisps the values of constant C were higher, which can suggest that in the process taking place, apart from physical sorption there was also an interaction with a chemical character, related to reactions between water and the product components.

Sorption specific surface area, being a derivative of monomolecular layer capacity, showed higher values in disintegrated products, both in rice crisps and in corn crisps (Tab. 1).

The kinetics of vapour adsorption of rice and corn crisps was determined in an environment with water activity levels of 0.07; 0.55; 0.69; 0.75; 0.85; 0.98 and is presented in Figures 3 and 4.



**Fig. 3.** Influence of the environment water activity on the kinetics of vapour sorption in rice crisps



**Fig. 4.** Influence of the environment water activity on the kinetics of vapour sorption in corn crisps

On the basis of kinetics curves (Fig. 3 and 4) and rate curves (Fig. 5 and 6) of vapour sorption process it was noted that differences in their shape appeared only in an environment with the lowest water activity. The biggest changes of water content in environment with water activity of 0.07, in both researched products, appeared not earlier than in the 8th hour of the process. In rice crisps the water content decreased

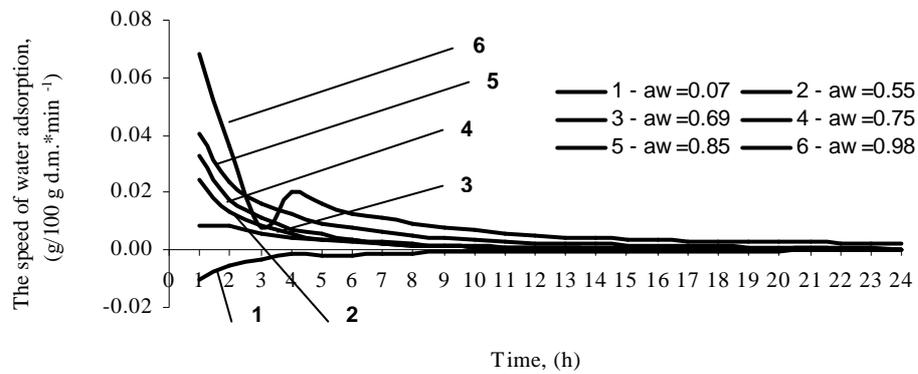
by about 23% in proportion to the initial value, achieving a value of 5.43 (g (100 g d. m.)<sup>-1</sup>) (Fig. 3), at desorption rate of -0.012 (g (100 g d. m. min)<sup>-1</sup>) (Fig. 5). Further process (24 h) caused a fall of the water content in rice crisps by about 6%, which corresponded to a water content of 5.10 g (100 g d.m.)<sup>-1</sup> and rate of -0.0001 (g (100 g d.m.·min)<sup>-1</sup>). In corn crisps the water content in the 8<sup>th</sup> hour of the process decreased by about 34% (5.40 g/100 g d. m.) in proportion to the initial value. However, in next hours of the process corn crisps started to absorb water. In 24<sup>th</sup> hour increase of water content by about 3% was observed, the water content being estimated at 5.56 (g (100 g d. m.)<sup>-1</sup>) at the rate of 0.0003 (g (100 g d.m.·min)<sup>-1</sup>) (Fig 4, 6).

In the case of other evaluated environment water activities, that is 0.55; 0.69, 0.75, 0.85; 0.98, it was observed that the course of kinetics curves and vapour adsorption rate curves of researched products proceeded similarly (Fig. 3-6). However, rice crisps in the studied activities were always characterized by insignificantly higher kinetics and initial vapour adsorption process rate in comparison with the corn crisps. After 24 hours of tests on the vapour adsorption process kinetics rice crisps achieved higher water content. Therefore, it can be assumed that the course of kinetics curves and vapour adsorption rate curves of researched products was conditioned by the environment water activity and the initial water content in the studied products. Differences of product humidity and its environment condition the humid potential difference and determine the propelling force of the processes under study (Ruszkowska *et al.* 2006). Most likely also the difference in rice and corn starch molecules structure plays an important role in the formation of the process rate and kinetics.

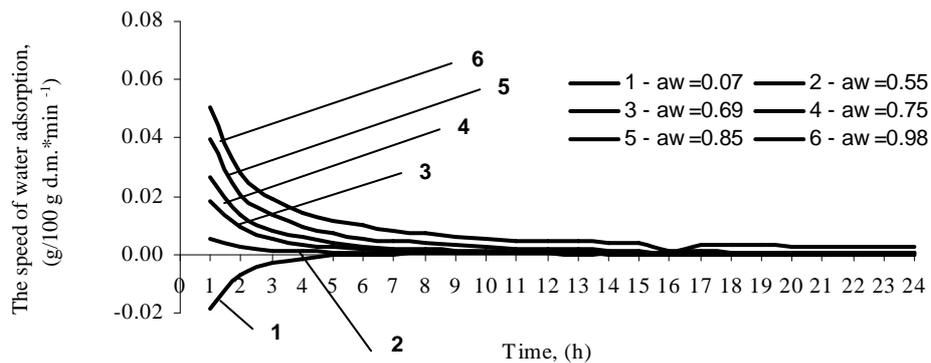
Also a comparison of water content was performed for the studied products, which was determined after 24 hours and on the basis of adsorption isotherms (Tab. 2). In corn crisps, at average environment water activity  $a_w = 0.55-0.85$ , the water content calculated on the basis of vapour adsorption kinetics after 24 hours was higher than the one determined from the vapour sorption isotherms. In rice crisps the water content determined after 24 hours was higher than the water content determined on the basis of sorption isotherms in the environment with water activities of 0.55 and 0.85 (Tab. 2).

Achieved results indicate that after 24 hours the researched products did not achieve an equilibrium state. However, higher values defining the water content in the tested samples after 24 hours can certify that the adsorption process proceeded in an incidental way. Probably there are places with a privileged position showing a bigger affinity to vapour molecules. Results of the Smirnow-Kolmogorow conformity test at the level of significance  $\alpha = 0.05$  showed that differences between the equilibrium water content calculated from the adsorption kinetics and the one achieved from the vapour adsorption process were not statistically significant. Taking into account the fact that the hydrogen bond strength

between food matrix and water molecule is higher than the hydrogen bond strength of the water-water type, it can be assumed that all function groups able to accept water will first be the subject to filling with adsorbed water molecules. In next order there will be further layers of loosely bonded water being formed. However, achieved results show that during 24-hour adsorption there was a formation of multilayer complexes in a non-uniform situation, and from the thermodynamics view point – filling in with some function groups. That is why in order to achieve a state of real product's relative humidity equilibrium a longer time is necessary. During pursuit to equilibrium relative humidity in the product there are adsorption and desorption processes, as a result of which water molecules uniformly cover the food matrix.



**Fig. 5.** Vapour adsorption process rate for rice crisps



**Fig. 6.** Vapour adsorption process rate for corn crisps

**Table 2.** Correlation of equilibrium water content achieved in the vapour adsorption kinetics process determined from the vapour adsorption isotherms in researched rice and corn crisps.

| Rice crisps   |      |       |       |       |       |       |
|---|------|-------|-------|-------|-------|-------|
| $a_w$   | 0.07 | 0.55  | 0.69  | 0.75  | 0.85  | 0.98  |
| Water content after the 24 h sorption process (g (100 g d. m.) <sup>-1</sup> )                    |      |       |       |       |       |       |
|   | 5.10 | 10.83 | 12.23 | 13.81 | 17.31 | 25.08 |
| Equilibrium water content calculated from the sorption isotherms (g (100 g d. m.) <sup>-1</sup> ) |      |       |       |       |       |       |
|   | 4.23 | 9.82  | 12.45 | 13.85 | 16.73 | 25.42 |
| Corn crisps   |      |       |       |       |       |       |
| $a_w$   | 0.07 | 0.55  | 0.69  | 0.75  | 0.85  | 0.98  |
| Water content after the 24 h sorption process (g (100 g d. m.) <sup>-1</sup> )                    |      |       |       |       |       |       |
|   | 5.56 | 9.58  | 11.85 | 13.66 | 17.07 | 22.48 |
| Equilibrium water content calculated from the sorption isotherms (g (100 g d. m.) <sup>-1</sup> ) |      |       |       |       |       |       |
|   | 3.48 | 9.34  | 11.69 | 12.88 | 16.13 | 26.04 |

Source: Own correlation.

### CONCLUSIONS

1. Vapour adsorption isotherms of researched crisps are characterized by a course conforming to type II sorption isotherms according to the Brunauer classification.
2. Differences in the shape and localization of sorption isotherms and parameters determined on their basis indicate the existence of differences in sorption features resulting from the type of product and its physical state.
3. Researched products achieved the state of relative humidity equilibrium in average water activities after 24 h.

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## WŁAŚCIWOŚCI SORPCYJNE CHRUPEK KUKURYDZIANYCH I RYŻOWYCH

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**Streszczenie.** Celem pracy było określenie właściwości sorpcyjnych produktów ekstrudowanych na przykładzie koncentratów spożywczych pochodzenia roślinnego, chrupki ryżowych i kukurydzianych. Pomiaru zjawiska sorpcji, w materiale rozdrobnionym i nierozdrobnionym dokonano metodą statyczną na podstawie analizy izoterm. Metodą dynamiczną przez określenie kinetyki i szybkości procesu adsorpcji pary wodnej produktów nierozdrobnionych, w środowisku o aktywności wody  $a_w = 0,07, 0,55, 0,69, 0,75, 0,85, 0,98$ , w ciągu 24 h pomiaru. Izotermy sorpcji wyznaczono w zakresie aktywności wody  $a_w = 0,07-0,98$ . Pojemność warstwy monomolekularnej  $V_m$  i odpowiadającą jej aktywność wody oraz powierzchnię właściwą adsorpcji obliczono z równania BET. Do oceny zjawiska sorpcji, zawartość wody obliczono na podstawie kinetyki adsorpcji pary wodnej oraz wyznaczono z izoterm adsorpcji. Izotermy adsorpcji pary wodnej badanych chrupki odpowiadały typowi II, w klasyfikacji Brunauera, a stwierdzone różnice w sorpcji materiału rozdrobnionego i nierozdrobnionego były prawdopodobnie wynikiem rozdrabniania, powodującego rozwinięcie powierzchni badanych produktów. W procesie adsorpcji wyższą pojemność monowarstwy oraz powierzchnię właściwą sorpcji uzyskano, bowiem w produktach rozdrobnionych. Przebieg krzywych kinetyki i szybkości adsorpcji pary wodnej uwarunkowany był aktywnością wody środowiska oraz początkową zawartością wody w badanych produktach. Wyniki testu zgodności Smirnowa-Kołmogorowa przy poziomie istotności  $\alpha = 0,05$ , wykazały że występujące różnice pomiędzy równowagową zawartością wody obliczoną z kinetyki adsorpcji a otrzymaną z izoterm adsorpcji pary wodnej nie były statystycznie istotne.

**Słowa kluczowe:** izotermy sorpcji, BET, powierzchnia właściwa, kinetyka i szybkość procesu sorpcji, chrupki