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ARTICLE

Effects of Drying Conditions of Corn Kernels and Storage at an Elevated Humidity on Starch Structures and Properties

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The objective of this study was to understand effects of sun drying (35 °C) and machine drying (80 °C) of corn kernels followed by storage at 27 °C and 85−90% relative humidity for up to 6 months on starch structures and properties. The peak viscosity and starch hydrolysis rate using porcine pancreatic α-amylase of finely ground samples decreased with storage of both sun-dried and machine-dried corn kernels. The rate of enzymatic hydrolysis of the isolated starch obtained from the sun-dried corn increased with storage time, but that from the machine-dried corn decreased. The gelatinization temperature, pasting temperature, and percentage crystallinity of the isolated starch increased but the gelatinization enthalpy-change and peak viscosity of the starch decreased with storage time. Numbers of damaged starch granules and starch granules with pinholes increased but the molecular weight of starch and long branch-chains of amylopectin decreased with storage time. The results indicated that endogenous enzyme activity remained after sun drying, which hydrolyzed starch and reduced viscosity.

KEYWORDS: Storage; tropical condition; starch structure; starch functional properties; hydrolysis of starch

INTRODUCTION

The storage of dried crops is a common practice in the food and agriculture industry. Changes in chemical structures and functional properties of the crops after storage impact their processing characteristics and the quality of the final products. For example, many grain crops after being harvested require storage for a period of time before they can be used for processing. After the storage, the grains can be extruded smoothly without generating excessive back pressure during extrusion. Extensive storage, however, reduces starch yield from the crops during wet milling because of starch degradation and interactions between starch and other components of the grain (*1*). Storage of grains results in increases in lipid oxidation and the free fatty acid content (*2*, *3*), and the free fatty acid can form a helical complex with amylose or long branch-chains of amylopectin and alter the physical and nutritional properties of the grain and its final products (*4*,*5*). The storage of crops also causes decreases in grain protein solubility and digestibility (*6*, *7*). Chrastil et al. (*8*, *9*) reported that storage increased the molecular weight of the protein in rice grain through disulfide bond formation. The storage of crops can also change the activity and properties of endogenous enzymes present in the grain, such as amylases, proteases, and phosphatase (*10*).

Starch is widely used in food and nonfood applications. Thus, changes in starch functional properties can significantly impact the quality of products made from the starch (*11*). Patindol et al. (*12*) reported that storage of rough rice at controlled temperatures of 38 °C up to nine months affected starch pasting and thermal properties and decreased long branch-chains of amylopectin.

The conditions used for drying corn kernels and the storing of corn at an elevated humidity can affect starch structures and functional properties, but the impact and mechanism are not well understood. Therefore, the objective of this study was to understand the effects of drying conditions, i.e., sun-dried at 35 °C (SD) or machine-dried at 80 °C (MD) of corn kernels followed by storage at 27 °C and 85−90% relative humidity (RH) on starch structures and functional properties. These storage conditions are commonly used in tropical countries. The results obtained from this study can also reveal effects of the storage of crops on their processing characteristics.

MATERIALS AND METHODS

Materials. Corn kernels of B-816 (27.8% moisture, db), a tropical maize variety, were grown, harvested, and dried using sun-drying (35 °C) and machine-drying methods (80 °C) until they reached the moisture contents of 12.5−13.1% (db). Dried corn kernels were stored at 27 °C and 85−90% RH for up to 6 months. Each of the stored corn samples was coarsely ground using a commercial blender (Panasonic MX-J1G, Indonesia) and sieved with 1.0 mm openings, which were conducted by scientists of Charoen Pokphand Indonesia. The ground corn samples were sent to Iowa State University by overnight mail and were kept in a sealed container at −15 °C prior to analyses. The dried corn samples without storage (0 month) were used as the control. Porcine pancreatic α-amylase (PPA) and amyloglucosidase from *Aspergillus niger* were purchased from Sigma Aldrich Corporation (St. Louis, MO). Glucose assay kits (GOPOD format) were purchased from Megazyme International (K-GLUC, Wicklow, Ireland).

Starch Isolation. Coarsely ground corn samples (50 g) were steeped in an aqueous solution of 0.45% sodium metabisulfite in a refrigerator

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overnight. The steeped sample was further ground using a commercial blender (Osterizer 14 speed blender, US) for 5 min, and the process was repeated three times. The ground sample was filtered through a nylon screen with a pore size of 53 μm and washed with excess water, following the method reported by Li et al. (*13*). The purified starch was washed twice with distilled water, rinsed twice with 100% ethanol, dried at 37 °C for 48 h, and kept in a sealed container until used for analyses (*13*).

Starch Hydrolysis. The rate of starch hydrolysis was determined with finely ground corn samples and isolated starch samples using PPA following the method of Hasjim et al. (*14*) with modifications. Isolated starch (200 mg, db) or finely ground corn (<0.5 mm particle size) containing 200 mg of starch (db) was suspended in a phosphate buffer solution (20 mL, 0.02 M, pH 6.9, containing 0.25 mM $CaCl_2$) and equilibrated at 40 °C for 1 h. An aliquot of each sample was withdrawn before adding PPA and was centrifuged, and the supernatant was analyzed for the initial soluble-sugar content. PPA (200 units/g of starch) was added to the corn or starch suspension, and the mixture was incubated at 40 °C. Aliquots (0.2 mL) of the hydrolysate were collected at different time intervals, and the supernatant was separated and hydrolyzed with amyloglucosidase (10 units). The glucose content of the hydrolysate was determined using the glucose assay kits (GOPOD format). The percentage of starch hydrolysis (%) was calculated using the following equation:

$$\text{percentage starch hydrolysis (\%)} = \frac{\text{glucose content} \times 0.9}{\text{initial starch weight (dry basis)}}$$

The analysis was done in duplicate.

Pasting Properties. Pasting properties of the finely ground corn (<0.5 mm particle size) and the isolated starch were analyzed using a Rapid Visco-Analyzer (RVA-4, Newport Scientific, Sidney, Australia) (*15*). Isolated starch (2.24 g, db) or finely ground corn containing 2.24 g of starch (db) was suspended in distilled water in an RVA canister making up to a total weight of 28 g. A constant paddle rotating speed (160 rpm) was used after premixing at 960 rpm for 10 s. The analysis was done in duplicate.

Thermal Properties of Starch. Thermal properties of the isolated starch were analyzed using a differential scanning calorimeter (DSC) (Diamond DSC, Perkin-Elmer, Norwalk, CT) (*16*). Each starch sample (2 mg, db) was precisely weighed in an aluminum pan, and deionized water (6 μL) was added. The mixture was sealed and allowed to equilibrate for 1 h. The sample was heated from 10 to 110 °C at a rate of 10 °C/min. An empty pan was used as the reference, and indium was used as a calibration standard. The analysis was done in triplicate.

Morphology of Starch Granules. Morphology of isolated starch granules was studied using scanning electron microscopy (SEM) following the method of Jiang et al. (*17*). Starch was coated with gold/palladium (60/40), and the images were captured at a magnification of 1500× using a scanning electron microscope (JEOL model, JSM-5800LV Tokyo, Japan) at the Microscopy and Nanoimaging Facilities, Iowa State University.

Starch Crystallinity. X-ray diffraction patterns and percentage crystallinity of the isolated starch were analyzed following the method of Jiang et al. (*18*). Samples were equilibrated in a chamber of 100% relative humidity at 22−24 °C for 24 h. The X-ray diffraction pattern of starch was obtained with copper Kα radiation using a diffractometer (D-500, Siemens, Madison, WI) at the Town Engineering X-ray Facility, Iowa State University. The diffractometer was operated at 27 mA and 50 kV. The scanning region of the two-theta angle (2θ) was from 4° to 40° at 0.05° step size with a count time of 2 s. Percentage crystallinity was calculated using the equation

$$\text{percentage crystallinity (\%)} = 100A_c/(A_c + A_a)$$

where A_c is crystalline area on the X-ray diffractogram and A_a is amorphous area.

Molecular Weight Distributions of Starch. Molecular weight distributions of the isolated starch were determined using gel permeation chromatography (GPC) (*19*). Starch was dispersed in 90% DMSO by heating and stirring the starch suspension in a boiling-water bath for 1 h and followed by stirring at 22−24 °C overnight to disperse the starch. The starch was recovered by precipitation with ethanol and redispersed in hot deionized water to make a dispersion (0.3%, w/v). The starch was analyzed using a GPC column (1.5 cm i.d. × 50 cm) packed with Sepharose CL-2B gel (Pharmacia, Inc., Piscataway, NJ), and the eluent (1.66 mL/fraction) was collected and analyzed for the total carbohydrate content (CHO) using a phenol−sulfuric acid method (*20*), and blue value (BV) using an iodine/potassium iodide solution (*21*). The colors developed from the CHO and BV analyses were quantified using an Ultra Microplate Reader (EL_X808, Bio-Tek Instruments, Inc., Winooski, VT) at 490 and 630 nm, respectively. The analysis was done in duplicate.

Branch-Chain Length Distribution of Amylopectin. Amylopectin branch-chain length distribution of the isolated starch was analyzed following the method of Morell et al. (*22*). Amylopectin was separated from amylose by complexing and precipitating the amylose molecule with *n*-butanol (*23*). The isolated amylopectin was collected and debranched using isoamylase (Megazyme, Ireland) at 40 °C for 16 h, dried, and derivatized with 8-amino-1,3,6-pyrenetrisulfonic acid (APTS) (*22*). The branch-chain length distribution was analyzed using fluorophore-assisted capillary electrophoresis (FACE) (P/ACE, MDQ, Beckman Courter, Fullerton, CA). The analysis was done in duplicate.

Statistical Analysis. Analysis of variance (ANOVA) with the General Linear Model procedure in SAS version 9.1 (SAS Institute, Inc., Cary, NC) was used for data analyses. Differences were evaluated by the *t* test using Tukey's adjustment. The significance level was set at *p*-value < 0.05.

RESULTS AND DISCUSSION

Results of starch hydrolysis by PPA using finely ground samples of corn kernels after being stored for up to 6 months are shown in **Table 1**. The soluble-sugar content of the sun-dried corn (0 h, determined before adding PPA) increased from 2.5% on 0 month to 4.4% after 6 months of storage (**Table 1**). In contrast, that of the machine-dried corn showed no clear trend of

Table 1. Starch Hydrolysis Rate of Finely Ground Sun-Dried and Machine-Dried Corn after Storage at 27 °C and 85−90% RH[a]

		percentage starch hydrolysis (%)[b]						
sample	storage (months)	0 h	1 h	2 h	4 h	6 h	8 h	24 h
B-816 SD[c]	0	2.5 ± 0.4 a	45.8 ± 0.4 a	52.0 ± 1.1 a	63.8 ± 3.7 a	71.4 ± 2.4 a	85.4 ± 1.7 a	97.4 ± 1.5 a
	2	2.3 ± 0.6 ab	39.7 ± 2.5 b	47.8 ± 1.0 ab	62.7 ± 0.1 a	67.4 ± 2.5 a	78.2 ± 0.9 b	90.1 ± 2.6 b
	3	3.4 ± 0.3 bc	38.1 ± 0.8 b	44.0 ± 1.9 b	58.4 ± 0.2 ab	60.2 ± 0.5 b	65.9 ± 0.7 c	75.6 ± 0.6 c
	4	3.9 ± 0.5 cd	35.7 ± 1.8 bc	43.6 ± 2.3 b	56.6 ± 0.1 b	59.9 ± 0.9 b	65.3 ± 0.9 c	74.3 ± 2.6 c
	6	4.4 ± 0.3 d	33.8 ± 1.2 c	43.9 ± 2.8 b	55.8 ± 1.1 b	57.9 ± 1.3 b	63.5 ± 1.1 c	74.1 ± 0.9 c
LSD[d]		0.92	4.84	5.73	5.45	5.16	3.32	5.34
B-816 MD[e]	0	1.8 ± 0.5 a	43.7 ± 0.2 a	52.4 ± 0.9 a	62.1 ± 0.3 a	72.3 ± 1.8 a	80.6 ± 1.4 a	94.9 ± 0.8 a
	2	1.6 ± 0.8 a	38.0 ± 2.1 b	48.9 ± 1.9 ab	57.3 ± 1.1 b	65.6 ± 0.9 b	72.3 ± 1.3 b	82.8 ± 1.3 b
	3	2.4 ± 0.6 a	36.8 ± 0.7 b	43.4 ± 0.3 bc	55.4 ± 0.2 b	58.8 ± 0.8 c	66.1 ± 0.5 c	77.3 ± 2.1 c
	4	1.8 ± 1.3 a	35.1 ± 0.6 b	41.9 ± 0.9 c	49.7 ± 1.9 c	56.8 ± 2.9 c	65.8 ± 0.8 c	76.4 ± 1.9 c
	6	2.1 ± 1.2 a	35.2 ± 1.7 b	41.3 ± 2.1 c	49.4 ± 1.1 c	56.4 ± 1.8 c	61.9 ± 0.3 d	76.9 ± 0.4 c
LSD		3.50	3.72	5.94	3.32	4.65	3.55	5.36

[a] The ground corn had particle size <0.5 mm; the starch was hydrolyzed using porcine pancreatic α-amylase. [b] The percentage starch hydrolysis was calculated as follows: glucose content × 0.9/initial starch weight (dry basis). Data in the same column with different letters are significantly different ($p < 0.05$). [c] SD: Sun-dried. [d] Least significant differences. [e] MD: Machine-dried.

changes with storage time. The increase in the soluble-sugar content of the sun-dried corn after storage was attributed to starch hydrolysis during the storage. It is plausible that endogenous amylases and/or amylases of contaminating microorganisms present in the sun-dried corn hydrolyze the starch and produce soluble sugars during the storage (*24*, *25*). Most of the amylases, however, were inactivated during machine drying at 80 °C, and, thus, there was no trend for an increase in the soluble-sugar content with the storage time of machine-dried corn samples. Both the sun-dried and machine-dried corn samples showed decreases in the starch hydrolysis rate after storage (**Table 1**). Pasting properties of finely ground samples of corn kernels after being stored for up to six months are shown in **Figure 1**. The peak viscosity (PV) of the ground corn decreased after the 6-month storage, from 164.0 to 107.3 Rapid Visco Units (RVU) and 168.3 to 113.3 RVU for sun-dried and machine-dried corn, respectively. These results agree with the results reported by Zhou et al. that peak viscosity decreases in rice flour after storage (*26*).

The enzymatic hydrolysis rate of isolated starch that was obtained from the same corn sample after storage, however, showed a different trend of change from that of the ground corn sample (**Table 2**). The percentage hydrolysis (8 h) of the starch isolated from sun-dried corn after storage increased from 77.2 (0 month) to 84.9% (6-month storage), whereas that of the starch isolated from the machine-dried corn decreased from 79.1 (0 month) to 75.6% (6 month) (**Table 2**). The soluble-sugar content of the isolated starch from sun-dried corn (0 h, before adding PPA) increased from 2.4 to 5.1% after 0 to 6 months of storage, whereas that of the machine-dried counterpart showed little difference (**Table 2**). Starch isolated from the machine-dried corn without storage showed a greater initial rate of enzyme

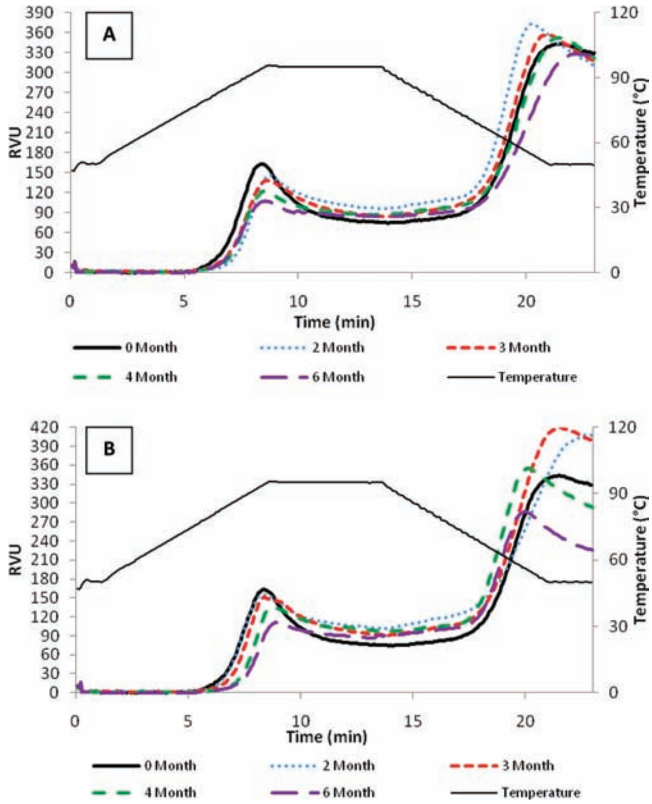

Figure 1. Pasting profiles of finely ground (<0.5 mm particle size) (**A**) sun-dried and (**B**) machine-dried corn after 0 to 6 months of storage at 27 °C and 85−90% RH.

Table 2. Enzymatic[a] Hydrolysis of Starch Isolated from the Sun-Dried and Machine-Dried Corn after Storage at 27 °C and 85−90% RH

		percentage starch hydrolysis (%)[b]						
sample	storage (months)	0 h	1 h	2 h	4 h	6 h	8 h	24 h
B-816SD[c]	0	2.4 ± 0.2 a	32.6 ± 1.1 a	44.1 ± 1.6 a	60.3 ± 1.4 a	70.7 ± 1.3 a	77.2 ± 1.3 a	99.3 ± 1.5 a
	2	3.3 ± 0.6 ab	34.6 ± 1.3 a	45.6 ± 1.3 a	60.1 ± 1.8 a	71.7 ± 1.5 ab	78.9 ± 0.9 ab	96.0 ± 1.6 a
	3	2.8 ± 0.6 cb	37.4 ± 0.8 ab	48.1 ± 1.8 ab	61.1 ± 1.3 a	72.5 ± 1.6 ab	80.7 ± 1.3 bc	98.0 ± 1.7 a
	4	4.6 ± 0.2 c	39.4 ± 1.1 bc	51.4 ± 0.6 b	64.0 ± 1.4 a	73.5 ± 0.9 ab	83.1 ± 1.2 cd	97.1 ± 1.8 a
	6	5.1 ± 0.3 c	40.4 ± 0.7 c	52.4 ± 1.2 b	64.9 ± 2.1 a	74.4 ± 1.1 ab	84.9 ± 1.9 d	98.5 ± 1.1 a
LSD[d]		1.48	3.94	4.95	5.53	4.14	3.76	5.68
B-816MD[e]	0	0.8 ± 0.3 a	34.2 ± 0.6 a	47.5 ± 0.5 a	63.4 ± 1.6 a	73.1 ± 1.3 a	79.1 ± 1.4 a	96.9 ± 0.9 a
	2	0.6 ± 0.1 a	33.4 ± 0.6 a	45.0 ± 0.8 ab	61.0 ± 0.3 a	70.7 ± 0.4 ab	78.4 ± 1.3 a	94.3 ± 1.3 a
	3	1.1 ± 0.3 a	34.2 ± 0.7 a	44.3 ± 1.4 ab	62.6 ± 0.9 a	72.4 ± 1.3 ab	79.5 ± 1.9 a	96.7 ± 0.4 a
	4	0.9 ± 0.2 a	33.2 ± 1.2 a	43.3 ± 1.3 b	58.6 ± 1.1 b	69.7 ± 0.9 ab	76.6 ± 1.4 a	93.2 ± 1.3 a
	6	1.2 ± 0.4 a	32.5 ± 0.8 a	44.6 ± 0.9 ab	58.8 ± 0.8 b	69.5 ± 1.1 b	75.6 ± 1.5 a	94.4 ± 1.5 a
LSD		1.01	2.73	3.81	3.60	4.06	4.41	2.53

[a] Porcine pancreatic α-amylase. [b] Percentage starch hydrolysis was calculated as follows: glucose content × 0.9/initial starch weight (dry basis). Data in the same column with different letters are significantly different ($p < 0.05$). [c] SD: Sun-dried. [d] Least significant differences. [e] MD: Machine-dried.

Table 3. Thermal Properties of Starch Isolated from the Sun-Dried and Machine-Dried Corn after Storage at 27 °C and 85−90% RH[a]

sample	storage (months)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
B-816SD[b]	0	68.74 ± 0.21 a	74.59 ± 0.12 a	80.71 ± 0.28 a	13.21 ± 0.42 a
	2	70.45 ± 0.17 b	75.71 ± 0.34 b	81.97 ± 0.28 bc	13.62 ± 0.23 a
	3	71.25 ± 0.13 c	75.31 ± 0.26 ab	82.42 ± 0.13 c	11.37 ± 0.33 b
	4	71.32 ± 0.22 c	76.02 ± 0.35 b	81.92 ± 0.33 bc	10.91 ± 0.22 b
	6	71.21 ± 0.33 c	75.88 ± 0.12 b	81.33 ± 0.42 ab	10.54 ± 0.28 b
LSD[c]		0.69	0.86	0.90	0.95
B-816MD[d]	0	68.76 ± 0.02 a	74.82 ± 0.12 a	80.31 ± 0.06 a	12.28 ± 0.22 a
	2	69.35 ± 0.19 ab	75.22 ± 0.24 b	80.85 ± 0.17 ab	12.06 ± 0.03 ab
	3	70.48 ± 0.08 b	76.02 ± 0.15 c	81.49 ± 0.22 bc	11.58 ± 0.17 b
	4	71.68 ± 0.06 c	75.75 ± 0.22 c	82.11 ± 0.36 c	10.85 ± 0.24 c
	6	71.95 ± 0.19 c	75.88 ± 0.24 c	82.42 ± 0.53 c	10.71 ± 0.38 c
LSD		1.04	0.55	1.00	0.61

[a] Data in the same column with different letters are significantly different ($p < 0.05$). [b] SD: Sun-dried. [c] Least significant differences. [d] MD: Machine-dried.

hydrolysis (47.5% at 2 h hydrolysis) than that of the sun-dried counterpart (44.1%) (**Table 2**). This difference could be a result of heating the corn kernels at 80 °C during machine drying, which caused partial gelatinization of the starch. Gelatinized starch is known to be more easily hydrolyzed (*27*). After storage, the gelatinized starch would retrograde and became resistant to enzyme hydrolysis (**Table 2**). Effects of drying method/temperature on starch properties will be further discussed later.

Thermal properties of starch isolated from sun-dried and machine-dried corn samples after different periods of storage are shown in **Table 3**. The onset gelatinization temperature (T_o) of the starch increased from 0- to 6-month storage (68.74 to 71.21 °C and 68.76 to 71.95 °C for sun-dried and machine-dried samples, respectively). The starch isolated from the machine-dried corn without storage showed a lower gelatinization enthalpy-change (12.28 J/g) than that isolated from the sun-dried counterpart (13.21 J/g). This result further supported that drying corn kernels with 27.8% moisture content at 80 °C caused partial gelatinization of starch. Gelatinization enthalpy changes (ΔH) of starch isolated from both sun-dried and machine-dried corn decreased with storage time. The decrease in the gelatinization enthalpy change after 6 months of storage was greater for the starch isolated from sun-dried corn (2.67 J/g) than that from the machine-dried counterpart (1.57 J/g) (calculated from data in **Table 3**).

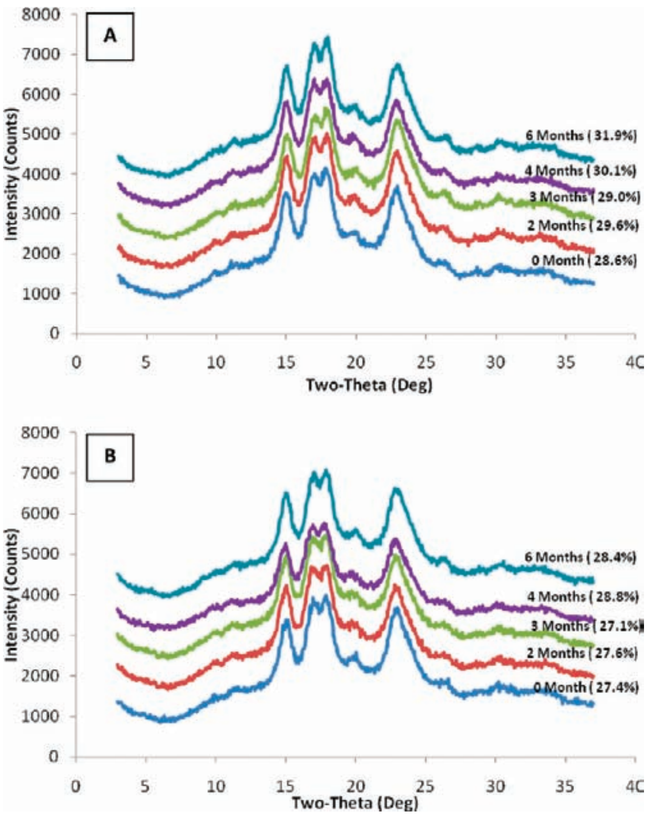

Figure 2. X-ray diffraction pattern of starch isolated from (**A**) sun-dried and (**B**) machine-dried corn after 0 to 6 months of storage at 27 °C and 85−90% RH. The number in parentheses represents the percentage crystallinity of the isolated starch.

X-ray diffraction patterns and percentage crystallinity of starch isolated from sun-dried and machine-dried corn after storage are shown in **Figure 2**. All the starch samples showed the typical A-type diffraction pattern with major 2θ peaks at 15°, 17°, 18°, and 23° (*28*). Starch isolated from the sun-dried corn without storage showed a greater percentage crystallinity (28.6%) than that from the machine-dried corn (27.4%). The lower percentage crystallinity of the starch from machine-dried corn confirmed the observation of partial-gelatinization of starch in the machine-dried corn. The percentage crystallinity of the starch increased with storage time, from 28.6 (0 month) to 31.9% (6 month) and 27.4 (0 month) to 28.4% (6 month) for the starch isolated from sun-dried and machine-dried corn, respectively. The increase in the percentage crystallinity of the starch with storage time, measured using X-ray diffractometry, was attributed to the growing in the size of starch crystallites after storage at 27 °C and 85−90% RH (*29*). The large crystallite could generate more diffractive beam, intensified the 2θ peaks, and increased the percentage crystallinity. This result differed from the decrease in the starch double helices with storage time, measured as gelatinization enthalpy changes (**Table 3**). The difference in the percentage-crystallinity change with storage time between the starch isolated from sun-dried and machine-dried corn will be discussed later.

Pasting properties of starch isolated from sun-dried and machine-dried corn after storage are summarized in **Table 4**. The pasting temperature (PT) of starch isolated from dried corn stored from 0 to 6 months increased from 72.5 to 75.6 °C and 73.6 to 75.4 °C for the sun-dried and machine-dried corn, respectively. The starch from sun-dried corn after 0 and 2 months of storage showed a peak viscosity at 158.2 and 160.9 RVU, whereas that of the corn after 3 to 6 months of storage showed remarkable decreases in the peak viscosity, 128.5−132.5 RVU (**Table 4**). The peak viscosity of the machine-dried starch samples gradually decreased, from 154.6 to 133.8 RVU after 0- to 6-month storage. The decrease in the peak viscosity of the ground corn after storage (**Figures 1A** and **1B**) showed a similar trend to the decrease in the peak viscosity of the isolated starch. The decreases in the peak

Table 4. Pasting Properties of Starch Isolated from the Sun-Dried and Machine-Dried Corn after Storage at 27 °C and 85−90% RH[a]

sample	storage (months)	pasting temp (°C)	peak viscosity (RVU)[b]	breakdown (RVU)	setback (RVU)	final viscosity (RVU)
B-816SD[c]	0	72.5 ± 0.4 a	158.2 ± 2.3 a	60.1 ± 1.3 a	84.7 ± 0.4 a	183.2 ± 2.2 a
	2	74.1 ± 0.1 b	160.9 ± 0.5 a	58.9 ± 0.3 a	86.0 ± 0.2 b	184.2 ± 1.3 a
	3	75.1 ± 0.4 bc	128.5 ± 0.3 b	30.7 ± 0.5 b	78.9 ± 0.5 c	177.9 ± 0.8 b
	4	74.8 ± 0.2 bc	131.3 ± 1.4 b	27.6 ± 1.3 b	78.6 ± 0.1 c	177.5 ± 1.3 b
	6	75.6 ± 0.5 c	132.5 ± 0.3 b	28.4 ± 1.8 b	79.2 ± 0.4 c	178.4 ± 1.1 b
LSD[d]		1.28	4.24	3.89	1.27	4.78
B-816MD[e]	0	73.6 ± 0.4 a	154.6 ± 1.3 a	59.3 ± 1.6 a	117.3 ± 1.4 a	212.4 ± 1.8 a
	2	74.5 ± 0.2 a	156.5 ± 1.2 a	60.2 ± 1.8 a	112.4 ± 1.7 b	211.3 ± 1.3 a
	3	74.1 ± 0.5 a	144.8 ± 0.9 b	42.3 ± 0.9 b	92.8 ± 1.1 c	193.8 ± 0.9 b
	4	74.7 ± 0.6 ab	136.8 ± 1.0 b	38.7 ± 2.9 b	78.1 ± 1.4 d	173.8 ± 0.9 c
	6	75.4 ± 0.7 b	133.8 ± 1.2 b	39.9 ± 1.4 b	76.3 ± 0.9 d	170.4 ± 1.9 c
LSD		1.47	4.06	4.79	4.38	5.29

[a] Data in the same column with different letters are significantly different ($p < 0.05$). [b] RVU: Rapid Visco Units. [c] SD: Sun-dried. [d] Least significant differences. [e] MD: Machine-dried.

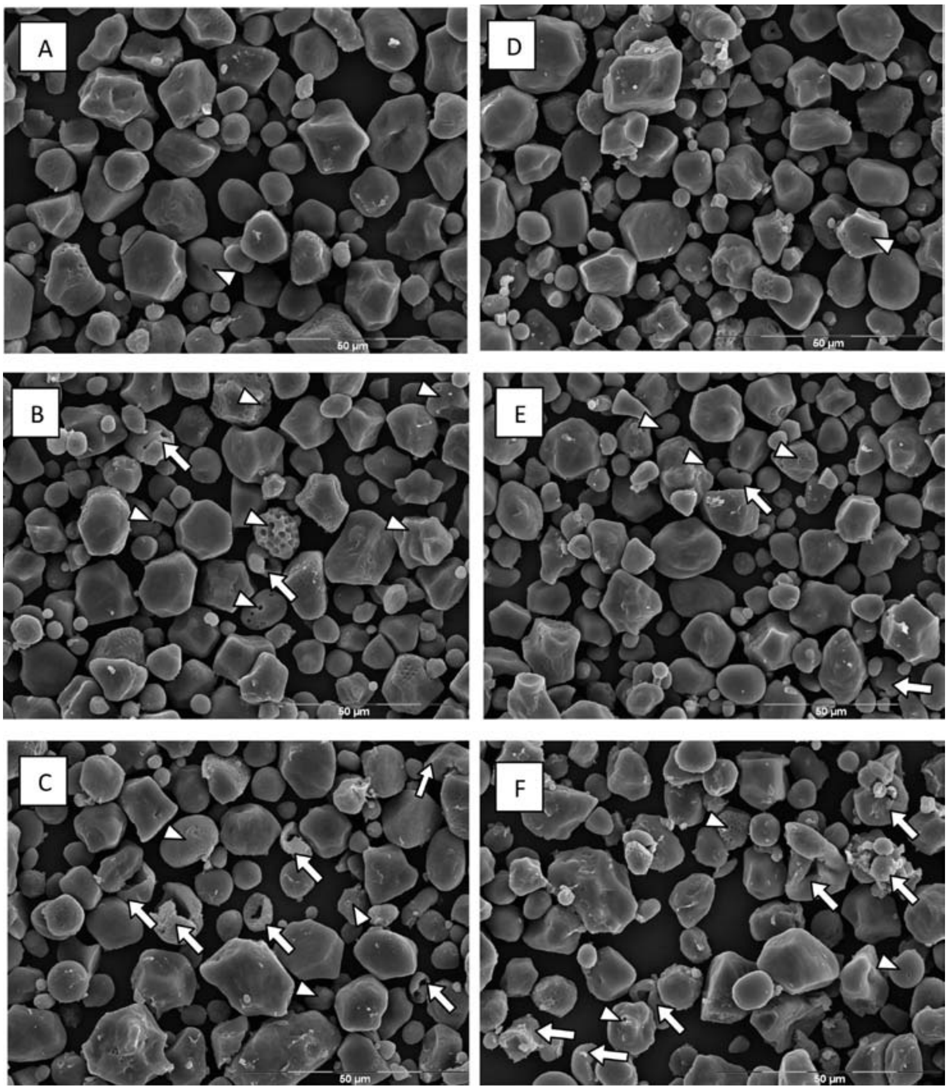

Figure 3. Scanning electron micrograph (1500×) of isolated starch. **A**−**C**, starch isolated from sun-dried corn after storage for (**A**) 0, (**B**) 2, and (**C**) 6 months. **D**−**F**, starch isolated from machine-dried corn after storage for (**D**) 0, (**E**) 2, and (**F**) 6 months at 27 °C and 85−90% RH. Full arrows: damaged starch granule. Arrowheads: starch granule with pinholes on the surface.

viscosity of the ground corn samples after 6-month storage (56.7 and 55.0 RVU for sun-dried and machine-dried corn, respectively) were, however, more pronounced than that of the isolated starch samples (25.7 and 20.8 RVU for starch isolated from sun-dried and machine-dried corn, respectively), indicating that nonstarch components of the grain, such as free fatty acids from lipids, which complex with starch, and disulfide bond formation of protein also contributed to the reduced peak viscosity of the ground corn after storage.

Representative SEM images of starch granules isolated from dried corn after storage are shown in **Figure 3**. The SEM images showed increases in the number of damaged starch granules (broken granules and debris) after storage of both sun-dried and machine-dried corn. The number of damaged starch granules was larger in the starch isolated from sun-dried corn than that from machine-dried corn (**Figure 3**). Starch isolated from machine-dried corn showed fewer starch granules with pinholes on the surface than that from sun-dried corn after the same period of storage (**Figures 3B** and **3E**). The difference was attributed to less starch-hydrolyzing enzyme activities in the machine-dried corn, resulting from high-temperature drying (80 °C). The larger number of damaged starch granules in the starch from sun-dried corn after storage coincided with its greater rate of enzymatic hydrolysis (**Table 2**). Damaged starch granules had more internal structures exposed, which were more susceptible to enzymatic hydrolysis (*14*). The presence of damaged-starch

Table 5. Molecular Weight Distribution of Starch Isolated from the Sun-Dried and Machine-Dried Corn after Storage at 27 °C and 85−90% RH Determined Using Gel Permeation Chromatography (GPC)[a]

sample	storage (months)	amylopectin/ 1st peak (%)	amylose/ 2nd peak (%)	BV: CHO[b] of 2nd peak
B-816 SD[c]	0	71.1 ± 0.4 a	28.9 ± 0.4 a	4.94 ± 0.01 a
	2	69.4 ± 0.4 b	30.6 ± 0.4 b	4.40 ± 0.04 b
	3	67.5 ± 0.0 c	32.5 ± 0.0 c	4.21 ± 0.02 c
	4	64.4 ± 0.4 d	35.6 ± 0.4 d	4.12 ± 0.02 c
	6	64.3 ± 0.3 d	35.7 ± 0.3 d	3.88 ± 0.03 d
LSD[d]		1.23	1.23	0.09
B-816MD[e]	0	71.8 ± 0.2 a	28.2 ± 0.2 a	3.84 ± 0.01 ab
	2	70.8 ± 0.1 b	29.1 ± 0.1 b	3.86 ± 0.01 a
	3	69.9 ± 0.3 bc	30.1 ± 0.3 bc	3.82 ± 0.04 ab
	4	69.3 ± 0.4 c	30.6 ± 0.4 c	3.74 ± 0.03 b
	6	68.2 ± 0.1 d	31.7 ± 0.1 d	3.61 ± 0.05 c
LSD		0.89	0.89	0.11

[a] Data in the same column with different letters are significantly different ($p < 0.05$). [b] Blue value (BV) to total carbohydrate (CHO) ratio of the second peak. [c] SD: Sun-dried. [d] Least significant differences. [e] MD: Machine-dried.

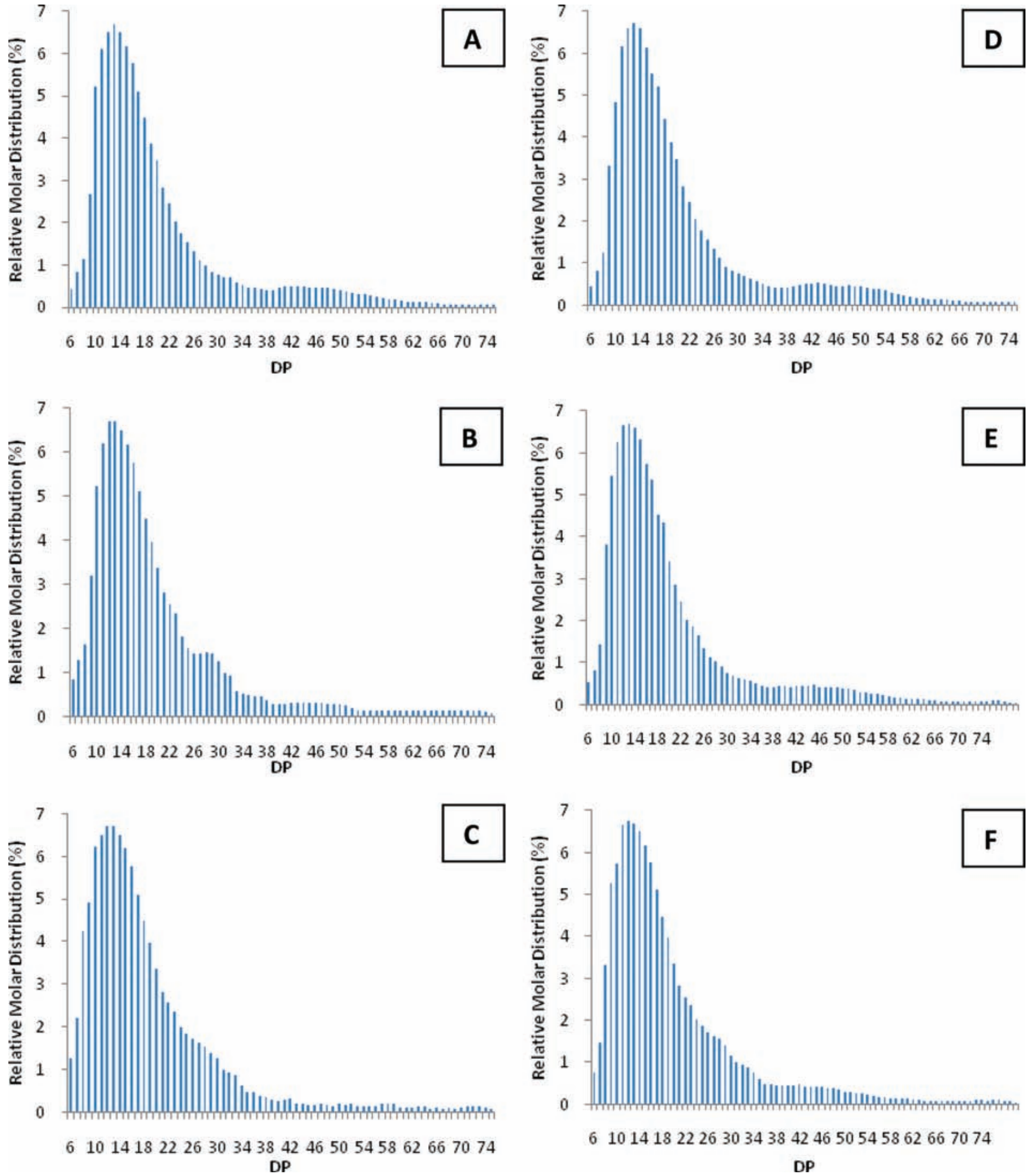

Figure 4. Amylopectin branch-chain length distribution profile of isolated starch. **A**−**C**, starch isolated from sun-dried corn after storage for (**A**) 0, (**B**) 3, and (**C**) 6 months. **D**−**F**, starch isolated from machine-dried corn after storage for (**D**) 0, (**E**) 3, and (**F**) 6 months at 27 °C and 85−90% RH.

granules also decreased the peak viscosity of the isolated starch (**Table 4**) (*30*).

Molecular weight distributions of the isolated starches analyzed using GPC displayed two peaks, representing the amylopectin (first peak) and the amylose (second peak) (data not shown). The proportion of the second peak of the starch isolated from the sun-dried and the machine-dried corn increased from 28.9 to 35.7% and 28.2 to 31.7%, respectively, after 0- to 6-month storage (**Table 5**). The increase in the proportion of the second peak was attributed to the hydrolysis of amylopectin molecules. The partially hydrolyzed amylopectin molecule had smaller molecular weight, which was coeluted with amylose and increased the proportion of the second peak. The hydrolysis of the amylopectin molecules was more pronounced in the starch isolated from sun-dried corn after storage than that from the machine-dried counterparts. These results confirmed that the activity of starch-hydrolyzing enzyme was reduced after machine drying at 80 °C. The coelution of the partially hydrolyzed amylopectin molecules with amylose in the chromatogram was evident by decreases in the ratio of blue value (BV) to the total-carbohydrate content (CHO) of the second peak, from 4.94 to 3.88 and 3.84 to 3.61 (**Table 5**) for the sun-dried and machine-dried starch samples, respectively, after 0- to 6-month storage of the dried corn kernels. The reduction in the BV of the peak resulted from the presence of partially hydrolyzed amylopectin molecules that were highly branched and gave less blue-color when complexed with iodine.

Table 6. Amylopectin Branch-Chain Length Distribution of Starch Isolated from Sun-Dried and Machine-Dried Corn after Storage at 27 °C and 85−90% RH[a]

sample	storage (months)	branch-chain length distribution (%)			
		DP6−12	DP13−24	DP25−36	DP > 36
B-816SD[b]	0	25.4 ± 0.2 a	52.8 ± 0.1 ab	9.8 ± 0.1 a	12.1 ± 0.4 a
	2	24.7 ± 0.4 b	53.1 ± 0.7 a	9.6 ± 0.5 a	11.7 ± 0.1 a
	3	25.8 ± 0.2 b	51.3 ± 0.8 ab	10.4 ± 0.1 a	10.4 ± 0.5 b
	4	26.3 ± 0.2 bc	51.2 ± 0.3 b	10.3 ± 0.3 a	9.8 ± 0.3 bc
	6	27.3 ± 0.1 c	51.4 ± 0.4 ab	11.9 ± 0.4 b	8.8 ± 0.1 c
LSD[c]		0.95	1.76	1.17	1.17
B-816MD[d]	0	24.8 ± 0.2 abc	52.8 ± 0.2 a	9.6 ± 0.1 a	12.7 ± 0.2 a
	2	24.6 ± 0.4 ab	52.7 ± 0.3 a	9.9 ± 0.5 a	12.6 ± 0.4 a
	3	24.2 ± 0.4 a	53.1 ± 0.4 a	9.7 ± 0.1 a	11.8 ± 0.2 ab
	4	25.7 ± 0.5 bc	52.1 ± 0.6 a	10.6 ± 0.3 a	10.8 ± 0.4 b
	6	25.9 ± 0.1 c	52.3 ± 0.5 a	10.5 ± 0.4 a	10.7 ± 0.3 b
LSD		1.28	1.37	1.16	1.13

[a] Data in the same column with different letters are significantly different ($p < 0.05$). [b] SD: Sun-dried. [c] Least significant differences. [d] MD: Machine-dried.

Furthermore, the enzymatic hydrolysis of starch molecules in the corn samples during storage reduced the structural integrity of the starch granules and resulted in a greater number of damaged starch granules after storage (**Figure 3**). The reduced molecular weight of starch after storage of the corn resulted in lower viscosities as shown in **Figure 1** and **Table 4**.

Representative amylopectin branch-chain length distributions of starch isolated from the dried corn samples after storage are shown in **Figure 4**. The amylopectin branch-chain length of the starch sample without storage showed a typical bimodal distribution, consisting of a large proportion of short A and B1 chains (DP 6−24) (**Figures 4A** and **4D**) (*15*,*31*). The branch-chain length distribution profiles of starch isolated from sun-dried corn showed obvious increases in DP 22 to 32 and decreases in the long branch-chains (DP 40−60) after 3-month storage (**Figure 4B**). After 6 months of storage of sun-dried corn, the percentage of long branch-chains (DP > 36) of amylopectin decreased from 12.1 to 8.8% and the percentage of intermediate branch-chains (DP 25−36) increased from 9.8 to 11.9% (**Figure 4C** and **Table 6**). Starch isolated from the machine-dried corn samples did not show any obvious changes in branch-chain length distribution up to 3 months of storage (**Figures 4D** and **4E** and **Table 6**). The decrease in the percentage of long branch-chains was more pronounced in the starch isolated from sun-dried corn (12.1 to 8.8% after 6-month storage) than that from the machine-dried counterparts (12.7 to 10.7%) (**Table 6**). The results of decreases in long branch-chains of amylopectin after storage were in agreement with the findings of Patindol et al. (*12*). The change in the amylopectin branch-chain length distribution of isolated starch was attributed to the enzymatic hydrolysis of starch, which took place during storage as previously suggested in rice (*32*, *33*). Alpha-amylase attacked the amorphous region of amylopectin, which consisted of long branch-chains, and hydrolyzed the long branch-chains to chains of intermediate lengths and reduced the molecular weight of amylopectin. Reduction in the molecular weight of starch has been reported to accelerate crystallization of starch and increase the resistant starch content (*34*). The smaller starch molecules in the sun-dried corn after storage facilitated crystallization of starch. Thus, the percentage crystallinity of the sun-dried starch increased from 28.6 to 31.9% after 6 months of storage, which was substantially greater than the machine-dried counterparts (27.4 to 28.4%) (**Figure 2**). Tester and Morrison reported that hydrolysis of amylopectin by both enzymatic and chemical treatments decreased the starch swelling power (*35*, *36*). Accordingly, the enzymatic hydrolysis of starch molecules after storage of corn (**Table 5** and **Figure 4**) resulted in lower peak viscosity of the isolated starch (**Table 4**) and ground corn samples (**Figure 1**).

In conclusion, storage of sun-dried and machine-dried corn kernels at 27 °C and 85−90% relative humidity for up to 6 months altered structures and functions of their starch. Starch hydrolysis rate and the peak viscosity of ground corn decreased with storage. The decrease in the peak viscosity of the ground corn was partially attributed to the decrease in the peak viscosity of the starch. The gelatinization temperature, pasting temperature, and percentage crystallinity of the isolated starch increased with the storage of the corn. Numbers of damaged starch granules and starch granules with pinholes increased and the molecular weight of starch and the percentage of long branch-chains of amylopectin decreased with the storage of corn, indicating that starch hydrolysis took place during the storage of corn. Starch isolated from sun-dried corn after storage displayed greater levels of enzymatic hydrolysis than that from the machine-dried counterparts, suggesting more amylase activities remaining in the corn samples after sun-drying at 35 °C than machine-drying at 80 °C.

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