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Hydration-induced crystalline transformation of starch polymer under ambient conditions

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ABSTRACT

With synchrotron small/wide-angle X-ray scattering (SAXS/WAXS), we revealed that post-harvest hydration at ambient conditions can further alter the starch crystalline structure. The hydration process induced the alignment of starch helices into crystalline lamellae, irrespective of the starch type (A- or B-). In this process, non-crystalline helices were probably packed with water molecules to form new crystal units, thereby enhancing the overall concentration of starch crystallinity. In particular, a fraction of the monoclinic crystal units of the A-type starches encapsulated water molecules during hydration, leading to the outward movement of starch helices. Such movement resulted in the transformation of monoclinic units into hexagonal units, which was associated with the B-type crystallites. Hence, the hydration under ambient conditions could enhance the B-polymorphic features for both A-type and B-type starches. The new knowledge obtained here may guide the design of biopolymer-based liquid crystal materials with controlled lattice regularity and demanded features.

1. Introduction

Nanopattern with controlled regularity has an enormous advantage in designing anisotropic materials because of their broad utility and versatility in optics [1], electronics [2,3], and bioengineering [4]. Liquid crystals, as anisotropic mesophases existing between solid crystal and isotropic liquid, have attracted increasing attention [2]. The molecules with liquid crystal behaviors, *viz.*, mesogens, are generally organized into regular nanoscale units (*i.e.*, lattices) via non-covalent forces (*e.g.*, hydrogen bonding) [5]. The functionalities (optical, electronic and sensing properties [1,2,5]) of liquid crystals highly depend on the shape and size of the lattices. Hence, manipulating the lattice pattern of liquid crystals stands at the core of tailoring their performance. For controlling the morphology of liquid crystal cells, mesogens with different sizes and shapes have been reported, including the smectic, columnar, cubic and discotic forms [6] originated from metal, ionic and polymeric materials [2]. However, the development of liquid crystals using these mesogens requires tedious multi-step reactions and purification processes, as well as severe experimental conditions.

In contrast, natural polymers such as cellulose and starch provide fascinating models for creating nano-materials with precisely controlled dimensions [7–10]. These polymers are not only widely available and sustainable but also biodegradable and biocompatible, and thus have several economic and environmental advantages. Starch is a typical natural polymer with the liquid crystal property [11], and it includes two major glucan polymers, *i.e.*, amylose and amylopectin [12,13]. These two biopolymers form crystalline and amorphous areas in the native starch granule to construct a multi-level semicrystalline structure [14–16]. In particular, the double helices of starch chains exist as mesogens [11] and are also the key structural units in the starch granule. The organization of the starch helices within the nanoscale crystal cells

Abbreviations: WMS, waxy maize starch; RMS, regular maize starch; GMS, Gelose 50 high amylose maize starch; PS, potato starch; SAXS, small-angle X-ray scattering; WAXS, wide-angle X-ray scattering.

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governs the crystalline structure of starch. There are mainly two types of crystalline structures of starch including A-type with monoclinic crystal cells and B-type with hexagonal crystal units [17]. The understanding of how the external conditions influence the organization of starch helices into the different crystal cells could open research avenues into artificially designing liquid crystals with regular nanoscale patterns.

The organization of post-harvest starch helices into either the A- or B-type crystal cell closely relates to the amount of water molecules. While A-type starch crystallites contain only eight interhelical water molecules in each monoclinic crystal unit with tightly packed helices, the B-type crystallites have 36 water molecules in each hexagonal crystal unit with a more open packing of helices [17]. The cereal starches (*e.g.*, wheat, rice) normally contain A-type crystallites, whereas tuber, fruit and stem starches (*e.g.*, potato, banana) often have B-type crystallites. Nonetheless, the mechanism on how the growth of plants relates to the starch crystalline type, *i.e.*, the manner of helices organized into the crystal cells, is still not fully understood. Moreover, besides the cultivar, the thermal processing of starch with water, *e.g.*, extruding and compression molding, also tends to change starch crystalline structure [18,19]. This change might result from the disruption of original crystallites and the realignment of helices into the crystal cells to form new crystallites with the same or an altered type. However, while in these cases a combination of multiple conditions (such as temperature, moisture, and so forth) with complex variation patterns are involved, it is challenging to derive general bionic inspirations for the design of liquid crystals where artificial (*e.g.*, post-harvest) and spontaneous (*e.g.*, at ambient conditions) processes are preferred.

Considering the crucial role of water molecules in constructing starch crystal cells, here we test whether the hydration alone under ambient conditions can spontaneously alter the manner of the starch helical organization into crystal cells, *i.e.*, the type of starch crystallites. If so, the related evolution in the assembly of starch helices (mesogens) within the crystal units would provide valuable information for the rational and simple development of natural, starch-based liquid crystals with regulated nanoscale morphology and thus demanded performance. Though earlier findings show that hydration might increase the starch crystallinity [20,21], it is unaccounted for whether post-harvest hydration can induce any changes in the crystalline type. To this end, we evaluated the effects of hydration under ambient conditions (*ca.* 26 °C) on the crystalline structure of four starches using synchrotron SAXS/WAXS techniques. Based on the results, we discussed the underlying mechanism regarding how hydration changes the starch crystalline features.

2. Materials and methods

2.1. Materials

Waxy maize starch (WMS), regular maize starch (RMS), and Gelose 50 maize starch (GMS) were supplied by Penford Australia Ltd. (Lane Cove, NSW Australia). WMS, RMS, and GMS had amylose contents of *ca.* 3%, 24% and 56%, respectively, as measured using an iodine colorimetric method [22]. Potato starch (PS) with an amylose content of *ca.* 36% was purchased from Avebe (Netherlands). A moisture analyzer (MA35, Sartorius Stedim Biotech GmbH, Germany) was used to measure the moisture content (MC) of starch. The MC for the maize starches was *ca.* 13%, while that for PS was *ca.* 14%.

2.2. Small/wide angle X-ray scattering (SAXS/WAXS)

SAXS/WAXS measurements with 1s acquisition were carried out on the SAXS/WAXS beamline (flux, 10^{13} photons/s) installed at the Australian Synchrotron (Clayton, Australia) [23], at a wavelength $\lambda = 1.54$ Å. The 2D scattering patterns were recorded using a Pilatus 1 M camera (active area 169 × 179 mm and pixel size 172 × 172 μm) and a Pilatus 200 K camera (active area 169 × 33 mm and pixel size 172 × 172 μm). The 1D data were acquired from the 2D scattering patterns using the Scatterbrain software. The starch powders without adding any water were used as the dry (*i.e.*, non-hydrated) starch samples. Also, to fully hydrate those four starches, the starch slurries containing 40% starch were prepared in vials with careful blending, and then kept under ambient conditions (*i.e.*, 26 °C) for 1 h. The resulted starch slurries were used as the hydrated starch samples. Both non-hydrated and hydrated starches were tested. The scattering of a Kapton tape (5413 AMBER 3/4IN X 36YD, 3 M, USA) on the stage window was used as the background for the starches before hydration, and the scattering of pure water with the Kapton tape was used as the background for the hydrated starches. All data were collected at 26 °C and were background subtracted and normalized. Each test was conducted in triplicate to obtain reliable scattering results.

The configuration covered $0.015 < q < 2.9$ Å^{-1} simultaneously by establishing a slight overlap in q (see Fig. S1 in Support information). The scattering vector, q, was defined as $q = 4\pi\sin\theta/\lambda$, in which 2θ is the scattering angle and λ is the wavelength of the X-ray source. The data in the range of $0.015 < q < 0.20$ Å^{-1} were used as the SAXS patterns. The data in the range of $0.28 < q < 2.8$ Å^{-1} (*ca.* $4^\circ < 2\theta$ for Cu Kα $< 40^\circ$) were used as the WAXS patterns. The relative crystallinity (X_c, %) of starch was calculated using the PeakFit software (Ver. 4.12) [24], according to Eq. (1):

$$X_c = \frac{\sum_{i=1}^{n} A_{ci}}{A_t} \quad (1)$$

where A_{ci} is the area under each crystalline peak with the index i, and A_t is the total area of the WAXS pattern.

2.3. Statistical analysis

Data were expressed as means ± standard deviations, and were analyzed by the one-way ANOVA and multiple comparison tests with a least significant difference using the IBM SPSS software version 20.0 (Chicago, IL, USA). A statistical difference of $P < 0.05$ was considered significant.

3. Results and discussion

3.1. Synchrotron SAXS analysis

Fig. 1 shows the double-logarithmic and Lorentz-corrected synchrotron SAXS patterns of WMS, RMS, GMS, and PS before hydration. Dry RMS displayed a modest peak at *ca.* 0.07 Å^{-1} (q_{peak1} for dry samples) (see Table 1 and Fig. 1A), ascribed to the semi-crystalline lamellar structure of starch [25,26]. Also, dry RMS featured a second less-resolved peak at *ca.* 0.15 Å^{-1} (q_{peak2} for dry samples), which was probably the second order reflection of the lamellar arrangement [21]. Dry WMS and dry PS had a lamellar peak at *ca.* 0.09 Å^{-1} and 0.08 Å^{-1} respectively, though the peak has never been detected by the bench-scale SAXS instrument for dry PS. From the Lorentz-corrected SAXS patterns in Fig. 1B, a very weak peak at *ca.* 0.08 Å^{-1} was seen for dry GMS powder. All these results indicate that, before hydration, only a small part of starch helices could be aligned into the crystalline lamellae to construct the semi-crystalline lamellar structure.