

Pasting Property Differences of Commercial and Isolated Rice Starch with Added Lipids and β -Cyclodextrin

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ABSTRACT

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Lipids are known to generally affect starch properties but the effects of lipid structure and β -cyclodextrin (β -CD) on different starches has not been investigated. This study compared the effects of lipids and β -CD on pasting properties of isolated rice starch with commercial rice starch. Flour was defatted by Soxhlet extraction and deproteinated by alkaline protease digestion. Fatty acids, monopalmitin (MP), tripalmitin, lysophosphatidylcholine (LC), lysophosphatidylethanolamine (LE), each added at 0.2 and 0.6% (starch db), and β -CD added at 2 and 6% (starch db) were tested. Pasting temperature (PT) increased with added

phospholipid, particularly in the commercial starch, while all lipids except tripalmitin increased final viscosity (FV) and total setback (TSB). Breakdown (BKD) was mainly affected and increased by up to 39 RVU for fatty acids while decreasing by up to 80 RVU for other lipids in both starches. TSB doubled by the addition of 0.6% MP but decreased to one-third by 0.6% LE or LC. Addition of β -CD decreased minimum viscosity (MV) and FV while increasing BKD in isolate but decreased TSB in commercial starch.

Lipids influence viscoelastic properties of cereal starches by forming the inclusion complexes with the helical structure of amylose (Maningat and Juliano 1980; Juliano et al 1987; Zobel 1988a). Those complexes might also affect the solubility of the granules and the pasting characteristics (Ryu and Walker 1993; Roach and Hosney 1995b; Ravi et al 1999).

Addition of surfactants or emulsifiers may restrict granule swelling and influence the rheological properties of starch paste. Those influences vary depending on the type and the concentration of the surfactant, as well as other conditions such as the presence of other additives (sugars, salts, and enzymes), moisture content, and heating temperatures (Ryu and Walker 1993; Roach and Hosney 1995a; Ravi et al 1999). However, further study is needed to compare and analyze individual lipid effects on the pasting characteristics of rice starch.

Cyclodextrin molecules contain hydrophobic cavities that can form inclusion complexes with various hydrophobic compounds including lipids. Kim and Hill (1984) observed that β -cyclodextrin (β -CD) could increase the swelling power and solubility of wheat starch granules during gelatinization, which was linked to the disruption of amylose-lipid complexes. Li et al (2000) found decreased PV of wheat starch when β -CD was present.

Starch retrogradation is the process that occurs when starch molecules reassociate and form an ordered structure during cooling and storage. A crystalline order is formed and a physical phase separation occurs (Atwell et al 1988). Starch retrogradation is usually associated with quality defects in food products, such as bread staling and loss of viscosity and precipitation in soups and sauces (Miles et al 1985; Morris 1994). The rate and extent of starch retrogradation depend on several variables including 1) botanical source, 2) amylose and amylopectin ratio, 3) temperature, 4) concentration, 5) presence and concentration of other food ingredients (such as lipids and surfactants, sugars, acids, and salts) (Orford et al 1987; Eliasson and Ljunger 1988; Kalichevsky et al 1990; Shi and Seib 1992; Eliasson and Gudmundsson 1996; Fredriksson et al 1998). How this process is affected by interactions between starch and other food components needs to be understood for better quality control of food products.

X-ray diffraction (XRD) has been used to study the crystallinity of starch. Under XRD, cereal starches usually give A-type patterns

(Zobel 1988a,b). V-type crystalline structure is mainly attributed to the formation of helical complexes of amylose with lipid in gelatinized starch (Hibi et al 1990). However, the change of crystalline structures from V-type to B-type XRD pattern was observed during cold storage, which might indicate that the starch-lipid complexes were metastable and changed to a more stable B-type structure following an amorphous state (Hibi et al 1990).

Normal starches from rice usually contain 0.5–1.3% granule associated lipids. It is generally accepted that starch lipids influence the behavior of starch in gelatinization and retrogradation processes (Ohashi et al 1980; Juliano 1984; Morrison et al 1984; Azudin and Morrison 1986). Studies using XRD and differential scanning calorimetry (DSC) have shown the formation of helical complexes of amylose with lipids after starch gelatinization (Zobel et al 1988a). Amylose-monoglyceride complex studies showed that long chain, saturated monoglyceride complexes were more resistant to enzymic breakdown than the short chain, unsaturated complexes (Eliasson and Krog 1985). Addition of certain lipids or surfactants may retard the firming and retrogradation of starchy foods (Legendijk and Pennings 1970; Germani et al 1983; Batres and White 1986; Eliasson and Ljunger 1988; Krog et al 1989; Chang and Liu 1991).

The objectives of this study were to 1) determine the effects of lipids and β -cyclodextrin on pasting properties of rice starch; 2) examine the influence of lipids and β -cyclodextrin on starch granule XRD pattern; 3) compare the effects of additives on commercial rice starch with white rice starch isolate (WSI).

MATERIALS AND METHODS

Materials

White rice flour was obtained from local sources (Riviana Foods, Inc., Abbeville, LA). Materials and chemicals purchased from Sigma Chemical (St. Louis, MO) included commercial rice starch (S-7260), free fatty acids (palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid), phospholipids (lysophosphatidylcholine [LC], lysophosphatidylethanolamine [LE]) and glycerides (monopalmitin [MP], tripalmitin [TP], β -cyclodextrin [β -CD] [C-4767], amylose [A0512], amylopectin [A8515], and protease [P5147]).

Lipids Extraction from Rice Flour

Defatting of rice flour was performed by the modified Soxhlet extraction method (Yang and Chang 1999). A 30-g flour sample was weighed and transferred into an extraction thimble 80 mm high. The thimble was then covered with cotton and put into a Soxhlet extraction tube. A 100-mL aliquot of petroleum ether was added to a 500-mL flask. An Allihn condenser, the Soxhlet extraction tube, and the flask were connected and placed on a hot plate set at 45°C. A

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cooling system was then connected to the condenser with the coolant temperature setting at -5°C . Petroleum ether extraction for 12 hr was followed by extraction with 100 mL of methanol at 65°C for 12 hr. Finally, the defatted flour sample was air-dried under a vacuum hood. Duplicate samples were prepared.

Protein Removal of Rice Flour

The modified alkaline protease digestion method (Lumdubwong and Seib 2000) was applied to remove protein from defatted rice flour. A 40-g defatted flour sample was weighed and transferred into a 500-mL flask. Then 150 mL of 0.001M NaOH solution was transferred to the flask and 0.2 g of protease powder was weighed and added to the mixture. The mixture was then stirred and adjusted to pH 10 by adding 1M sodium hydroxide solution. Then the flask was covered with parafilm and placed in a shaking water bath for 18 hr at 55°C .

The slurry was centrifuged at $3,000 \times g$ for 20 min. The supernatant was discarded while the sediment was washed twice with 150 mL of distilled water and centrifuged at $3,000 \times g$ for 15 min. The residue was then suspended in 150 mL of distilled water and adjusted to pH 7 by adding 1M hydrochloric acid. The pH-adjusted slurry was centrifuged at $10,000 \times g$ for 20 min. The supernatant was removed by decantation, and the dark tailings layer atop the residual starch was carefully scraped off and discarded. The starch was finally washed three times with 100 mL of distilled water until the tailing fraction became negligible after centrifuging. The isolated starch was dried in a convection oven at 40°C for 48 hr. Duplicate samples were prepared.

Chemical Composition Analysis

White rice flour, defatted flour, WSI, and commercial starch were analyzed (AOAC 1995) for moisture (Method 985.14), lipid (Method 945.16), protein ($N \times 5.95$) (Method 992.15), and ash content (Method 920.153). The amylose content of the samples was determined using the standard iodine colorimetry method proposed by Juliano et al (1981). Duplicate samples were used for analysis. All values were reported on a dry weight basis except moisture. Commercial rice starch had 11.1% moisture, 0.6% protein, 0.0% lipid, 0.3% ash, and 25.3% amylose. WSI had 7.3% moisture, 1.4% protein, 0.1% lipid, 0.5% ash, and 29.2% amylose.

Standard Rapid Viscosity Analysis

Lipids and β -CD were used as additives to test the effects at two levels: 0.2 and 0.6% (starch db) for lipids, and 2 and 6% (starch db) for β -CD. Commercial rice starch and WSI were mixed with each additive.

The Rapid Visco Analyser (RVA, Newport Scientific, Warriewood, Australia) was used to measure the apparent viscosity of samples as a function of temperature, time, and stirring. A modified procedure of the manufacturer's rice method was followed (Newport Scientific 1997). Each additive was carefully weighed into an RVA canister. Distilled water (25 mL) was transferred into the canister. A sample (2.65 g, db) was weighed and transferred to the canister, and distilled water was added to reach a total weight of 28 g. A plastic paddle was placed into the canister and vigorously jogged through the sample up and down 10 times. The canister with the paddle was then inserted into the instrument. The measurement cycle was initiated by lowering the motor tower of the instrument into position.

The starch suspension was stirred rapidly at 960 rpm for 10 sec before the shear input was decreased and held constant at 160 rpm for the heating and cooling cycles. The suspension was heated from 50 to 95°C in 3 min and 48 sec, then held at 95°C for 2 min and 30 sec before cooling to 50°C over 3 min 48 sec. All pasting curves were performed in duplicate. The viscosity was expressed in RVA units (RVU). Peak viscosity (PV), minimum viscosity (MV), final viscosity (FV), pasting temperature (PT), and time to peak (TP) were reported. Total setback (TSB = FV - MV) and breakdown (BKD = PV - MV) viscosity were determined (Ravi et al 1999).

The gelatinized sample gels obtained from the RVA tests were refrigerated for three days to accelerate retrogradation. Those gels were then freeze-dried and milled to 100 mesh powders using a rice miller. Samples were hydrated at 75% rh in a sealed vessel using saturated NaCl before the XRD test.

XRD

A portion of each sample (≈ 1 g) was pressed into a 10×25 mm pellet with a hydraulic press. XRD patterns were obtained using a Siemens D5000 X-ray diffraction instrument. Conditions for XRD were 40 KV, 30 mA, with the scanning angle 2θ set from 2 to 36° at a scanning rate of $0.6^{\circ}/\text{min}$. Relative crystallinity (RC) of the starch was determined by the method of Hermans and Weidinger (1948) as described by Nara et al (1978). The area of the crystalline fraction (A_c) is divided by the diffraction area for a 100% crystalline substance (A_c). In this study, the area of the crystalline fraction in raw commercial starch XRD pattern was used as the value of A_c (Dragsdorf and Varriano-Marston 1980). X-ray patterns were designated according to the d -spacings and intensities given by Zobel (1988a,b). The diffraction patterns were recorded and compared.

Statistical Analysis

Statistical Analysis System software (v. 8.0, SAS Institute, Cary, NC) was used for data analysis. Analysis of variance (ANOVA), with Tukey's studentized range (HSD) test, was performed to examine the additive effects (lipids and β -CD) on the pasting characteristics (PV, MV, FV, PT, TP, TSB, and BKD) of commercial starch and WSI. Duplicate samples were used and the significance level was $P \leq 0.05$.

RESULTS AND DISCUSSION

The RVA viscosity curves reflect the pasting characteristics of starch during processing and use (Deffenbaugh and Walker 1989). The PT is the temperature at which the viscosity starts to rise. Usually PT is higher than the gelatinization temperature, meaning the starch granules are gelatinized before the viscosity begins to rise and be detected by RVA. Lower PT means faster swelling. PV reflects the extent of granule swelling. Most of the time, we must cook through this stage to obtain a usable starch paste. TP indicates the time required for cooking. The drop in viscosity from a maximum value (PV) to a minimum value (MV) is the breakdown value (BKD). BKD reflects the stability of the paste during cooking, whereas the FV at 50°C indicates the stability of the cooked paste. TSB shows the viscosity increase on cooling to 50°C , indicating the extent of retrogradation of the starch product. Rice flours with higher amylose contents and which showed greater retrogradation properties in bread had greater TSB than other flours. Therefore, TSB has been correlated with retrogradation (Juliano et al 1964; Bean 1986; Leelavathi et al 1987).

Effects of Lipids on Pasting Properties of Commercial Starch

For commercial starch, the presence of monopalmitin (MP) increased the PV, MV, and FV values (Table I, Fig. 1A). The influence of monoglyceride (MG) on starch swelling, as related to PV, depends on the chain length of the constituent fatty acid and may also depend on the type of starch used. Hoover and Hadziyev (1981) found lower swelling power with MG of various chain lengths (C_8 to C_{18}) added to potato starch than without. Roach and Hosney (1995a) found increased swelling with C_{10} MG added to wheat starch, but decreased swelling with C_{18} MG added. In our study, the PT was increased by 6°C when 0.2 or 0.6% MP were added. Addition of 0.6% MP significantly increased the FV and TSB by 72 and 45 RVU, respectively, while increasing BKD by 11 RVU. The increase in BKD is expected with the increase in PV, as starches with greater swelling, such as potato starch, tend to break down easier. TSB is associated with retrogradation tendency

and firming of a starch gel, so greater TSB would be expected to occur when more amylose is free to associate into crystallites. Emulsifiers such as monoglyceride (MG) are typically added to bread products to delay retrogradation and maintain softness through their interaction with starch. C₁₈MG added at 2% (fwb) reduced bread crumb firmness, indicating that amylose-lipid complexes prevented the amylose from forming crystallites through inhibition of starch swelling (Roach and Hosenev 1995a). There may also be an effect of the MG preventing amylose leaching as was observed by Hoover and Hadziyev (1981). We used a much smaller quantity of MG in our study so there may have not been enough lipid to prevent the amylose from leaching and forming crystallites. The presence of tripalmitin showed no influence on pasting properties of commercial starch, which might be due to stearic hindrance by the fatty acid chains, prohibiting interaction with the amylose (Table I). Roach and Hosenev (1995b) found similar results. They observed no effect of triglyceride on swelling of wheat starch.

The addition of lysophosphatidylcholine (LC) to commercial starch increased the MV, FV, TP, and TSB values. At 0.6%, LC also increased the PV (Table I, Fig. 1B). The PT was increased by 4°C while the TP was increased slightly. However, the BKD of the commercial starch was reduced. Compared with the control, addition of 0.6% lysophosphatidylethanolamine (LE) increased the PV and MV (Table I, Fig. 1C). The PT was increased by 6°C. Compared with the control, the TSB was increased by 22 RVU when 0.2% LE was used. BKD was reduced. LC and LE stabilized the starch while enhancing swelling, but TSB again unexpectedly increased.

Palmitic acid, oleic acid, linoleic acid, and linolenic acid increased the FV of the commercial starch at both levels (0.2 and 0.6%) while the stearic acid showed no influence on FV (Table I). The presence of 0.6% palmitic acid, oleic acid, linoleic acid, and linolenic acid also increased the TSB. Only linoleic and linolenic acids at 0.6% increased BKD. Saturated fatty acids at 0.2% increased MV and no fatty acids had an effect on PV, PT, or TP.

TABLE I
Effects of Lipids^a on Pasting Properties^b of Commercial Starch

Additive	% ^c	PV (RVU)	MV (RVU)	FV (RVU)	PT (°C)	TP (min)	TSB (RVU)	BKD (RVU)
Control	...	162.17d ^d	141.17ef	217.34ij	89.38d	6.70c-e	76.17d-f	21.01c-f
Palmitic	0.2	167.55cd	152.13c	244.25d-g	90.13b-d	6.86a-c	92.13bc	15.42fg
	0.6	162.00d	142.21d-f	260.5bc	89.53d	6.80a-e	118.29a	19.79c-f
Stearic	0.2	168.84b-d	150.75cd	220.13ij	90.13b-d	6.80a-e	69.38f	18.09d-g
	0.6	166.09d	144.84c-f	227.38h-j	89.25d	6.85a-c	82.54c-e	21.25c-e
Oleic	0.2	164.42d	147.88c-e	235.71f-h	91.20a-d	6.83a-d	87.84b-d	16.54e-g
	0.6	167.42cd	149.29c-e	247.63de	89.50d	6.89ab	98.34b	18.13d-g
Linoleic	0.2	167.79cd	145.83c-e	236.75f-h	90.05cd	6.73b-e	90.92bc	21.96c-e
	0.6	166.05d	136.21f	252.13c-e	90.95a-d	6.67de	115.92a	29.84ab
Linolenic	0.2	167.83cd	143.38c-f	234.67gh	89.78cd	6.80a-e	91.30bc	24.46bc
	0.6	167.96cd	136.13f	253.66cd	89.7cd	6.64e	117.54a	31.84a
MP	0.2	197.63a	174.29a	258.75c	95.25a	6.72b-e	84.46cd	23.34cd
	0.6	199.88a	167.84ab	289.25a	95.25a	6.72b-e	121.42a	32.04a
Tripalmitin	0.2	165.79d	147.67c-e	217.42ij	89.88cd	6.80a-e	69.75ef	18.13d-g
	0.6	167.88cd	147.17c-e	216.63j	90.50b-d	6.80a-e	69.46ef	20.71c-f
LC	0.2	170.25b-d	152.42c	242.29e-g	92.83a-d	6.93a	89.87bc	17.83d-g
	0.6	176.88bc	170.38ab	271.04b	93.93a-c	6.97a	100.67b	6.50h
LE	0.2	166.92cd	147.08c-e	246.04d-f	94.45ab	6.93a	98.96b	19.84c-f
	0.6	177.80b	164.59b	228.00hi	95.23a	6.97a	63.42f	13.21g

^a MP, monopalmitin; LC, lysophosphatidylcholine; LE, lysophosphatidylethanolamine.

^b PV, peak viscosity; MV, minimum viscosity; FV, final viscosity; PT, pasting temperature; TP, time to peak; TSB, total setback; BKD, breakdown.

^c Based on starch dry weight.

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

TABLE II
Effect of Lipids^a on Pasting Properties^b of White Starch Isolate

Additive	% ^c	PV (RVU)	MV (RVU)	FV (RVU)	PT (°C)	TP (min)	TSB (RVU)	BKD (RVU)
Control	...	197.75b-e ^d	119.46bc	183.63f-j	77.25bc	4.87fg	64.17e	78.29f
Palmitic	0.2	207.54ab	107.50c-e	191.46e-g	76.90c	4.84fg	83.96bc	100.04b-d
	0.6	201.33a-d	99.92d-f	186.75f-j	76.93c	4.86fg	86.83b	101.42bc
Stearic	0.2	206.54ab	121.33bc	200.71c-f	77.03bc	4.86fg	79.38b-d	85.21ef
	0.6	211.25a	113.04b-d	195.04d-g	77.35bc	4.87fg	82.00bc	98.21b-d
Oleic	0.2	198.13b-e	108.17bc-e	180.83g-j	77.03bc	4.99f	72.67c-e	89.96de
	0.6	195.79b-e	94.96ef	169.79jk	77.85bc	4.97fg	74.83b-e	100.83bc
Linoleic	0.2	195.33b-e	100.25d-f	172.83h-k	77.58bc	4.95fg	72.58c-e	95.08cde
	0.6	193.13c-f	86.29f	161.33k	77.28bc	4.92fg	75.04bcde	106.83ab
Linolenic	0.2	211.83a	108.71bc-e	183.38fg-j	77.33bc	4.89fg	74.67b-e	103.13bc
	0.6	211.67a	94.54ef	171.67i-k	77.55bc	4.85fg	77.13b-d	117.13a
MP	0.2	180.29f	119.67bc	206.13c-e	78.20b	6.00d	86.46b	60.63g
	0.6	185.21ef	120.63bc	247.63a	77.75bc	6.44b	127.00a	64.58g
Tripalmitin	0.2	211.54a	121.54bc	189.38e-i	77.15bc	4.81g	67.83de	90.00de
	0.6	212.63a	122.83b	190.33e-h	76.90c	4.86fg	67.50de	89.79de
LC	0.2	212.75a	185.21a	235.29ab	78.23b	5.74e	50.08f	27.54h
	0.6	202.67a-c	198.17a	217.63bc	80.00a	6.97a	19.46h	4.50i
LE	0.2	205.46a-c	199.50a	231.50ab	77.63bc	6.24c	32.00g	5.96i
	0.6	189.04d-f	191.79a	211.83cd	77.95bc	6.97a	20.04gh	-2.75i

^a MP, monopalmitin; LC, lysophosphatidylcholine; LE, lysophosphatidylethanolamine.

^b PV, peak viscosity; MV, minimum viscosity; FV, final viscosity; PT, pasting temperature; TP, time to peak; TSB, total setback; BKD, breakdown.

^c Based on starch dry weight.

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

Among all lipids, monopalmitin (MP) caused the greatest increase of PV, MV, and FV. The highest TSB was observed when 0.6% MP was applied, with 0.6% palmitic acid giving the second greatest TSB, both enhancing retrogradation tendency of the starch. Both MP and LE had the largest increase in pasting temperature. Both LC and LE had greatest TP. In a study by Perez et al (1993), non-waxy rice flours with greater lipid content, mainly due to starch lipids, showed greater PV and BKD values. Nonwaxy rice starch lipids were composed of 48–67% lysophospholipids and 29–45% fatty acids, mainly LC, LE, palmitic acid, and linoleic acid, while only 3–4% of the starch lipids were MG (Azudin and Morrison 1986). We observed few differences in the pasting properties of the starches between lipid types added. We did see increases in PV for LC and LE, but decreases in BKD as compared with the control, while palmitic and linoleic acids had no affect on PV but increased BKD. Although the level of MG in rice starch lipids is low compared with other lipid types, our study and others showed that MG can play a large role in affecting starch pasting properties.

Effects of Lipids on Pasting Properties of WSI

Compared with commercial starch, WSI generally had greater PV and BKD and lower MV, FV, PT, TP, and TSB values. With the addition of 0.2% MP, WSI had decreased PV and BKD and increased FV and TSB compared with WSI control (Table II, Fig. 2A). An

increase in MP to 0.6% increased FV and TSB further by 41 RVU each. MP also delayed the TP as compared with the control. Tripalmitin increased the PV and BKD at both 0.2 and 0.6% levels (Table II). Tripalmitin had no other influence on the pasting properties of the WSI. Addition of glycerol monostearate at 2% to a bread formula, wheat starch itself or wheat starch before extrusion resulted in decreased swelling and lower PV of the starch, but a C10MG resulted in increased swelling (Ryu and Walker 1993; Roach and Hosney 1995a,b). TP of wheat starch as well as MV was increased by the addition of 0.75–1.5% glycerol monostearate (GMS) before extrusion of wheat starch (Ryu and Walker 1993). We observed the same result for TP, but no effect for MV by adding MP at lower levels for isolated starch only. Ravi et al (1999) found that GMS did not affect PV in a weak (low protein content) wheat flour, but decreased PV in a medium strength (medium protein content) wheat flour, which they attributed to the absorption of surfactants on the surface of the starch granules to inhibit swelling. This was similar to our results. The isolated starch had greater protein content than commercial starch (1.4 vs. 0.6%) and addition of MP to the WSI decreased the PV value. The commercial starch, which had less protein, showed an increase in PV with added MP, which seemed to indicate in our study that protein along with the lipid interacted with the granule inhibiting the swelling of the starch. Ravi et al (1999) also found that TSB increased in both strength wheat flours when GMS was added,

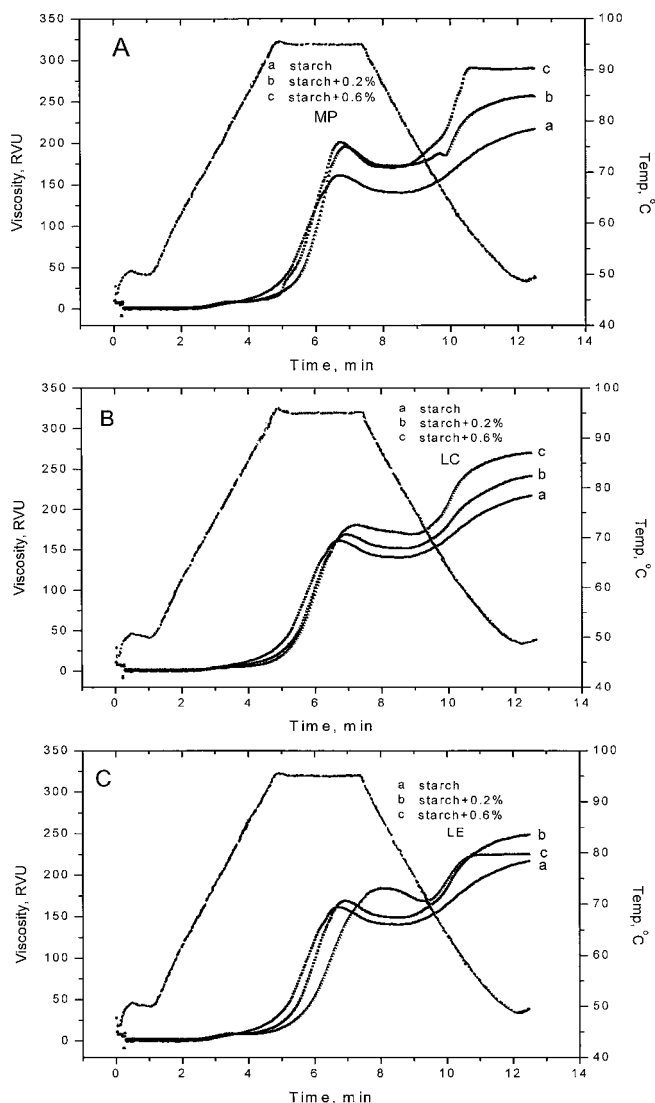


Fig. 1. Effects of monopalmitin (A), lysophosphatidylcholine (B), and lysophosphatidylethanolamine (C) on pasting properties of commercial starch

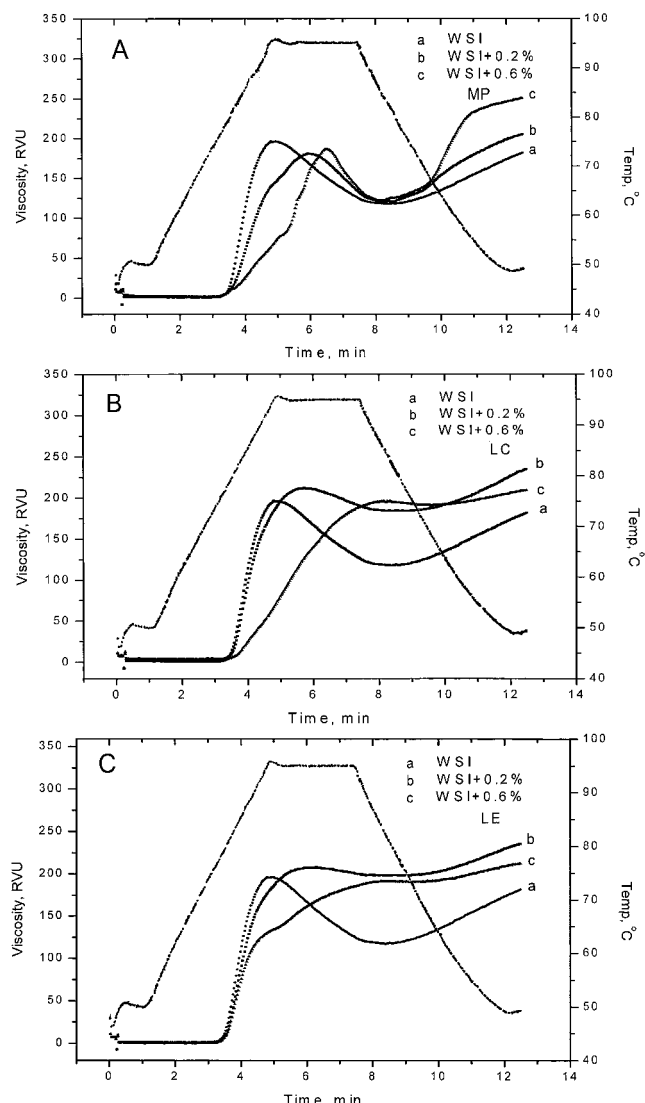


Fig. 2. Effect of monopalmitin (A), lysophosphatidylcholine (B), and lysophosphatidylethanolamine (C) on pasting properties of rice starch isolate (WSI)

which is what we found with both of our starches when MP was added.

LC and LE tended to stabilize the WSI to the cooking process and against retrogradation. The presence of 0.6% LC greatly increased the MV and FV, resulting in a substantial drop in BKD and TSB (Table II, Fig. 2B). The PT was increased by 3°C, whereas the TP was increased by 2.1 min. LC at 0.2% had less of an effect on MV, TP, TSB, and BKD, but a greater influence on PV and FV than LC at 0.6%. Similar results were observed with LE when 0.2 or 0.6% was added. Increases were observed in MV, FV, and TP with decreases in TSB and BKD at both levels, but the effects on MV and FV were greater at 0.2%. With the presence of 0.6% LE, starch viscosity continued to increase after passing the initial 95°C, resulting in no BKD (Table II, Fig. 2C). The TP was increased while the TSB was reduced.

Fatty acids tended to destabilize the WSI. Among the individual fatty acids, linolenic acid caused the greatest increase in PV and BKD. All fatty acids caused the BKD to increase, resulting in less cooking stability, with stearic having an effect only at 0.6%. TSB was increased with palmitic and stearic acids, resulting in greater tendency for retrogradation, but was not affected by any other fatty acids. Addition of 0.6% stearic acid and linolenic acid increased the PV value (Table II). The presence of 0.6% palmitic, oleic, linoleic, and linolenic acid decreased the MV by 20–33 RVU and increased the BKD.

WSI contained a greater level of amylose and protein residues than the commercial starch, but both starches had little lipid. Starches with lower amylose tend to have greater PV and BKD but lower FV (Zeng et al 1997). Results from this study do not support that finding; we saw the opposite result where our isolate, with greater amylose content than commercial starch (29.2 vs. 25.3%), had greater PV and BKD values. Our result indicated that the amylose content is not the only influence on the pasting characteristics. Other factors, such as source and minor components, might also play an important role in determining the pasting properties of rice starch.

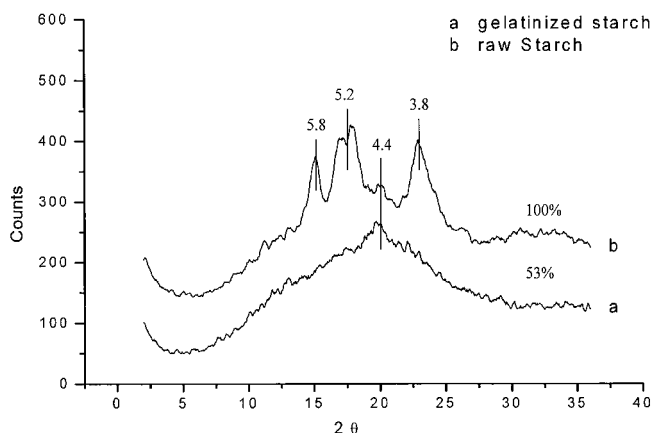


Fig. 3. Influence of gelatinization on X-ray diffraction pattern of commercial starch

Effects of β -Cyclodextrin on Pasting Properties of Starches

Addition of 2% β -CD to commercial starch increased the MV slightly as compared with the control (Table III). However, further increase of the concentration to 6% caused the MV to stay at a level similar to that of the control. In addition, the presence of 6% β -CD reduced the FV. The presence of 2 and 6% β -CD reduced the TSB slightly. PV and BKD were not affected. Cyclodextrins were reported to increase the swelling power and solubility of wheat starch granules through amylose-lipid complex disruption and cyclodextrin-lipid inclusion (Kim and Hill 1984). Our results on commercial starch showed that β -CD had only a slight influence on the pasting properties of rice starch.

More dramatic differences were observed for the WSI than for the commercial starch with β -CD added. WSI started with a greater PV than commercial starch and this can lead to greater BKD value. Whereas BKD was not affected by the addition of β -CD to commercial starch, BKD was affected significantly in the WSI. The presence of 2 and 6% β -CD decreased the MV and FV, causing the BKD to increase (Table III). The PV, PT, TP, and TSB were not changed by either level of β -CD, except TSB increased slightly for 2% β -CD. Differences in pasting properties between starch types in the presence of β -CD were also found by Li et al (2000). Wheat starches with higher PV by themselves had increases in PV with added β -CD, while wheat starches with lower PV had decreased PV with added β -CD present. Cold paste viscosity of all but one of the wheat starches tested increased in the presence of β -CD. TSB is related to retrogradation tendency, which, in turn, is related to amylose helix interaction. Therefore, it would be expected that if cyclodextrin can preferentially complex with lipid over amylose, then more amylose would be free to associate during cooling, resulting in a greater TSB. Also a greater TSB would be expected for samples containing more amylose, such as the WSI, which contained 15.4% more amylose than commercial starch, but this was not observed. It is possible that the cyclodextrin itself could have physically interfered with the amylose complexing.

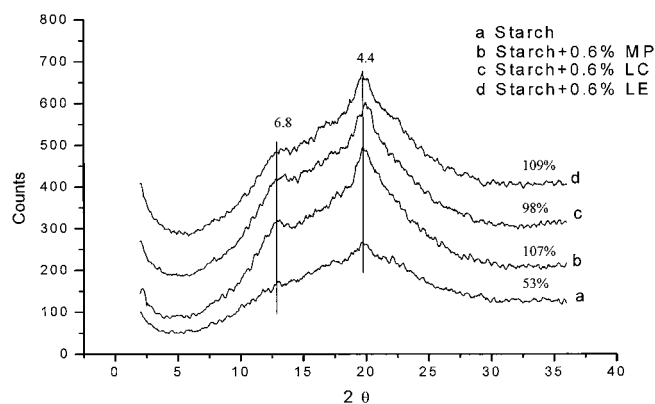


Fig. 4. Influence of lipids on X-ray diffraction pattern of commercial starch. All samples were gelatinized and refrigerated for three days. MP, monopalmitin; LC lysophosphatidylcholine; LE, lysophosphatidylethanolamine.

TABLE III
Effect of β -Cyclodextrin on Pasting Properties^a of Commercial Starch and Starch Isolate

Additive	% ^b	PV (RVU)	MV (RVU)	FV (RVU)	PT (°C)	TP (min)	TSB (RVU)	BKD (RVU)
Control comm.	...	162.17a ^c	141.17b	217.34a	89.38a	6.70a	76.17a	21.01ab
β -CD	2	166.63a	147.13a	217.55a	87.10a	6.72a	70.42b	19.50b
	6	162.67a	140.92b	208.79b	85.93a	6.59a	67.87b	21.75a
Control isolate	...	197.75a	119.46a	183.62a	77.25a	4.87a	64.17b	78.29c
β -CD	2	201.16a	105.21b	173.55b	77.60a	4.79a	68.34a	95.95b
	6	199.50a	93.15c	157.03c	76.65a	4.70a	63.89b	106.35a

^a PV, peak viscosity; MV, minimum viscosity; FV, final viscosity; PT, pasting temperature; TP, time to peak; TSB, total setback; BKD, breakdown.

^b Based on starch dry weight.

^c Values followed by the same letter in the same column are not significantly different ($P < 0.05$).

Effect of Lipids on Commercial Starch XRD Pattern

The crystalline nature of raw and gelatinized commercial starches was investigated by X-ray diffraction (Fig. 3). In raw starch, A-type X-ray diffraction patterns were characterized by clear diffraction peaks at ≈ 3.8 , 5.2 , and 5.8\AA . The A-type pattern was generally regarded as cereal starch crystal forms (Zobel 1988b), resulting from the formation of double helical structures of the amylopectin fraction (Jenkins et al 1993). During starch gelatinization, the double helices of amylopectin can be destroyed, whereas part of the free lipids present in the cereal starches can form a helical inclusion complex with the amylose molecules (Hoover and Hadziyev 1981; Zobel 1988b). This results in the V-type X-ray diffraction pattern, which was characterized by peaks at ≈ 4.4 , 6.8 , and 12\AA . In this study, the X-ray pattern had an enhanced peak at 4.4\AA and no peaks were present at 6.8 and 12\AA , which was similar to the findings by Hibi et al (1990) for defatted rice. Therefore, the gelatinized commercial rice starch seemed to be forming a V-complex, which is known to occur during heat treatment of rice starches (Zobel 1988b). Gelatinization resulted in a 47% reduction of the relative crystallinity (RC).

Compared with the gelatinized commercial starch (control) at 53% crystallinity of raw starch, the presence of 0.6% MP increased the intensity of the peak at 4.4\AA and gave rise to the development of another peak at 6.8\AA , resulting in a more evident V-type crystalline structure (Fig. 4). The RC was also increased by 102%. Similarly, the addition of LC and LE resulted in an increase of the RC by 85 and 106%, respectively, with the X-ray pattern changed to a more evident V-type crystalline structure. Results from this study indicated that addition of lipids led to the development of a V-type X-ray pattern, which was attributed to the enhanced lipid-amylose complexes formation (Zobel 1988b).

Effect of Lipids on WSI XRD Pattern

Gelatinized WSI had 64% RC compared with raw rice commercial rice starch. There were two main peaks at 4.4\AA (weak) and 5.2\AA (moderate), indicating a mixed A- and V-type pattern (Zobel 1988b). Compared with the gelatinized WSI (control), the presence of 0.6% MP increased the intensity of the peak at 4.4\AA , resulting in enhanced V-type complex XRD pattern, but the peak at 5.2\AA was still observed and was slightly weaker (Fig. 5). The RC was increased by 13%. Addition of 0.6% LC increased the RC by 3% and again increased the peak at 4.4\AA compared with that of the control. However, the presence of 0.6% LE caused a decrease of the RC for 3% while still increasing the 4.4\AA peak intensity. For LC and LE though, the peak at 5.2\AA decreased in intensity to almost zero. WSI had 15.4% more amylose than commercial starch (29.2 vs. 25.3%, respectively). Biliaderis et al (1993) found different results for milled rice flours from parboiled (100°C) rice samples, where starch with 25.8% amylose (IR-5) showed a stronger V-type complex pattern than the

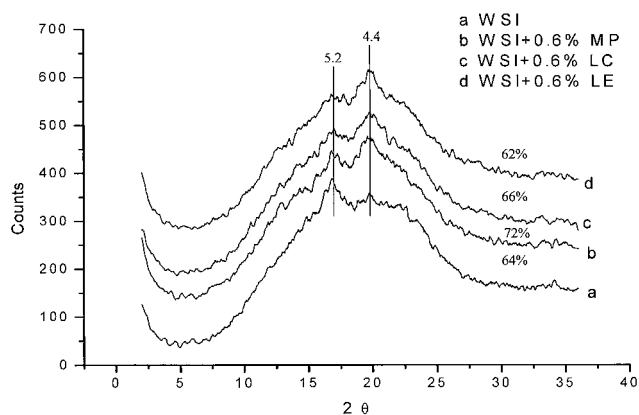


Fig. 5. Influence of lipids on X-ray diffraction pattern of rice starch isolate (WSI). All samples were gelatinized and refrigerated for three days. MP, monopalmitin; LC lysophosphatidylcholine; LE, lysophosphatidylethanolamine.

sample with 21.9% amylose (IR-64). They found that greater temperatures of parboiling resulted in more intense V-type complex patterns. Our samples only reached 95°C because they came from the RVA, which may be why our V-type complexes were weak.

Effect of β -CD on Commercial Starch and WSI XRD Patterns

Compared with the commercial starch control, the presence of 6% β -CD in WSI led to the development of a weak peak at 6.8\AA and increased the intensity of the 4.4\AA peak, indicating a weak V-type pattern was formed (Fig. 6A). The RC was increased by 85%. For WSI, the peak at 5.2\AA decreased somewhat, with a very small increase in the peak at 4.4\AA (Fig. 6B). The RC decreased greatly. Kim and Hill (1987) found that addition of cyclomaltoheptaose interfered with the formation of V-type complexes between amylose and lysolecithin. In their study, the V-type pattern in XRD was lost and a pattern that was more complex developed for a mixture with a ratio of 10:1:10 (w/w) amylose, lysolecithin, cyclomaltoheptaose. The effect of β -CD on rice starch crystalline structure has not been documented previously. Our study results provided some evidence about the β -CD influence on rice starch X-ray diffraction pattern.

CONCLUSIONS

This study showed that addition of lipids to commercial starch generally caused a delay in the granule swelling, but an increase in the extent of swelling. Addition of lipids increased gel viscosity and enhanced the retrogradation tendency, but cooking stability varied depending on the type of lipid and starch source. No specific influence pattern was observed regarding the effect of the degree of fatty acid saturation on pasting properties of starch. Investigators reported the antifirming property of monoglycerides in breadmaking, and attributed this property to the formation of monoglyceride and amylose complexes (Eliasson and Krog 1985; Roach and Hosney 1995a). However, results from this study indicated that amylose-lipid complex formation enhanced the retrogradation tendency of commercial starch. Removal of lipids from starch decreased the retro-

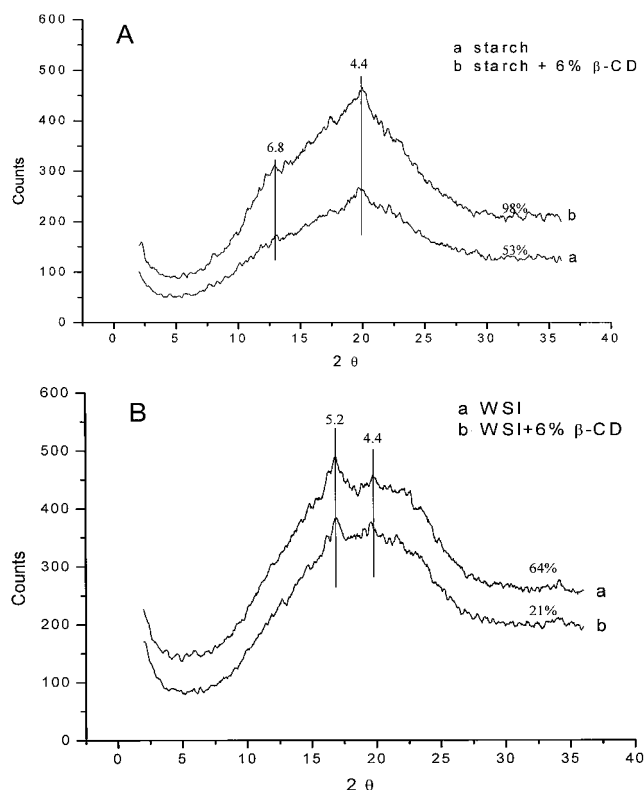


Fig. 6. Influence of β -CD on X-ray diffraction pattern of commercial starch (A) and rice starch isolate (WSI) (B). All samples were gelatinized and refrigerated for three days.

gradation tendency. Evidence indicated that amylopectin could interact with monoglycerides in model systems (Batres and White 1986; Huang and White 1993). Therefore, the antifirming effect of lipids is most likely due to the amylopectin-lipid complex formation. β -CD had a slight influence on pasting properties of rice starches. The variation in the effects of lipids and β -CD on commercial starch and WSI might be due to differences in source and isolation method.

The gelatinization process destroyed the double helix structure of starch granules, resulting in an amorphous starch. Addition of lipids to commercial starch induced the development of a new peak at 6.8Å and increased the intensity of the 4.4Å peak. The enhanced V-type pattern may be due to the formation of amylose-lipid complexes. The presence of β -CD competed with amylose for lipids, resulting in less amylose-lipid complex formation in the retrograded gel. The enhanced V-type pattern of the β -CD added starch may be due to the complex formation of β -CD and lipids. Further research is needed to explore the β -CD and lipid complex crystalline structure.

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