

# Thermal and Functional Characterization of Starch from Argentinean Corn<sup>1</sup>

K. Seetharaman,<sup>2</sup> A. Tziotis,<sup>3</sup> F. Borrás,<sup>4</sup> P. J. White,<sup>3,5</sup> M. Ferrer,<sup>4</sup> and J. Robutti<sup>4</sup>

## ABSTRACT

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Screening accessions in a germplasm bank aids in the identification of plants with unusual properties ranging from agronomic traits to functional and compositional traits of the seed itself. Results from this study confirm the presence of a wide variation in the thermal and functional properties of starch from several landraces of corn in the Argentinean germplasm. Thermal properties of starch measured using differential scanning calorimetry (DSC) identified several corn landraces with properties of potential commercial interest. The pasting and textural properties of gels obtained from starch of different corn landraces also exhibited considerable variability. The degree of variation in thermal and functional properties of corn reported in this study is comparable to the thermal properties of

starch from several other crop species. These corn races show promise for further regeneration to create inbred lines with unusual traits. The potential for further improvement of corn races exists not only based on thermal properties, but directly for specific functional attributes as well. Correlation analyses suggest that the variability in thermal and functional attributes are a function of amylose content, granule size distribution and, possibly, differences in the structural makeup of amylose and amylopectin. The strong correlation observed between the thermal properties and pasting and textural properties will allow for the estimation of starch properties from small sample sizes.

Quality specifications of corn for food and feed uses are diverse and exacting. Achieving the quality attributes for different uses traditionally has been accomplished by using a range of postharvest processing techniques such as milling or modifying starch and proteins. Breeding and genetic tools can be used effectively to achieve several end-use quality attributes. Incorporating unusual traits from exotic germplasm materials into the narrow germplasm base commercially grown by the agricultural industry worldwide is another alternative. Past attempts to incorporate tropical germplasm into existing breeding programs have had little success (Goodman 1985), primarily due to the lack of information about the agronomic, physiological, pathological, and other potentially useful traits. Further characterization of the germplasm materials, therefore, is essential to fully utilize their potential. The Germplasm Enhancement of Maize (GEM) project, coordinated through United States Department of Agriculture (USDA) researchers at Iowa State University, is one such attempt to characterize and identify traits relating to starch, protein, or oil content and composition. Our laboratory has been involved actively in this project for several years and has identified several corn lines with unusual starch and oil properties that are being further evaluated and crossed with Iowa corn lines. The identification of unusual starch thermal properties is based on a database obtained from screening normal corn starches over several years; a summary of those properties is listed in Table I.

The Maize Active Germplasm Bank at Pergamino, Argentina, has collected more than 2,500 accessions of different landraces of corn and classified them into 44 races. The diversity in the corn germplasm in Argentina is extensive because of the wide variation in the latitude and altitude within the country. To maximize the benefits of this diversity in corn races, comprehensive assessments of their characteristics and traits are necessary. A cooperative research effort between PROCIM (Maize Quality Research Project) and USDA-Agricultural Research Service (ARS) was established to thoroughly characterize the different races to expand the poten-

tial of Argentinean corn for domestic and export uses. This cooperation has resulted in the documentation of the hardness, amylose, and starch contents of a number of these races (Robutti et al 2000b). Reverse-phase high-pressure liquid chromatography (RP-HPLC) also was used to analyze zein content as a means to group and identify corn races (Robutti et al 2000a).

Most studies investigating the thermal properties of starches from corn have focused on mutant corn types such as waxy (*wx*), amylose-extender (*ae*), dull (*du*), or sugary (*su*) in different backgrounds (Stevens and Elton 1971; Inouchi et al 1984; Krueger et al 1987; Brockett et al 1988; Sanders et al 1990). Our laboratory has conducted extensive investigations on the thermal properties of starch from several open-pollinated corn populations and has shown significant variation among and within populations (White et al 1990). Li et al (1994) characterized the thermal properties of 35 tropical and semitropical corn populations and reported significant differences for all measured thermal properties. The granule size distribution of the same 35 corn populations also was examined, and a significant difference in the average granule size was reported within and among populations (Campbell et al 1996). Several significant correlations also were established between granule size and thermal properties based on results from these populations.

The objectives of this study were to characterize the thermal and functional starch properties of several corn races from the Argentinean germplasm and to identify unusual corn races with potential for further improvement, thus adding to the existing database of information on the different races of corn.

## MATERIALS AND METHODS

### Materials

Several landraces of corn collected from different regions in Argentina were stored at the Active Maize Germplasm Bank, Pergamino, Argentina (Table II). All of the samples under study had been characterized previously for hardness, amylose, starch, and zein contents (Robutti et al 2000a,b). Several of the corn races also were regrown at the Agricultural Experiment Station at Pergamino,

TABLE I  
Desired Starch Characteristics of Differential Scanning Calorimetry (DSC) Parameters

DSC Parameter	Target Value
Onset temperature of gelatinization ( $T_{oG}$ )	<61°C
Enthalpy of gelatinization ( $\delta_G$ )	<9.5 J/g or >14.5 J/g
Range of gelatinization ( $R_G$ )	<5.5°C or >14.5°C
Enthalpy of retrogradation ( $\delta_R$ )	<3.8 J/g
Percent retrogradation (%R)	<20% or >80%

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<sup>2</sup> Dept. of Food Science, The Pennsylvania State University, University Park, PA.

<sup>3</sup> Dept. of Food Science and Human Nutrition, Iowa State University, Ames, IA.

<sup>4</sup> EEA Pergamino INTA, CC31, 2700 Pergamino, BA, Argentina.

<sup>5</sup> Corresponding author. E-mail: pjwhite@iastate.edu Phone: 515-294-9688. Fax: 515-294-8181.

Argentina. Corn was categorized based on endosperm type, such as dent, flint, floury, semident, or semiflint. Corn accessions originally collected are labeled "O" in this study and those that were regrown in Pergamino, Argentina, are labeled "P". A corn belt inbred, Mo-17, grown and harvested in Ames, IA, in 1998 was used as a control for comparison.

### Starch Isolation

Starch for differential scanning calorimetry (DSC) analysis was extracted using procedures previously described by White et al (1990) and modified by Krieger et al (1997). For the initial screening of the 35 landraces from the germplasm, starch was extracted from five randomly selected seeds per race. Based on the results of the initial screening, 13 landraces were selected for further analyses (Table II). DSC analyses of the starch from these 13 landraces were conducted on starch extracted using the single-kernel extraction procedure from 10 randomly selected seeds from each race. This sampling protocol allowed for the determination of the variability in starch thermal properties within each race. Larger quantities of starch, needed to analyze starch pasting properties using a Rapid Visco Analyser (RVA) and to measure textural properties of starch gels, were extracted from 50 g of seed using the procedure described by Singh et al (1997).

### DSC Analysis

The thermal properties of the starch samples were analyzed with a differential scanning calorimeter equipped with a Pyris software

for Windows package (V2.04, Perkin-Elmer, Norwalk, CT) using procedures previously described (White et al 1990). To measure the degree of retrogradation, the gelatinized starch in the DSC pan was stored for 7 days at 4°C, the optimum temperature for retrogradation, then equilibrated at 25°C for 1.5 hr before being rerun using DSC from 30 to 120°C at 10°C/min (White et al 1989).

All analyses were conducted in duplicate, and the average results were reported. Starch gelatinization properties that were computed automatically were peak onset temperature ( $T_{oG}$ ), range of gelatinization ( $R_G$ ), and enthalpy of gelatinization ( $\delta_G$ ). Starch retrogradation properties that were computed were onset of retrogradation ( $T_{oR}$ ), range of retrogradation ( $R_R$ ), and enthalpy of retrogradation ( $\delta_R$ ). Also, peak height index (PHI) was calculated as the ratio of  $\delta_G$  and half of  $R_G$ , and  $R_G$  or  $R_R$  was computed as twice the difference between peak temperature and onset temperature.

### Pasting Properties

The pasting properties of 13 selected races were analyzed by using an RVA model 4 (Newport Scientific Pty. Ltd., Warriewood, NSW, Australia) and an STD2 temperature profile equipped with ThermoLine for Windows software (V1.2) (Jennings 1996). Two RVA profiles were obtained for each sample and results averaged. A starch slurry (8% dwb) with a final weight of 28 g was used for each RVA analysis.

The temperature profile involved heating the slurry for 1 min at 50°C, then heating the slurry to 95°C in 7.5 min. The temperature was held at 95°C for 5 min, decreased to 50°C in 7.5

TABLE II  
List of 35 Corn Landraces Used in the Study from the Argentinean Germplasm

Sample <sup>a</sup>	Race	Year of Collection <sup>b</sup>	Province of Collection	Endosperm Type	Amylose <sup>c</sup>	Starch <sup>c</sup>	Reason for Selecting Landrace for Further Analyses
01-102-P	Cristalino Colorado	1989	Buenos Aires	Flint	18.9	72.1	
03-021-P	Cristalino Amarillo Anaranjado	1988	Entre Rios	Flint	18.5	69.7	
03-029-P	Camelia	1988	Entre Rios	Flint	18.2	65.9	
03-032-O	Camelia	1978	Entre Rios	Flint	19.1	69.6	O vs. P comparison
03-032-P	Camelia	1988	Entre Rios	Flint	18.4	67.0	O vs. P comparison
03-044-O	Avatí Morotí Ti	1978	Entre Rios	Floury	19.2	71.0	
04-035-P	Dentado Amarillo	1989	Corrientes	Dent	16.4	62.9	Lowest starch content
04-040-P	Avatí Morotí Ti	1988	Corrientes	Floury	19.0	70.3	
04-087-O	Complejo Tropical	1978	Corrientes	Semiflint	19.5	69.7	
05-081-P	Dentado Amarillo	1989	Misiones	Dent	16.1	63.0	Lowest amylose content
05-087-O	Dentado Amarillo	1977	Misiones	Dent	18.8	67.9	
07-031-O	Canario Formosa	1977	Formosa	Semident	23.5	77.8	Highest amylose content
07-031-P	Canario Formosa	1988	Formosa	Semident	20.5	74.5	O vs. P comparison
07-061-P	Canario Formosa	1977	Formosa	Semident	21.8	76.6	
07-061-O	Canario Formosa	1989	Formosa	Semident	22.0	75.7	
07-126-O	Canario Formosa	1977	Formosa	Semident	23.3	79.0	Highest starch content
08-085-O	Pisingallo	1977	Salta	Flint	18.7	71.1	
08-096-O	Amarillo de Ocho	1977	Salta	Floury	17.0	70.7	Lowest amylose to starch ratio
08-173-O2	Capia Garrapata	1977	Salta	Floury	19.2	71.5	Low gelatinization onset temperature
08-173-O3	Capia Rosado	1977	Salta	Floury	19.0	72.5	Low gelatinization onset temperature
10-020-O	Pisingallo	1977	Tucuma	Flint	18.9	69.9	
12-080-O	Dentado Blanco	1977	Catamarca	Dent	18.7	68.8	
13-035-P	Cristalino Colorado	1989	La Rioja	Flint	18.7	67.6	
13-049-O	Dentado Blanco	1977	La Rioja	Dent	19.3	70.3	O vs. P comparison
13-049-P	Dentado Blanco	1989	La Rioja	Dent	20.4	66.4	Highest amylose to starch ratio
13-064-O	Cristalino Amarillo Anaranjado	1977	La Rioja	Flint	19.6	72.0	
13-165-O	Complejo Tropical	1977	La Rioja	Semiflint	20.7	75.0	Low $T_{oG}$ and low $\delta_R$
16-007-P	Dentado Blanco	1988	Mendoza	Dent	18.5	68.1	
16-018-O	Cristalino Blanco	1986	Mendoza	Flint	19.1	73.9	
16-024-O	Cristalino Blanco	1986	Mendoza	Flint	20.0	72.8	
17-026-O	Cristalino Colorado	1986	San Luis	Flint	18.6	69.9	
18-026-O	Avatí Morotí Ti	1981	La Pampa	Floury	19.0	71.6	
19-033-O	Cristalino Amarillo	1986	Neuquen	Flint	19.1	71.7	
19-036-86/87	Cristalino Amarillo	1986	Neuquen	Flint	19.4	70.1	
19-075-O	Cristalino Amarillo	1986	Neuquen	Flint	19.4	72.3	

<sup>a</sup> O = suffix denoting landraces originally collected from different regions of Argentina; P = suffix denoting landraces that were replanted at the Agriculture Experiment Station in Pergamino, Argentina.

<sup>b</sup> Year of original collection for samples with suffix O; year of regeneration at Pergamino, Argentina, for samples with suffix P.

<sup>c</sup> Amylose and starch values were provided by our collaborators at INTA, Argentina.

min, and held at 50°C for 2 min. Pasting temperature ( $P_{onset}$ ), peak viscosity (PV), hot paste viscosity (HPV), cold paste viscosity (CPV), breakdown, and setback were recorded.

### Gel Strength

The starch pastes from the RVA analysis were analyzed for gel strength with a texture analyzer (Stable Micro Systems TA.XT2, Texture Technologies Corp., Scarsdale, NY) equipped with Texture Expert for Windows software (V1.11) (Takahashi and Seib 1988). After each RVA run, the gelatinized paste was transferred into an aluminum container (27 mm diameter and depth) and surrounded on the top by aluminum foil to increase the height by 10 mm. The container was covered with foil and stored in another plastic container with a lid to minimize dehydration. Gel strength was tested after 1 day at 25°C and after 7 days at 4°C. Samples stored under refrigeration were equilibrated to room temperature before analysis. Due to limited sample size, texture analysis data reported were an average of five punches per gel, run only once under each storage condition. Texture analysis was repeated for a few samples for which there was enough starch, and the standard deviations were recorded.

For gel strength measurement, the aluminum foil was removed and the top surface sliced with a wire cheese cutter. The gels were compressed at a speed of 0.9 mm/sec to a distance of 7.5 mm using a stainless steel probe (P/4, 4-mm diameter). The peak force at 7.5 mm was reported as the firmness of the gel for each storage condition.

### Image Analysis

The single starch sample extracted from 50 g of corn was mounted on a glass microscope slide and viewed with a Zeiss axiophot microscope (Zeiss-Kontron, Thornwood, NY) at  $\times 50$  magnification ( $\times 20$  by  $\times 2.5$  Optivar). Starch granule sizes were obtained by following the procedure described by Jane et al (1992) on 200 individual granules per each corn landrace.

### Statistical Analysis

Analysis of variance (Steel and Torrie 1980) was used for data analysis. Relationships between starch and amylose content, granule size distribution, DSC, RVA, and texture parameters were determined using Pearson's simple correlation test (SAS Institute, Cary, NC).

TABLE III  
Differential Scanning Calorimetry Values<sup>a</sup> from Initial Screening  
of 35 Argentinean Corn Landraces<sup>b</sup>

Landrace <sup>c</sup>	Endosperm Type	$T_{oG}$ (°C)	$R_G$ (°C)	$\delta_G$ (J/g)	$T_{oR}$ (°C)	$R_R$ (°C)	$\delta_R$ (J/g)	PHI
MO-17 (control)	Dent	65.0	10.8	13.8	40.2	21.2	6.7	2.60
04-035-P	Dent	64.2	12.4	13.3	40.7	19.4	4.5	2.15
05-081-P	Dent	62.0	12.5	11.5	40.0	19.8	6.0	1.83
05-087-P	Dent	65.9	9.1	11.0	39.4	23.1	5.8	2.41
12-080-O	Dent	63.5	10.1	12.4	39.7	22.5	7.2	2.45
13-049-O	Dent	64.5	12.1	12.0	39.8	21.9	5.9	1.98
13-049-P	Dent	63.2	11.3	12.4	39.7	21.5	6.2	2.20
16-007-P	Dent	64.8	11.3	12.9	39.1	23.3	6.1	2.29
01-102-P	Flint	62.4	14.2	11.6	40.5	20.0	6.0	1.64
03-021-P	Flint	64.8	11.6	12.4	40.6	22.4	6.5	2.14
03-029-P	Flint	64.1	11.9	10.8	39.8	21.4	5.2	1.81
03-032-O	Flint	65.1	10.6	12.0	40.9	21.4	6.1	2.27
03-032-P	Flint	63.3	12.4	12.3	39.5	23.5	6.4	1.98
08-085-O	Flint	57.7	13.5	11.6	40.0	19.8	5.8	1.71
10-020-O	Flint	52.9	17.9	10.2	40.8	19.4	5.2	1.14
13-035-P	Flint	63.1	12.7	12.3	39.2	25.8	5.9	1.93
13-064-O	Flint	64.6	10.7	11.9	42.0	19.3	6.1	2.22
16-018-O	Flint	60.5	12.9	12.2	40.2	21.3	5.5	1.88
16-024-O	Flint	63.2	11.4	12.4	39.5	22.8	7.2	2.17
16-036-O	Flint	64.3	10.0	12.3	40.5	20.5	5.5	2.46
17-026-O	Flint	63.5	10.9	12.7	40.2	21.6	6.7	2.34
19-033-O	Flint	59.3	14.4	12.7	39.6	20.9	5.3	1.76
19-036-O	Flint	66.5	8.7	12.1	39.2	22.4	6.0	2.78
19-075-O	Flint	63.3	11.1	12.9	40.2	22.1	6.4	2.31
03-044-O	Floury	65.2	10.8	12.9	40.5	21.5	6.4	2.39
04-040-P	Floury	61.6	11.7	12.1	39.8	20.2	5.8	2.05
08-096-O	Floury	57.1	17.1	12.3	40.4	20.0	5.5	1.44
08-173-O2	Floury	58.0	13.0	12.7	39.9	19.8	5.4	1.95
08-173-O3	Floury	58.8	12.8	12.5	40.7	20.0	5.6	1.95
18-026-O	Floury	61.4	15.2	12.3	40.4	21.1	6.0	1.62
07-031-O	Semident	65.4	10.7	11.9	40.7	21.9	6.4	2.22
07-031-P	Semident	62.6	11.4	12.5	39.9	23.4	6.5	2.19
07-061-O	Semident	64.1	11.5	11.6	40.4	21.6	5.8	2.02
07-126-O	Semident	65.0	9.8	11.8	39.9	22.2	5.9	2.42
04-087-O	Semiflint	65.5	10.5	12.5	40.3	20.9	5.4	2.38
13-165-O	Semiflint	60.5	13.5	11.9	41.4	19.2	4.6	1.77
Mean		62.8	12.0	12.1	40.2	21.4	5.9	2.1
Minimum		52.9	8.7	10.2	39.1	19.2	4.5	1.1
Maximum		66.5	17.9	13.3	42.0	25.8	7.2	2.8
Range		13.7	9.2	3.1	2.9	6.6	2.7	1.6
Confidence level (95.0%)		1.0	0.7	0.2	0.2	0.5	0.2	0.1

<sup>a</sup>  $T_{oG}$  = gelatinization onset temperature;  $R_G$  = range of gelatinization temperature;  $\delta_G$  = enthalpy of gelatinization;  $T_{oR}$  = retrogradation onset temperature;  $R_R$  = range of retrogradation temperature;  $\delta_R$  = enthalpy of retrogradation; PHI = peak height index ( $\delta_G/(0.5 \times R_G)$ ).

<sup>b</sup> Values are averages of duplicate runs from starch extracted from five randomly selected seeds.

<sup>c</sup> O = suffix denoting landraces originally collected from different regions of Argentina; P = suffix denoting landraces that were replanted at the Agriculture Experiment Station in Pergamino, Argentina.

## RESULTS AND DISCUSSION

### DSC Characterization of Starch

Starches from 35 corn landraces were screened for thermal properties using DSC to identify starches with thermal properties of potential research or commercial interest. Starches were considered to possess unusual thermal properties based on criteria listed in Table I, which draws upon the extensive database of thermal properties of normal cornstarch from the United States. The landraces of corn screened included different endosperm types such as dent, flint, floursy, semident, and semiflint and varied in the levels of starch, amylose, and protein contents (Robutti et al 2000b). These samples are a subset of the germplasm available at the Argentinean Germplasm Bank.

The thermal properties of starch from the different landraces exhibited considerable variability (Table III). Value ranges were  $T_{oG}$  52.9–66.5°C,  $R_G$  8.7–17.9°C,  $R_R$  19.2–25.8°C, and PHI 1.1–2.8 for all the accessions screened. The  $T_{oG}$  values of the different landraces were skewed by one corn landrace, a flint corn (10-020-O) with a  $T_{oG}$  value of 52.9°C. This corn is of the Pisingallo race, which is the type of corn used for popcorn. Upon comparing the

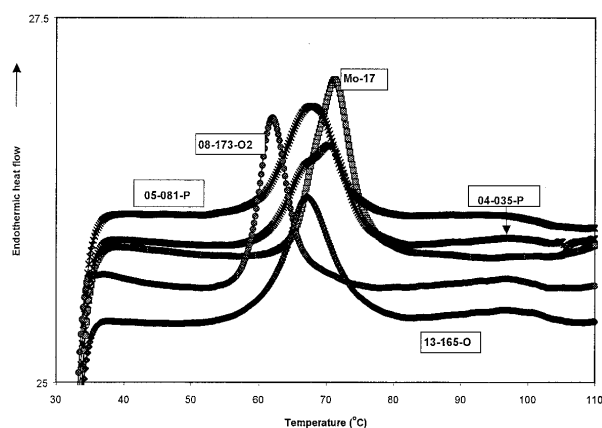


Fig. 1. Representative differential scanning calorimetry thermograms of selected maize starches. Mo-17 is a Corn Belt inbred used as a control.

thermal properties based on endosperm types, floursy corn had the lowest mean value for  $T_{oG}$  (60.8°C) and the highest for  $R_G$  (13.5°C). Representative thermograms of starches exhibiting unusual DSC properties are shown in Fig. 1.

Earlier studies investigating the thermal properties of nonmutant corn inbreds reported  $T_{oG}$  values for starch from flint corn at 62.6–68.1°C,  $R_G$  values at 7.6–13.5°C, and  $R_R$  values at 16.7–19.2°C (Campbell et al 1995; Pollak and White 1997). The same studies also reported  $T_{oG}$  values for starch from dent corn at 61.2–71.2°C,  $R_G$  values at 7.8–17.6°C, and  $R_R$  values at 15.8–19.7°C. Flint corn landraces from the present study showed a greater variation for these properties than previously reported, whereas the dent corn races exhibited lesser variation. Li et al (1994) reported the DSC properties of starch from 35 Latin American corn accessions. Although significant differences in various thermal properties were reported in their study, the range of thermal properties among the different accessions was smaller than the results obtained in this study. Jane et al (1999) reported DSC values for a variety of A-type starches. The  $T_{oG}$  values of these A-type starches were 56.3°C for barley to 70.3°C for normal rice starch, and the  $R_G$  values were 6.6°C for barley to 14.4°C for dull-waxy starch from corn. The range of DSC attributes from the corn landraces in the present study exhibited about the same degree of variability as for other A-type starches, if not higher. Thus, sufficient variability exists within corn germplasm for a range of thermal properties, making it possible to create corn lines with unusual thermal properties using the accessions from Argentinean germplasm.

### DSC Properties of Starch from Selected Landraces of Corn

Based on the DSC characteristics such as low  $T_{oG}$  or broad  $R_G$ , and parameters such as low or high starch or amylose contents, 13 of the 35 corn landraces were selected for further functional analyses (Table II). The degree of genetic variability within each of the selected landraces for thermal properties was characterized by analyzing starch thermal properties on several single kernels with the DSC. The analysis was conducted on starch extracted from 10 randomly selected single kernels per race. Analyzing individual seeds from an ear of corn highlights the genetic variability for thermal properties within a corn race. The thermal properties of the selected landraces are listed in Table IV.

TABLE IV  
Differential Scanning Calorimetry (DSC) Values<sup>a</sup> of Starch from 13 Selected Argentinean Corn Landraces<sup>b</sup>

Endosperm Type and Landrace <sup>c</sup>	$T_{oG}$ (°C)				$R_G$ (°C)				$\delta_G$ (J/g)			
	Mean	Min	Max	Range	Mean	Min	Max	Range	Mean	Min	Max	Range
Mo17 (Control)	65.0				10.8				13.8			
Overall	64.0	58.2	68.2	10.0	9.7	6.4	17.9	11.5	12.0	8.8	13.8	5.0
Dent	64.3a–c <sup>d</sup>	60.0	67.8	7.8	10.2a	7.2	17.6	10.4	12.1a	9.6	13.8	4.2
04-035-P	65.3	61.5	67.8	6.3	11.6	8.4	17.6	9.2	11.7	11.1	12.4	1.3
05081-P	62.1	60.0	64.4	4.4	11.1	8.4	14.8	6.4	12.1	11.0	12.9	1.9
13-049-O	64.7	60.6	66.9	6.8	9.0	7.2	11.4	4.3	12.4	9.6	13.8	4.2
13-049-P	65.2	63.5	66.9	3.4	8.9	7.2	11.6	4.4	12.2	9.7	13.8	4.1
Flint	65.7a	61.5	68.0	6.5	9.5a	7.2	14.1	6.8	11.7a	8.8	12.9	4.1
03-032-O	66.7	65.9	67.7	1.9	8.5	7.6	9.9	2.3	11.9	10.6	12.9	2.4
03-032-P	64.9	61.5	68.0	6.5	10.4	7.2	14.1	6.8	11.4	8.8	12.4	3.6
Floursy	60.8d	58.0	65.2	7.2	8.7a	6.9	10.8	3.9	12.3a	11.0	13.1	2.1
08-096-O	60.7	59.0	64.3	5.2	8.1	6.9	10.7	3.8	11.8	11.0	12.7	1.7
08-173-O2	61.5	58.2	65.2	7.0	8.7	7.6	9.9	2.3	12.3	11.4	12.9	1.4
08-173-O3	60.2	58.0	63.3	5.3	9.1	7.8	10.8	3.0	12.6	11.4	13.1	1.7
Semident	64.8ab	58.7	68.2	9.5	10a	6.4	17.9	11.5	12.1a	9.4	13.7	4.2
07-126-O	65.4	62.9	67.0	4.1	8.7	6.6	10.6	4.0	11.3	9.4	12.1	2.7
07-031-O	66.1	64.8	68.2	3.4	8.1	6.4	9.4	3.0	12.9	12.2	13.7	1.4
07-031-P	62.9	58.7	64.9	6.1	13.3	10.2	17.9	7.6	11.9	10.9	13.3	2.4
Semiflnt (13-165-O)	62.3bd	59.4	64.0	4.6	9.5a	7.6	10.7	3.2	11.6a	10.5	12.3	1.8

<sup>a</sup>  $T_{oG}$  = gelatinization onset temperature;  $R_G$  = range of gelatinization temperature;  $\delta_G$  = enthalpy of gelatinization;  $T_{oR}$  = retrogradation onset temperature;  $R_R$  = range of retrogradation temperature;  $\delta_R$  = enthalpy of retrogradation.

<sup>b</sup> Values are average of duplicate runs on DSC of starch extracted from 10 single kernels from each corn landrace.

<sup>c</sup> O = suffix denoting landraces originally collected from different regions of Argentina; P = suffix denoting landraces that were replanted at the Agriculture Experiment Station in Pergamino, Argentina.

<sup>d</sup> Values followed by the same letter in the same column are not significantly different ( $P < 0.05$ ).

Starch thermal properties from individual kernels within a landrace exhibited considerable variability. Starch from several individual kernels from most landraces exhibited lower  $T_{oG}$  values than did Mo-17, and several of these values also were unusual ( $<61^{\circ}\text{C}$ ). The mean  $R_G$  values of starch from several landraces were lower than that of Mo-17 and, although considerable variation within each landrace was observed for  $R_G$  values, starch from only a few kernels exhibited unusual  $R_G$  values ( $<5.5$  or  $>14.5^{\circ}\text{C}$ ). Dent landraces 04-035-P and 05-081-P, and semident landrace 07-031-P, had individual kernels with  $R_G$  values  $>14.5^{\circ}\text{C}$ . The mean  $\delta_G$  values of starch from all the landraces were lower than the  $\delta_G$  values of starch from Mo-17, but only one kernel each from landraces 13-049-P and 03-032-P exhibited  $\delta_G$  values  $<9.5$  J/g. The mean  $\delta_R$  values of starches from most landraces were lower than the  $\delta_R$  value of Mo-17, and starches from several kernels in most landraces exhibited  $\delta_R$  values  $<3.8$  J/g.

Statistical analyses of the data revealed significant differences in the thermal properties of starches when endosperm types were compared. But the thermal properties of starches between different landraces were not significant because considerable variability was observed in the thermal properties within each landrace based on the data obtained from 10 individual seeds per landrace. This lack of significance denotes variation for each starch thermal attribute within each landrace of corn. Identifying landraces and kernels of corn that are the outliers for different properties was the objective of this screening process because the outliers reveal accessions possessing traits of potential use. The high degree of variability for different thermal attributes shows the promise for identifying landraces and kernels within the landraces that possess new thermal properties for use in breeding programs.

Statistical analyses also were conducted to compare the thermal properties between corn landraces of different endosperm types. Although the analysis is skewed because of the uneven, small sample size within each endosperm type, significant differences were observed in the thermal properties between the endosperm types for  $T_{oG}$ ,  $R_R$ , and  $\delta_R$  (Table IV). Flourey corn starch had a lower mean  $T_{oG}$ ,  $R_R$ , and  $\delta_R$  than did starch from all other corn types. Flint corn had a higher  $T_{oG}$  and lower  $\delta_R$  than did the other endosperm types, except for flourey endosperm corn. Semident corn starch had the highest variability in  $T_{oG}$  and  $R_G$  values. More

specifically, starches from one dent landrace, 05-081-P, one semident landrace, 07-031-P, and the semiflour landrace 13-165-O had lower mean  $T_{oG}$  values than those of Mo-17 starch.

Thermal properties also were compared between races that were originally collected (suffix "O" in the label) and then replanted (suffix "P") in the Agriculture Experiment Station at Pergamino, Argentina. A comparison of the thermal properties of these samples reveals that there was greater variability for  $T_{oG}$  in two of the O samples (03-032-O and 07-031-O) than for those that were re-grown (P), whereas race 13-049 had the opposite trend. The differences between the O and P samples reflect the influence of environment on the thermal properties and highlight the potential difficulty in incorporating unusual traits into adapted corn backgrounds.

### Pasting Properties of Starch from Selected Corn Landraces

Significant differences were observed in the pasting properties of starch from different landraces of corn (Table V). Overall, the pasting viscosities of the starches from the Argentinean germ-plasm were greater than those for normal dent corn (Mo-17). Mean  $P_{onset}$  temperature for all the landraces was  $78.7^{\circ}\text{C}$ , with values of  $74.9$ – $84.7^{\circ}\text{C}$ . The mean PV value for all the samples was 158.9 RVU, with values of 120.6–172.0 RVU, and the mean HPV value for all the samples was 92.2 RVU, with values of 76.8–101.3 RVU. The mean CPV value for all the samples was 190.8 RVU, with values of 150.6–210.0 RVU. The average breakdown value for all the samples was 66.7 RVU, and the values were 40.2–77.3 RVU for starches from different corn landraces. The mean setback value was 98.5 RVU, and the values for the different landraces were 73.3–115.3 RVU. The average slope of the curve from  $P_{onset}$  to PV was 17.6 RVU, and the values were 12.5–25.6 RVU for starches from the different landraces.

When comparing the pasting properties of starch from the different endosperm types, only flourey endosperm corn was significantly different from other endosperm types. Starch from flourey corn had the highest  $P_{onset}$  and the lowest average PV, CPV, breakdown, and setback viscosities. Flourey corn generally also reached the pasting viscosity earlier than the other corn types, as measured by the slope of the curve from  $P_{onset}$  to PV.

Jane et al (1999) reported pasting properties of a variety of A- and B-type starches from different botanical sources using the

TABLE IV  
(continued)

Endosperm Type and Landrace	$T_{oG}$ ( $^{\circ}\text{C}$ )				$R_G$ ( $^{\circ}\text{C}$ )				$\delta_G$ (J/g)			
	Mean	Min	Max	Range	Mean	Min	Max	Range	Mean	Min	Max	Range
Mo17 (Control)	40.2				21.2				6.7			
Overall	39.9	35.3	43.0	7.7	21.0	15.6	32.3	16.7	5.4	2.7	8.6	6.0
Dent	39.3c	35.3	42.6	7.2	21.8a	17.2	32.3	15.1	5.7ab	3.6	8.6	5.1
04-035-P	40.0	39.6	40.6	1.0	19.6	17.2	20.6	3.4	5.3	3.9	5.9	2.0
05081-P	39.6	38.0	40.1	2.1	20.2	19.4	21.2	1.8	5.3	4.6	6.6	2.0
13-049-O	39.2	35.3	42.6	7.2	26.2	19.2	32.3	13.2	7.5	6.1	8.6	2.6
13-049-P	38.6	37.8	39.5	1.7	21.9	20.4	24.4	4.0	5.2	3.6	6.1	2.6
Flint	39c	37.2	41.0	3.8	21.5a	16.3	25.2	8.9	4.9c	3.3	5.8	2.5
03-032-O	39.4	37.4	41.0	3.6	20.3	16.3	23.2	6.9	4.9	3.3	5.8	2.5
03-032-P	38.6	37.2	39.5	2.3	22.6	21.0	25.2	4.2	5.0	4.1	5.6	1.4
Flourey	40.9b	38.8	42.4	3.6	19.3b	15.6	22.0	6.4	5c	2.7	6.2	3.6
08-096-O	41.3	40.6	41.8	1.2	19.8	18.4	21.0	2.6	5.7	5.0	6.2	1.2
08-173-O2	40.6	38.8	42.0	3.2	19.3	15.6	22.0	6.4	4.5	2.7	5.3	2.7
08-173-O3	40.8	39.8	42.4	2.6	18.8	16.6	21.4	4.8	5.0	4.1	5.8	1.7
Semident	39.5c	37.9	41.9	4.0	20.9ab	15.8	25.6	9.8	5.4ab	3.8	6.9	3.1
07-126-O	40.2	39.1	41.8	2.7	20.0	18.8	21.8	3.0	5.1	3.8	6.9	3.1
07-031-O	38.7	37.9	39.9	2.0	22.2	20.2	25.6	5.4	5.4	5.1	6.2	1.1
07-031-P	39.7	38.6	41.9	3.3	20.4	15.8	22.4	6.6	5.5	4.8	6.3	1.5
Semiflour (13-165-O)	42.2a	41.7	43.0	1.3	19.7ab	18.0	21.0	3.0	6a	5.4	6.7	1.2

RVA. The  $P_{onset}$  values of these starches were 63.5°C for potato to 91.2°C for barley. The PV values were 58 RVU for barley to 250 RVU for green banana, with a high of 702 RVU for potato. Setback values were 6 RVU for waxy amaranth starch to 202 RVU for mung bean starch. The pasting properties of starches from the different landraces of corn in the present study also exhibited considerable variability. The variability in the pasting properties of corn starch in the present study also was significantly higher than the variability reported by Yamin et al (1999) characterizing the pasting properties of starches from mutagenized corn.

### Textural Properties of Starch Gels from Selected Corn Races

Significant differences were observed in the textural properties of the starch gels among the different corn landraces (Table VI). The average force required to break the gel after 1 day was 16.8 g, with values for the different landraces at 12.8–21.3 g. The average force required to break the gel after 7 days of storage at refrigeration temperature was 24.0 g, with values for the landraces at 16.7–35.0 g. Starches from landraces of the floury type corn generally required the least amount of force to break the gel among all starch types after both 1 and 7 days. Yamin et al (1999) reported texture values for starch gels obtained from mutagenized corn that were lower for gels stored for 1 and 7 days than reported in the present study. But the variability induced in gel strength by mutagenized corn was lower than the natural variability reported in this study among the various landraces from the germplasm.

### Starch Granule Size Distribution

The granule size distributions of starch from the different corn landraces and endosperm types are listed in Table VII. The data for each landrace were then divided into two size ranges, <10- $\mu$ m and >10- $\mu$ m diameter, and reported as a percentage of the total number of granules measured. Variability in starch granule size distribution is, therefore, a measure of the skewness in the distribution of granule sizes within each landrace of corn.

The average diameter of the starch granules across all landraces and endosperm types was 8.96  $\mu$ m, with a range of 17.56  $\mu$ m.

Floury endosperm corn landraces had a greater mean starch granule size than did starch from all other endosperm types. Floury corn 08-096-O and dent corn 13-049-O had starch with most granules >10  $\mu$ m in diameter and dent corn 13-049-P had starch with most granules <10  $\mu$ m.

**TABLE VI**  
Textural Properties of 13 Selected Argentinean Corn Landraces<sup>a</sup>

Endosperm Type and Landrace <sup>b</sup>	1 Day Force (g)	7 Day Force (g)
Control (Mo-17)	13.1	20.3
Overall ( $n = 13$ )	16.8	24.0
Dent	17.3x <sup>c</sup>	24.7x
04-035-P	17.7b–d <sup>d</sup>	25.4b–d
05-081-P	14.7ef	21.1c–e
13-049-O	17.7b–d	28.4b
13-049-P	19.2a–c	26.7bc
Flint	16.4xy	24.4x
03-032-O	15.3d–f	23b–d
03-032-P	17.7b–d	25.4bc
Floury	13.3y	18.3y
08-096-O	12.8f	16.7f
08-173-O2	13.5f	19.5d–f
08-173-O3	13.6f	18.2ef
Semident	19.1x	28.1x
07-126-O	19.3ab	26.5b
07-031-O	21.3a	35.0a
07-031-P	16.1c–e	23.3c–e
Semiflint	18.8x	25.9x
13-165-O	18.8a–c	25.9bc
Minimum	12.8	16.7
Maximum	21.3	35.0
Range	8.5	18.3

<sup>a</sup> Values are the averages of five measurements from a gel sample.

<sup>b</sup> O = suffix denoting landraces originally collected from different regions of Argentina; P = suffix denoting landraces that were replanted at the Agriculture Experiment Station in Pergamino, Argentina.

<sup>c</sup> Different letters (x,y) within the same column indicate significant differences at  $P < 0.05$  between endosperm types.

<sup>d</sup> Different letters (a–f) within the same column indicate significant differences at  $P < 0.05$  between different landraces.

**TABLE V**  
Pasting Properties<sup>a</sup> of 13 Selected Argentinean Corn Landraces<sup>b</sup>

Endosperm Type and Landrace <sup>c</sup>	$P_{onset}$ (°C)	HPV (RVU)	PV (RVU)	CPV (RVU)	Breakdown (RVU)	Setback (RVU)	Slope (RVU/sec)
Control (Mo-17)	76.7	84.5	136.6	183.8	52.1	99.3	11.9
Overall ( $n = 13$ )	78.7	92.2	158.9	190.8	66.7	98.5	17.6
Dent	77.7x <sup>d</sup>	95.6x	166.2x	198.1x	70.6x	102.6x	17.7xy
04-035-P	77.6c–f <sup>e</sup>	101.3a	163.0ab	205.6a	61.7ef	104.3a–d	14.2gh
05-081-P	80.1bc	82.7b–d	159.9ab	170.5cd	77.3a	87.8de	21.2b
13-049-O	75.9d–f	97.3a	172.0a	206.5a	74.8a–c	109.3a–c	18.0c–e
13-049-P	77.4c–f	101.0a	169.8a	210.0a	68.8a–e	109.0a–c	17.4c–f
Flint	77.9x	90.4xy	165.5x	200.7x	75.1x	110.3x	16.3z
03-032-O	78.9b–d	91.9a–c	165.5	197.3ab	73.5a–d	105.3a–c	16.6d–f
03-032-P	76.9c–f	88.8a–d	165.5ab	204.2ab	76.6ab	115.3a	15.9e–g
Floury	83.3y	81.9y	135.8y	162.5y	53.9y	80.6y	20.5x
08-096-O	84.7a	88.6a–d	151.5b	183.3bc	62.9ef	94.6cd	25.6a
08-173-O2	83.5a	80.4cd	120.6c	153.7d	40.2g	73.3e	18.5cd
08-173-O3	81.6ab	76.8cd	135.3c	150.6d	58.5f	73.8e	17.6c–e
Semident	76.0x	96.7x	165.0x	200.4x	68.3x	103.7x	15.5z
07-126-O	75.4ef	100.1a	165.5ab	202.8ab	65.5c–f	102.7a–d	14.9f–h
07-031-O	74.9f	93.6a–c	158.3ab	190.4a–c	64.6d–f	96.7b–d	12.5h
07-031-P	77.7c–f	96.3ab	171.2a	208.0a	74.9a–c	111.7ab	19.2bc
Semiflint	78.2x	100.0x	167.5x	197.2x	67.5xy	97.2xy	16.7yz
13-165-O	78.2c–e	100.0a	167.5a	197.2ab	67.5b–f	97.2b–d	16.7d–f
Minimum	74.9	76.8	120.6	150.6	40.2	73.3	12.5
Maximum	84.7	101.3	172.0	210.0	77.3	115.3	25.6
Range	9.6	24.5	51.4	59.4	37.1	42.0	13.1

<sup>a</sup>  $P_{onset}$  = pasting onset temperature; HPV = hot paste viscosity; PV = pasting viscosity; CPV = final viscosity; Slope = slope from  $P_{onset}$  to  $P_{V_{temp}}$ .

<sup>b</sup> Values are average of duplicate runs.

<sup>c</sup> O = suffix denoting landraces originally collected from different regions of Argentina; P = suffix denoting landraces that were replanted at the Agriculture Experiment Station in Pergamino, Argentina.

<sup>d</sup> Different letters (x–z) within the same column indicate significant differences at  $P < 0.05$  between endosperm types.

<sup>e</sup> Different letters (a–h) within the same column indicate significant differences at  $P < 0.05$  between different landraces.

Campbell et al (1996) reported mean starch granule diameters at 16.2–18.2  $\mu\text{m}$  for starches from 35 corn populations from the Latin American germplasm. Starch granule diameters in the present study from the different corn landraces were significantly lower than data reported by Campbell et al (1996). Campbell et al (1996) did not, however, report the distribution of starch granule size for the different corn populations.

### Correlation of Data

Although correlation data do not signify causality, correlation analyses of the physical and compositional attributes of the starches with the thermal and pasting properties of starches potentially provide valuable insights into the mechanisms contributing to the functional properties of the starches. The correlation data with levels of significance  $P < 0.05$  or greater are listed in Table VIII.

Starch content correlated positively with amylose content, but did not correlate with any functional property. The amylose content of the starch, however, correlated significantly with several functional attributes.

Amylose content did not significantly correlate with DSC parameters. Sasaki et al (2000), investigating the thermal and pasting properties of waxy and nonwaxy wheat, reported a negative correlation between the gelatinization endpoint temperature and  $\delta_G$  with amylose content. In this study, we did not observe a relationship between amylose content and gelatinization properties measured using DSC, probably because the range of amylose content of corn in this study was low (18–22%) compared with the study reported by Sasaki et al (2000), in which amylose content was 0.8–20%. Amylose content exhibited a positive correlation with the RVA measurement of HPV and a negative correlation with the  $P_{\text{onset}}$  and the slope of the curve from pasting onset to the peak pasting temperature.

Sasaki et al (2000) reported a negative correlation between amylose content and pasting viscosity measured using an RVA. Although this study showed no relationship between amylose content and pasting viscosity, it did show that starch with lower amylose content achieved peak viscosity at a faster rate, as measured by the slope of the curve from pasting onset to peak viscosity. Amylose content further correlated positively with gel texture after both 1 and 7 days of storage. This result is in agreement with that reported by Gaines et al (2000), who investigated the various physicochemical attributes of wheat cultivars.

Starch granule size correlated only with the onset temperature measured using a DSC and with  $P_{\text{onset}}$ , HPV, and slope measured using the RVA. Larger average granule size resulted in lower gelatinization and pasting onset temperatures and higher HPV. Granule size correlated strongly with starch textural properties with larger granule size resulting in firmer gel texture at both 1 and 7 days.

Several significant relationships also were observed between starch thermal properties measured using a DSC and the functional properties measured using the RVA. Starches with lower  $T_{\text{OG}}$  had higher  $P_{\text{onset}}$ , achieved PV earlier, and had lower PV, breakdown, and setback values.

### CONCLUSIONS

Germplasm banks are valuable resources for identifying natural variability of different plant and seed traits. Screening the accessions in a germplasm bank aids in the identification of plants with unusual properties ranging from agronomic traits to functional and compositional traits of the seeds. Results from this study confirm the presence of a wide variation in the thermal and functional properties of starch from several landraces of corn in the Argentinean germplasm.

Thermal properties of starch measured using a DSC identified several corn landraces with unusual properties. The thermal properties of some of the corn reported in this study are comparable to the thermal properties of starch from several other crop species. Furthermore, several of these corn races exhibited unusual properties in several kernels that were analyzed, indicating a certain degree of genetic homogeneity for that trait. These corn races show promise for further regeneration to create inbred lines with unusual traits.

The pasting and textural properties of starch gels obtained from starch from different corn races also exhibited considerable variability comparable with those properties reported for starch from other crop species. Thus, the potential for further improvement of corn races exists not only based on thermal properties, but directly for specific functional attributes as well.

The correlation analyses suggest that the variability in thermal and functional attributes is a function of amylose content and starch granule size. The strong correlation observed between the thermal properties analyzed using a DSC and the functional properties measured using an RVA and texture analyzer will allow for

TABLE VII  
Starch Granule Size Distribution of 13 Selected Argentinean Corn Landraces<sup>a</sup>

Endosperm Type and Landrace <sup>b</sup>	Mean ( $\mu\text{m}$ )	Minimum ( $\mu\text{m}$ )	Maximum ( $\mu\text{m}$ )	Range ( $\mu\text{m}$ )	<10 $\mu\text{m}$ (%)	>10 $\mu\text{m}$ (%)
Control (Mo-17)	8.60	2.28	19.22	16.94	71.0	29.0
Overall ( $n = 13$ )	8.96	1.88	19.44	17.56	63.3	36.7
Dent	8.68ab <sup>c</sup>	1.96	19.28	17.32	68.0	32.0
04-035-P	8.32	2.60	19.20	16.60	71.6	28.4
05-081-P	8.66	3.42	16.74	13.34	69.2	30.8
13-049-O	9.88	1.96	19.28	17.32	54.2	45.8
13-049-P	7.86	3.20	15.38	12.18	77.1	22.9
Flint	9.38a	2.26	18.86	16.60	60.9	39.6
03-032-O	9.10	2.26	18.44	16.18	63.7	36.3
03-032-P	9.66	2.60	18.86	16.26	58.2	41.8
Floury	9.64a	2.10	18.94	16.84	57.9	42.1
08-096-O	9.92	2.98	18.52	15.56	54.7	45.3
08-173-O2	9.38	2.10	18.94	16.84	63.2	36.8
08-173-O3	9.66	2.50	18.70	16.20	55.7	44.3
Semident	8.58b	1.88	19.54	17.56	66.8	33.2
07-126-O	8.44	1.88	16.18	14.30	66.2	33.8
07-031-O	7.98	3.16	17.68	14.32	75.1	24.9
07-031-P	9.32	2.94	19.44	16.50	59.2	40.8
Semiflint (13-165-O)	8.80b	2.38	18.36	15.98	62.7	37.3

<sup>a</sup> Values are averages of diameters of 200 starch granules.

<sup>b</sup> O = suffix denoting landraces originally collected from different regions of Argentina; P = suffix denoting landraces that were replanted at the Agriculture Experiment Station in Pergamino, Argentina.

<sup>c</sup> Different letters within the same column indicate significant differences at  $P < 0.05$  between endosperm types.

**TABLE VIII**  
Correlation Coefficients for 13 Argentinean Corn Landraces<sup>a</sup>

Variable	Granule		Pasting Properties <sup>b</sup>						Textural Properties		
	Amylose	Size (mean)	P <sub>onset</sub>	HPV	PV	CPV	BD	SB	Slope	1 Day Force	7 Day Force
Starch	0.82*										
Thermal properties											
<i>T</i> <sub>OG</sub>		-0.43****	-0.77*	0.61*	0.52***	0.62*		0.55**	-0.71*	0.68*	0.69*
<i>R</i> <sub>G</sub>											
$\delta$ <sub>G</sub>											
<i>T</i> <sub>OR</sub>				0.51***	0.71*	0.64*	0.64*	0.64*		0.39****	0.47****
<i>R</i> <sub>R</sub>			-0.52***								
$\delta$ <sub>R</sub>						-0.40****	-0.60*	-0.50***			
Pasting properties											
P <sub>onset</sub>	-0.59**	0.47***									
HPV	0.40****										
PV											
CPV											
BD											
SB											
Slope	-0.53***	0.44****									
Texture properties											
1 day force	0.70*	-0.50***	-0.86*	0.69*	0.58**	0.64*		0.53**	-0.74*		
7 day force	0.70*	-0.40***	-0.87*	0.55**	0.52***	0.54**		0.47****	-0.71*		

<sup>a</sup> \*, \*\*, \*\*\*, \*\*\*\* =  $P < 0.001, 0.005, 0.01, \text{ and } 0.05$ , respectively.

<sup>b</sup> P<sub>onset</sub> = pasting onset temperature; HPV = hot paste viscosity; PV = pasting viscosity; CPV = final viscosity; BD = breakdown (PV - HPV); SB = setback (CPV - PV); slope = slope from P<sub>onset</sub> to PV<sub>temp</sub>; *T*<sub>OG</sub> = gelatinization onset temperature; *R*<sub>G</sub> = range of gelatinization temperature;  $\delta$ <sub>G</sub> = enthalpy of gelatinization; *T*<sub>OR</sub> = retrogradation onset temperature; *R*<sub>R</sub> = range of retrogradation temperature;  $\delta$ <sub>R</sub> = enthalpy of retrogradation.

extrapolation of starch properties using the smaller sample sizes allowed for DSC analyses.

Further collaborative studies are underway to develop inbred lines using these exotic races of corn to create lines with unusual starch properties and improved agronomic traits.

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