

# Properties of Some Starch Blends<sup>1</sup>

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## ABSTRACT

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Normal corn, high-amylose corn, waxy corn (waxy maize), wheat, rice, potato, cassava (tapioca), and a modified waxy corn starch were blended in various combinations and ratios. Pasting behavior, paste and thermal properties, and retrogradation tendency were determined. Differential scanning calorimetry (DSC) traces of the mixtures did not resemble those of either of the two components, nor did any DSC trace have

two peaks suggestive of a mixture of two distinct starches. Amylograph data suggested that some mixtures behaved like a chemically modified starch. Observations from light microscopy suggested that intermolecular, molecular-supermolecular, and intersupermolecular interactions may be responsible for this behavior.

Commercial starches are obtained from various botanical sources. Each starch has unique functional properties, but much of that used industrially is modified before use, giving a wider range of useful products. Blending of starches has not been a common practice. Stute and Kern (1994) patented blends of starches for use in pudding preparation. The patent claims that use of blends of unmodified pea and corn starches in ratios of 9:1 to 1:9 as gelling and texturing agents in the formulation of food products reduces syneresis. Liu and Lelièvre (1992) studied the melting transitions of blends of native wheat and rice starches. They found that, at starch concentrations <30%, the differential scanning calorimetry (DSC) curves of the blends was the sum of the outputs for each individual component of the mixture. However, when starch concentrations were high, a nonadditive behavior was observed. Under these conditions, competition for water occurred and the starch with the lower gelatinization temperature (wheat) melted first (Liu and Lelièvre 1992). Jane and Chen (1992) blended amyloses and amylopectins from various botanical sources and reported synergistic effects on paste viscosities.

When blends of a native or modified starch and a water-soluble gum are heated together in water, the general effects commonly seen were an apparent lowering of the pasting temperature as determined in a Brabender ViscoGraph or a Rapid Visco-Analyzer, a lower temperature of peak viscosity, a higher peak viscosity, a decreased rate of setback, a decreased gel strength, and a more rapid increase in the storage modulus of the paste. The specific effects and magnitudes are dependent on the nature of the starch or modified starch, the nature of the gum, and their ratio, with  $\iota$ -type carrageenans being an exception to the generalities (Crossland and Favor 1948, Racciato 1978, Christianson et al 1981, Sanderson 1982, Sajjan and Rao 1987, Tye 1988, Alloncle et al 1989, Alloncle and Doublier 1991, Kohyama and Nishinari 1992, Bahnassey and Breene 1994, Eidam et al 1995, Liehr and Kulicke 1996, Kulicke et al 1996). Christianson et al (1981) suggested that strong associations of wheat starch amylose with guar gum, xanthan, and carboxymethylcellulose were developed during pasting.

Based on the available information, it might be speculated that a starch with a lower pasting temperature might affect the properties of a starch with a higher gelatinization temperature. However,

behaviors of starch and starch blends have received little attention. The objective of this study was to examine the cooking behaviors, paste properties, and thermal properties of starch and starch blends. It was prompted by the finding of Obanni and BeMiller (1995) that certain maize endosperm double starch mutants are mixtures of different and distinct granule types.

## MATERIAL AND METHODS

### Botanical Sources of the Starches Used

Blends at various ratios (1:9 to 9:1) were formulated by mixing different combinations of the following starches: normal (common) and waxy corn (waxy maize) starches (A. E. Staley Mfg., Decatur, IL), high-amylose corn starch (Hylon V, National Starch and Chemical Co., Bridgewater, NJ), potato starch (Penwest Foods, Co., Englewood, CO), wheat starch (Midwest Grain Products, Inc., Atchinson, KS), tapioca starch (National Starch and Chemical), rice starch (California Natural Products, Lathrop, CA; A & B Ingredients, Inc., Fairfield, NJ). A chemically modified (stabilized) waxy corn starch, Polar-Gel 18 (PG18) (American Maize Products, now Cerestar USA, Hammond, IN), was also used. The starch with the highest proportion in the blend was slurried first in 450 mL of deionized distilled water (total starch concentration = 7.5% w/w, dsb). The second starch was then added, and stirring was continued for 30 min to assure homogeneity of the blend.

### Pasting Behavior

Paste properties of starch blends, as well as their individual components, were evaluated in a Brabender ViscoGraph (type VA-VE, C. W. Brabender Instruments, Inc., Hackensack, NJ). Aqueous suspensions (7.5%, dsb) of the blends and components were cooked at a shear rate of 75 rpm and a torque of 700 cm·g. Dispersions were heated to 95°C, held for 30 min, then cooled to 50°C and held for 10 min. Heating and cooling rates were 1.5°C/min.

### Thermal Characteristics and Retrogradation of Starch Blends and Components

DSC analysis was performed using a Mettler DSC30 differential scanning calorimeter (Mettler Toledo, Hightstown, NJ) with a TC10A control center and standard aluminum 40- $\mu$ L DSC pans (Mettler ME-27331). A 33% slurry (w/w, dsb) of each starch or starch blend was prepared in triplicate. Scans were made from 25 to 125°C at a rate of 10°C/min using an empty pan as a reference. The pans were then stored at 4°C for two weeks and rescanned as previously described to determine the degree of retrogradation.

### Light Microscopy

Paste samples from the viscograph bowl were taken at the end of the 95°C hold and stained with an iodine and potassium iodide

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solution and viewed under bright field in a Leitz Laborlux 12 Pol microscope equipped with a Wild MPS 28 photomicrographic system (Obanni and BeMiller 1995). Photomicrographs were taken at total magnification of 100× using Kodak 100 Gold day-light film and a blue filter.

## RESULTS AND DISCUSSION

### Pasting Behavior of Starch Blends and Components

The amylograms of common corn starch (CCS) and waxy corn starch (WCS) starches presented in Fig. 1 are typical of what has been reported many times previously. WCS produced a high peak viscosity as a result of starch granules swelling to the maximum, followed by granule breakdown. The viscosity was then maintained during the 95°C hold, and no major setback was observed. CCS did not give a high peak viscosity but gave a high setback viscosity as expected (Fig. 1).

When these two starches were mixed at a 1:1 ratio, the amylogram contained two maximum viscosity peaks, one slightly preceding that given by WCS alone (76°C), and the other at the position where CCS reached its maximum viscosity when pasted alone (92°C) (Fig. 1). Only minor reduction in viscosity following either peak was observed. One possible explanation is that, at the time WCS granules were breaking down, the CCS granules were producing a viscosity increase. A problem with this explanation is that, at the time the viscosity of WCS should have been diminishing, there should have been only a small viscosity build up from CCS to account for the total viscosity (Fig. 1). Another possible explanation is that leached starch molecules (probably primarily amylose) from CCS granules prevent major breakdown of WCS granules. However, microscopic observations of the paste at the end of the 95°C hold showed that WCS granules were completely cooked and the solubilized amylopectin of this starch formed a network in which the CCS granules were embedded (data not shown). We conclude that the presence of a discontinuous phase in a continuous phase probably accounts for the structure and properties of the paste (Morris 1990). The paste from the 1:1 blend of these two corn starches exhibited only a small amount of setback, again suggesting entrapment of unpasted CCS granules in an amylopectin network.

Potato starch, at the concentration used in this study (7.5% starch solids), gave a very high peak viscosity typical of this starch,

whereas wheat starch produced a very modest peak viscosity, similar to that of CCS. Both potato and wheat starches exhibited pronounced setback upon cooling. (Amylograms of wheat and potato starches are not given in Fig. 1.) When wheat and potato starches were mixed at a ratio of 3:1, the amylogram showed no peak viscosity or viscosity breakdown, even when holding at 95°C for 30 min (Fig. 1). The amylogram of 3:1 mixture of CCS and potato starch showed characteristics similar to those of the wheat and potato starch blend, but the CCS and potato starch blend had higher viscosity values throughout the amylogram (Fig. 1). The general shapes of the heating and 95°C hold portions of the amylograms of these two mixtures are those usually associated with chemically crosslinked starches. [It should be noted that duh and aedu mutant corn starches, both of which are mixtures of two principal granule types (Obanni and BeMiller 1995), have been patented (Friedman et al 1988a,b) as starches that exhibit the characteristics of chemically modified (crosslinked) starches.] Light microscopy of an iodine-stained paste of the CCS and potato starch blend at the end of the 95°C hold revealed that the potato starch granules were fully cooked and mostly disintegrated. Solubilized starch served as a matrix network in which were found large fragments of potato starch ghosts and CCS ghosts, with the CCS ghosts appearing to be not as highly swollen as they were when CCS was used alone. Again, this can be considered to be a structure-producing system (Morris 1990) and may be responsible for the viscosity stability of these blends at 95°C under moderate shear.

Several other examined combinations of unmodified starches from various other botanical sources showed pasting behaviors different from that of either individual component. Some starch blends, namely wheat and tapioca (8.5:1.5) and normal rice and potato (3:1 to 3:2), produced pasting curves similar to those of chemically crosslinked starch. The amylograms of normal rice and potato (3:1 to 3:2, especially 3:1) (Fig. 2) resembled closely that of a dual-modified tapioca starch (M. Obanni and J. N. BeMiller, unpublished data). Stability of the resulting gels was not investigated, but no apparent changes occurred in gels from the blends when stored at room temperature for several days.

Another interesting combination is the blend of PG18 and Hylon V starches at a 3:1 ratio. PG18 is a modified waxy corn starch and Hylon V a high-amylose (≈55%) corn starch. PG18 produced a high peak viscosity, followed by only slight setback, properties expected from a stabilized waxy corn starch (Fig. 3).

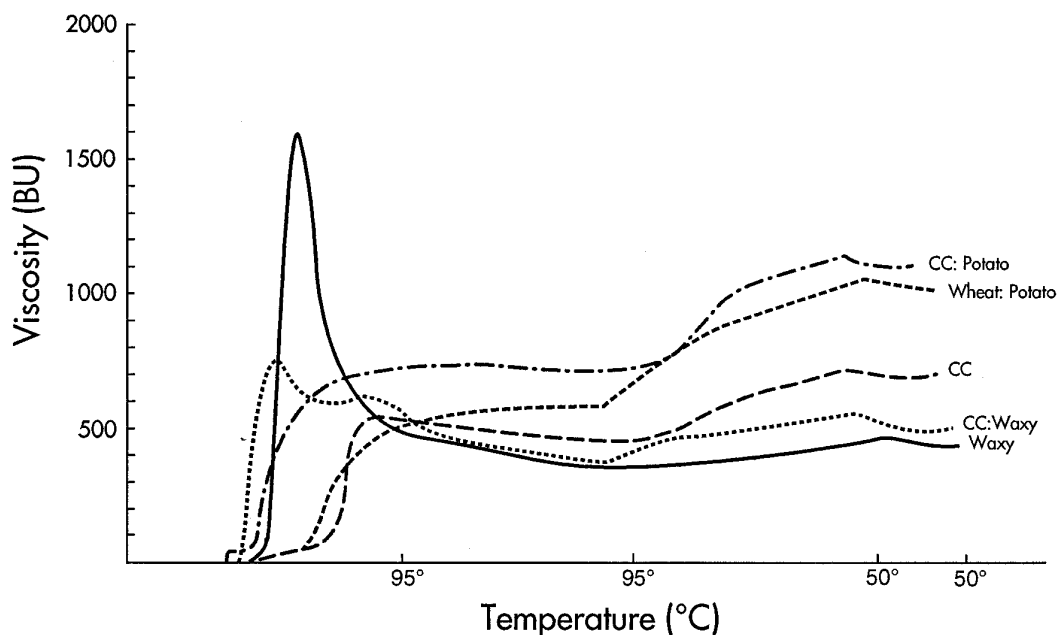


Fig. 1. Amylograms of individual starches and starch blends: common (CC) and potato (3:1), wheat and potato (3:1), CC and waxy (1:1). Starch solids = 7.5%.

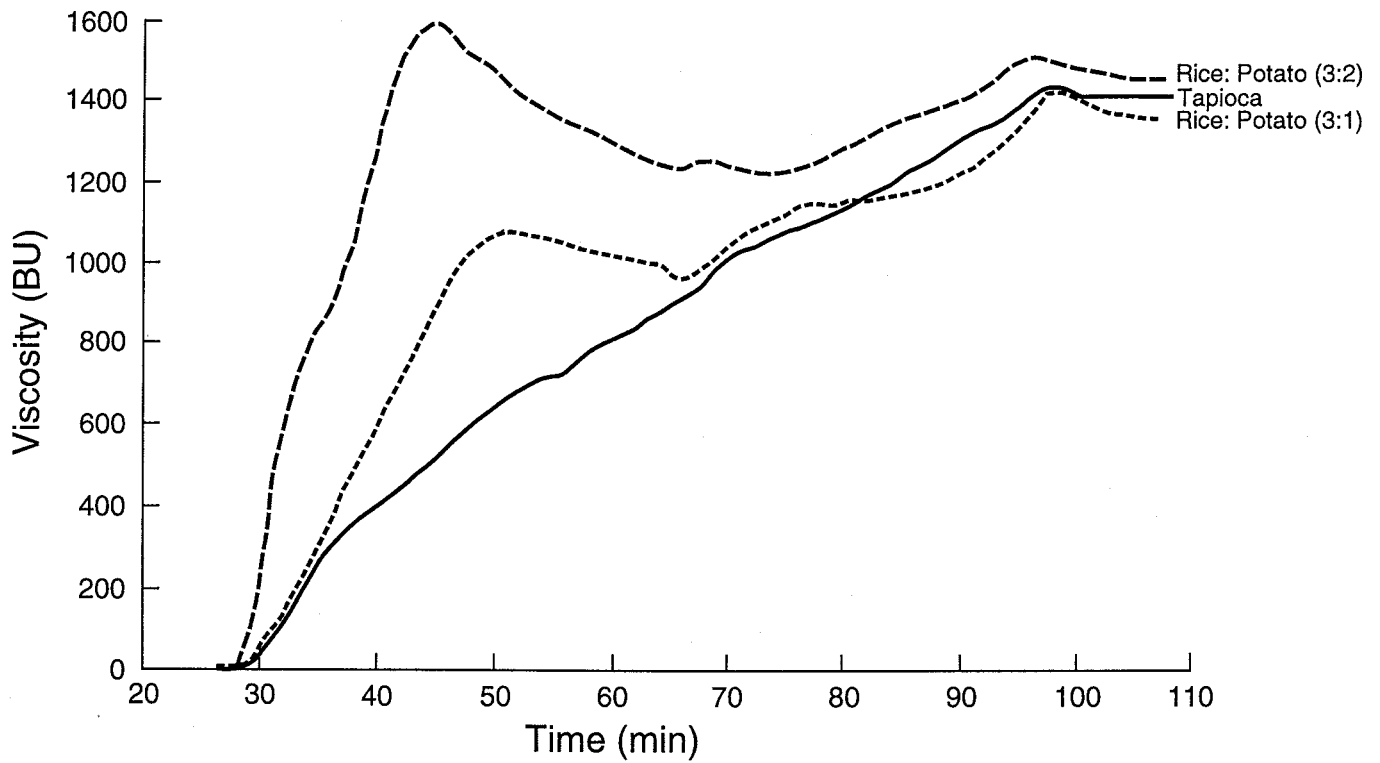


Fig. 2. Amylograms of tapioca starch and normal rice and potato starch blends. Starch solids = 7.5%.

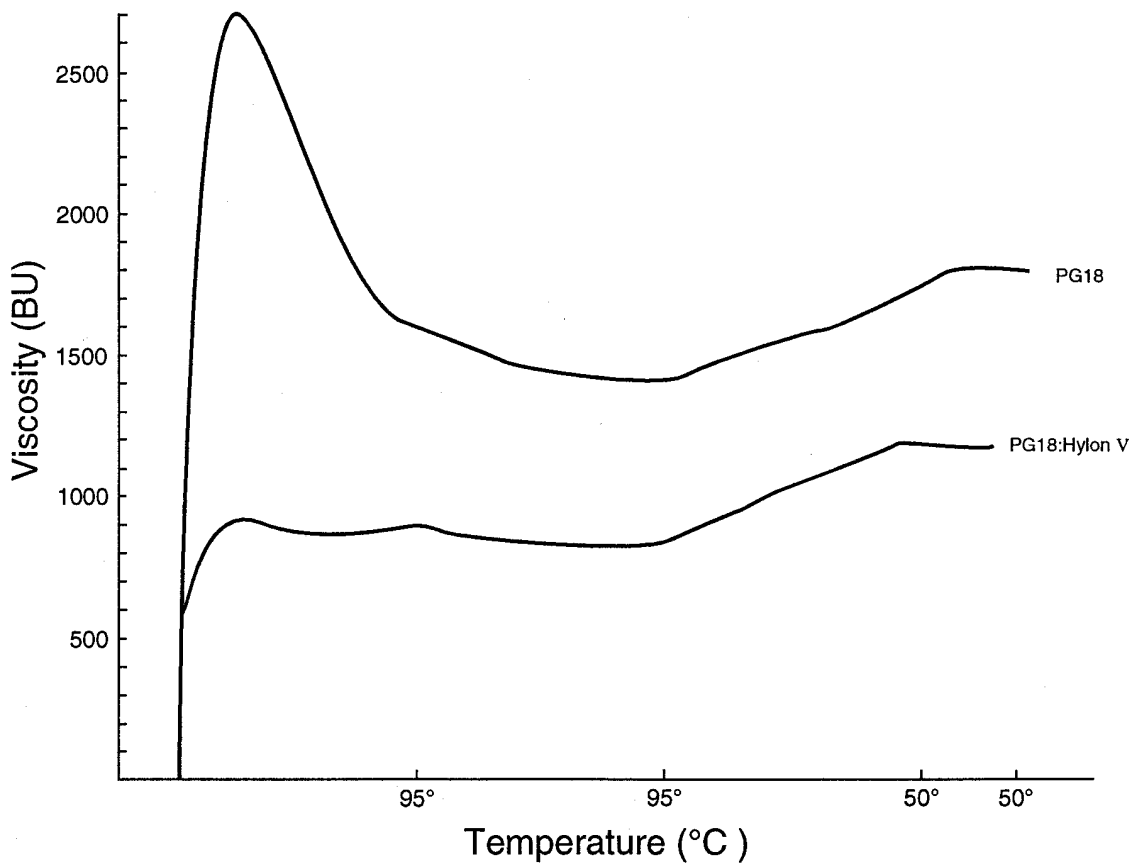
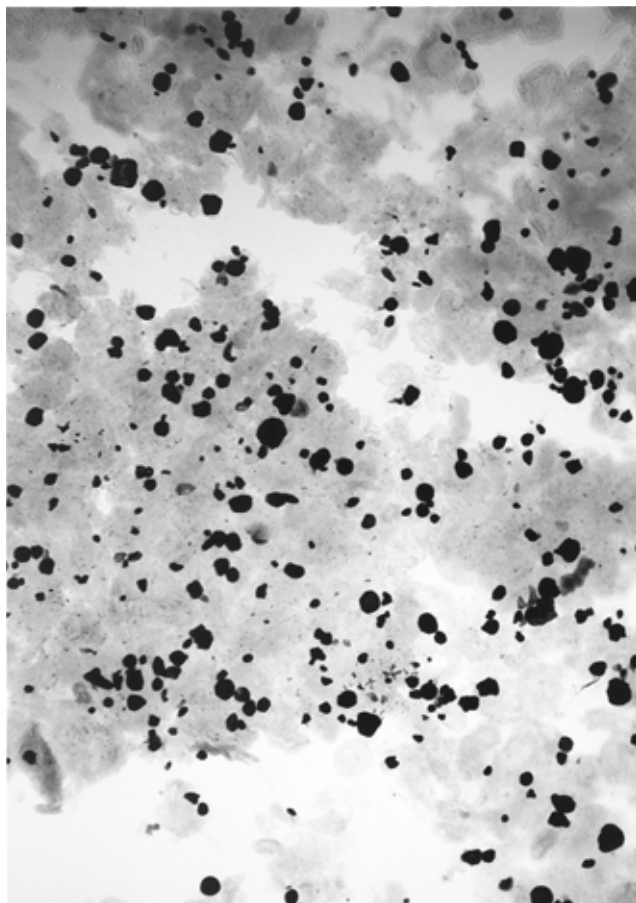


Fig. 3. Amylograms of Polar-Gel 18 alone and Polar-Gel 18 and Hylon V starch blend (3:1). Starch solids = 7.5%.

A 3:1 PG18 and Hylon V starch blend, however, produced no peak viscosity, and its paste exhibited even less setback than that from PG18 alone. Viscosity was maintained at relatively the same level during heating and shearing. Thus, the amylogram again resembled that of chemically crosslinked starch. Examination of the paste with a light microscope at the end of the 95°C hold surprisingly revealed that the PG18 starch granules in the cooked mixture had neither ruptured nor swelled to the maximum. Hylon V starch granules swelled very little, as expected. PG18 granule ghosts contained blue-staining particles, indicating that amylose leached from Hylon V starch granules was either entrapped in, or was bound to, the amylopectin of PG18 ghosts. Additionally, it was observed that Hylon V starch granules were always associated with PG18 ghosts and could not be found alone (Fig. 4). It is not known whether this is the sole reason, or the reason at all, why PG18 granules did not fully swell and disintegrate. The finding further supports the possibility of interaction among starch molecules and granule structures that results in a mimicking of the properties produced by chemical crosslinking. While the properties of any starch paste are functions of the nature of the continuous phase, the nature of the discontinuous phase (swollen granules, granule fragments, or products of retrogradation), and interactions between the two (Morris 1990), our results indicate that there can be greater interaction between molecules, granules, swollen granules, and granule fragments from at least certain different starches than between the same from a single starch.

We conclude that it is possible to formulate starch blends that behave like chemically modified starches with regard to pasting behavior as determined by amylography. Additional tests need to be done to determine functionalities imparted by blends of (modified and unmodified) starches.

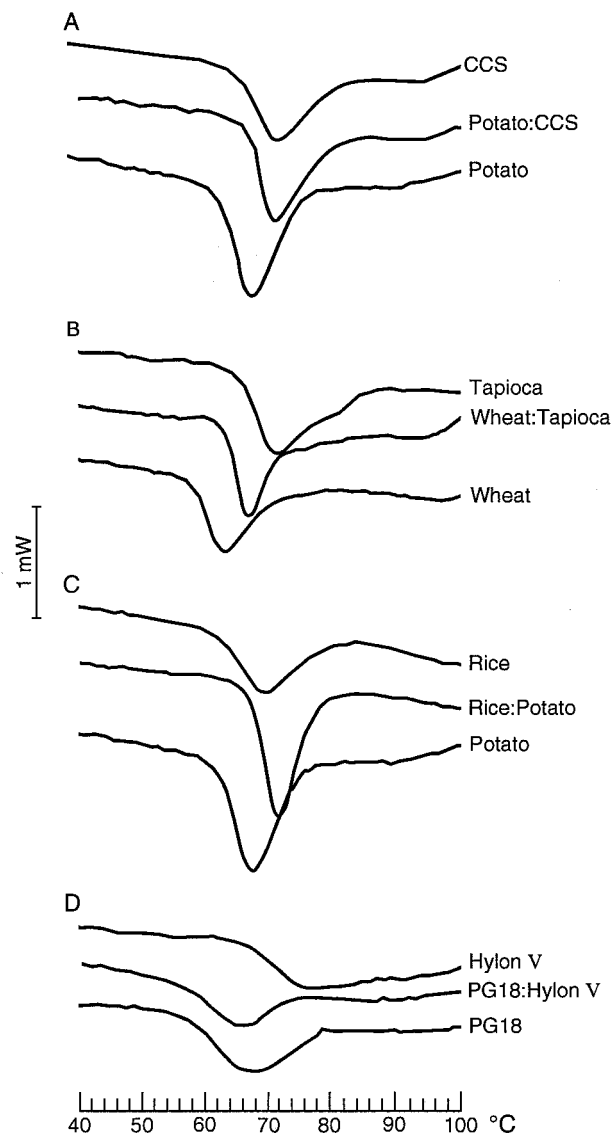


**Fig. 4.** Photomicrograph of Polar-Gel 18 and Hylon V starch blend paste taken from the viscosgraph bowl at the end of a 95°C hold and stained with I<sub>2</sub>/KI. (From a color photograph. 100×)

The mixing of other hydrocolloids with starches to reduce undesirable properties of native starches has been proposed (Christianson et al 1981, Tye 1988, Alloncle et al 1989, Eidam et al 1995, Kulicke et al 1996, Liehr and Kulicke 1996). However, starch blends should be more economical than starch-hydrocolloid blends.

### Thermal Characteristics of Starch Blends and Components

The DSC curves of four starch blends and their individual components are presented in Fig. 5. None of the DSC traces of blends had two endotherms, suggesting a mixture of two starches. [Neither were two peaks observed by DSC analysis of du, duh, or aedu mutant corn starches, all of which are mixtures of two principal granule types, although at the insistence of a reviewer, it was stated in the report (Obanni and BeMiller 1995) that double peaks indicative of two granule populations might be expected.] Liu and Lelièvre (1992), using the same heating rate used in this study, concluded that, at starch concentrations <30%, DSC traces of blends of wheat and rice starches were the sums of the outputs for each component in the mixture, but at higher concentrations, competition for water occurs and the behavior is nonadditive. At



**Fig. 5.** Differential scanning calorimetry traces of individual starches and blends. **A,** Common corn starch (CCS), potato, and 75:25 blend. **B,** Tapioca, wheat, and 15:85 blend. **C,** Rice, potato, and 50:50 blend. **D,** Polar-Gel 18, Hylon V, and 75:25 blend. Starch solids = 33%.

all concentrations, two endotherms corresponding to those of the two individual starches were observed when the minor component was present at a concentration >15% of the total concentration. In contrast to the results of Liu and Lelièvre (1992), none of the starch blends we examined originally, which did not include a wheat and rice starch mixture, showed evidence of two endotherms, suggesting again specificity of interaction between components of cooks of different starches. None of the peak temperatures of the endotherms of the four blends studied by DSC corresponded to the endotherm of the individual component that melted first when the starch was cooked alone. It was expected that the starch granule crystallites that required less energy to melt would melt first, probably tying up most, if not all, the available water, as reported by Liu and Lelièvre (1992), and that the starch granules of the second component would never fully gelatinize and, hence, would not

**TABLE I**  
Differential Scanning Calorimetry Parameters<sup>a</sup> for Starch Mixtures and Individual Components

Sample	$T_o$	$T_p$	$T_c$	$\Delta H$ (J/g)
Common corn and potato (75:25)	64.8	70.3	83.1	9.6
Wheat and tapioca (85:15)	61.7	65.4	71.6	4.6
Normal rice and potato (50:50)	65.1	70.9	80.0	9.5
Polar-Gel 18 and Hylon V (75:25)	54.9	64.9	75.0	4.4
Common corn	62.9	71.2	81.8	7.5
Wheat	56.5	61.8	70.7	5.7
Normal rice	60.4	68.3	79.0	8.5
Tapioca	63.1	69.9	85.9	10.5
Potato	60.8	66.6	75.7	9.5
Polar-Gel 18	54.5	65.6	78.3	7.6

<sup>a</sup>  $T_o$ ,  $T_p$ , and  $T_c$  = onset, peak, and conclusion temperatures, respectively.  $\Delta H$  = enthalpy of gelatinization.

produce a significant endotherm. Instead, our data showed that the peak temperatures of the melting endotherms of two starch blends (CCS and potato; wheat and tapioca) fell between those of the individual components (Fig. 5A and B, respectively). The normal rice and potato peak temperature was higher than that of either of the two components (Fig. 5C), and the endotherm of the PG18 and Hylon V starch mixture was lower than that of either of the two components (Fig. 5D). Each thermal characteristic (onset temperature [ $T_o$ ], peak temperature [ $T_p$ ], conclusion temperature [ $T_c$ ], enthalpy of gelatinization [ $\Delta H$ ]) (Table I) was specific to the mixture. No trend could be detected. For example, while  $T_o$ ,  $T_p$ , and  $T_c$  of the CCS and potato starch blend were closer to the values given by CCS, which represents 75% of the mixture, the  $\Delta H$  of the blend was closer to that of potato starch (Table I). Such seemingly complex behavior suggests that specific interactions between molecules of these biopolymers were occurring, rather than each starch gelatinizing and pasting independently, which is in agreement with observations made from amylography.

Because of the results of Liu and Lelièvre (1992), we had a 1:1 (w/w) wheat starch and rice starch mixture and a 1:1 (w/w) wheat starch and tapioca starch mixture examined by DSC by an independent investigator. The wheat starch and rice starch mixture was prepared in two ways: 1) dry mixture and 2) a dry mixture slurried in water and then dried. All three mixtures were examined at 33% solids. The two wheat starch and rice starch mixtures gave two endotherms with peak temperatures of 65.1 and 78.6°C for the dry mixture and 64.2 and 78.2°C for the slurried and dried mixture, confirming that there were two endotherms as reported by Liu and Lelièvre (1992). Both peak temperatures were shifted to higher temperatures; the endotherm peak temperature of the wheat starch alone was 61.8°C and that of the rice starch alone was 68.3°C (Table I), with the latter being shifted most. The 1:1 (w/w) wheat starch and tapioca starch mixture gave a single endotherm with a peak temperature of 65.6°C, confirming our results. Overall, these results confirm that the cooking behavior of a starch mixture will probably be specific to that mixture.

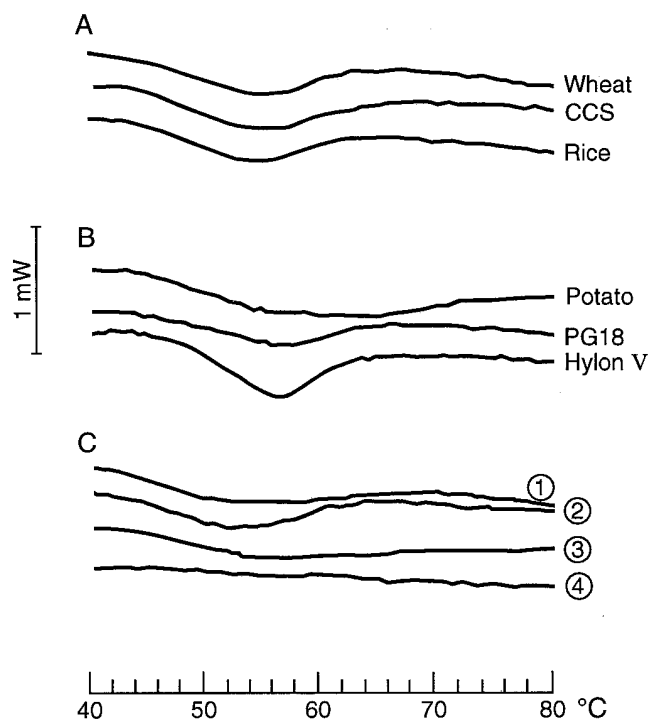
### Retrogradation of Starch Blends and Components

Starch retrogradation was investigated by rescanning DSC pans containing starch mixtures or their components after two weeks of storage at 4°C. Wheat starch, CCS, and normal rice starch all showed a small endotherm indicative of the retrogradation characteristic of these starches (Fig. 6A). Hylon V starch produced the largest retrogradation endotherm, which was expected since this starch has ≈55% amylose (Fig. 6B).

With the exception of the wheat and tapioca starch blend, the blends showed no major rescanning endotherm (Fig. 6C), indicating that only very small amounts of starch had retrograded. A possible explanation is that the amylose molecules in these blends have associated with amylopectin (see Fig. 4 and accompanying discussion), and therefore were not available for recrystallization. Most importantly, the blends, with the exception of the wheat and tapioca starch blend, have the additional property of low retrogradation, something otherwise only attained through chemical or genetic modification of starches.

### CONCLUSIONS

It is possible to formulate starch blends from unmodified starches that possess at least some of the desired characteristics of modified starches. It appeared that starch molecules from different starches interact to produce the attributes of the blends, and that at least some of the interactions occur very early in the heating process, before gelatinization or pasting occurs. These early interactions could be between leached amylose molecules from one starch and granules of the other starch or between molecules on the outer surfaces of granules of the two starches. Only a very limited number of blends was examined. Obviously, there should



**Fig. 6.** Differential scanning calorimetry traces of cooked starches and starch blends (33%, w/w) rescanned after two weeks at 4°C. **A** and **B**, Traces of individual starches. **C**, Traces of starch blends. 1 = Potato and common corn starch (CCS) (25:75). 2 = Wheat and tapioca (85:15). 3 = Normal rice and potato (50:50). 4 = Polar-Gel 18 and Hylon V (75:25).

be more work in this area. Further characterization of these and other blends and a determination of the ratio of the mixture that best mimics the desired behavior is necessary.

Starch mixtures could have a place in the food industry where all natural products are desirable and in the food and other industries where reduction in the use of chemicals for modification is desirable. Proprietary starch mixtures already exist in the food industry, both in the United States and Europe (Stute and Kern 1994).

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#### LITERATURE CITED

- Alloncle, M., and Doublier, J. L. 1991. Viscoelastic properties of maize starch/hydrocolloid pastes and gels. *Food Hydrocoll.* 5:455-467.
- Alloncle, M., Lefebvre, J., Llamas, G., and Doublier, J. L. 1989. A rheological characterization of cereal starch-galactomannan mixtures. *Cereal Chem.* 66:90-93.
- Bahnassey, Y. A., and Breene, W. M. 1994. Rapid Visco-Analyzer (RVA) pasting profiles of wheat, corn, waxy corn, tapioca and amaranth starches (*A. hypochondriacus* and *A. cruentus*) in the presence of konjac flour, gellan, guar, xanthan and locust bean gums. *Starch/Staerke* 46:134-141.
- Christianson, D. D., Hodge, J. E., Osborne, D., and Detroy, R. W. 1981. Gelatinization of wheat starch as modified by xanthan gum, guar gum, and cellulose gum. *Cereal Chem.* 58:513-517.
- Crossland, L. B., and Favor, H. H. 1948. Starch gelatinization studies. II. A method for showing the stages in swelling of starch during heating in the amylograph. *Cereal Chem.* 25:213-220.
- Eidam, D., Kulicke, W.-M., Kuhn, K., and Stute, R. 1995. Formation of maize starch gels selectively regulated by the addition of hydrocolloids. *Starch/Staerke* 47:378-384.
- Friedman, R. B., Gottneid, D. J., Faron, E. J., Pustek, F. J., and Katz, F. R. 1988a. Starch of the duh genotype and products produced therefrom. U.S. patent 4,774,328.
- Friedman, R. B., Gottneid, D. J., Faron, E. J., Pustek, F. J., and Katz, F. R. 1988b. Food stuffs containing starch of an amylose extender dull genotype. U.S. patent 4,790,997.
- Jane, J.-L., and Chen, J.-F. 1992. Effect of amylose molecular size and amylopectin branch chain length on paste properties of starch. *Cereal Chem.* 69:60-65.
- Kohyama, K., and Nishinari, K. 1992. Cellulose derivatives effects on gelatinization and retrogradation of sweet potato starch. *J. Food Sci.* 57:128-131, 137.
- Kulicke, W.-M., Eidam, D., Kath, F., Kix, M., and Kull, A. H. 1996. Hydrocolloids and rheology: Regulation of visco-elastic characteristics of waxy rice starch in mixtures with galactomannans. *Starch/Staerke* 48:105-114.
- Liehr, M., and Kulicke, W.-M. 1996. Rheologische Untersuchungen zum Einfluss von Hydrokolloiden auf die Giefrier-Tau-Stabilität von Stärkekleistern. *Starch/Staerke* 48:52-57.
- Liu, H., and Lelièvre, J. 1992. A differential scanning calorimetry study of melting transitions in aqueous suspensions containing blends of wheat and rice starch. *Carbohydr. Polym.* 17:145-149.
- Morris, V. J. 1990. Starch gelation and retrogradation. *Trends Food Sci. Technol.* 1:2-6.
- Obanni, M., and BeMiller, J. N. 1995. Identification of starch from various maize endosperm mutants via ghost microstructures. *Cereal Chem.* 72:436-442.
- Racciato, J. S. 1978. Thickening agent. Ger. Offen. 2,738,355; Thickening compositions containing xanthan gum, guar gum and starch. U.S. patent 4,105,461.
- Sajjan, S. U., and Rao, M. R. R. 1987. Effect of hydrocolloids on the rheological properties of wheat starch. *Carbohydr. Polym.* 7: 395-402.
- Sanderson, G. R. 1982. The interactions of xanthan gum in food systems. *Prog. Food Nutr. Sci.* 6:77-87.
- Stute, R., and Kern, H. 1994. Starch mixtures as pudding starches. U.S. patent 5,324,532.
- Tye, R. J. 1988. The rheology of starch/carrageenan systems. *Food Hydrocoll.* 2:259-266.

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