Int. Agrophysics, 2000, 14, 93-98

FRACTAL STRUCTURE OF STARCH EXTRUDATES-INVESTIGATION BY SMALL ANGLE X-RAY SCATTERING

S. Pikus[1], *J. Jamroz*[2], *E. Kobylas*[1]

[1]Department of Crystallography, University of Maria Curie-Skłodowska, Maria Curie-Skłodowska Square 3 20-031 Lublin, Poland
[2]Department of Biological Elements of Food Technology and Feed, University of Agriculture, Doświadczalna 48, 20-236 Lublin, Poland

Accepted April 17, 1998

A b s t r a c t. Small angle X-ray scattering has been applied to the study of structure of potato starch and wheat flour extrudates. The range changes of microstructure deformation after extrusion cooking processes was analysed from the fractal view point to some physical properties of these materials. Furthermore, relationship between some fractal magnitudes was shown.

K e y w o r d s: fractal structure, SAX scattering, starch extrudates

INTRODUCTION

Extrusion cooking technology is used to modify functional properties, such as water solubility, water absorption and paste viscosity of starches and cereal flours. In the extruder cooker, starch and protein-based flours are subjected to thermomechanical stress that can produce extrudates with smaller size macromolecules. Starch granules are gelatinized giving amorphous and expanded phase with partial degradation of biopolymers, proteins are denatured which results in texturisation [6]. The range of these changes is a function of extrusion cooking conditions and of starch source [5,13].

Enzymatic digestion, gel permeation chromatography and viscous analyses were used to demonstrate depolymerization of starch polymers during extrusion as well as to characterise their functional properties [16]. Little has been reported on the surface texture analysis of extruded product, which is usually difficult to define as smooth/rough and regular/irregular patterns [17].

Study of the material generated in this way may be done by various methods, among which a small angle X-ray scattering (SAXS) method becomes more and more important. SAXS appears when there is inhomogeneity of electronic density in the investigated material. The magnitude of these inhomogeneities should be in the diameter range of 1 to 1000 nm. The SAX scattering intensity depends on the difference in the electronic density of the area with inhomogeneities and its surroudings as well as on the shape and size of these inhomogeneities. The study by Pikus and Jamroz [8,14] proved the existence of inhomogeneities of electronic density which lead to SAX scattering effect in starch material after extrusion cooking. It was stated that SAX scattering intensity depends on the extrusion cooking process variables, as well as on the kind of starch material. However, a detailed interpretation of the SAXS effect in such complex configuration as extrudates causes numerous problems. Results of the SAXS theory development indicate, that the application of a fractal model may be one of the possible interpretations of the SAXS effect.

CHARACTERISTIC OF THE FRACTALS AND SAX SCATTERING FROM FRACTALS

The most important feature of fractals is their selfsimilarity, which means a type of structure which after consecutive divisions allows to obtain parts similar to the original unit [2]. A cauliflower head can be an example of such a fractal object can serve. However, the feature of selfsimilarity can be fulfilled just to a certain range of sizes which in literature is related to a and ξ. It is understandable, that by dividing a given fractal object (e.g., broccoli) into smaller and smaller pieces one will finally obtain objects, which are not similar to the original unit any more. Thus, the a value is referred to as the smallest size of the object still maintaining the shape of the whole fractal object, and ξ indicates the largest possible distance between two points of the fractal object.

Three primary types of fractal objects can be distinguished: mass fractal, surface fractal and porous fractal. Structural scheme of these three types of fractals are shown in Fig.1.

The most important magnitude, which characterises a fractal is fractal dimension D. For mass fractals its value is contained in the range $1<D_m<3$, and $2<D_s<3$ for surface fractals.

The intensity of SAXS $I(q)$ scattering for many objects, including fractal objects, can be described by the power law equation [1,15]:

$$I(q) = I_o q^{-\alpha} \qquad (1)$$

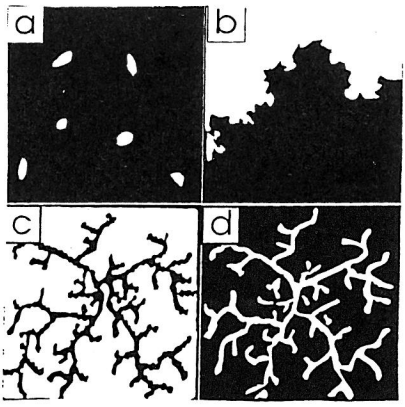

Fig. 1. Types of structures of porous materials: a-pores of a "particle" type; b-pores with a rough surface of pore-solid phase border (surface fractal); c-highly porous material with branched solid phase (mass fractal); d-branched net of pores (porous fractal).

where:

$$q = \frac{4\pi \sin\theta}{\lambda}, \qquad (2)$$

where 2θ is the scatering angle, λ is the X-ray wavelength. and I_o, α are constant values for mass and surface fractal objects.

Values of α are respectively:

$\alpha = D_m$ $\quad 1<\alpha<3$ for mass fractal

$\alpha = 6\text{-}D_s$ $\quad 3<\alpha<4$ for surface fractal.

One can see, that the SAXS method allows to determine fractal dimension of mass fractals as well as of surface ones. Usually the power law is fulfilled for a certain range of q values [1,15]; the extreme limit values of this range

Table 1. Some values of the magnitude α of the power-law-scattering exponent

Scattering system	α
Mass fractal with fractal dimension D_m	$1<D_m<3$
Surface fractal with fractal dimension D_s	$3<6\text{-}D_s<4$
Polydisperse system of fractal scatterers that have a mass-fractal dimension D_m	$0<\alpha<D_m$
Polydisperse system of fractal scaterers that have a surface-fractal dimension D_s	$0<\alpha<6\text{-}D_s$
Thin rod	1
Thin plane lamina	2
Non-fractal scatterer with smooth boundary	4
Porous solid with smooth pore boundaries and a continuous power-law density transition with a power-law-transition exponent β	$4<4+2\beta<6$

determine the a and ξ values thus, it is possible to make an additional characteristic of the fractal structure.

Apart from the fractal structures, the power law may refer to other types of objects; the value of α coefficient makes it possible to distinguish these different structures [15].

Table 1 contains data set of values and the respective types of scattering objects.

EXPERIMENT

Materials and extrusion cooking

Samples of commercial potato starch (PN-93/A-74710) and wheat flour (PN-91/a-74022) extrudates were studied. Native potato starch contained 0.26% of ash, 0.02% of protein (Nx6.25), 0.03% of lipids and 19.5% of moisture. Commercial wheat flour contained 0.46% of ash, 12.01% of protein (Nx6.25), 1.82% of lipids, 79.89% of starch, 1.93% of fiber and 14.50% of moisture. Extrudates were made in the Department of Biological Elements of Food Technology and Feed of the University of Agriculture, Lublin, Poland. Extrusion cooking was carried out in an industrial twin screw Polish extruder cooker 2S 9/5, at a changing temperature of process and moisture level of feed material [11]. This way extrudates of various expansion ratio, density and shearing stress were obtained (Table 2). The exact description of the extrusion cooking process and the physical properties of the products was provided in the earlier works [8,9,14].

SAXS measurements

Measurements were performed on a slit -collimated Kratky camera using a Cu anode tube with nickel filter as the radiation source. A scintillation counter with a pulse-height analyser were used to measure the scattered intensity. The samples for the SAXS experiments were prepared as follows:

- the extrudates were ground in a coffee mill to pass through a 0.2 mm screen, next, they were dried in an electric dryer and placed in special 1 mm capillaries. The scattering curve of a given sample was measured several times and so was the background scattering curve (e.g., scattering of the air, empty capillary, parasitic scattering of the slits, etc) curve. The background scattering curves were corrected for absorption. The measurements were carried out in the range 2θ from 0.076 to 6.52 degrees with changing step from 0.0076 to 0.038 degrees and a counting time of 100 s. After a slight smoothing of the scattering curves properly and substracting the value of the background scattering curve from that of the sample, further slight smoothing of the curve was obtained. At the end the desmearing curve was calculated and as a result the SAX scattering curve $I(q)$ vs. q was obtained. The above calculations were carried out using a modiffied Vonk's programme [18].

RESULTS AND DISCUSSION

Previous studies applying SAXS method to examine potato starch extrudates proved that the power law was fulfilled by q in a certain range of its value, and the obtained values of α factor suggested the presence of the fractal structure of the extrudates [8,14].

Thus, the present study was focused on the analysis of the intensity of the SAXS radiation in the aspect of the fulfilment of the power law.

Table 2. Physical and textural propferties of potato (I*p*-IV*p*) and wheat (I*w*, II*w*) extrudates and data obtained from SAXS measurements

Sample	Expansion ratio	Density (kg m^{-3})	Shearing stress (N cm^{-2})	α	ξ (nm)	a (nm)
I*p*	6.10	51.94	4.03	3.00	3.13	0.62
II*p*	4.78	87.49	13.30	2.99	3.60	0.62
III*p*	3.38	196.57	51.24	2.99	3.69	0.62
IV*p*	1.86	365.14	301.93	3.60	5.43	0.62
I*w*	2.39	365.30	48.47	2.02	1.39	0.66
II*w*	3.55	145.86	13.26	2.04	1.54	0.68

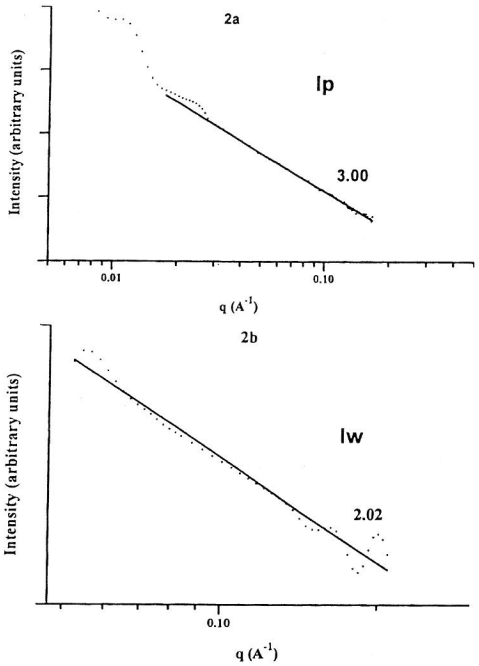

Fig. 2. SAX scattering curves (in log-log axes) for *Ip* (2a) and *Iw* (2b) samples (see also Table 2).

As a result of the fulfilment of the power law by SAX scattering curve (or a part of it) the graph of the relation between $\log I(q)$ and $\log (q)$ should form a straight line.

In Fig. 2 the relation between $\log I(q)$ and $\log (q)$ for the scattering curves of potato starch extrudate (2a) and wheat flour extrudate (2b) are shown. The shape of SAXS curves for other examined extrudates is similar. As can be seen in Fig. 2 part of the curve is almost an ideally straight line. From the slope of this straight-line a part the α coefficient was derived (Eq. (1), the values obtained are depicted in Table 2). Its value indicates that all the examined extrudates are fractals. As was mentioned before, for the characteristic of a fractal object, except a fractal dimension D, it is important to evaluate also the "fractal range", i.e., a and ζ values, which are calculated from the following equations:

$$a = 1/q_{\max} \text{ and } \zeta = 1/q_{\min}$$

where the values $q_{\max}$ and $q_{\min}$ are in the range which fulfils the power law (see Fig. 2).

The values of a and ζ calculated this way are shown in Table 2 together with some physical characteristics of the extrudates. In detailed analysis of the SAXS data first it is necessary to determine, whether pores of the extrudate are not the source of SAX scattering. Pore diameters determined by the porosimetric method were above the upper range of the SAXS method [7]. The intensity of scattering, which is much lower than for porous materials [14] as well as values of α in (Table 2), indicate that pores are not the cause of scattering. A question that arises from the analysis of data in Table 2 is type of the fractal structure of the extrudates. The values of α coefficient of potato starch extrudates are in the range of 2.99-3.6, depending on the extrusion cooking variables (Table 2) and much lower for wheat flour extrudates (from 2.02 to 2.04). Essential differences of ζ values, i.e., the maximum size of fractal object of both types of extrudates, also occur.

It's widely recognised [15] that for classic fractal structures differences between a and ξ should be in the ten fold range. As it can be seen for potato extrudate the difference is from about 6 to 9 fold, and for wheat extrudate it, is only about 2.5 fold (see Table 2, values were obtained by dividing ξ/a). Thus, doubts arise whether the SAX scattering originating from wheat extrudate can be considered as if it came from classical fractal structure. It is known that SAX scattering intensity of wheat extrudates is much greater than that of potato extrudates [14]. This fact can be explained by the different protein and fibre content in these extrudates. The value of α coefficient ($\alpha \approx 2$) suggests the presence of a mass fractal. Thus, the source of the SAX scattering of wheat extrudates could be highly dispersed protein particles (1.3-1.5 nm) in starch matrix. This thesis is confirmed by the value of ζ for wheat extrudates and, as mentioned above, high intensity of the SAX scattering for these extrudates.

Potato extrudates contain almost pure starch [3,4,10,12], other substances only in trace levels, thus the source of SAX scattering can

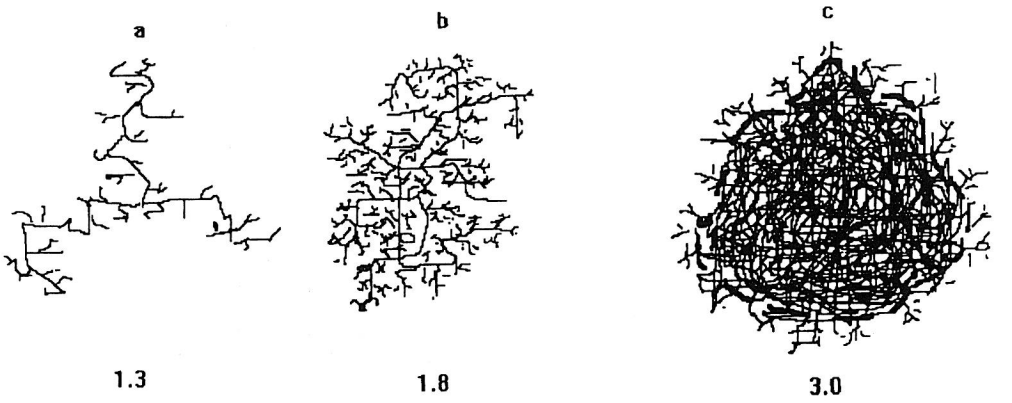

Fig. 3. Two-dimensional skeleton tracery of structures with different fractal dimension.

only be differences in the electronic inhomogeneities of the extrudates.

The values of α coefficient of potato extrudates are of 2.99 and more, which would indicate the absence of mass fractal. For a mass fractal an increase of D coefficient (equal to α - see Table 1) from 1 to 3 indicates increase of branching of the fractal structure (see an example in Fig. 3). When the value of α approaches 3, so many branches are present that distances between them are close to those between atoms. In this situation the object may be considered as having an uniform electronic density and only on its surface a somewhat looser structure occurs. The image of this object is presented in Fig. 3c. Further increase of the coefficient value causes also compaction of the surface and when α equals 4, the surface can be considered smooth. Thus, for potato extrudates the existence of fractals resembling those in Fig. 3c could be imagined. These objects are steeped in the starch structure of a different electronic density than that of the fractal. The density difference is, however, very small, and so the SAX scattering intensity is low.

The explanation of appearance of such fractal objects may be done on the basis of semicrystalline structure of the original material [3,4,10]. It is composed of crystalline and amorphous areas which have different conformations and different electronic densities. It seems that both areas behave differently during extrusion cooking processes. Thus, in the extruded material in spite of the destruction of the semicrystalline ordering objects differing in electronic density are present.

CONCLUSION

Values of α coefficient of potato starch extrudates (2.99-3.6) and of wheat flour extrudates (2.02-2.04) suggest their fractal structure. As it results from a and ξ parameters, potato products have a typical fractal structure, whereas in wheat extrudates some other type of structure may be the source of scattering. It seems that scattering intensity in potato extrudates results from the inhomogeneities of packing in the starch structure, whereas in wheat extrudates it may originate from certain protein or fibrous structures in the starch matrix.

REFERENCES

1. **Bale H.D., Schmidt P.W.:** Small angle X-ray scattering investigations of submicroscopic porosity with fractal properties. Phys. Rev. Lett., 53, 596-601, 1984.
2. **Barrett A.H., Peleg M.:** Applications of fractal analysis to food structure. Lebensm. -Wiss. u. -Technol., 28, 553-563, 1995.
3. **Cameron R.E., Donald A.M.:** A small-angle X-ray scattering study of the annealing and gelatinization of starch. Polymer., 33, 2628-2636, 1992.
4. **Cieśla K., Żółtowski T., Diduszko R.:** Physicochemical changes occurring in gamma irradiated flours studied by small-angle X-ray scattering. Food Structure, 12, 175-180, 1993.
5. **Colonna P., Doublier J.L., Melcion J.P., Monredon F., Mercier C.:** Extrusion cooking and drum drying of wheat starch. I. Physical and macromolecular modifications. Cereal Chem., 61, 538-543, 1984.

6. **Guy R.C.E.:** Raw materials for extrusion cooking processes. In: The technology of extrusion cooking (Ed. N.D. Frame). Blackie Academic and Professional, London-Glasgow-NewJork-Tokyo-Melbourne-Madras, 65-67, 1994.
7. **Jamroz J., Hajnos M., Sokołowska Z.:** The use of the mercury porosimeter for the evaluation of micropore size distribution in potato extrudates. Int. Agrophysics, 10, 295-302, 1996.
8. **Jamroz J., Pikus S.:** New aspects of small angle X-ray scattering investigations on potato extrudates. Ital. J. Food Sci., 9, 205-214, 1997.
9. **Jamroz J., Pikus S., Rogalski J.:** The influence of the extrusion on some properties of the products from potato starch. Żywność, Technologia, Jakość, 2, 191-199, 1996.
10. **Jenkins P.J., Cameron R.E., Donald A.M.:** A universal feature in the structure of starch granules from different botanical sources. Starch, 12, 417-420, 1993.
11. **Mościcki L.:** Review of the extrusion-cookers design produced all over the world (in Polish). Post. Techniki Przetwór. Rol. Spożyw., 1, 46, 1994.
12. **Nagai T., Yano T.:** Fractal structure of deformed potato starch and its sorption characteristics. J. Food Sci., 55, 1334-1337, 1990.
13. **Owusu-Ansach J., Voort F.R., Stanley D.W.:** Textural and microstructural changes in corn starch as function of extrusion variables. Can. Inst. Food Technol. J., 17, 65-70, 1984.
14. **Pikus S., Jamroz J.:** Small-angle X-ray scattering investigations of extrudates. X-Ray Investigations of Polymer Structures, SPIE., 3095, 167-173, 1997.
15. **Schmidt P.W.:** Small angle scattering of disordered, porous and fractal systems. J. Appl. Cryst., 24, 413-435, 1991.
16. **Tang J., Ding X.L.:** Relationship between functional properties and macromolecular modifications of extruded corn starch. Cereal Chem., 71, 364-369, 1994.
17. **Tan J., Gao X., Hsieh F.:** Extrudate characterization by image processing. J. Food Sci., 59, 1247-1250, 1994.
18. **Vonk C.G.:** FFSAXS - computer program for SAXS data treatment. J. Appl. Cryst., 8, 340-344, 1975 .