

## Apparent surface area of selected meal extrudates

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**A b s t r a c t.** We have investigated water vapour adsorption and calculated the specific surface area of meal extrudates. The Brunauer-Emmet and Teller (BET) equation was used to analyse experimental data on water vapour adsorption and to calculate the apparent surface area ( $S_{app}$ ) from both adsorption and from desorption branches of the adsorption isotherm. Values of  $S_{app}$  estimated from adsorption isotherms ranged: from 214 to 294; from 202 to 210; and from 199 to 232  $m^2g^{-1}$  for potato, wheat and rice extrudates, respectively. If the desorption isotherms have been used, the ranges of  $S_{BET}$  were 327-347, 274-281, and 287-295  $m^2g^{-1}$ , respectively. We have observed linear relationship between adsorption- and desorption-apparent surface areas. In the case of rice extrudates the correlation coefficients,  $R^2$ , were very high. Similar linear relationship has been found for potato and wheat extrudates, but correlation coefficients were lower. The surface area,  $S$ , is directly proportional to the monolayer capacity  $N_m$  and the value of apparent surface area obtained from desorption data may be treated as a measure of the amount of strongly bounded water. Therefore the desorption surface area seems to be a better parameter to characterize the solid surface of meal extrudates.

**K e y w o r d s:** water vapour adsorption, specific surface area, potato, and wheat and rice extrudates

### INTRODUCTION

Studies in the surface chemistry of solids frequently include determinations of surface area that is one of the major parameters describing solid surfaces. Many investigators have attempted to measure surface area as means of describing better the solid body under study or understanding better particular processes or reactions. The specific surface can be used as a measure of surface activity. In relation to processes taking place at solid-gas phase boundaries, the specific surface is viewed as the surface accessible to gas molecules. It encompasses the external surface of a solid body as well as

its internal surface produced by its porosity. It is defined as the actual surface of the adsorbent per unit mass and is commonly expressed in  $m^2g^{-1}$ . Usual method of determining the surface area of textured solids is based on the adsorption of gases or vapours, and on the application of the Brunauer-Emmet and Teller (BET) equation (Ościak, 1982; Gregg and Sing, 1978).

Adsorption of gases or vapours and surface area depend on nature of solids. Adsorption is proportional to the surface area, which may be determined assuming the model of adsorption that involves not only the characteristics of an adsorbent (as the BET model does), but which is also dependent on some parameters characterizing the adsorbate. The water molecules are highly polar because of asymmetry of electrical charges and possess a permanent dipole moment. The polarity results in intermolecular attractive forces between water molecules and polar groups of the solid surface. Various kinds of the polar and nonpolar functional groups have been identified in mineral and organic solids. The most important are the carboxylic-, phenolic-, hydroxylic-groups. These groups create primarily hydrogen bonding or van der Waals forces. Several polar functional groups serve as sorption sites for water molecules. Because of a high dipole moment and the ability to form hydrogen bonds, water can be form a quite complex adsorbed layers that can exhibit different properties depending on the kind of surface functional groups binding water molecules. The hydration or coordination reactions between surface cations and water molecule also influence adsorption of water vapour. Chiou *et al.* (1990) and Peenell *et al.* (1995) pointed out that polar compound such as ethylene glycol (EG) can partition into soil organic matter, hampering its use for reliable measurement of the

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specific surface area. For the surface area determined by the EG method, Chiou *et al.* (1990) proposed term 'apparent surface area', which is based on measured by the uptake of an adsorbate that either changes the structure of the solid or dissolves in it, or both.

The sorption of water vapour by foods has received much attention because of its importance in dehydration processes, in packaging, and in changing their quality during storage. The changes in chemical, physical and biological properties of foods, which do not appear to be related directly to either moisture content or water relative pressure (water activity), often can be revealed in terms of the moisture sorption isotherm. The monolayer moisture content value is an important parameter in food storage and deterioration. The monolayer concept is useful because of its relationship with several aspects of the physical and chemical deterioration of dry products (Chirife and Iglesias, 1978). Moisture sorption isotherms have been used to explain the relation between water content of food and the equilibrium relative humidity of the food surrounding. They provide information about the mechanisms of water binding during sorption in foods (Labuza, 1984).

The objective of this work is to determine the apparent surface area of potato, wheat and rice extrudates, using the BET methods.

#### MATERIALS AND METHODS

The commercial potato starch (PN-93/A-74710), flower wheat (PN, 1991) and rice gruel from commercial rice (Sigma) were used as raw materials. Extrusion was carried out in Polish S 45 and S 9/5 twin extruder, described by Mościcki (1994). Native potato starch contained 0.26% of ash, 0.02% of protein, 0.03% of lipids and 19.5% of moisture. The barrel temperature was differentiated over the length of the barrel from feed to die as follows: 1) 80-120-150-170-100°C, 2) 80-120-150-170-100°C, 3) 145-165-120°C, 4) 100-140-180-200-120 °C, and 5) 80-110-140-160-100°C. The feed moisture contents were 10.5, 14, 10.5, 14, and 19.5% for samples Nos P1, P2, P3, P4, P5, respectively. Wheat flower contained 0.46% of ash, 12.01% of protein, 1.82% of lipids and 14.5% of moisture. The barrel temperature was differentiated over the length of the barrel from feed to die as follows: 1) 80-120-180-200-100°C, 2) 145-165-120°C, 3) 100-140-180-200-100°C, 4) 80-150-190-210-140°C, 5) 140-160-120°C, 6) 80-150-190-210-140°C. The feed moisture contents were 14.2, 11.2, 13.4, 14.5, 11.8, and 14.5% for samples Nos W1, W2, W3, W4, W5, W6, respectively. Milled rice contains approximately 80% of starch, 8.1% of protein and 0.9% of lipids. The barrel temperature was differentiated over the length of the barrel from feed to die 110-160-145°C, the feed moisture were 10, 15, 20 and 30% for samples Nos R1, R2, R3 and R4, respectively. The dry mass in the raw material was measured by drier method according to AACC, Method 44-15A.

The adsorption-desorption isotherms of water vapour were measured using the gravimetric method. Before the adsorption measurement, the samples were gently ground and dried in a vacuum chamber with the concentrated sulphuric acid until the sample masses reached constant values. The subsample of about 3 g was put into the glass vessel and was placed over sulphuric acid solutions of stepwise decreasing concentrations (to increase of the relative water vapour pressure *ie* to determine the adsorption branch of isotherm) and next over sulphuric acid solutions of stepwise increasing concentrations (to decrease of the relative water vapour pressure *ie* to measure the desorption branch of isotherm). The sample was equilibrated with water vapour during two days. The amount of adsorbed water vapour was computed as the difference between the weight of the sample after the equilibration and the dry sample (dried in an oven at 105°C). The adsorption measurements were replicated three times at temperature  $T=20^{\circ}\text{C}\pm 0.5$ . Twenty levels of relative pressure were selected in the range from 0.015 to 0.95. The variation in replicated data did not exceed  $\pm 5\%$  at the lowest vapour pressure and  $\pm 1\%$  at the highest vapour pressure. The average values at each pressure level were used to obtain the specific surface areas and to prepare the figures.

The surface area of extrudates was evaluated from adsorption-desorption isotherms in the BET range of relative water vapour pressure ( $0 < pp_0^{-1} < 0.35$ ), using the Brunauer-Emmett-Teller (BET) method (Gregg and Sing, 1978; Ościk, 1982; Sing, 1982). The experimental data have been described using the BET equation. The parameters of this equation *ie*  $N_m$ , and  $C_{\text{BET}}$ , as well as the correlation coefficient,  $R^2$  were estimated from the linear form of the BET equation:

$$\frac{x}{N(1-x)} = \frac{1}{C_{\text{BET}}N_m} + \frac{(C_{\text{BET}} - 1)}{C_{\text{BET}}N_m}x,$$

where:  $x = p/p_0$  is the relative pressure of water vapour,  $N$  is the amount of adsorbed water vapour, and  $C_{\text{BET}}$  is a constant.

The first step in the application of the BET method is to obtain the monolayer capacity ( $N_m$ ) from the BET plot at lineal range of water vapour pressure  $0 < pp_0^{-1} < 0.35$ . The second step is to calculate the surface area  $S$  from the dependence  $S = N_m M^{-1} L \cdot \omega$ , where  $L$  is the Avogadro number ( $6.02 \cdot 10^{23}$  molecules per mole),  $M$  is the molecular weight of water (in gram per mole) and  $\omega$  is the molecule cross-sectional area ( $10.8 \cdot 10^{-20} \text{ m}^2$  for water molecule). If  $N_m$  is expressed in grams of water per gram of solid and  $\omega$  is  $10.8 \cdot 10^{-20} \text{ m}^2$  for water molecule the specific surface area  $S (\text{m}^2 \text{g}^{-1})$  is estimated from the monolayer capacity as:  $S = 3612 N_m$ . This procedure is described by the Polish Standard PN-Z-19010-1 for measuring the surface area of soil.

## RESULTS AND DISCUSSION

Figure 1a shows an example of experimental adsorption-desorption isotherms obtained for starch, wheat and rice extrudates. In general, the shape of adsorption and desorption curves is similar. According to the BET classification of the adsorption isotherms (Gregg and Sing, 1978; Ościk, 1982) all the curves belong to the same class, namely to the type II that is typical for many food materials (Blahovec, 2004). A hysteresis effect was observed for all investigated extrudates. The samples possess relatively large hysteresis loops (Fig. 1a), especially potato starch extrudates. Generally, the difference between the adsorption and desorption data can be attributed to capillary condensation, which takes place in mesopores (Gregg and Sing, 1978), as well as to some irreversible changes occurring in the samples during adsorption *eg* swelling or hydration. In the case of potato starch products, the hysteresis loop seems to be related to the change of their porosity during adsorption (Jamroz *et al.*, 1999a; 1999b). Also Boki and Ohno (1991) interpreted the hysteresis loop for kudzu and sweet potato starch as a change in mesopore volume, caused by the water adsorption.

The parameters of BET equation *ie*  $N_m$ , and  $C_{BET}$ , as well as the correlation coefficient,  $R^2$  are given in Table 1. Figure 1b shows an example of applying the transformed BET equation (or the so-called BET plot) to the isotherms given in Fig. 1a.

The values of the correlation coefficient  $R^2$  indicate that the BET equation provides a good fit to the experimental data. In all cases the values of  $R^2$  vary from 0.987 to 0.997, if the calculations were performed for the relative pressures lower than  $p/p_0 \approx 0.35$ .

The adsorption and desorption data have been used to evaluate the values of the surface area. Figure 2 shows the apparent surface area ( $S_{app}$ ) for potato starch, wheat, and rice extrudates. For the samples under study the BET surface area estimated from the adsorption isotherms ranged from: 214-294, 202-210, and from 199 to 232  $m^2g^{-1}$  for potato starch, wheat, and rice extrudates, respectively. However, when the desorption isotherms have been used, the BET surface area was higher and equal to 327-347, 274-281, and 287-295  $m^2g^{-1}$  for potato starch, wheat and rice extrudates, respectively. Similar effect has been reported for extruded corn derivatives (Świtka and Fornal, 1989) and for different kind of starch extrudates (Włodarczyk-Stasiak, 2006, 2007).

The apparent surface areas the potato starch products were greatest. For remaining investigated extrudates the values of  $S_{app}$  were generally similar and only slight differences between particular samples were observed (Fig. 2b and c). Small variations in apparent surface area of investigated extrudates obtained from desorption data suggest similarity of mechanisms of desorption and similarity of physico-

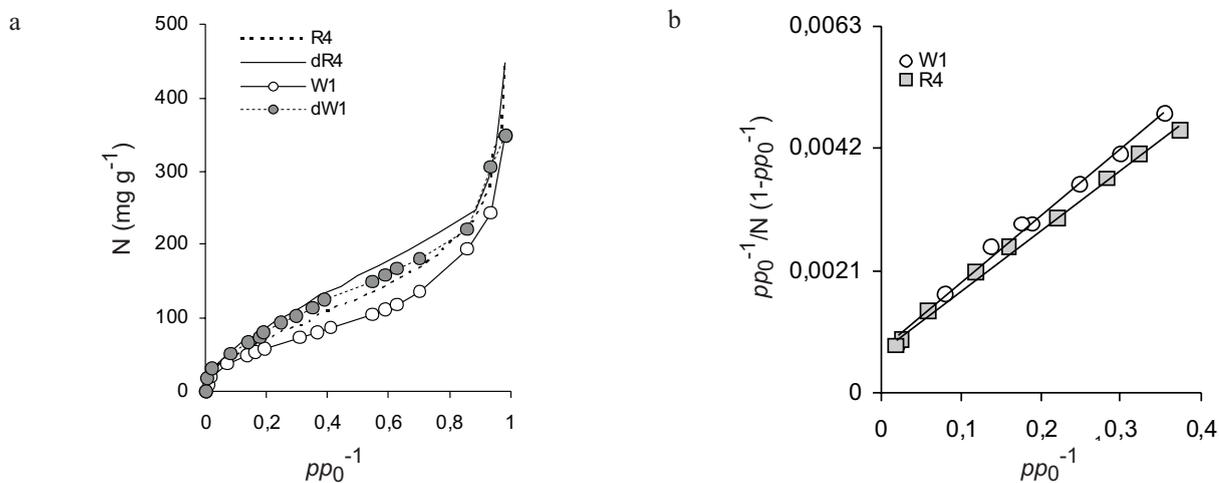
chemical character of the extrudates. The higher values of apparent surface area obtained from desorption data result from the existence of hysteresis loops on the sorption isotherms. In the case of investigated samples, the water vapour adsorption hysteresis is not fully understood, although there is general agreement that some thermodynamically irreversible processes must occur during desorption or adsorption or both (Ait Mohamed *et al.*, 2006). Various hypothetical explanations for this phenomenon have been reported in the literature (Boki, 1991; Kaminski and Kudra, 2000; Kapsalis, 1981; Wolf *et al.*, 1972).

Generally, the values of the surface area of investigated extrudates are relatively high and the obtained values agree with the results reported for other organic materials such as peat, moorsh or plant roots (Józefaciuk and Szatanik-Kloc, 2003; Sokołowska, 2004; Szatanik-Kloc, 2003). In the cases quoted above, the values of  $S_{app}$  obtained from desorption data were also higher than those obtained from adsorption data.

There exist several additional criteria for testing the correctness of the monolayer capacity evaluation from the BET equation. In particular, the BET transformed into a linear equation should lead to a reasonable estimation of the monolayer capacity if its prediction is close to the position of the inflection point of the isotherm. In several cases desorption data may better satisfy the last requirement (Sokołowska, 2002). We have found the linear correlation between adsorption- and desorption-apparent surface areas (Fig. 3). For rice extrudates the value of  $R^2$  that characterizes the above correlation was high (0.93), but it was rather low (0.51 and 0.26) for potato and wheat extrudates, respectively.

The surface area,  $S$ , is directly proportional to the monolayer capacity  $N_m$ , and the relationship between these two quantities is given above. The value of apparent surface area obtained from desorption data may be treated as a measure of the real amount of the strongly bounded water. The results displayed in Fig. 3 confirm that the desorption isotherm is a better base to obtain the amount of water which is strongly bounded with the surface and, consequently, desorption surface area is also a better parameter which characterizes the solid surface of meal extrudates.

Sposito (1984) commented that as its definition implies, the specific surface area is an operational concept. Usually, the numerical value found for a given solid material depends on the experimental method that was used. The operational nature of specific surface area precludes any interpretation of its numerical values in an absolute geometric sense. There is no specific surface area of solid, but only specific surface areas, each determined with some surface chemical application in mind. A chemical measurement of specific surface area in general provides only information about the solid surfaces that were reactive under the conditions of the measurement.



**Fig. 1.** Examples of water vapour adsorption data: a – original adsorption isotherms, and b – the BET plot for investigated samples. Explanations: R4,W1, dR4, dW1 – rice extrudate, W1, dW1 – wheat extrudate,  $N$  - amount of adsorbed water,  $pp_0^{-1}$  – relative pressure, white symbols - adsorption, d and black symbols – desorption.

**Table 1.** Parameters of the BET equation at its lineal range  $0 < pp_0^{-1} > 0.35$

Sample	Adsorption isotherm Nm (mg g <sup>-1</sup> )	C <sub>BET</sub>	R <sup>2</sup>	Desorption isotherm Nm (mg g <sup>-1</sup> )	C <sub>BET</sub>	R <sup>2</sup>
Potato extrudates						
P1	86.7	21.3	0.994	90.6	25.8	0.996
P2	68.8	18.6	0.993	96.1	17.7	0.996
P3	69.0	17.7	0.994	96.1	17.7	0.996
P4	66.8	18.6	0.996	95.2	17.6	0.995
P5	59.3	21.3	0.997	90.8	21.8	0.992
Wheat extrudates						
W1	58.5	18.0	0.998	76.4	21.3	0.992
W2	58.1	20.9	0.998	77.8	22.7	0.992
W3	57.5	19.8	0.998	76.8	21.4	0.991
W4	53.4	24.1	0.998	76.0	22.9	0.992
W5	55.2	23.5	0.998	77.0	24.7	0.991
W6	56.0	23.5	0.999	76.2	25.2	0.991
Rice extrudates						
R1	64.4	37.3	0.990	81.7	28.5	0.987
R2	58.9	39.6	0.991	79.6	27.6	0.989
R3	60.2	36.2	0.989	80.3	25.3	0.982
R4	55.1	40.9	0.992	79.2	29.1	0.987

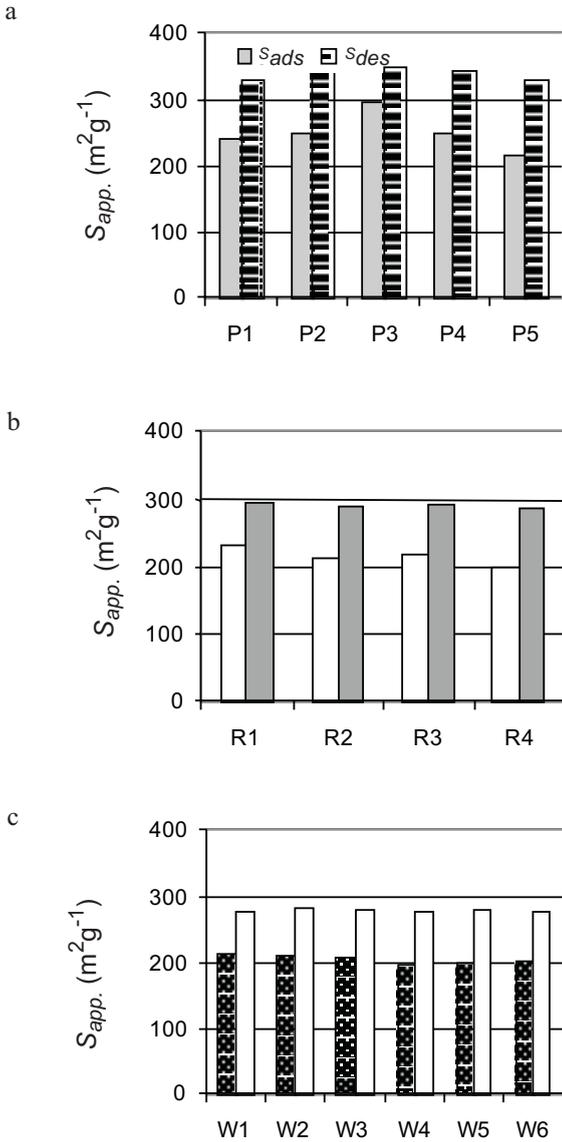


Fig. 2. Apparent surface area of the: a – potato-starch, b – rice, and c – wheat extrudates.

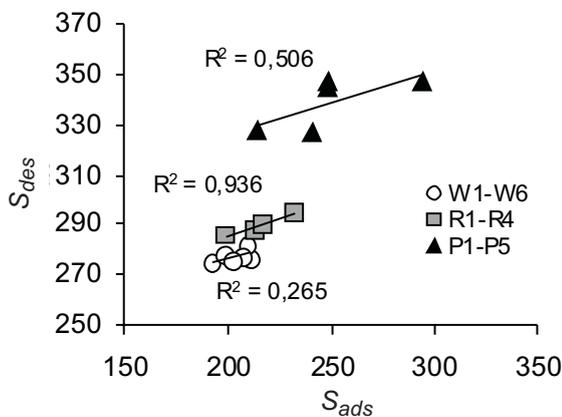


Fig. 3. Relationship between the sorption ( $S_{ads}$ ) and desorption ( $S_{des}$ ) apparent surface area of the investigated extrudates.

CONCLUSIONS

1. The shapes of experimental adsorption isotherms for investigated extrudates are similar, but the amount of adsorbed or desorbed water varies from sample to sample. This is obviously related to different basic properties of particular samples. The values of the correlation coefficient,  $R^2$ , indicate that the BET equation provides a good fit to the experimental data.

2. The BET surface areas for the studied materials place the samples under study in the rather high range of surface areas of organic materials. For potato starch extrudates the apparent specific surface area are higher than for those for wheat and rice extrudates. The values of the apparent specific surface area obtained from adsorption and desorption data are different. Specific surface areas evaluated from desorption data are higher. The higher values of apparent surface area obtained from desorption data result from the occurrence of hysteresis loop on the sorption isotherms.

3. The linear relationship between the adsorption- and desorption-apparent surface areas has been found. In the case of rice extrudates the correlation coefficient,  $R^2$ , was very high. Similarly, a linear relationship has been found for potato and wheat extrudates, but correlations are much weaker. The surface area,  $S$ , is directly proportional to the monolayer capacity  $N_m$  and the value of apparent surface area obtained from desorption data may be assumed as a measure of the amount of strongly bounded water. The desorption isotherm seems to be a better base for obtaining the amount of water which is a strongly bounded with surface and, consequently, the desorption-surface area should also be a better parameter, which characterizes the solid surface of meal extrudates.

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