

The Fine Structure of Ball-milled Corn Starches with Different Amylose Contents Investigated by SAXS Technique

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Small angle X-ray scattering (SAXS) was applied to investigate the average thickness of the lamellar repeating unit of ball-milled corn starches with different amylose contents, and conditioned in different relative humidities (54, 100% RH) or hydrated. The position of the SAXS peak is related to the average lamellar repeating length in granular starch, whereas peak width and intensity are mainly dependent on the regularity of the arrangement of lamellae and the electron density differences between the amorphous and crystalline regions of the lamellar structure [1]. Our investigations show that the intensity of SAXS peaks of normal, waxy and Hylon VII corn starches (conditioned at 54% RH) were decreased while the time of ball milling were increased. It means that the crystallinity of starch was decreased after ball milling which was a kind of physical modification that could destroy the semi-crystalline structure by collision between granules and milling balls.

The $q_{\max}$ value of the SAXS peak (Fig. 1 (a)) was at $0.065 \text{ \AA}^{-1}$ before ball milling, but disappeared after ball milling (Fig. 1 (b to d)). However, Fig. 1 (e to g) showed that the position and intensity of SAXS peaks recovered after being conditioned at 100% RH, and the SAXS peak of hydrated native corn starch (Fig. 1 (i)) was higher than those conditioned at 54 and 100% RH. The above phenomenon agreed with previous studies, suggesting that on adding excess water, the peak associated with the 9 nm d -spacing characteristic of native corn starch ($q \sim 0.07 \text{ \AA}^{-1}$) appears obviously [2]. Cameron and Donald indicated that an increase in the water content of starch granule lead to an increase in the molecular order, as molecular motion and, therefore, chain reorganization was favored [2]. Although adjusting starches to 100% RH or hydrated them in water would lead to rearrangement of the starch molecular order, the ball milling did decompose the structure of the crystalline lamella and this change was irreversible. The evidence was that the ball-milled corn starch conditioned at the same RH showed decreased peak intensity and increased peak width in SAXS pattern. The broader peak means the smaller repeating number of lamella.

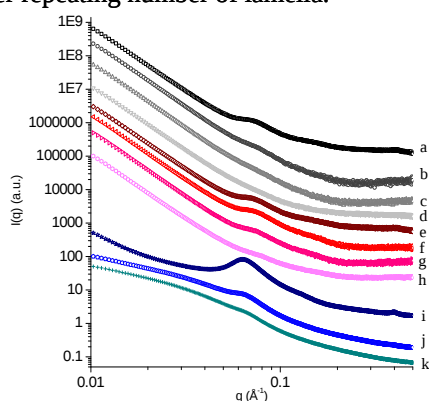


Fig. 1: SAXS patterns of normal corn starches ball milled for 0 (a, e, and i), 30 (b, f, and j), 60 (c, g, and k) or 120 (d and h) min, followed by conditioning at 54% RH (a-d) and 100% RH (e-h), and hydrated (i-k).

In Table 1, the parameters of the ball-milled waxy corn starches conditioned at 100% RH were different from those of normal corn starches. The intensity of SAXS peaks and d -spacing (average thickness of the lamellar repeating unit) were increased gradually with increasing milling time. Because the waxy corn starch granule was lack of the entanglement of amylose, the structure was decomposed easier while being stroken by milling balls. The loosened structure of ball-milled waxy corn starches lead to easier reorganization of amylopectin at 100% RH. However, the Δq (peak width) of SAXS peaks of ball-milled waxy corn starch were increased with increasing milling time. It means that the mounts of lamellar repeating unit were decreased after ball milling. Table 1. Parameters obtained by fitting the scattering data of waxy corn starch samples conditioned at 100% RH based on "Power Law plus Cauchy" model [3].

Sample*	$I_{\max}$ (rel. units)	$q_{\max}$ ($\text{\AA}^{-1}$)	Δq ($\text{\AA}^{-1}$)	d -spacing (nm)
WCS0 ^a	0.4175	0.0833	0.0381	7.54
WCS30 ^b	0.5509	0.0835	0.0503	7.52
WCS60 ^c	1.4112	0.0800	0.0493	7.85
WCS120 ^d	1.2847	0.0724	0.0657	8.67

* The characters a to d represented waxy corn starch ball milled for 0, 30, 60 and 120 min, respectively.

The two peaks, $q \sim 0.07$ and $0.4 \text{ \AA}^{-1}$ shown in Fig. 2 (a) were associated with the 9 nm d -spacing and the 100 reflection from B-type crystallinity [4], respectively. The SAXS patterns of ball-milled Hylon VII displayed the same trend with ball-milled normal corn starch. The intensity of SAXS peaks were decreased and the width of SAXS peaks became broader.

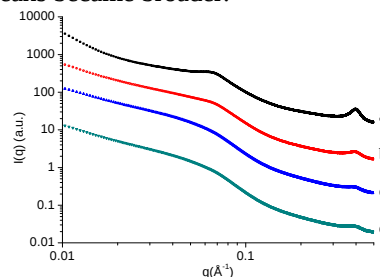


Fig. 2: SAXS patterns of ball-milled Hylon VII corn starches for 0 (a), 30 (b), 60 (c) or 120 (d) min, followed by conditioning in excess water.

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