

Interpretation of small angle X-ray scattering from starch on the basis of fractals

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Using small-angle X-ray scattering, the behaviour of corn and potato starches during gelatinization, swelling, and retrogradation was investigated. The scattering patterns were analysed on the basis of the fractal concept. The main scattering source from low moisture starches could be interpreted as a 'surface fractal' obeying a power law with an exponent of *ca* -4 . When the starch swelled, the surface fractal characteristic was recognised only at very low angles, and on heating it disappeared at *ca* 80°C. For gelatinised starches, the whole scattering pattern obeyed the power law with the power around -2.0 . This result suggests that the physical arrangement of gelatinised starch molecules is a 'mass fractal', i.e. a self-similar structure, in nature. Further, it was found that the scattering of the retrograded starch showed a shoulder like peak superimposed the background scattering representing the mass fractal. The corresponding Bragg spacing was estimated to be 31~15 nm. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

It is well known that the properties of starch such as digestibility and rheological properties are influenced by the physical arrangement of amylose and amylopectin and the branched structure of amylopectin. To obtain information on such structures, much research has been carried out using electron microscopy (Oostergetel and Van Bruggen, 1989), enzymatic methods (Robin *et al.*, 1974) and X-ray diffraction. The latter have been reviewed by Zobel (1988a, b). Wide-angle X-ray (WAX) diffraction is used for determination of short range information (less than 1 nm) such as crystallinity in starch granules, and small-angle X-ray scattering (SAXS) is usually used for the determination of longer range information (1–100 nm) such as micelle structure. Although the structural information obtained by SAXS is important for understanding starch structure, studies have been limited due to the difficulties of the technique. Using the SAXS technique, Sterling (1962) and Hizukuri *et al.* (1964) found the existence of a long range periodicity occurring at about 10 nm in moist starch

granules below the gelatinization temperature, which disappears as the starch gelatinises. This long-range periodicity was believed to represent the distance between the amorphous centres that have intervening crystalline molecular clusters. Blanshard *et al.* (1984) suggested the possibility of an alternative interpretation for the periodic peak, which supports a racemose model of amylopectin. In recent years, a new model for starch internal structure, which consists of a paracrystalline lamella stack embedded in an amorphous background medium, was proposed by Cameron and Donald (1992, 1993a, b) and Jenkins *et al.* (1994). The behaviour of their own experimental SAXS profile during gelatinization, swelling, and annealing could be explained in terms of this model. Cameron and Donald (1991) also reported that SAXS patterns from gelatinised and retrograded starches show no characteristic periodicity of *ca* 10 nm which was observed for native starch. Using Guinier and the Debye–Bueche approaches, they showed that the effective sizes of the scattering object such as correlation length develop as the retrogradation progresses. However some data obtained from SAXS measurement of starch, which may be important, still remains to be interpreted because of the lack of an

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appropriate method for analysis. For example, the SAXS profiles of a completely gelatinised starch, for which the intensity decreases continuously with increasing scattering angle, have not been used efficiently. Further, the fact that the very low moisture starch shows no peak in the SAXS profile, which had already reported by Hizukuri *et al.* (1964), has not been analysed.

However, in the fields of synthetic polymer and colloid science, data on the scattering of X-rays, light and neutrons have begun to be analysed using the fractal concept (Daoud and Martin, 1989; Martin and Hurd, 1987). This fractal concept is based on 'self-similarity' and introduces a non-integer dimension, called the fractal dimension, which provides a novel way for the quantitative evaluation of irregular structures of bio-materials such as protein structures (Colvin and Stapleton, 1985; Farin *et al.*, 1985; Pfeifer *et al.*, 1985). However, there is no research on applying fractal analysis to SAXS data of starch itself, even though the small-angle neutron scatterings of amylose gels have been analysed as a fractal structure (Vallera *et al.*, 1994).

While a series of reports on SAXS study of starch was being published by Cameron and Donald (1992, 1993a, b and Jenkins *et al.*, 1994), we have also measured the SAXS profile of gelatinised and retrograded starch at lower angles for a range of moisture contents using a Kratky type camera able to measure to $q=0.0419\text{ nm}^{-1}$. We observed that the scattering at low angles from retrograded starches show a different pattern to that predicted from extrapolation from high angles $q > 0.2\text{ nm}^{-1}$.

In this paper, we analyse SAXS data of starches during swelling, gelatinization and retrogradation by using the fractal concept, and discuss the changes in the surface of the starch granules and their molecular arrangement.

FRactal ANALYSIS METHOD FOR SMALL-ANGLE X-RAY SCATTERING

Theoretically, it has been known that the scattering patterns from a fractal object generally obey the following power law

$$I \propto q^\alpha \quad (1)$$

where I is the scattering intensity and q is the scattering vector (Schaefer and Keefer, 1984; Schaefer and Martin, 1984; Martin and Hurd, 1987). Particularly, in the case of X-ray scattering, q is represented by using the scattering angle 2θ and X-ray wavelength λ as follows,

$$q = \left(\frac{4\pi}{\lambda}\right) \sin(2\theta) \quad (2)$$

If Bragg's law is applied, q is proportional to the inverse of the apparent periodic length d :

$$q = 2\pi/d \quad (3)$$

The exponent α in Eq. (1), which can take the range from -1 to -4 , relates to the fractal characteristics of the scattering object. When fractal relations are observed from scattering experiments, i.e. the linear relationship between $\log I$ and $\log q$ following Eq. (1), it is possible to determine the character of the scattering sources according to the value of α (Martin and Hurd, 1987).

In the case of $-4 < \alpha < -3$, the scattering can be judged to be the reflection from the surface or interface which is classified as a 'surface fractal'. The surface fractal dimension, D_s , which indicates the irregularity of the surface, is then expressed as follows:

$$D_s = 6 + \alpha \quad (-4 < \alpha < -3). \quad (4)$$

Although D_s is capable of assuming the value of 2.0–3.0, when the surface of the scattering object is smooth, the D_s value becomes 2.0 ($\alpha = -4.0$), which corresponds to the well-known Porod's law for SAXS (Gratzer and Kratky, 1982; Bale and Schmidt, 1984). Conversely, a large D_s means that the surface is rough.

In the case of $-3 < \alpha < -1$, the scattering source is classified as a 'mass fractal', which means that the density profile of the scattering object has a self-similar nature. Thus, the relation between the mass fractal dimension D_m and α is defined as follows:

$$D_m = -\alpha \quad (-3 < \alpha < -1) \quad (5)$$

According to conventional concepts, the D_m value, which indicates the physical arrangement of the mass such as polymer segments, becomes 1.0 for a linear arrangement, 2.0 for a surface-like arrangement, and 3.0 for a regular arrangement such as a cube or sphere. However, when polymer segments or aggregated particles distribute in a self-similar form, i.e. a fractal, the D_m values have noninteger intermediate values. According to the fractal concept, D_m is thought to be an indicator of the degree of compactness.

MATERIALS AND METHODS

Two kinds of starches, corn and potato starches, were used as typical samples of starches that show different types of wide angle X-ray diffraction (A and B types, respectively). The corn starch was provided by Nihon Shokuhin Kako Co.; this is called white spice and has granules of about $16\text{ }\mu\text{m}$ in diameter. The potato starch was a commercial product, the granules of which have an average diameter of $40\text{ }\mu\text{m}$. These starches were completely dried under reduced pressure without further purification before all experiments. The low-moisture starches, i.e. less than 40 g water per 100 g solid, were prepared by storage in humidity-controlled

desiccators for 3 days. The precise moisture content of these samples was determined by the oven-drying method, 24 h at 110°C, before X-ray measurement. Sample water contents of more than about 50 g water/100 g solid were prepared by dripping a given amount of water on pre-weighed starches or by dispersing a given weight of the starch in a unit of water. Heating for gelatinization and ageing for retrogradation were carried out by using the SAXS measurement system described below.

SAXS measurement

A Kratky camera system (Anton Parr Co.) on an X-ray generator (Phillips Co.) was used. The X-ray source used was CuK_α (wavelength $\lambda = 1.54 \text{ \AA}$) from the X-ray tube operated at 35 kV, 60 mA. Samples were packed in 0.7-mm-diameter quartz capillary tubes and sealed. These sealed tubes were placed on the sample holder, which was able to control the temperature of a sample. The samples of more than 1 g water/g solid in moisture content were measured at different temperatures from nearly room temperature to *ca* 100°C, provided that the samples were preheated at each measuring temperatures for 30 min before scanning in order to attain thermal equilibrium. Other samples of less than 1 g water/g solid were measured at 24°C. In particular, the gelatinised samples of 1 g water/g solid were kept at 4°C, and measured at 24°C after 1 and 2 days. The intensities of the scattered X-ray were detected using a proportional counter, and the time during counting for each angle was fixed so that the integral intensity was at least over 1000 counts. The relationship between X-ray intensities and angles measured from the slit collimation system of a Kratky camera were desmeared to the point collimation system using the method of Guinier and Fournet (1955) after subtraction of the blank scattering from the capillary tube. The X-ray path was in a vacuum chamber in order to prevent any scattering due to air.

RESULTS AND DISCUSSION

Swelling

Figure 1(a and b) shows the respective scattering patterns at 24°C from corn and potato starches of different moisture content, in which the relative intensities are represented as a function of the scattering vector q on a double-logarithmic scale. It was found that the scattering patterns from low moisture starches except for the sample of 1 g water/g solid, whether corn or potato, showed a good linearity over a wide range of q on the log-log graph. The linearities on the log-log graph were retained in the ranges of $0.04 < q < 0.2$ [1/nm] for corn and

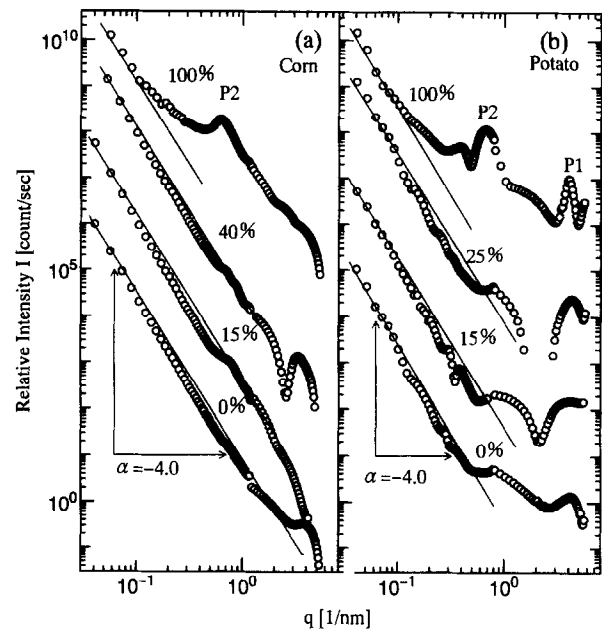


Fig. 1. The small angle X-ray scattering patterns from corn (a) and potato (b) starches of different moisture contents at 24°C. The moisture percent values shown in figure are the weight percents on dry base. The real lines show the relationship; $I \propto q^{-4}$ in the case of smooth surface. The intensities are shifted along the ordinate in order to avoid overlapping of the symbols.

$0.04 < q < 0.6$ [1/nm] for potato. According to Eq. (1), this result implies that the scattering objects are fractal in nature. Furthermore, with regard to the kind of fractal, it was judged that the scatterings from low moisture starches are mainly due to the surface fractal structure of the corn and potato starch granules because the slopes of these linear relations, α , were close to -4.0 , and that were at least in the range of less than -3.0 . From Eq. (4) the 'surface fractal dimension' D_s was estimated to be *ca* 2.0 for both starches. Therefore, it can be presumed that the surfaces of low moisture starches are smooth when observed in the scale of $3 < d (= 2\pi/q) < 150$ [nm] for corn and $10 < d (= 2\pi/q) < 150$ [nm] for potato. This scattering can also be interpreted as a reflection of a sharp surface according to Porod's Law (Gratzer and Kratky, 1982) because the gradient is alternatively close to -4.0 , even though it is a special case of a surface fractal.

When the moisture increased to 1 g water/g solid, the linearities between I and q on the log-log scale came to hold only within a narrow range on the low angle side for both starches. As shown in Figs 1 and 2, at ambient temperature, the scattering patterns of the low angle side approach the real lines, which are calculated from Eq. (1) in the case of $\alpha = -4.0$, i.e. a smooth surface. Simultaneously, the scattering patterns of potato starch came to show two characteristic peaks, P1 and P2, indicated by arrows in Fig. 1, whereas that of corn starch showed only one peak, P2. The P1 peak

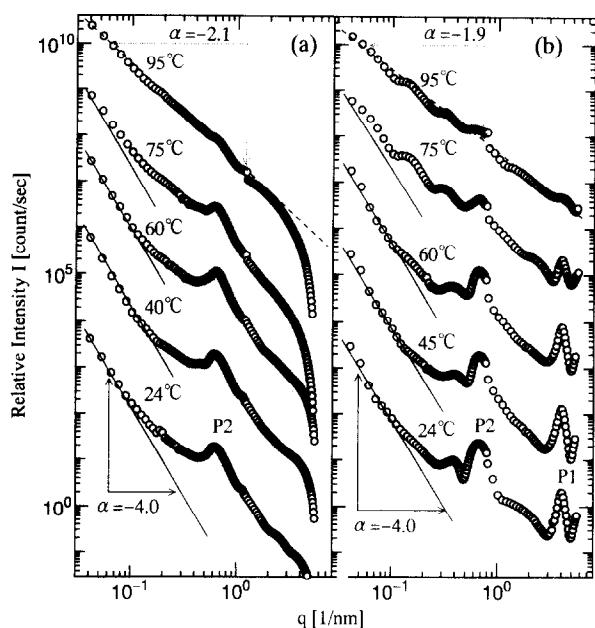


Fig. 2. The small angle X-ray scattering patterns from corn (a) and potato (b) starches during gelatinization. The moisture content of all samples was 100 wt% on a dry basis. The intensities are shifted along the ordinate in order to avoid overlapping of the symbols. The real lines show the curves calculated by the equation; $I \propto q^{-1}$ as same as those in Fig. 1. The broken lines in both figures, (a) and (b), show the fitting curves to $I \propto q^{-1}$, which represents fractal relationship. From the values of the slopes, α , the scattering patterns at 95°C are categorised as a 'mass fractal'.

on the high angle side, which was recognised only for potato starch, is thought to correspond to one of the end peaks, which are usually detected using wide angle X-ray diffraction for a B-type starch (Zobel (1988a, b)). Since an A-type starch is known to lack this peak (Zobel (1988a, b)), it is reasonable that for corn starch of the A-type, the peak on the high angle side was not observed. However, the P2 peaks of about $q = 0.62 [1/\text{nm}]$ ($d = 10 \text{ nm}$) were recognised for both starches, which were in good agreement with the results of similar investigations using SAXS by Stirling (1962), Hizukuri *et al.* (1964), and Cameron and Donald (1992, 1993a, b and Jenkins *et al.*, 1994)). Although it seemed that, for a lower-moisture starch, there were some small peaks, they were considered to be due to noise. This was enlarged by the desmearing treatment because the net scattering intensities were small relative to the noise in the range of large q values.

With regard to the effects of swelling on the scattering, we considered the following: the intensity of SAXS is affected in principle by the electron density difference in a sample, in other words, the density contrast rather than the absolute density itself (Guinier and Fournet, 1955). When the powdered starch samples of low moisture content were packed in a capillary tube for SAXS experiments, the large density difference at the interface or surface, which lies

between the average density of the starch granules and the air density of the gaps, will become more significant for scattering intensity than the density fluctuation in the starch granules. Therefore, for the low-moisture starches, the scattering may be detected as a surface fractal. However, when water fills the gaps between the starch granules and is absorbed by the amorphous regions inside the granules on swelling, the density difference between the amorphous and the crystalline regions inside the starch granules becomes prominent rather than that at the interface or surface of the granules. Cameron and Donald (1993a) applied the lamella stack model to analyse the SAXS pattern for the swelling process of wheat starch slurries (45–55% w/w). They then concluded that the density difference between the amorphous and the lamella regions enlarges as the water is absorbed by the amorphous region, because the density of the lamella crystal does not change with absorbed water, but the electron density of the amorphous region decreases. The swelling of the starch granules on water absorption might cause an enhancement of the peaks in the scattering pattern. As a result, it may become difficult to detect the scattering from the surface, despite the existence of the surface. Though Cameron and Donald (1993a) did not discuss the scattering from the surface, it seems that their conclusions do not contradict our view regarding surface scattering. This suggests that the surface of starch granules is rigid and remains smooth at room temperature, even if the starches swell. Reversibly, the scattering from the inner structure of dry starches is thought to be masked by the surface scattering. If the air around the dry starch granules is replaced with a fluid of density close to that of starch granule, then the surface scattering disappears, and the scattering reflects only the inner structure of the dry starch. We have attempted SAXS measurements on samples when the gaps between the starch granules are filled liquids that would not penetrate inside the granules. However, at the present time, we have not yet attained definitive conclusions because of conditions from the scattering of the liquid itself.

Gelatinization

Figure 2(a and b) shows the scattering curves at different temperatures for corn and potato starches with 1 g water/1 g solid. We can recognise the remarkable structure changes on a nanometre scale during gelatinization of the starches. The two previously mentioned peaks, P1 and P2, became gradually smaller as the temperature rose. Although many DSC experiments show an endothermic transition due to the gelatinization at 60–70°C, the behaviour of the SAXS peaks was not observed as a critical transition at that temperature. The melting of

the crystalline regions inside the starch granules is thought to progress in conjunction with swelling of the amorphous regions as reported by Cameron and Donald (1992, 1993b). In our experiment, the water content was not high enough for starch to gelatinise, and consequently, the transitional melting temperature as observed by DSC would become high or obscure.

However, with regard to the surface structure, it was found that the surface structures for both starches remain smooth below about 60°C because the gradients of the scattering profiles were almost unchanged on the low angle side. However, near 75°C, the slopes changed dramatically from *ca* 4.0 to less than 3.0. These results mean that the equation governing the scattering patterns changed from Eq. (4) to Eq. (5). On the basis of the fractal concept, it can be said that the source substances inducing the scattering changed from a 'surface fractal' to a 'mass fractal'. That is, the surface of the starch granules disappeared near 75°C, and then macroscopically, the suspension state became a polymer solution.

Further, when the sample temperature reached 95°C for both starches, the peaks in the scattering patterns disappeared completely. The relationship between I and q for gelatinised starches is then linear over a wide angle range on the double-logarithmic graph. That is to say, the scattering from the completely gelatinised starches show a fractal relation obeying Eq. (1). The gradients of the straight lines, $-\alpha$, were -2.1 for corn and -1.9 for potato. These values of α imply that the physical arrangement of starch molecules is a 'mass fractal' entirely at 95°C. The 'mass fractal dimension', D_m , was then estimated to be 2.1 for corn starch and 1.9 for potato.

Blanshard *et al.* (1984) applied Guinier's method to the analysis of the data on small angle neutron scattering from gelatinised starch, which is similar to SAXS in principle, and determined the dimensions of the racemose model of amylopectin. Cameron and Donald (1991, 1992, 1993b) and Jenkins *et al.* (1994) explained the change in the SAXS profiles on gelatinization of starch by using the lamella stacking paracrystalline model. However it seems difficult to explain the very wide range linearity of $\log I$ and $\log q$ observed in our experiments using those models.

Figure 3 shows the scattering patterns of the gelatinised corn starches prepared at various concentrations. The logarithmic scattering patterns at each concentration showed a good agreement in the slopes, though their absolute intensities were dependent on the concentrations. Although we did not show the results for potato starch, the results were the same as that for corn starch. These results not only verify the reproducibility of our experiment, but also mean that the conformations of gelatinised starch polymers keep the same fractal formation over the semi-dilute concentration range examined. Generally, a semi-dilute

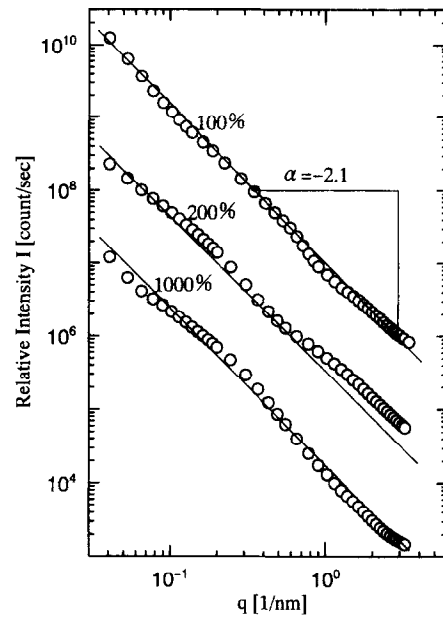


Fig. 3. The effect of concentration on the small angle X-ray scattering of gelatinised corn starch at 95°C. The intensities are shifted along the ordinate in order to avoid overlapping of the symbols. The real lines show the curves calculated by the equation assuming $\alpha = -2.1$. The percent values in this figure represent the water contents on a dry basis.

concentration is defined as the concentration between the pure melt and the so-called overlap concentration when polymers must contact each other. For such a concentration, it is expected that the mass fractal dimension D_m for a linear polymer is $5/3$ or 2.0, depending on the q range, and D_m for a branched polymer is within $8/5$ to $5/2$ (Daoud and Martin, 1989). Compared with these values of D_m , our results, 2.1 for corn and 1.9 for potato, appear to be reasonable. However, it is thought that the difference in the D_m values between corn and potato was so small that it should not be considered at this stage. Further tests for confirmation of the difference would be needed. Although amylose is one of the main components of starch, Vallera *et al.* (1994) showed, using small-angle neutron scattering, that the amylose gels and sols have different fractal dimensions, 2.6 and 2.0, respectively; and those values were almost independent of concentration. Their result is very similar to ours. Since, in our experiment, the sample temperature was *ca* 95°C when the scatterings of starches showed a mass fractal, the state of the starches is thought to be sol. It is interesting that the fractal dimensions of the gelatinised starches, which were around 2.0, are close to that of amylose sols rather than its gel. In the sol state, starch and amylose may have similar conformations. However, to account for the structure of gelatinised starch in more detail, the existence of another component, i.e. amylopectin, should be taken into consideration. Furthermore, the effects of

polydispersity on the fractal dimension must also be considered.

Retrogradation

Figure 4 shows the distinctive scattering pattern of the retrograded potato starches. For a comparison, the scattering patterns of the gelatinised starch and the swollen state starch at ambient temperature are shown in the same figure. It is found that even after 1 day's storage at 4°C, the scattering pattern changes remarkably, and that is clearly different from the scattering of the gelatinised starch and the swollen starch. We can recognise that the scattering profile of the retrograded starch has a shoulder-like pattern at $q=0.2\sim 0.4\text{ nm}^{-1}$, and the surface scattering of low angle side is not recovered. The pattern did not change after 2 days' storage. Cameron and Donald (1991) also reported similar results; SAXS patterns from retrograded starches showed no periodicity of *ca* 10 nm; this was observed for native starch. However, they did not describe the shoulder at $q=0.2\sim 0.4\text{ nm}^{-1}$. Probably, since the smallest scattering vector, q , measured by them was $q=0.2\text{ nm}^{-1}$, the shoulder would be located on the edge of the scattering profile. Thus, it is probable that they would not be able to observe it.

As for the scattering pattern of the retrograded starch, two kinds of interpretation may be considered; one is that the pattern is a convolution of the fractal scattering of the gelatinised starch, the broad Bragg's peak due to a new, large lamella stacking, another is that it has two fractal scattering regions at high and low q values, with different fractal dimensions. At present, it is impossible to determine which is true. However, as shown in Fig. 4, it seems that the imposed real lines, representing the

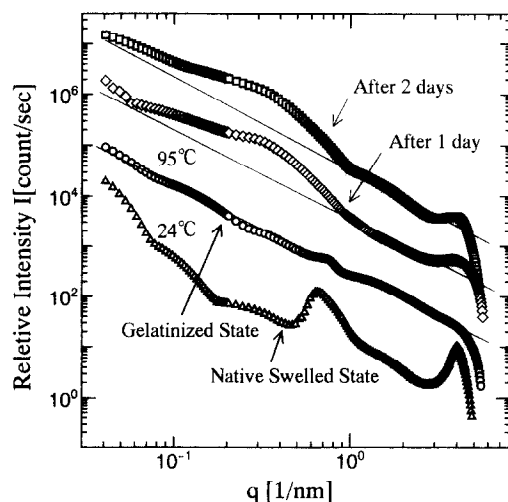


Fig. 4. The scattering patterns of the retrograded potato starches. For reference, the data of the gelatinized and native potato starches are shown. The real lines show the curves calculated by the equation; $I \propto q^\alpha$, assuming $\alpha = -1.9$.

fractal scattering of $D_m=1.9$, are the background scattering of the retrograded starch. At least, what we can say from this result is that the long-range structure of retrograded starch has a characteristic size of some kind; this is similar not to the structure of the native starch but to the gelatinised starch. That is to say, the retrogradation phenomena is irreversible also in the long length structure. The Bragg spacing corresponding $q=0.2\sim 0.4\text{ nm}^{-1}$ is 31~15 nm. Since this size is of the same order as the diameter of digestive enzymes such as amylase, the structural change of this size is thought to affect the digestibility of starch. To understand the relation between the digestibility and the retrogradation of starch, it may be of interest to clear the origin structure of the shoulder in the scattering profile. Although we did not show the results for corn starch, the result was the same as that for potato starch.

In conclusion, small-angle X-ray scattering from starches during each stage of swelling, gelatinization and retrogradation could be interpreted on the basis of the fractal concept. The SAXS from dry starches showed a surface fractal response and reflected entirely the scattering from a smooth surface. Since scattering at low angles from the swollen starch also showed the same behaviour as the dry starch, the surface of starch was thought to remain smooth at ambient temperature, even when the starch was swollen. On melting of crystalline portions (the so-called gelatinization process), at *ca* 80°C, the disappearance of the surface of the starch granules was suggested from the change in slope of the scattering profile at low angles. It was found that the physical arrangements of the completely gelatinised starch molecules for both corn and potato can be evaluated as a mass fractal, giving different non-integer dimensions. Although those values of D_m were in a reasonable range, they were not yet sufficiently precise to discuss the difference between corn and potato starch. Furthermore, we found that the scattering of the retrograded starch showed a shoulder-like peak, with the mass fractal scattering as a background. Indeed, the retrograded starch may form irreversibly a different lamella stacking structure to that of the native starch. It is expected that the detailed structural analysis for the retrograded starch can be conducted using a combined lamella and mass fractal model.

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