Structure of the Starch Granule – A Curved Crystal

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A structure model of the molecular arrangement in native starch proposed earlier is further considered, with special regard to the lateral packing of cluster units. The amylopectin molecules are radially distributed, with branches concentrated in clusters. Within each cluster the polyglucan chains form double helices which are hexagonally packed. The clusters form spherically concentric crystalline layers with amylose in an amorphous form acting as a space-filler. A translational mechanism for the change of helical direction at boundaries between clusters is proposed which can account for variations in the curvature of the concentric layers. The model is related to X-ray diffraction data and optical birefringence, considering dissembly at gelatinization.

The structure is also discussed in relation to biosynthesis. Some aspects of gelatinization, such as the recent glass-transition approach, are then considered.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

Starch is the main form in which carbohydrates are stored in plants, and it is found in all organs in the majority of the higher plants. Starch is produced in amyloplasts and chloroplasts. Amyloplasts are organelles specialized for starch storage which are developed from proplastids like the chloroplasts. Chloroplast starch is degraded and used as energy during night-time in the living plant. From a food point of view starch is of utmost importance, as is gives more than half of the energy intake to the world population. Furthermore, the physical/structural changes associated with starch gelatinization play a central role in food processes, e.g. in the baking of bread.

The ordered structure of the starch granule is unique, with crystalline layers forming a mainly spherically concentric arrangement. Liposomes exhibit a related structure, but their molecular organization is liquid-crystalline. Starch might, owing to its curvature, be described as a quasicrystal with a two-dimensional dilation of the lattice. It should be pointed out that there are other types of curved crystalline structures in Nature, for example the cylindrical arrangement of cellulose molecules in the cell wall of wood.

This paper is an extension of earlier work of the structure of native starch,[1] and is focused on the mechanisms behind the assembly of crystalline clusters into curved layers.

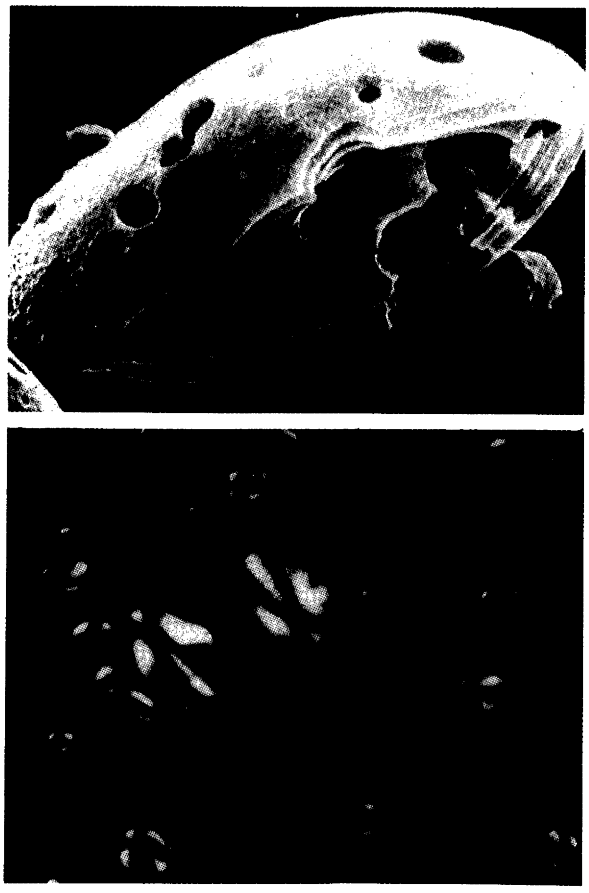

Fig. 1. Potato starch granules viewed in the polarizing microscope are shown below, and the concentric crystalline layers viewed by SEM are shown above.

Amylopectin structure in starch granules

The main features of the proposed structure of the starch granule[1] will be summarized here. The radial symmetry of starch granules and the arrangements of crystalline regions into closed concentric layers are illustrated in Fig. 1. The

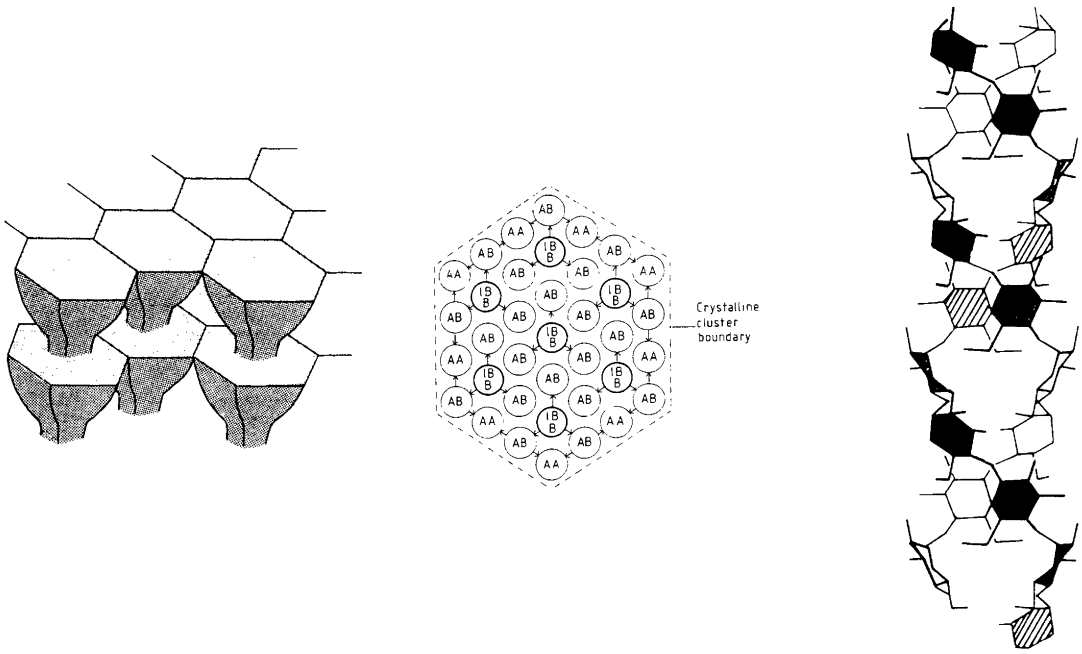

Fig. 2. The arrangement of crystalline cluster units into concentric layers is shown to the left. Between these units (shaded) amylose in an amorphous state fills the space. To the right a segment of a double helix is shown, and in the middle a cross-section view of a cluster is illustrated. Each ring is a double helix, and the branch linkages are shown by arrows. A long B-chain (I-B) goes through many clusters. This is branched into a B-chain, which in turn is branched into an A-chain.

branches of the huge amylopectin molecule are concentrated into groups, termed clusters. The length of the whole molecule is 1200–1400 Å and the size of the clusters along this chain is about 100 Å. The pioneering study of the order of the starch structure was reported by Wu and Sarko,[2] who analysed its X-ray diffraction pattern. The linear polyglucan chains have a strong tendency to form double helices, which in turn are hexagonally arranged (Fig. 2). The pitch contains six sugar units and is about 21 Å in length. A most remarkable feature of the starch structure is that the branched amylopectin molecule only forms crystalline regions,[3] whereas the linear amylose component is amorphous, appearing as a space-filler.

The arrangement of the double helices into a crystalline cluster unit is also shown in Fig. 2, as well as the lateral arrangement of amylopectin molecules into concentric crystalline layers. Our earlier work[1] concerned the relation between chemical branching and the helical packing arrangement within a cluster. The structure is very similar to that of quartz, and it can be described by an infinite periodic minimal surface (zero average curvature), which in fact is the interface between each helix (the Q^*-surface). The space group is $P6_422$. It should be pointed out that this structure model concerns cereal starch; its relationship to other starches is discussed in a later paragraph.

The proposal that the size of the crystalline regions is identical to the cluster size is based on X-ray line-broadening analysis.[4] Thus line-broadening corresponds to a size of ca. 100 Å in the different directions defined by the planes of the observed reflexions. Furthermore, no difference due to different granule size fractions could be seen, consistent with periodicity disorder over cluster boundaries.

Cluster packing into curved layers

The X-ray diffraction analysis described below is consistent with conically shaped units, about 100 Å in thickness and 150 Å in diameter. The fact that the granules exhibit birefringence, however, must mean that there is also a periodicity of the cluster arrangement, although it is obviously not perfect on the atomic level. It is also evident that the forces between double helices within a cluster are very similar to packing forces over cluster boundaries, as the thermal dissembly of helices in excess of water (gelatinization) takes place at a discrete temperature. Also, the simultaneous disappearance of X-ray diffraction and optical birefringence indicates a simultaneous dissembly of all the double helices.

Although the packing forces between double helices over the cluster boundary must be almost identical to those within the cluster, as argued above, there is also a need for a change in curvature. The only reasonable locations for such distortions are along these boundaries, as they are free from covalent linkages. It is thus reasonable to assume that adjacent clusters show differences in the directions of the helical axes. A possible mechanism for tilt change at the cluster boundary is shown in Fig. 3. A short double helix can be quite closely packed with a neighbouring helix in a different direction if they are moved in relation to the packing of parallel helices by a translatory displacement.

Fig. 3. Mechanism proposed in order to form the curved layers of clusters. The normal close-packing arrangement of double helices is shown to the right, and the proposed translation in order to account for a change in the direction of the helical axes is shown to the left.

Starch structure in different plants

The main structure in granules from all starch varieties is the same, with the concentric crystalline layers of clusters described above. There is, however, a difference within the cluster. The structure in Fig. 2 is obtained in cereals, whereas in tuber starch one double helix out of three is replaced by water (the rest is very similar).[2] There is a third type of starch structure in plants, occurring in legumes (e.g. beans and peas). The structure in these starch granules[5] is a mixture of a cluster structure like that in tuber starch and a cluster structure like that in cereals (Fig. 2). The relative localization of these two types, however, is not known.

Why is different molecular packing obtained at the crystallization of tuber starch compared to cereal starch, independent of variations in the amylose/amylopectin ratios? The most striking difference is the amount of lipids present in the granule in the form of an amylose–monoacyl lipid helical complex in cereal starches (usually about 1 % lipid, but in oats up to 5 %). There is, however, no evident epitaxy if the lipid–amylose lattice (V-amylose) is compared to that of the cluster. Furthermore it has not been possible to observe any V-conformation diffraction, even at high contents of lipid complexes in the starch granule. This indicates that, as there is high phospholipase-C activity at the site of amylose synthesis, the insoluble complex simply forms an amorphous coprecipitate, acting as a space-filler like amylose.

Retrogradation of a starch gel can give an X-ray diffraction pattern corresponding to the cluster structure of either tuber starch or cereal starch, depending upon the water content. Therefore, the fact that starch formation in tuber starch takes place in the presence of more water than in the cereal endosperm indicates that it is simply the aqueous environment that determines whether the cluster structure will consist of close-packed double helices or whether there will be absences occupied by water molecules. This is consistent with the observation that maize starch granules show birefringence after a growth period of 18 days and have the same X-ray pattern as tuber starch, contrary to the diffraction pattern of mature kernels formed when there is less water.[8]

Biosynthetic aspects

Little is known about the initial stages of starch granule formation. An attractive model suggesting by Badenhuizen[6] involves the separation of an aqueous droplet, a coacervate. Such two-phase separation into separate aqueous compartments is a common colloidal phenomenon. A droplet rich in amylopectin should then be expected to solidify into a microgranule, which will be a nucleus for further growth. From radiochemical studies it is furthermore clear that the granules grow by apposition, i.e. by the addition of gluycose units to the surface.[7] A tempting hypothesis is the localization of the synthezising enzyme system at a two-phase boundary, where amylopectin in water is the dispersed phase.

Granule shape

The final shape of the starch granules is characteristic for different species of plants, and the cellular organization of the synthetic apparatus is the primary factor determining the final topography. However, there is reason to assume that the strive toward a minimum in the surface free energy will also influence the shape. This equilibrium shape should be equal to σA, where σ is the specific surface energy of the layer structure and A is the area. Small granules, in wheat for example, are globular, whereas large granules have a lens-like shape; in some cases even biconcave shapes like erythrocytes can be seen. Such curvature will give a closer cluster packing in the crystalline layer, thus reducing the specific surface free energy as a compensation for the increased surface-to-volume ratio.

There are striking textual similarities between starch granules and polymer spherulites when viewed in the polarizing microscope. In addition to the spherulitic habit at crystallization, the radial symmetry is the same, as is evident from the birefringence and an extinction cross parallel to the directions of the polarizer and analyzer. There is, however, a fundamental structural difference. The polymer spherulite has the polymer chain oriented perpendicular (or slightly inclined) to the radial direction, unlike the polyglucan chains in the starch granules.

The starch gel

A dried starch gel is structurally equivalent to a glass. The glass concept has been introduced by Levine and Slade in connection with food gel systems (cf. Ref. 9). Many organic molecules can be transformed into a vitreous state if they are cooled rapidly enough. A glucose melt, for example, forms a glass around room temperature. The glass transition is characterized by a reduction in heat capacity by a factor of 2, whereas the molar volume or enthalpy shows no abrupt change. From a structural point of view there is no long range order in a glass, although the molecular

mobility is like that in a solid, and the viscosity is typically about 10^{13} poise. Glass transitions are common in polymers (cf. Ref. 10).

In food systems the significance of this approach is mainly related to the role of water. Thus water is regarded as a plasticizer, much in the way phtalates and other small molecules influence organic polymers such as polyvinyl chloride. In native starch only the amorphous regions will be plasticized by water. The plasticizer will increase the free volume of the polymer, leading to increased polymer chain mobility and therefore a reduction in the glass-transition temperature. The agreement between the effect of water on the glass-transition temperature, as seen from DSC curves and calculations of effects on free volumes, is very good. One important aspect of this approach has been a modified view of water as "free" and "bound" in aqueous systems of biopolymers. Thus mobility effects, rather than specific hydrogen bonding, are dominating in water interaction phenomena such as gelatinization.

Concluding remarks

There are a number of crucial questions which remain to be answered before we have a complete picture of the structure of starch. To mention a few of them:

Why is amylose amorphous in the granule?
How can the characteristic granule of a particular plant species adopt wide variations in the amylose/amylopectin ratio?
Is branching monitored by curvature?
How are adjacent clusters assembled during biosynthesis?

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