

# Relationship of Gelatinization and Recrystallization of Cross-Linked Rice to Glass Transition Temperature

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## ABSTRACT

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Nonwaxy rice starch was cross-linked with sodium trimetaphosphate and sodium tripolyphosphate to obtain different degrees of cross-linking (9.2, 26.2, and 29.2%). The objective was to investigate the influence of cross-linking on thermal transitions of rice starch. Starch suspensions (67% moisture) were heated at 2°C/min using differential scanning calorimetry (DSC) to follow melting transition of amylopectin. Biphasic transitions were observed at ≈60–95°C in all samples. Melting endotherms of amylopectin shifted to a higher temperature (≤5°C) with an increasing degree

of cross-linking, while there was no dramatic change in enthalpy. Recrystallization during aging for 0–15 days was significantly suppressed by cross-linking. The delayed gelatinization and retrogradation in cross-linked starch were evident due to restricted swelling and reduced hydration in starch granules. Glass transition temperature ( $T_g$ ) measured from the derivative curve of heat flow was –3 to –4°C. No significant change in  $T_g$  was observed over the storage time studied.

Gelatinization and retrogradation are two important starch functional properties that vary due to the ratio of amylose to amylopectin, starch crystallinity, granule size distribution, and the amount of minor constituents (e.g., phosphorus, lipids, proteins, and enzymes). Although present in small quantities, those minor constituents can affect the properties of the starch (Lineback and Rasper 1988, Deffenbaugh and Walker 1989). Among them, phosphorus has gained a great deal of interest due to its important role in starch functional properties (Jane et al 1996). Phosphorus in starch is found naturally in three major forms: phosphate monoesters, phospholipids, and inorganic phosphate (Lin and Czuchajowska 1998). In addition, the amount of phosphorus in starch can be adjusted by phosphorylation, a chemical modification, resulting in different functional properties (paste clarity, viscosity).

The Code of Federal Regulation (CFR) of the U.S. Food and Drug Administration (1995) allows the use of monosodium orthophosphate (SOP), sodium trimetaphosphate (STMP), sodium tripolyphosphate (STTP), and phosphorus oxychloride (POC) to phosphorylate food-grade starch. The CFR specifies that the residual phosphate in the starch should not exceed 0.04% when STMP is used alone and 0.4% phosphorus for a mixture of STMP and STTP. The pH of starch phosphorylation is important to the properties of the products. At pH 7–9, STMP and STTP produce small amounts of diester linkage (cross-linking). But at pH 9–11.5, cross-linking reaction of starch predominates (Kerr and Cleveland 1959). Both STTP and STMP can cross-link starch in aqueous slurry reactions at pH 11 (Solarek 1986).

Gelatinization and retrogradation have been studied by various means such as thermal analysis (Wada et al 1979, Nakazawa et al 1984, Shiotsubo and Takahashi 1984, Slade and Levine 1987), X-ray diffraction (I'Anson et al 1988, Zobel et al 1988), and nuclear magnetic resonance (NMR) (Chinachoti et al 1991, German et al 1992). Differential scanning calorimetry (DSC) is the most common technique used in thermal studies of starches (Nakazawa et al 1984, Biliaderis et al 1986, Yook et al 1993, Huang et al 1994). Yook et al (1993) reported a lower value of gelatinization heat in cross-linked rice compared with native rice as cross-linking reduced the portion of starch able to be gelatinized. Yeh and Yeh (1993), however, reported the increase in heat of gelatinization by 30% and a decrease in solubility of cross-linked rice starch.

It has been generally accepted that starch gelatinization is a non-equilibrium process, and melting of the crystalline region requires previous softening (glass transition and swelling) of the amorphous parts of the granule (Slade and Levine 1984, Maurice et al 1985). The glass transition is proposed to be responsible for the phase transition of rice starch (Blanshard 1987). However, characterization of glass transition in starch has been far from clear, particularly for granular starch when analyzed by DSC only. The objective of this work was to study the influence of cross-linking using phosphate compounds (sodium tripolyphosphate and sodium trimetaphosphate) on thermal properties of rice starch including gelatinization, glass transition, and retrogradation.

## MATERIALS AND METHODS

### Materials

Rice starch (indica, nonwaxy with 26–28% amylose) was the product of Choheng Co. (Thailand). Sodium trimetaphosphate, sodium tripolyphosphate, sodium carbonate, sodium hydroxide and hydrochloric acid were supplied by Fisher Scientific (Springfield, NJ).

### Cross-Linking

Cross-linking reaction of rice starch was performed with 300 mg of sodium tripolyphosphate (STPP), 9 g of sodium carbonate and variable amounts (0, 18, 27, and 39 g) of sodium trimetaphosphate (STMP) dissolved in 300 mL of water. The variable amounts of STMP were to vary the degree of cross-linking. Starch subjected to the cross-linking without STMP was used as the control sample. Rice starch (150 g) was added and the mixtures were adjusted to pH 11 with 0.1N NaOH and kept at 50°C for 20 hr with stirring. The starch suspensions were then adjusted to pH 6.5 with 0.1N HCl, centrifuged (1,000 rpm or 207 g) and the clear solution was discarded. Distilled water (5,000 mL) was added to wash the mixtures further. Samples were then centrifuged. The starch portions were dried at 50°C for 24 hr in an air oven. The starch samples were then ground in a mortar and sieved (80 mesh). The final moisture content of the starches was obtained by drying in a vacuum oven at 60°C and 27 mmHg for 24 hr (AOAC method 925.09) were all in 8–11% moisture range.

Phosphorus content was determined from the starch ash. The starch was mixed with 0.25N NaOH, dried, and ignited in a furnace at 600°C. The phosphorus content in the ash was determined spectrophotometrically and calculated according to the method described (Rand et al 1975). The phosphorus content of all cross-linked samples was 0.3–0.4%.

The rheological properties of rice starch slurries (25% starch in distilled water) were recorded (Viscoamylograph Type E, Brabender

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OHG Duisburg, Germany). The temperature heating program was heat 30–95°C at 1.5°C/min, hold at 95°C for 15 min, and cool 95–50°C at 1.5°C/min. The viscosity was measured at the torque of 1,000 g·cm (0.01 Nm).

The physical properties of cross-linked starch such as viscosity by viscoamylograph and swelling power are generally used to estimate the degree of cross-linking (Jarowenko 1971, Rutenberg and Solarek 1984). The degree of cross-linking was estimated (Varavint et al 1998, 1999) as:

$$\text{Degree of cross-linking} = (A - B/A) \times 100$$

where *A* is the peak viscosity in Brabender units of the control sample (0% STMP) and *B* is the peak viscosity of highly cross-linked starch. The estimated degree of cross-linking for all samples was 0, 9.2, 26.2, and 29.2%.

### Gelatinization

Native and cross-linked (control, 9.2, 26.2, and 29.2%) starch samples were hydrated to 67% moisture content. The starch slurries were stored overnight at ambient temperature. Each starch suspension (8–10 mg) was then transferred to an aluminum pan (ME 26763, Mettler-Toledo, Westerville, OH) and hermetically sealed. The rice starch samples were gelatinized in a DSC chamber (DSC 100, Seiko Instruments, Torrance, CA) from –40 to 120°C at 2°C/min. The endothermic melting transition of amylopectin was observed at 60–95°C. An empty pan was used as the reference and the calorimeter was calibrated using indium. All measurements were done at least in duplicate. The onset (*T<sub>o</sub>*), peak (*T<sub>p</sub>*), and conclusion (*T<sub>c</sub>*) temperatures and the melting enthalpy ( $\Delta H$ ) in J/g of dry starch were calculated. Experimental errors for these parameters were within 2%.

### Recrystallization on Aging

After completely gelatinization, rice starch gels and pastes were cooled down immediately to room temperature in a DSC chamber using cool air and liquid nitrogen and kept refrigerated (4°C) for 5, 10, and 15 days before rescanning. Two of eight replicates were rescanned immediately by heating at 2°C/min to 120°C. Changes in thermal characteristics were observed.

### Glass Transition During Aging

Gelatinized starch was used to measure glass transition temperature (*T<sub>g</sub>*) by using the derivative curve of heat flow to time (dCp/dt) (Huang et al 1994). Slade and Levine (1988, 1989) and

Liu and Lelievre (1991, 1992) reported the same results in wheat starch. The ice melting peaks of samples obtained from the rescan of gelatinized starch were analyzed. The first derivative curve of heat flow was used to define the *T<sub>g</sub>* of starches.

## RESULTS AND DISCUSSION

A reaction with STTP and STMP results in cross-linking at pH > 10 and 8, respectively (Lim 1990). Our experimental level was pH 11 (resulting in a predominant cross-linking reaction). Exposure to STTP and STMP at pH 11 would likely lead mainly to distarch phosphate and perhaps residual monostarch phosphate. The latter is expected to be more predominant if the reaction is performed in a more acidic condition. The amount of phosphorus residue in starch allowable by the CFR (1995) are 0.04 and 0.4% for STMP alone and for a combination of STMP and STTP, respectively. This study applied a combination of STTP and STMP at pH 11 resulting in 0.3–0.4% phosphorus, which was within the CFR allowance.

Viscoamylograms of the starch modified with only STTP (control sample) showed the highest viscosity (Fig. 1). The highly cross-linked starches (9.2–29.2%) showed higher pasting temperature and lower viscosity than that of the control. The higher degree of cross-linking of starch resulted in higher pasting temperature and lower viscosity.

### Gelatinization

Gelatinization thermograms of native, control and highly cross-linked (9.2, 26.2, and 29.2%) rice starches at a water-to-starch ratio of 2:1 (67% moisture content) showed biphasic melting (more details presented by Chatakanonda et al, *in press*). Endotherms were observed at ≈60–95°C in all samples (Table I). Rice starches with 9.2, 26.2, and 29.2% cross-linking showed deep and sharp endotherms, 20–22°C wide, while native and control samples exhibited broader endotherms, ≈30°C wide. Control sample showed a lower gelatinization temperature (≈3°C) when compared with native rice starch. Gelatinization temperatures significantly increased ≤5°C with an increasing degree of cross-linking. The results suggested that the introduction of phosphate groups by STMP into starch tightened the molecular structure and thus gelatinized at a higher temperature. However, the enthalpy was not significantly changed (≈15% decrease), suggesting a complete melting of crystalline regions regardless of cross-linking.

The amylose-lipid complex endotherm (90–110°C) was only found in native and control rice starches. It was possible that sodium trimetaphosphate (STMP) or other cross-linking treatment conditions (alkalinity) might have interfered with the molecular structure of amylose-lipid complex, resulting in a small or unstable complex that is not detectable by DSC. Similarly, Eliasson (1994) reported less enthalpy of amylose-lipid complex in chemically modified starches, indicating that small or relatively unstable complexes might have been formed. A high degree of modification can prevent the complex formation (Kim et al 1992). No conclusion can be made whether amylopectin-lipid complex was also affected because its endotherm could not be identified from the thermograms obtained.

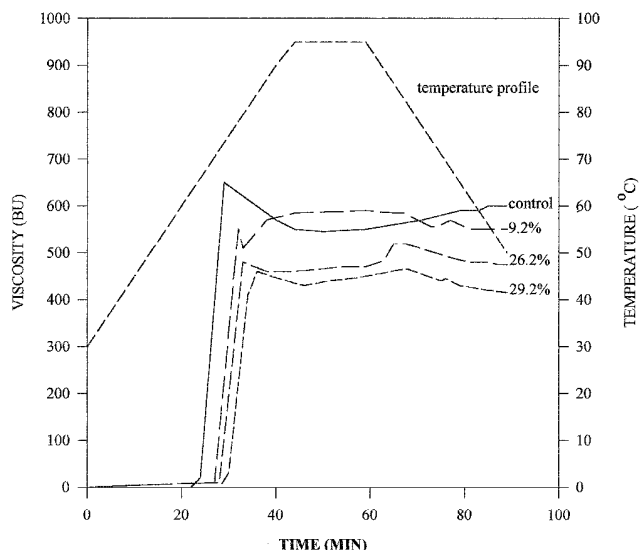


Fig. 1. Viscoamylograms of slurries (25% dsb) of native and cross-linked rice starches in water.

TABLE I  
Gelatinization Characteristics<sup>a</sup> of Native and Cross-Linked Rice Starches

% Cross-Linking	<i>T<sub>o</sub></i>	<i>T<sub>p</sub></i>	<i>T<sub>c</sub></i>	$\Delta H$
Native	58.0 ± 0.0a <sup>b</sup>	74.6 ± 0.2a	88.4 ± 1.4a	15.3 ± 1.4a
Control	57.6 ± 0.0a	72.7 ± 0.1b	85.2 ± 0.8bc	15.0 ± 0.2a
9.2	61.9 ± 0.1b	76.5 ± 0.1c	83.6 ± 0.4c	14.4 ± 0.2a
26.2	63.2 ± 0.2c	77.6 ± 0.2d	85.8 ± 0.5bc	14.7 ± 0.5a
29.2	66.6 ± 0.2d	79.5 ± 0.1e	86.9 ± 0.9ab	14.2 ± 0.0a

<sup>a</sup> Onset peak and conclusion temperatures (°C) (*T<sub>o</sub>*, *T<sub>p</sub>*, *T<sub>c</sub>*) and enthalpy ( $\Delta H$ , J/g).

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

## Retrogradation

All samples exhibited broad endotherms that contributed to amylopectin recrystallization (Fig. 2). Those endotherms were observed at 30–65°C for native and control samples and at 30–60°C for cross-linked samples. Control rice starch seemed to show the same crystalline properties as that of native samples because the endotherms were in the same temperature range and shape. The results indicated that, after recrystallization, the crystallites are broadly distributed and relatively unstable or imperfect, leading to broad endotherms and a low melting temperature range.

The enthalpy of recrystallization increased with time in all samples but at different rates (Fig. 3). Recrystallization of the native and control samples increased dramatically over a short period (five days) and slightly increased during long-term storage. On the other hand, highly cross-linked samples showed a gradual increase in the degree of recrystallization throughout the storage period (15 days). The maximum recrystallization enthalpies of native and control samples stored at 4°C for 15 days are ≈40%, while those of highly cross-linked samples only reached 15–25% of the total original melting enthalpies. The restricted mobility of cross-linked amylopectin branches caused by the phosphate groups could have retarded the reassociation of starch chains and inhibited the recrystallization. However, the degree of cross-linking at 9.2–29.2% did not much affect the degree of recrystallization. After gelatinized starches were cooled down, the native and control samples formed a gel (nongranular) structure, whereas the highly cross-linked samples became a paste (no gel structure) in which starch granules were intact as observed under a microscope.

Reassociation of starch molecules could have been facilitated within intact granules because molecules were closer to each other when compared with widely distributed molecules in the gel system. However, the fact that fewer water molecules are associated to starch chains could be antiplasticizing and prevent further recrystallization, that is, mobility of starch chains was expected to decrease. The ionic phosphate groups present in distarch phosphate could induce repulsive force throughout the negative charges, thus retarding the reassociation of starch chains in granules. Such chemical

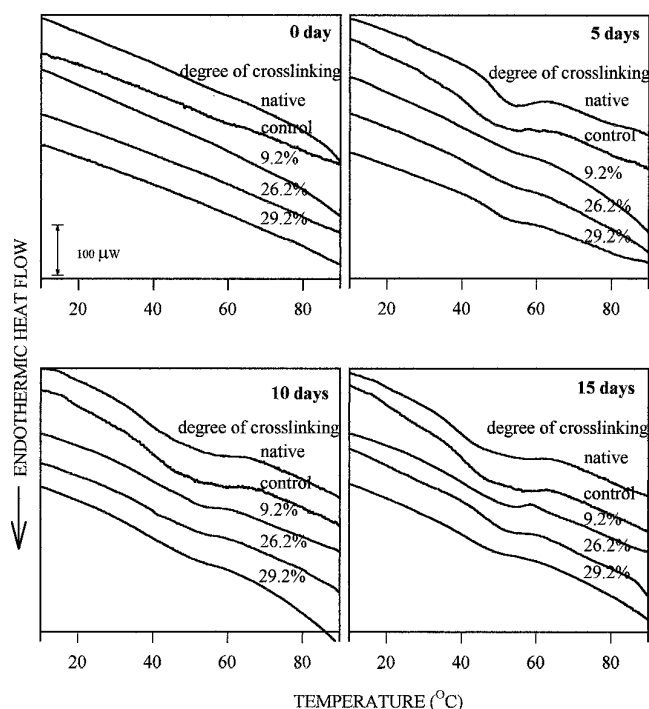


Fig. 2. Amylopectin melting thermograms of gelatinized native and cross-linked rice starches stored at 4°C for 15 days.

and physical changes could greatly interfere with the alignment of starch polymers and increase starch chain rigidity. These could be the explanation for the recrystallization enthalpies of highly cross-linked samples which are much lower than those of native and control starches. It can be concluded that phosphate groups have a strong effect that partially blocks or delays the reassociation of starch molecules.

## Glass Transition

The  $T_g$  was determined from the derivative ( $dC_p/dt$ ) curve of heat flow versus time (Fig. 4) as earlier reported (Biliaderis et al 1986; Slade and Levine 1988, 1989; Liu and Lelievre 1991, 1992; Huang et al 1994). The measured  $T_g$  of all gelatinized starch samples was -3 to -4°C (Table II). This  $T_g$  is not  $T_g'$  as samples were

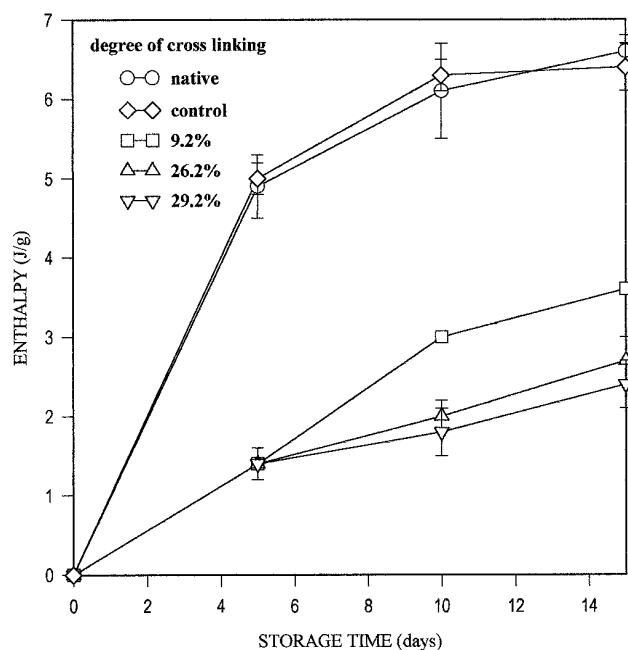


Fig. 3. Recrystallization enthalpies of gelatinized native and cross-linked rice starches kept at 4°C for 15 days.

TABLE II  
Glass Transition Temperatures ( $T_g$ ) of Gelatinized Native and Cross-Linked Rice Starches Stored at 4°C

% Cross Linking	Storage Time (days)	$T_g$ (°C)	
Native	0	-4.3 ± 0.0	
	5	-4.1 ± 0.2	
	10	-3.5 ± 0.3	
	15	-3.7 ± 0.2	
	Control	0	-4.2 ± 0.1
Control	5	-4.0 ± 0.1	
	10	-3.5 ± 0.1	
	15	-3.7 ± 0.1	
	9.2	0	-3.9 ± 0.2
		5	-3.9 ± 0.1
10		-3.4 ± 0.1	
15		-3.6 ± 0.1	
26.2		0	-4.1 ± 0.1
	5	-3.6 ± 0.1	
	10	-3.5 ± 0.1	
	15	-3.4 ± 0.1	
	29.2	0	-3.8 ± 0.1
5		-3.8 ± 0.1	
10		-3.4 ± 0.1	
15		-3.6 ± 0.0	

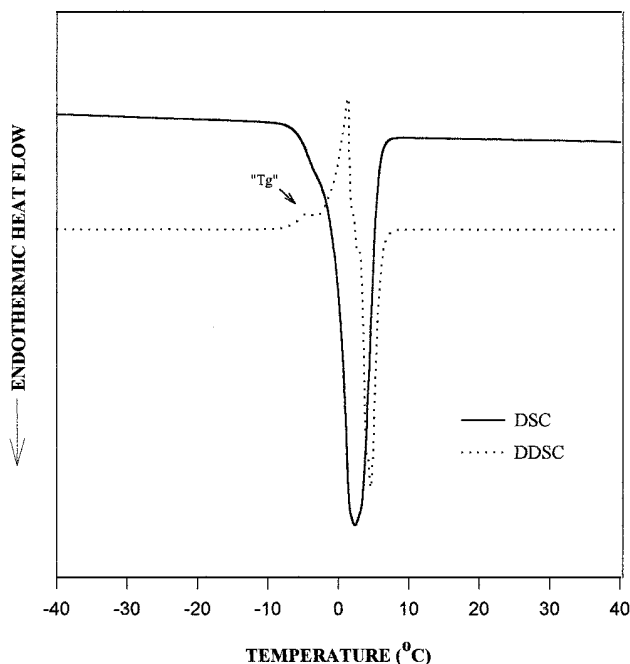


Fig. 4. Typical ice melting endotherm of gelatinized rice starch.

not annealed to obtain a maximally freeze-concentrated dispersion. It was expected that the presence of bulky groups or cross-links between chains should decrease chain mobility and increase  $T_g$  (Armeniades and Baer 1977). Additionally,  $T_g$  of rice starch gel has been reported to increase with increasing time and degree of starch recrystallization (Huang et al 1994, Baik et al 1997). The trend of  $T_g$  increase was small ( $<1^\circ\text{C}$ ) and statistically insignificant ( $P < 0.05$ ) observed with the progressive increase in degree of recrystallization with time. Although the sample remained unchanged in total moisture content, aging of starch gels could lead to an increase in more mature network expelling water from local amorphous regions and increasing  $T_g$ . Without further evidence on a local or molecular level, this remains only speculation.

All aging samples were further analyzed by dynamic mechanical analysis (data not shown). The  $T_g$  transition was also observed but showed no frequency dependence normally expected in a glass transition of a polymer (Kalichevsky 1993). In some cases, such as wheat starch at lower moisture content, this transition showed behavior (frequency dependence) similar to that of a glass transition (Vodovotz and Chinachoti 1998). In this work, for rice starch at 67% moisture, the data were opposite. The  $T_g$  transition observed might not solely be a glass transition but rather a combination with a melting transition of some imperfect ice crystals that perhaps occurred simultaneously and thus overlap the glass transition.

## CONCLUSIONS

Introduction of phosphate groups by cross-linking reaction significantly shifted gelatinization of rice starch to a higher temperature but did not significantly affect enthalpy. Although dramatic effect on the melting of amylopectin was not detectable, physical structure changes in rice starch granules after gelatinization were more pronounced, that is, a gel network was formed in native and control samples while a paste structure was formed in highly cross-linked samples.

Recrystallization of rice starch was suppressed by cross-linking. The enthalpies of crystallization were 40% in native and control samples and 15–25% in highly cross-linked samples after 15 days of storage at  $4^\circ\text{C}$  compared with their original gelatinization enthalpies. However,  $T_g$  of gelatinized samples did not change significantly with degree of cross-linking or with storage time. It is im-

portant to keep in mind that the commercial sample used here may be subject to variation, and more investigation is necessary to confirm these results.

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