

Starch: the most challenging polymer colloid

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Starch is at first sight a simple polymer, being a homopolymer of glucose. However, it has an extraordinary complexity, covering six identifiable structural levels, at scales from nm to mm. This is because of its branching structure, the ways these branches are arranged in spaces in lamellae, the way the lamellae are arranged, and so on. Starch's major component, amylopectin, is particularly challenging: a hyperbranched polymer with molecular weight up to 10^9 , and 10^5 branches per molecule. The structure of this complex polymer colloid in solution, whose size is ~ 300 nm,¹ can be characterized by multiple-detection size separation techniques, which requires a solvent system able to dissolve all of the starch. The water-based systems usually employed for this do not dissolve the bigger chains,² requiring the use of DMSO-based solvents³ and both SEC and field-flow fractionation. The interpretation of multiple-detection size-separation data requires novel theory. This starts with a multi-variable distribution function $P''(V_h, M, N)$, the number of chains with hydrodynamic volume V_h , total molecular weight M and a branch of degree of polymerization N . The integral of this distribution over N gives the function P'_N , which is the basis for a new means of obtaining structural information from size-exclusion data,⁴ and whose integral over M provides a new distribution function P'_M which can be found experimentally by combining preparative size separation and debranching.^{5,6} This provides the only unambiguous means to determine amylose fraction and biosynthetic processes. Relating multi-detection size-exclusion data to structural characteristics is through a randomly-branched reference distribution function, which has the same debranched chain-length distribution as the actual sample.^{7,8} This enables the complex structure to be reduced to a small number of physically meaningful parameters.

These means of obtaining structural characteristics provide a new battery of tools to obtain structure-property and synthesis-structure relations, which can reveal the mechanistic basis linking molecular architecture to material behaviour for starches. This will allow rational selection of plant molecular breeding targets and food processing conditions for desired nutritional properties, as well as for industrial uses of starch. Starch comprises 50% of the food energy in Western diets, and the long-term goal is to establish the structural characteristics which are of significance in the present epidemic levels of obesity and diabetes.

References

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