

Crystallinity of Rice Starch and its Fractions in Relation to Gelatinization and Pasting Characteristics

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Synopsis

The x-ray diffraction intensities of rice starch and its fractions and the gelatinization and pasting characteristics of the starch were studied. The results obtained from blends of two rice starches with amylose contents ranging from 13.7 to 32.8% indicate that amylose content affects the degree of crystallinity of granular starch. Further, the intensities of five characteristic diffraction peaks of the starch were consistently correlated with its gelatinization and pasting characteristics. The C_A type x-ray diffraction patterns of rice starch showed no appreciable differences in line intensities among varieties. However, when these intensities were considered in the light of concentration dependence with respect to amylose, significant differences were revealed which could be correlated with the gelatinization and pasting characteristics of starch. Amyloses from seven rice varieties showed different crystalline orders. These differences seemed to account for the unpredictability of the pasting characteristics of the starch of certain varieties, as reported by many investigators.

INTRODUCTION

Although the composition of the starch of the rice grain has been studied extensively,¹⁻⁴ the gelatinization and pasting characteristics and the cooking behavior of many varieties cannot be predicted on the basis of either the amylose or the amylopectin content alone.⁵⁻⁹ Several investigators^{1,5-9} have reported the apparent independence between the gelatinization temperature and the amylose content of granular rice starch. The unpredictability of this relationship is further shown by the results of our studies.^{1,2} In a study of 16 rice varieties,¹ these two properties were positively correlated for 14 of the varieties; the varieties Century Patna 231 and Taichung (Native) 1 behaved differently. A study of 51 nonwaxy rice varieties from Southeast Asia did not reveal any correlation between amylose content and gelatinization temperature.²

Although granular starches are not highly crystalline, they exhibit sufficient crystal perfection to produce recognizably different x-ray diffraction patterns. Katz and van Itallie¹⁰ have classified these patterns into the A, B, and C types. The C type is intermediate between A and B. Also they recognized a fourth and entirely different type V, which is obtained by precipitating solutions of starch with alcohol.

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The property of starch to form crystalline modifications has been ascribed by some investigators¹¹⁻¹⁶ to the amylose fraction. Bear and French¹¹ stated that the amylose fraction may account for the diffraction rings in the x-ray pattern of starch. Amylose can form films in which molecular orientation can be induced by stretching to yield a product with a fiber diagram which is very similar to that of the granular starch.^{12,13} Under the same conditions, the amylopectin fraction shows a poor pattern.¹⁴ Similarly, Storey and Merrill¹⁵ showed that when solutions of amylose and of amylopectin are placed under shear, amylose molecules reassociate more readily than amylopectin. Also, Foster and Sterman¹⁶ have demonstrated the rigidity of amylose.

The amylopectin fraction may also contribute to the crystallinity of the starch granule, although this requires that the molecule possess sufficiently long straight-chain portions which may associate. The crystallinity of granules of waxy starch, which has a negligible content of amylose, supports this possibility. It has been suggested¹⁴ that the branch points in the amylopectin molecule may be in the amorphous part of the granule. Nikuni and Hizukuri^{17,18} likewise reported that the crystalline part of granular starch is in the linear portion of the amylopectin molecule and not in the longer amylose component. In fact, sweet potato amylopectin, with a range in the mean degree of polymerization of 12-15, was more crystalline than granular starch.^{18,19} These values are of similar magnitude to the outer chain lengths of rice amylopectin, with 12-18 glucose units.²⁰

Various investigators,²¹⁻²⁵ using the x-ray diffraction method, attempted to correlate the different crystal types A, C_A, and C_C with other physical properties of rice starch, but disregarded the degree of crystal perfection. As the associative bonding and physical properties of a starch film may be controlled by using the proper proportion of amylose,²⁶ inherent differences in crystalline order may likewise alter the physical properties of the granular starch. Our preliminary work²⁷ has revealed that starches of certain rice varieties which have essentially the same type of crystal pattern may differ widely in their gelatinization and pasting characteristics. This indicates that some factor other than crystal type is involved.

Our study was based on the hypothesis that, aside from the crystal type, the extent of crystal perfection of granular starch influences some of its physical properties, especially gelatinization temperature and degree of swelling. Starch of rice varieties with a high degree of crystalline order would be expected to have strong associative bonding and would necessarily have a high gelatinization temperature.

The present investigation aimed to determine (1) the effect of starch composition, as indexed by amylose content, on the crystallinity of rice starch, using blends of rice starches, and (2) the effect of the crystallinity of the starch and its fractions on the gelatinization and pasting characteristics of rice flour.

EXPERIMENTAL

Sample Preparation

Alkali-Treated Starch. Starch was prepared from the milled rice of 13 nonwaxy (nonglutinous) varieties. All were grown at the Institute during the 1962 dry season, except the sample of the variety Nahng Mon S-4 which was obtained from Thailand. The 12 other varieties were Radin Kling, Chinsurah 35, Kolamba 42, Taichung (Native) 1, Bir-me-fen, Gulfrose, Century Patna 231, Toro, Rexoro, Texas Patna, Peta, and Milfor 6(2). Certain physicochemical properties of the grain of these varieties have been determined.¹

Rice flour that passed through a 40-mesh sieve was repeatedly shaken with 0.2% sodium hydroxide and centrifuged until the washings were negative to biuret reagent. It was subsequently washed with water until the washings were neutral to phenolphthalein. The starch preparation was then air-dried and the top and bottom crusts discarded.

Different proportions of the prepared starches of the varieties Peta (32.8% amylose, 1.53% protein) and Toro (13.7% amylose, 2.39% protein) were blended to give mixtures with amylose contents of 15, 20, 25, and 30%.

Detergent-Treated Starch and Its Fractions. Starch was prepared from milled rice samples of seven nonwaxy varieties by extracting the protein with a solution of sodium dodecylbenzene sulfonate.²⁸ Amylose and amylopectin fractions were isolated from these starches as described by Tsai, Phillips, and Williams.⁸ Amyloses were recrystallized once from aqueous 1-butanol. Starch and amylopectin of the local waxy variety, Malagkit Sungsong Puti, were similarly prepared.

Methods

Amylose content of the starches was determined by potentiometric iodine titration.²⁹ Protein was calculated from the Kjeldahl nitrogen contents using the factor 5.95.

X-ray diffraction diagrams were obtained with a General Electric XRD-3 unit and a Speedomax type G recorder with a chart speed of 0.5 in./min. The powdered starch materials were packed into aluminum frames at a constant packing density of about 1.14×10^{-3} g./mm.³ and were scanned through the 2θ range of 5–45°. The diffraction conditions were: $\text{CuK}\alpha$ radiation with Ni filter, 40-kv. high tension voltage, 15-ma. current, and scanning speed of 2°/min. Precise intensity data in counts per second of the principal indexes were then obtained from the exposure time data in seconds with the scaler set at 16,384 counts (probable error, 0.5%). All results reported are the means of duplicate determinations.

The gelatinization and pasting characteristics of the milled rice flours and Peta-Toro starch blends were determined with a Brabender Visco-amylograph with a 700 cm.-g. sensitivity cartridge, following the procedure of Halick and Kelly.⁹ A 50-g. portion of rice flour (40-mesh) or rice starch and

300 ml. of water were mixed for 1.5 min. in a Waring Blender and quantitatively transferred to the amylograph bowl with 150 ml. of water. The gelatinization temperature, the peak viscosity η_{\max} , the drop in viscosity after 20 min. at 94°C. $\Delta\eta_{94^\circ\text{C.}}$, and setback $\Delta\eta_{50^\circ\text{C.}}$ were obtained from the amylograms. The gelatinization temperature of rice starch corresponds to the temperature at which the starch suspension shows an initial increase in viscosity. The gelatinization temperature of rice flour, however, is 3°C. lower than the temperature at the initial rise in viscosity. η_{\max} is the hot paste peak viscosity irrespective of the temperature. The difference between the η_{\max} and the measured viscosity after cooking for 20 min. at 94°C. is $\Delta\eta_{94^\circ\text{C.}}$. $\Delta\eta_{50^\circ\text{C.}}$ is the difference between the η_{\max} and the viscosity of the paste when it has been cooled to 50°C.

RESULTS AND DISCUSSION

The x-ray diffraction patterns of the different samples of rice starch were essentially of the C_A type,³⁰ which is intermediate between A and C (Fig. 1). The characteristic line 1 ($2\theta = 5.6^\circ$) of the B pattern was not observed in any of the samples. The principal indexes of the patterns were at $2\theta =$

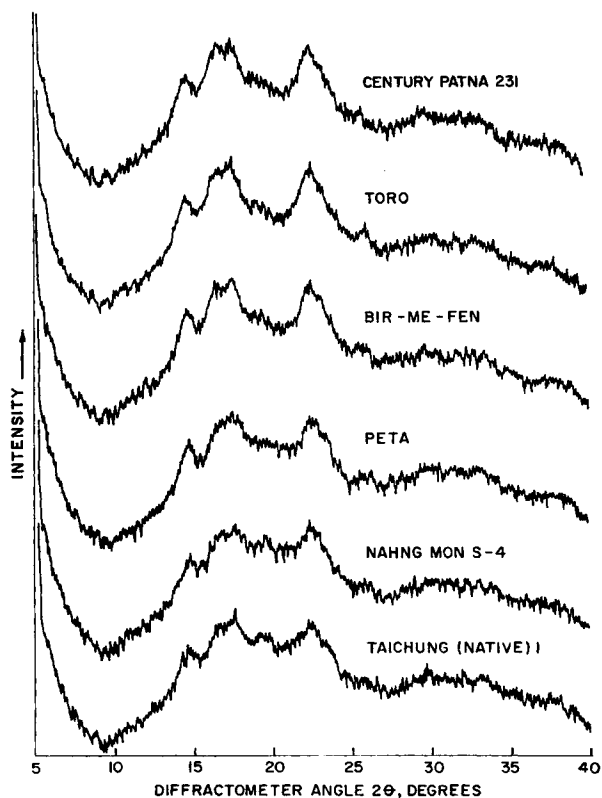


Fig. 1. Representative x-ray powder diffractograms of rice starch.

TABLE I
X-Ray Powder Diffraction and Amylograph Data of Mixtures of Starches from Rice Varieties Peta and Toro

	Amylose concentration, %					
	13.7 (Toro)	15	20	25	30	32.8 (Peta)
	X-Ray Diffraction Data ^a					
<i>d</i> spacing, Å.	6.03 m ⁻	6.03 ms ⁺	6.03 s ⁺⁺	6.03 s ⁺	6.03 s ⁺⁺	6.03 s ⁺⁺
Intensity, counts/sec.	650	895	1030	1080	1060	1070
<i>d</i> spacing, Å.	5.31 ms ⁺	5.31 s ⁻	5.31 s	5.31 vs ⁻	5.31 vs ⁺⁺	5.31 vs ⁺
Intensity, counts/sec.	849	1050	1190	1250	1260	1220
<i>d</i> spacing, Å.	5.04 ms ⁺	5.07 s	5.04 vs ⁻	5.04 vs	5.07 vs ⁺⁺	5.04 vs ⁺⁺
Intensity, counts/sec.	890	1070	1210	1310	1310	1300
<i>d</i> spacing, Å.	4.53 m	4.53 ms	4.58 ms ⁺	4.58 s ⁺	4.58 s ⁻	4.53 s ⁺⁺
Intensity, counts/sec.	741	872	993	1040	1010	1030
<i>d</i> spacing, Å.	3.95 ms	3.95 s	3.95 vs ⁺⁺	3.95 vs ⁺	3.95 vs ⁺	3.95 vs ⁺
Intensity, counts/sec.	936	1080	1240	1270	1260	1240
<i>d</i> spacing, Å.	3.43 w ⁻	3.43 w	3.43 mw	3.43 mw ⁺	3.43 mw ⁻	3.43 mw ⁺
Intensity, counts/sec.	661	777	876	900	867	890
	Amylograph Data					
Gel temp., °C.	66	66	67	67.5	71	71.5
η_{max} , B.U. ^b	1150	945	695	665	660	655
$\Delta\eta_{94^\circ C.}$, B.U. ^b	710	485	205	155	95	75
$\Delta\eta_{50^\circ C.}$, B.U. ^b	-490	-255	+190	+420	+680	+650

^a Relative intensities and sharpness of interplanar spacing with respect to the different mixtures. s = strong, m = moderate, w = weak, v = very;

+⁺ = very sharp, + = sharp, - = broad.

^b B.U. = Brabender units.

$14.7^\circ \pm 0.2^\circ$, $16.7^\circ \pm 0.1^\circ$, $17.6^\circ \pm 0.2^\circ$, $19.4^\circ \pm 0.2^\circ$, and 22.5° . In this study, only these five indexes were considered. These peaks corresponded to interplanar distances of 6.03, 5.30, 5.03, 4.55, and 3.94 Å, respectively. A weak peak of poor to moderate sharpness was observed at $2\theta = 25.5^\circ$. The x-ray diffraction pattern of rice starch has been reported as C,²² C_A,^{21,25} or A.^{23,25}

Rice Starch Blends

The x-ray powder diffraction data and the gelatinization and pasting characteristics of Peta and Toro starches and their blends are presented in Table I. The five diffraction peaks showed optimum intensities at 25% amylose. The maximum increase in crystallinity ranged from 35% for the $2\theta = 22.5^\circ$ plane to 66% for the 14.7° plane.

With the increase in crystallinity, a concomitant increase in gelatinization temperature was observed. Gelatinization temperature may be interpreted as a measure of the ease of swelling of the starch granules. The increased concentration of the crystalline fraction in granular starch, which for the present study is attributed to the amylose fraction, results in a greater associative bonding and a resultant higher gelatinization temperature.

Diffraction intensity and η_{\max} of the starch mixtures showed a negative linear relationship. In contrast, η_{\max} showed an optimum value at 25% amylose. The η_{\max} measures the extent of swelling of the starch granules. Hence the increase in crystallinity, which results in increased associative bonding, suppresses the extent of swelling of the granules during gelatinization and pasting. Halick and Kelly⁹ noted that higher-amylose United States rices tend to have lower η_{\max} values than low-amylose samples.

Diffraction intensity and $\Delta\eta_{94^\circ\text{C}}$ of the starch blends showed a negative relationship. Amylose content and $\Delta\eta_{94^\circ\text{C}}$ were also negatively correlated. This drop in viscosity during cooking is a measure of the extent of disintegration of the gelatinized starch granules.³¹ Amylose content and the $\Delta\eta_{94^\circ\text{C}}$ were also negatively correlated for 51 samples of nonwaxy rice.²

Setback $\Delta\eta_{50^\circ\text{C}}$ was positively correlated with diffraction intensity and amylose content of the starch blends. It represents the extent of starch retrogradation and has been ascribed to the amylose fraction.²⁶ It appears that mixtures with high amylose content are less readily disorganized due to the higher degree of crystallinity, and any residual crystallinity enhances retrogradation, possibly by nucleation. Hofstee³² noted that, although the chemical structure of the starch molecules is the main factor influencing the rheological properties of highly dispersed starch pastes, the residual granular structure which may not be destroyed during pasting may still influence the rheological behavior of the cooled gels. Amylose content and $\Delta\eta_{50^\circ\text{C}}$ of 51 samples of nonwaxy rice were also found to be positively correlated.²

The relation of the original spectrum of granular starch to the pasting characteristics of gelatinized starch may not be due to its crystallinity *per se*. Hizukuri et al.³³ found that the original spectrum of rice starch disappeared even at half of the maximum viscosity in the viscogram and was replaced by

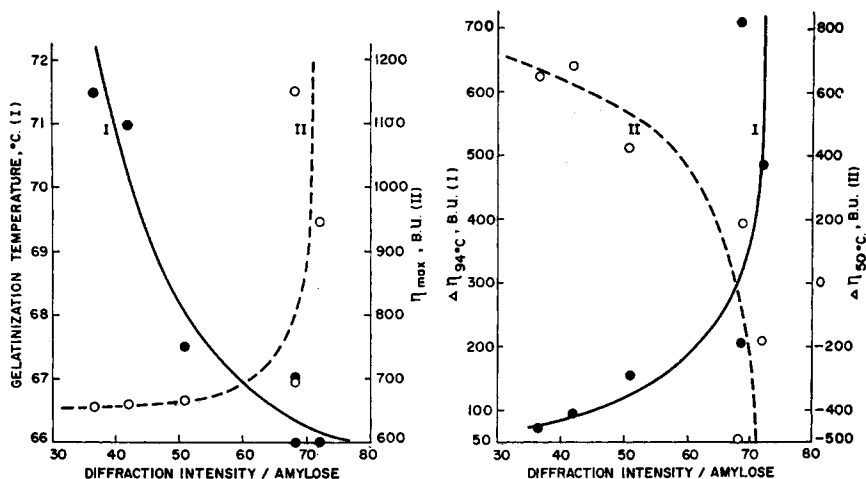


Fig. 2. Relation of diffraction intensity at $2\theta = 22.5^\circ$ per unit of amylose to gelatinization and pasting characteristics of mixtures of starches from rice varieties Peta and Toro.

a weak V spectrum. Ueda and Ota,²¹ working with six varieties, reported the complete conversion of rice starch from β to α form ($C_A \rightarrow V$) at hot water temperatures ranging from 56 to 60°C. This residual V pattern in gelatinized starch has been demonstrated to be free fatty acid-amylose complexes.³⁴ This may explain in part the dependence of the viscosity of the starch pastes on amylose content.

Results identical with the Peta-Toro rice starch blends were obtained with mixtures of AMIOCA waxy corn starch and normal corn starch.²⁷ Diffraction intensities were also optimum at 25% amylose. The same relations between diffraction indexes and gelatinization and pasting characteristics which were observed for rice starch mixtures were noted for these corn starch blends. These results with blends of starches of different amylose contents indicate that the molecular organization of granular starch may be responsible for the differences in the gelatinization and the pasting characteristics, particularly the peak viscosity, of rice starch.

When the effect of amylose content on diffraction intensity was minimized by substituting diffraction intensity per unit of amylose for diffraction intensity, such intensity per unit of amylose showed curvilinear relations with gelatinization and pasting characteristics (Fig. 2). The curves for intensity/amylose with η_{max} and with $\Delta\eta_{94^\circ C}$ were exponential.

Rice Starch

The diffraction intensity values for starch purified by treating with sodium dodecylbenzene sulfonate were higher than those of the same varieties purified by alkali treatment (Table II). The alkali may have caused a more extensive gelatinization of the granular starch than the detergent.

TABLE II
X-Ray Diffraction Intensity at $2\theta = 22.5^\circ$ of Rice Starch and at $2\theta = 20.25^\circ$ of Amylose, Amylose Content of Starch, and Pasting and Gelatinization Characteristics of Rice Flour

Sample no.	Variety	Intensity, counts/sec.		Amylose, %	Intensity at $2\theta = 22.5^\circ$ / amylose	Gel. temp., $^\circ\text{C}$.	η_{max} , B.U. ^a	$\Delta\eta_{74^\circ\text{C}}$, B.U. ^a	$\Delta\eta_{90^\circ\text{C}}$, B.U. ^a	
		At $2\theta = 22.5^\circ$ (starch)	At $2\theta = 20.25^\circ$ (amylose)							
Alkali-treated										
1	Radin Kling	832		31.4	26.5	72	690	150	+360	
2	Chinsurah 35	745		33.0	22.6	70	800	165	+470	
3	Kolamba 42	741		35.4	20.9	66	530	75	+460	
4	Taichung (Native) 1	700		35.7	19.6	62	570	60	+480	
5	Bir-me-fen	769		36.6	21.0	72	490	35	+110	
6	Gulfrose	758		20.4	37.2	66.5	560	175	+85	
7	Century Patna 231	763		18.8	40.6	75	660	255	+20	
8	Toro	774		15.9	48.7	67	550	190	+40	
9	Rexoro	753		25.0	30.1	71	570	170	+170	
10	Texas Patna	747		28.0	26.7	71	605	185	+175	
11	Peta	672		36.0	18.7	73	690	100	+440	
12	Milfor 6(2)	746		29.9	24.9	70	625	220	+110	
13	Nahng Mon S-4	670		25.9	25.9	58.5	660	190	+260	
Detergent-treated										
14	Century Patna 231	933	1570	15.5	60.2	74.5	640	270	-70	
15	Taichung 65	958	1380	18.5	51.8	68.5	615	265	+35	
16	Taichung (Native) 1	1140	1180	37.2	30.6	64.5	700	35	+740	
17	Peta	1110	711	28.6	38.8	69.5	660	50	+550	
18	Nahng Mon S-4	1080	807	28.4	38.0	58.5	660	190	+260	
19	Bengawan	1120	1400	21.0	53.3	68	660	105	+10	
20	Leuang Yai 34	1170	1130	25.8	45.3	58	850	40	+620	
21	Malagkit Sungsong Puti	773	—	0.9	859	61	375	145	-55	

^a B.U. = Brabender units. Cited from Juliano et al.¹

TABLE III
X-Ray Diffraction Data of Starch and Amylose from Seven Nonwaxy Rice Varieties and of Starch of One Waxy Variety

	Interplanar spacing, Å. ^a							Waxy variety ^b
	Century Patna 231	Bengawan	Taichung 65	Taichung (Native) 1	Leuang Yai 34	Nahng Mon S-4	Peta	
Starch	6.03 m	6.03 m ⁺	6.03 m	6.03 m	6.03 m	6.03 m	6.03 m	6.03 mw
	5.31 vs	5.31 s	5.31 vs ⁺	5.31 s	5.31 s	5.34 s ⁻	5.31 s	5.31 m
	5.10 vs ⁺	5.04 s	5.04 vs ⁺	5.04 s	5.04 s	5.04 s	5.04 s	5.04 m
	4.44 m ⁻	4.52 m ⁺	4.58 m ⁻	4.58 m ⁺	4.52 m	4.62 m	4.58 m	4.58 mw
	3.95 vs ⁺	3.95 s ⁺	3.95 vs	3.95 s ⁺	3.91 s	3.93 s	3.95 s ⁺	3.95 m
—	—	3.71 w ⁺	—	—	—	—	—	—
3.43 mw	3.43 mw ⁻	3.43 mw	3.43 mw	3.43 mw ⁻	3.43 mw	3.43 mw	3.43 mw	3.43 w
Amylose	12.5 m ⁺	12.5 w ⁻	12.6 w ⁻	12.6 vw	12.1 vw ⁻	13.4 vw ⁻	12.6 vw	12.6 vw
	7.02 s ⁺	6.82 s ⁺	6.82 s ⁺	7.14 s	6.86 s	7.08 s ⁺	7.02 s ⁺	7.02 s ⁺
	5.22 m	5.28 w ⁻	5.15 w ⁻	5.22 vw ⁻	5.28 vw ⁻	—	5.28 vw ⁻	5.28 vw ⁻
	—	—	4.82 vw ⁻	—	—	—	—	—
	—	—	4.60 vw ⁻	4.60 m	4.62 vw ⁻	4.60 ms	4.58 s	4.58 s
	4.44 s ⁺⁺	4.39 s ⁺	4.37 s ⁺	4.38 s	4.37 s	4.38 w ⁺	43.7 m	43.7 m
	—	—	—	—	4.09 w	4.11 mw	4.06 mw	4.06 mw
	3.47 m	3.51 m ⁻	3.50 vw ⁻	—	3.54 vw ⁻	—	—	—
	3.00 m	2.96 m ⁻	2.96 vw ⁻	—	2.98 vw	—	—	—
	2.49 w ⁻	—	—	—	—	—	—	—

^a CuK α radiation. Relative intensity and sharpness with respect to the different varieties, s = strong, m = moderate, w = weak, v = very; ++ = very sharp, + = sharp, - = broad.

^b Malagkit Sungsong Puti.

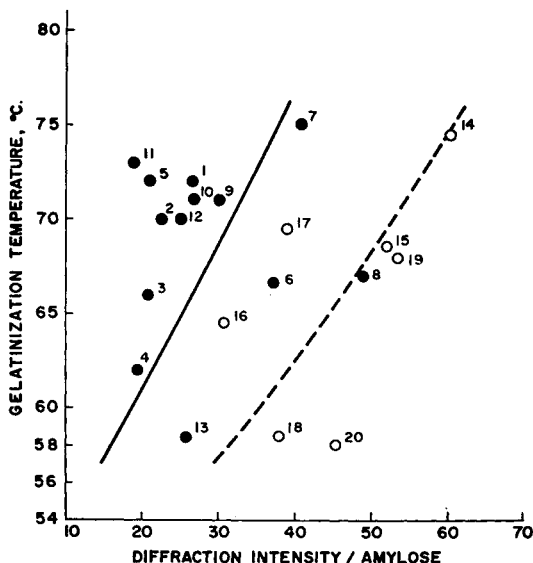


Fig. 3. Relation of diffraction intensity at $2\theta = 22.5^\circ$ of starch per unit of amylose to gelatinization temperature of 13 alkali-treated and seven detergent-treated nonwaxy rice starches. See Table II for identification of samples.

The waxy rice starch was the least crystalline of the starches prepared by the detergent method (Table III).

Notable differences were observed in the degree of crystallinity among the alkali-washed samples represented in Figure 1. Nahng Mon S-4, Taichung (Native) 1, and Peta showed a broad peak at $2\theta = 22.5^\circ$ and unresolved diffraction bands which correspond to the 16.7° and 17.6° lattice planes. Bir-me-fen and Gulfroze showed moderately resolved bands, while the rest of the samples exhibited a higher state of crystallinity. As the trends shown by the major peaks were identical, only the $2\theta = 22.5^\circ$ peak (d spacing of 3.95 Å.) is considered in the discussion below.

A close examination of the data in Table II indicates poor linear correlations between diffraction intensity at $2\theta = 22.5^\circ$ of the purified starches and the gelatinization and pasting characteristics of the corresponding rice flours. However, the diffraction intensity per unit of amylose and the gelatinization temperature for both the alkali- and detergent-treated starches were positively correlated (Fig. 3). This contrasts with the negative relationship between these two properties for the blends of Peta and Toro starches (Fig. 2). This implies that some factor other than amylose concentration-dependent crystallinity of granular starch (I_c) influences the gelatinization temperature of rice starch. Apparently there are variations in the inherent crystalline order (I_0) which affect the gelatinization temperature.

In both sets of purified samples, Century Patna showed high crystallinity per unit of amylose, whereas Nahng Mon S-4 showed low values.

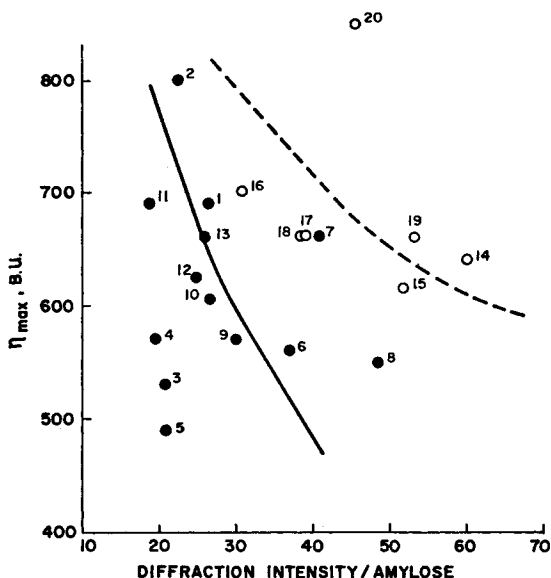


Fig. 4. Relation of diffraction intensity at $2\theta = 22.5^\circ$ per unit of amylose to maximum viscosity of 20 samples of nonwaxy rice starch. See Table II for identification of samples.

The relation between diffraction intensity at $2\theta = 22.5^\circ$ per unit amylose and η_{\max} as shown in Figure 4 is also the reverse of that shown by the Peta-Toro mixtures (Fig. 2). Such conflicting trends again reflect the presence of factors other than I_c which alter this relationship.

In contrast, the relations of intensity per unit amylose with $\Delta\eta_{94^\circ\text{C.}}$ of rice starch and $\Delta\eta_{50^\circ\text{C.}}$ (not presented) were similar to those of the blended mixtures. Presumably, any inherent state of crystallinity of the starch of the different rice varieties does not affect the viscosity of the starch paste.

Rice Amylose

To verify the presence of inherent degrees of crystal perfection in granular starch, the degree of crystallinity was determined for amylopectin and once-recrystallized amylose which were prepared from seven nonwaxy varieties of rice. The amylopectin patterns were all amorphous. The patterns of the amyloses which were recrystallized from aqueous 1-butanol were all of the V hydrate (linear alcohol) type, as they are similar to the characteristic V monohydrate (linear alcohol) interplanar spacings of 12.0m, 6.75s, and 4.42s³⁰ (Table II). However, differences in degree of crystalline order were noted among the amyloses (Fig. 5). Nahng Mon S-4 and Peta had poor crystalline order, whereas Century Patna 231 had the highest degree of crystal perfection. These differences in degree of crystallinity of amylose are evident with the intensity data of the lattice plane at $2\theta = 20.15^\circ \pm 0.15^\circ$ (d value = 4.37–4.44 Å.).

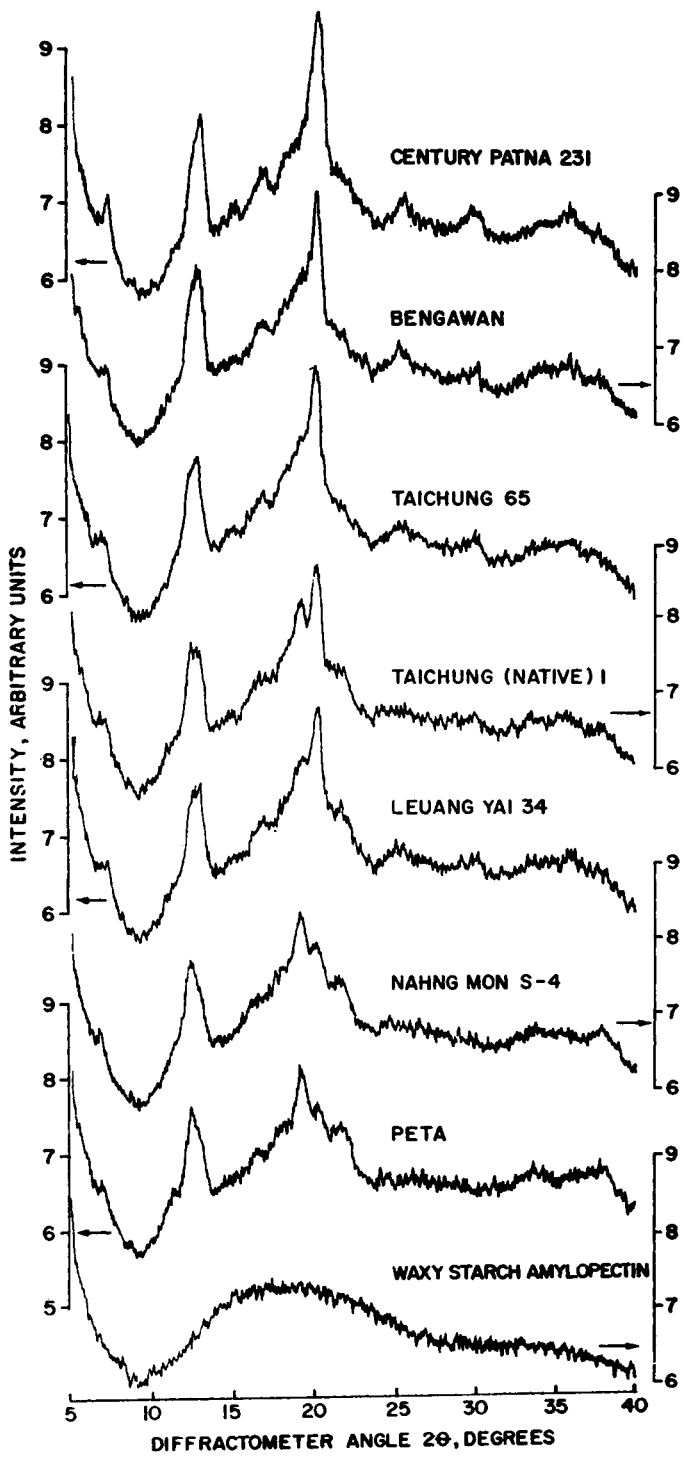


Fig. 5. X-ray diffractograms of amylose of seven varieties of rice and of amylopectin of waxy rice.

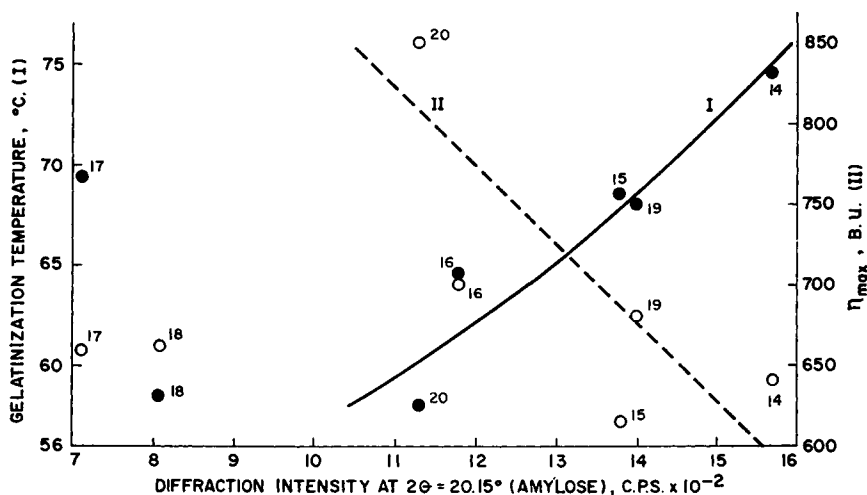


Fig. 6. Relation between diffraction intensity at $2\theta = 20.15^\circ$ of rice amylose to gelatinization temperature and maximum viscosity of rice starch of seven varieties. See Table II for identification of samples.

Figure 5 indicates the presence of two types of patterns depending on the relative intensities of the lattice planes at $2\theta = 19.3^\circ \pm 0.10^\circ$ and $20.15^\circ \pm 0.15^\circ$. With Nahng Mon S-4 and Peta, the former peak was more prominent than the latter, whereas the reverse was true for the five other amylose samples. In Century Patna 231, the diffraction bond at $2\theta = 19.3^\circ$ was absent.

The effect of these inherent states of crystalline order I_0 of the amyloses on the gelatinization temperature and η_{\max} of their rice flours are presented in Figure 6. The amylose diffraction intensity at $2\theta = 20.15^\circ$ was correlated positively with gelatinization temperature and negatively with η_{\max} , when data on Peta and Nahng Mon S-4 were excluded. The results for the five amyloses agree with the proposed hypothesis that the higher the degree of crystal perfection, the higher the gelatinization temperature of granular starch and the less its extent of swelling during pasting. These results are similar to those of the purified rice starches in Figures 3 and 4. The high degree of crystalline order shown by the amylose of Century Patna 231 would explain the high gelatinization temperature of the starch of this variety despite its low amylose content. Fukuba³⁵ demonstrated that the pasting characteristics of rice starch were mainly associated with the amylose fraction.

The varieties Peta and Nahng Mon S-4 did not fit into the linear relations between diffraction intensity and gelatinization temperature and peak viscosity shown by the five other varieties. The behavior of these two varieties may be explained by the fact that they have, as discussed above, an x-ray pattern that differs from the other varieties.

The role of I_0 of amylose on residual crystallinity of starch pastes becomes more apparent as the residual crystallinity of gelatinized starch is due to

amylose-fatty acid complexes. The residual crystallinity of the starch of cooked whole-milled rice is higher than that of stirred starch pastes. However, the texture of cooked rice is principally determined by the chemical composition of the starch, as indexed by amylose content, and not by gelatinization temperature.³⁶

Factors other than I_c and I_0 of the amylose may also be important in influencing the physical properties of granular starch. The crystallinity of waxy rice starch cannot be explained in terms of I_c and I_0 alone, as the amylose content of waxy starch is only about 1%. Recently, Zobel, Cotton, and Senti³⁷ reported that corn granular starches with a strong V pattern have a gelatinization temperature 15–20°C. lower than starches showing only an A, B, or C pattern. The characteristic spacings of the V pattern were not prominent, however, in samples of rice starch with low gelatinization temperatures.

While the trends reported here may be criticized as having been derived from relatively few samples, the data clearly establish the close relation between crystallinity and the gelatinization and pasting properties of rice granular starch. Varietal differences in the x-ray structure of granular starch and its amylose fraction contribute greatly to the unpredictability of the relationship between gelatinization temperature and amylose content. Further investigation of the nature of the micellar organization of the starch granule and the role of amylopectin in this organization is needed.

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Résumé

On a étudié les intensités de diffraction aux rayons X de l'amidon de riz et de ses fractions ainsi que les caractéristiques de gélatinisation et de collage de l'amidon. Les résultats obtenus à partir de mélanges de deux amidons de riz possédant des teneurs en amylose se situant entre 13,7 et 32,8% montrent que la teneur en amylose influence le degré de cristallinité du grain d'amidon. En plus, les intensités de cinq pics de diffraction caractéristiques de l'amidon, ont été reliées à ses caractéristiques de gélatinisation et de collage. Les diagrammes de diffraction aux rayons X, du type CA, de l'amidon de riz ne présentent pas de différences appréciables dans l'intensité des lignes suivant les variétés. Cependant lorsqu'on examine ces intensités en fonction de la dépendance vis à vis de la concentration en amylose, on remarque des différences importantes qui peuvent être reliées aux caractéristiques de gélatinisation et de collage de l'amidon. Des amyloses provenant de sept variétés de riz présentent différents ordres de cristallinité. Ces différences semblent rendre compte de l'impossibilité de prévoir les caractéristiques de collage de l'amidon de certaines variétés comme cela est décrit par plusieurs auteurs.

Zusammenfassung

Die Röntgenbeugungsintensitäten von Reisstärke und ihren Fraktionen sowie die Gelatinierungs- und Kleisterbildungscharakteristik der Stärke wurden untersucht. Die an Mischungen von zwei Reisstärken mit Amylosegehalt im Bereich von 13,7 bis 32,8% erhaltenen Ergebnisse zeigen, dass der Amylosegehalt den Kristallinitätsgrad von Stärkekörnern beeinflusst. Weiters bestand eine bestimmte Korrelation von fünf charakteristischen Beugungsmaxima der Stärke zu ihrer Gelatinierungs- und Kleister-

bildungscharakteristik. Das Röntgendiagramm vom CA-Typ von Reisstärke zeigte bei den verschiedenen Varietäten keine nennenswerte Unterschiede in der Linienintensität. Bei Betrachtung der Intensitäten in ihrer Konzentrationsabhängigkeit in bezug auf die Amylose ergaben sich jedoch signifikante Unterschiede, welche zur Gelatinierungs- und Kleisterbildungscharakteristik der Stärke in Korrelation gesetzt werden konnten. Die Amylosen von sieben Varietäten zeigten verschiedene kristalline Ordnung. Diese Unterschiede scheinen für die Unmöglichkeit verantwortlich zu sein, die Kleisterbildungscharakteristik der Stärke verschiedener Varietäten vorherzusagen zu können, wie sie in vielen Arbeiten berichtet wurden.

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