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Porosity of starch–proteins extrudates determined from nitrogen adsorption data

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ABSTRACT

Extrudates of potato starch with selected proteins (concentrate of soybean proteins, whey proteins and acidic casein) were produced at 22% raw material moisture, and at various process temperatures and extruder screw speeds. Increase of screw speed and temperature had a significant effect on changes in the specific surface area and porosity of products which were tested with the use of low-temperature sorption of nitrogen. The nitrogen adsorption isotherms plotted are of types II and III according to IUPAC, both for the raw material and for the product. Equation BJH was used to determine the surface area (S_{BJH}), volume (V_{BJH}) and average pore diameter (D_{BJH}). For diameters from 35 Å to 74 Å, the calculated pore volumes assumed values within the range of $23 \cdot 10^{-5}$ cm^3/g $-55 \cdot 10^{-5}$ cm^3/g. Curves of pore size distribution based on average pore diameter within the range of 19.7–23.2 Å indicate a large cumulative volume of pores.

Extrusion caused a decrease in the specific surface area of the product, from 0.19 m^2/g to 0.32 m^2/g. A high correlation was noted between increase in porosity and expansion, and the optimum screw speed and temperature profile.

1. Introduction

Extrusion is a method of physical texturing of a raw material for the purpose of its refinement and for imparting to it the features of a semi-product or product. In the food industry that technology is used for the production of a broad array of products such as breakfast flakes, diet supplements, functional foods, pastries and confectionery, snacks, and feeds from e.g. waste materials from the agricultural and food industry (Fornal, 1998; Guy, 2001; Mercier & Feillet, 1975; Miller, 1990; Moore, 1994; Obuchowicz & Michniewicz, 1993; Rokey, 1994; Rzedzicki & Zarzycki, 2006; Thymi, Krokida, Pappa, & Maroulis, 2005). The direction and degree of physicochemical transformations of raw materials modified with that technique can be regulated through the choice of suitable chemical composition of raw materials and degree of their moistening, extruder cylinder temperature distribution, pressure, mixing intensity, etc. (Anderson, Conway, Pfeifer, & Griffin, 1969; Barres, Vergnes, Tayeb, & Della Valle, 1990; Bhattacharya & Hanna, 1987; Kirby, Ollet, Parker, & Smith, 1988; Mason & Hoseney, 1986; Meuser & van Lengerich, 1992; Miller, 1990; Moore, 1994; Rokey, 1994). Optimisation of those processes has a fundamental impact on the formation of the porous structure of the product, which is in the focus of interest of many researchers (Fortuna, Januszewska, Juszczak, Kielski, & Pałasiński, 2000; Fortuna, Juszczak, & Palasinski, 1999, Jamroz, 1999; Jamroz & Pikus, 1997; Karathanas & Saravacos, 1993; Pikus, Jamroz, & Kobylas, 2000; Śmietana, Szpendowski, Soral-Śmietana, & Świgoń, 1996; Sokołowska, Jamroz, & Bańka, 2008; Thymi et al., 2005; Włodarczyk-Stasiak & Jamroz, 2008, 2009; Yano & Nagai, 1989). The prediction of pore formation in food during processing is needed for technology process design, in prediction of properties, and in characterising the quality of a product (Rahmann, 2001). Porosity of food is correlated with physical properties, such as mass diffusion coefficient, thermal conductivity, thermal diffusivity, mechanical and textural properties. Porosity plays the most important role for the apparent density. The lower the porosity of a product, the higher the apparent density of food (Hussain, Rahman, & Ng, 2002).

A porous product is characterised by a structure with irregular surface with numerous indentations, and a network of empty spaces within. The porous structure is non-homogeneous, with observable pores of various shapes, closed and/or open, connected with the surface or not. The presence of closed pores determines the mechanical and thermal strength of the product, and its density (Hajnos & Świeboda, 2004; Lowell & Shields, 1991; Paderewski, 1991). Surface irregularities and open pores participate in the

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Nomenclature

a_m	monolayer value (g N_2/1 g d.m.)
D	extrudate diameter (mm)
D_{BJH}	average diameter of mesopores (Å)
d	extruder nozzle diameter (mm)
E_x	radial expansion index
M	molecular weight of nitrogen (14.01 g/mol)
m	weighed portion, converted to value per 1 g of dry matter (g)
$\max f(E_X)$	extreme function
m_m	weight of test tube with wet sediment (g)
N_o	Avogadro number ($6.023 \cdot 10^{23}$)
p/p_o	relative pressure
S_{BET}	specific surface area (m^2/g)
S_{BJH}	cumulative surface of pores (m^2/g)
V_{BJH}	volume mesopores (10^{-5} cm^3/g)
σ_o	settlement area of a molecule of nitrogen ($16.2 \cdot 10^{-20}$ m^2/molecule)

surface processes (adsorption, desorption, solubility), and affect also the degree of development of the specific surface area (Chibowski, 1992; Gregg & Sing, 1982; Hajnos & Świeboda, 2004; Lowell & Shields, 1991; Ościk, 1983; Paderewski, 1991). Apart from specific surface area, other important parameters describing porosity include the average diameter (D_{BJH}) and volume (V_{BJH}) of pores, and their average diameter distribution. Physical gas absorption often used for the study of surface and pore characteristics of porous materials. Gas adsorption measurements are widely used for the characterisation of a variety of porous materials (carbons, zeolites and organic polymers) and of particular importance is the application of physisorption (physical adsorption) for the determination of the surface area, pore size and distribution. IUPAC recommends nitrogen (at 77 K) for the characterisation of porous materials. Nitrogen as the apolar adsorbate allows to determine the inner surface. Nitrogen molecule is small and spherical in shape, has a hexagonal packing in a liquid state and relatively weak interaction with the functional groups on the surface of the adsorbent (Ciembroniewicz, Klinik, Korta, Nodzeński, & Rewilak, 1977). The isotherm obtained from experiments can provide information about the surface energetic and geometric heterogeneity, pore volume, average size and size distribution (Sokołowska, Bowanko, Boguta, Tys, & Skiba, 2013). Many investigators have attempted to measure surface area as a means of better description of the solid body under study or better understanding particular processes or reactions (Sing, 2001).

The porosity of starch and of starch–protein products is the object of studies by numerous researchers. The presented results of estimation and description of porosity are often ambiguous due to the accessibility of pores and to the choice of method/technique of their determination. The most frequently applied techniques include methods based on the phenomenon of physical adsorption on the boundary of the gaseous or liquid phase (Fornal et al., 2012; Fortuna et al., 1999; Juszczak, Fortuna, & Wodnicka, 2002; Nagai & Yano, 1990; Sokołowska et al., 2008; Włodarczyk-Stasiak & Jamroz, 2008, 2009). A separate group of research tools includes the microscopy techniques: SEM (Abdel-Aalet et al., 1992; Baldwin, Adler, Davies, & Melia, 1994; Chen & Zhang, 2012; Fannon, Hauber, & BeMiller, 1992, 1993; Gallant, Mercier, & Guilbot, 1972), TEM, (Fannon et al., 1992, 1993), as well as mercury porosimetry (Fornal et al., 2012; Jamroz, Hajnos, & Sokołowska, 1996, 1999; Karathanas & Saravacos, 1993) i SAXS, (Doutch & Gilbert, 2013; Jamroz & Pikus, 1997; Pikus et al., 2000).

Suntory (1991) investigated the phenomenon of physical adsorption to the least developed encapsulation method onto the surfaces of high surface area substrates. Highly porous carbohydrates have been recognised as flavour carriers/adsorbents. The porous carbohydrates could find an application in alternative to conventional flavour encapsulation, these materials being incorporated into foods to adsorb impurities and bitter components. Zelller, McKay & Saleeb (1987) indicate the possibility of the use of physical sorption on high porous material and adsorption carbon dioxide in the production of carbonated beverage powders.

Estimation of the porosity of extrudates enables the design of the technological process through the selection of optimal parameters under which the resulting product has the predicted physical and qualitative characteristics. In this study, the porosity of extrudates from mixed potato starch and various proteins produced at various process parameters was analysed using low-temperature nitrogen adsorption from the gaseous phase.

2. Materials and methods

2.1. Materials

Commercial potato starch (S), "Superior", conforming to the Polish standard PN-93/A-74710 (Table 1.).

2.2. Methods

2.2.1. Extrusion

Native potato starch (S) and protein components (B, C, W) were extruded. The qualitative and quantitative characteristics of blends are presented in Table 2. The process was conducted in a single-screw extruder (type S 45), manufactured by Metalchem, Gliwice (Poland). Temperature and extruder screw speed at constant 22% moisture content are presented in Table 2. Fragmented extrudates were screened through a sieve to isolate the fractions below 0.2 mm for further study.

2.2.2. Low-nitrogen adsorption/desorption

Measurements of specific surface area (S_{BET}), cumulative surface of pores (S_{BJH}), volume of mesopores (V_{BJH}) and average diameter of mesopores (D_{BJH}) were taken using the Sorptomat ASAP 2405 apparatus (Micromeritics Inc. USA). The sample material (~8 g) was degassed and immersed in liquid nitrogen (77.3 K). Sorption isotherm was determined within the range of 0.06–0.99 p/p_o. The monolayer value (a_m) was determined within the range of $p/p_0 = 0.06–0.20$.

Samples of the material, with weight of about 8 g, were degassed at 100 °C and pressure of 10^{-3}mm Hg, to establish a state of equilibrium at the temperature of liquid nitrogen. The sample was immersed in liquid nitrogen at a temperature of 77.3 K. The measurement was carried out for dispensing a specific portion of the nitrogen gas and measuring the relative pressure p/p_o. The Sorptomat ASAP 2405 records the pressure change depending on

Table 1
Approximate chemical composition of components made of extrudates (%).

Components[a]	Water	Protein	Lactose	Fat	Ash
Potato starch (S)	19.10	0.02	–	0.03	0.26
Acid casein (C)	8.21	88.45	0.21	1.37	1.49
Soybean protein preparation (B)	9.12	51.52	1.54	2.10	2.46
Whey protein preparation – WPC 60 (W)	5.57	58.26	23.15	10.66	4.58

[a] Protein determined by AACC (Method 46-08), [60], dry mass counting up water determined by AACC (Method 44-15A), [60], lactose determined by AACC (Method 80-04), [60], ash determined by AACC (Method 08-01), [60], fat determined by AACC (Method 30-16, 26), [60].