Some Characteristics of Hydroxypropylated and Cross-Linked Rice Starch

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ABSTRACT

Cereal Chem. 70(5):596–601

Rice starch was cross-linked with phosphorus oxychloride ($POCl_3$), hydroxypropylated with propylene oxide, and dual-modified with both reagents. The properties evaluated were: solubility in dimethyl sulfoxide, heat absorption during gelatinization, paste viscosity, and freeze-thaw stability. In addition, scanning electron microscopy was used to observe the morphology of the starch granules and their corresponding pastes. Cross-linking increased heat of gelatinization and shear stability, and it reduced solubility in dimethyl sulfoxide and freeze-thaw stability. Cross-linked starch exhibited a three-dimensional network structure under scanning electron microscopy. Opposite effects were found for hydroxypropylation. The hydroxypropylated starch paste had a planar structure. The procedure used to prepare dual-modified starches also affected the product properties. Cross-linking reduced the degree of subsequent hydroxypropylation, but hydroxypropylation increased the degree of subsequent cross-linking. The results indicate that hydroxypropylation of rice starch took place inside starch granules.

Rice is one of the major ingredients in Chinese foods. Starch is the predominant component of rice, and it contributes to rice product properties (Juliano 1985). Recently, some traditional rice foods have been prepared using canning, refrigeration, or other nontraditional processes. Native rice starch can not satisfy the needs of these newly developed processes. Chemical modification has improved the functional properties of starches, such as resistance to severe processing conditions or to cold and low-temperature storage conditions.

Cross-linking and substitution are two widely used methods for making modified starches. Cross-linked starch is more resistant to acid, heat, and shearing than is native starch (Wurzburg 1986). Therefore, cross-linked starch is suitable for canned food, surgical dusting powder, and other applications (Rutenberg and Solarek 1984). Hydroxypropylation is another method for making starch derivatives with improved properties for food applications. Tuschhoff (1986) proposed a mechanism for the reaction. The introduction of a hydroxypropyl group reduces the bond strength between starch molecules and, thereby, improves freeze-thaw or cold-storage stability. These modifications impart a desired texture property to the product.

Wu and Seib (1990) compared the paste properties of starch cross-linked by $POCl_3$ with those of hydroxypropylation in waxy barley starch. They pointed out that hydroxypropylation was more effective than acetylation in improving freeze-thaw stability. Inagaki and Seib (1992) added cross-linked waxy barley starches with varying degrees of cross-linking to white pan bread in place of wheat starch. They found that the swelling power of the cross-linked waxy barley starch declined as the level of cross-linking increased. Kim et al (1992) observed from light-microscopic photographs that native and hydroxypropylated potato starch granules were similar. Their work showed that the central region of the potato starch granule was the main site of hydroxypropylation. Hood et al (1974) pointed out that cross-linking occurred only in the outer region of the starch granule. The observations of Vihervaara et al (1990) about the structure of cationic potato starches were in agreement with the observations of Hood et al (1974). Jane et al (1992) found that more amylopectin than amylose molecules were cross-linked. However, it is very difficult to provide direct evidence of where the modification takes place.

For some traditional Chinese desserts prepared using new processes, starches with heat resistance and cold-storage stability are desirable. To meet these requirements, dual-modification is necessary. The objectives of this study were to evaluate, for future applications, the properties of rice starches after cross-linking and hydroxypropylation modification, including their paste properties.

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MATERIALS AND METHODS

Rice starch, isolated from Dutch variety, was purchased from Sigma Chemical Co. (St. Louis, MO). The amylose content was determined as 14.2% according to the method of Juliano et al (1981).

Cross-linking of rice starch was done with phosphorus oxychloride ($POCl_3$) in aqueous alkali (pH 10.5) containing sodium sulfate (Na_2SO_4, 5% based on dry weight of starch) as described by Wu and Seib (1990). The concentration of starch in the slurry was 35%. The concentration of $POCl_3$ was 0.1%, based on the dry weight of starch. Reaction temperature was maintained at 35°C. Samples were taken after reaction periods of 15, 30, 60, and 120 min. The samples were then neutralized using $1N$ HCl to terminate the reaction and washed with distilled water before drying at 40°C in a vacuum oven.

Hydroxypropylation of rice starch was done with propylene oxide at 25°C as described by Kesler and Hjermstad (1964). A jar-fermentor (model KMJ-2A, Mituwa, Japan) was used as the reactor. First, 20 g of 30% NaOH and 140 g of 26% NaCl were added to a starch slurry containing 40% starch. Then the solution was fed into the reactor. Propylene oxide (4 and 5%, based on dry weight of starch) was added to the solution. The reaction proceeded for 24 hr. It was terminated by adjusting the pH to 5.0 using $1N$ HCl. (See Table I.)

Degree of Substitution in Cross-Linking

The degree of substitution in cross-linking was analyzed according to Koch et al (1982). The starches were acidified to form H-starch using $0.1N$ HCl. Sodium ions bound to phosphate groups were replaced by hydrogen ions during acidification. H-starch was washed with distilled water and dried in a vacuum oven

TABLE I
Abbreviations for Native and Modified Rice Starches

Starch	Reaction Time	Abbreviation
Native rice starch		NR
Modified starch		
Cross-linked (DS × 10^{-4})		
3.66	120 min	X366
3.51	60 min	X351
3.22	30 min	X322
2.86	15 min	X286
Hydroxypropylated		
Propylene oxide, 5%[a]	24 hr	Hop5
Propylene oxide, 4%	24 hr	Hop4
Cross-linked—hydroxypropylated		
X351 reacted with 5% propylene oxide	24 hr	DX351-H5
X351 reacted with 4% propylene oxide	24 hr	DX351-H4
Hydroxypropylated—cross-linked		
Hop5 cross-linked with 0.1% $POCl_3$	120 min	DH5-X
Hop4 cross-linked with 0.1% $POCl_3$	120 min	DH4-X

[a]The percentage of propylene oxide was based on dry starch weight.

at 40°C. The dried H-starch was then titrated with $0.01N$ NaOH. The degree of substitution was calculated using the method of Rutenberg and Solarek (1984). The result is also included in Table I.

Molar Substitution for Hydroxypropylation

The hydroxypropyl content was determined using a spectrophotometric method (FAO 1983). Hydroxypropylated starch was heated with $1N$ H_2SO_4. The absorbance was measured at 590 nm after reacting with ninhydrin reagent. The content of hydroxypropyl groups was obtained. Molar substitution was calculated using the method of Rutenberg and Solarek (1984).

Solubility in Dimethyl Sulfoxide

The solubilities of the native and modified starches in anhydrous dimethyl sulfoxide (DMSO) were measured using the method of Leach and Schoch (1962). Native or modified starch (0.5 g, db) was suspended in 100 ml of anhydrous DMSO in four 250-ml centrifuge bottles. The bottles were closed with rubber stoppers and placed horizontally in a reciprocating shaker. The shaking was sufficient to keep starch granules continually suspended. After specified shaking times (4, 8, 16, and 24 hr), each bottle was removed and centrifuged (10,000 $\times$ g for 15 min). In all cases, a well-defined sedimentation of undissolved substance (either granular or swollen) left a clear supernatant. A 50-ml aliquot of the latter was removed by pipet and added to 150 ml of methanol with vigorous stirring. The mixture was heated in a steam bath for 20 min and then allowed to stand overnight. The heat treatment was repeated twice. The precipitated starch (A) was obtained by filtering the mixture on a medium-porosity, tared, fritted pyrex crucible that was thoroughly prewashed with methanol and dried in a vacuum oven for 4 hr at 120°C. The solubility calculation was:

$$\% \text{ solubility} = \text{wt. of A}/0.25 \times 100$$

Differential Scanning Calorimetry

The gelatinization temperature, heat of gelatinization, and glass transition temperature during starch gelatinization were determined using a differential scanning calorimeter (Setaram DSC121, Setaram Co., France) equipped with a liquid-nitrogen intercooler. About 120 mg of starch solution (20% starch, 80% distilled water) was hermetically sealed in a stainless steel crucible. The scanning temperature was increased from 40 to 110°C at 5°C/min. The data was analyzed using a differential scanning calorimetry (DSC) data-analysis system provided by Setaram.

Paste Viscosity

The viscosity of starch paste was measured using a Brabender Viscograph-E (C. W. Brabender Instruments, Hackensack, NJ). The torque was 700 cm·g, and the rotation speed was set at 75 rpm. Starch solution containing 8% solids was heated from 45 to 95°C, held at 95°C for another 60 min, and then cooled to 45°C. The heating and cooling rate was 3°C/min.

Freeze-Thaw Stability

The method reported by Wu and Seib (1990) was modified to conduct these tests. A starch solution (8% starch) was adjusted to pH 6 and heated at 95°C for 30 min. After cooling to room temperature, the paste was centrifuged (1,500 $\times$ g for 15 min). The supernatant (free water) was decanted. The remainder was frozen at −30°C for 24 hr and then thawed in a water bath at 30°C for 1 hr. The sample was centrifuged at 1,500 $\times$ g for 15 min. The weight of the supernatant (separated water) was determined. The percentage of separated water was the ratio of the weight of the separated water to the weight of the paste. In this study, 20 freeze-thaw cycles were conducted.

Scanning Electron Microscopy (SEM)

Unheated starch solution or heated starch paste (8% starch) was freeze-dried to a moisture content of less than 5%. Two heating conditions were used: 60°C for 30 min and 90°C for 30 min. Samples were sprinkled onto double-backed cellophane tape

attached to an SEM stub. The stub and samples were coated with gold-palladium, examined using a scanning electron microscope (Hitachi 5-550, 20 kV, Japan), and photographed. All chemicals used were reagent grade.

RESULTS AND DISCUSSION

Solubility of Starches in DMSO

Leach and Schoch (1962) pointed out that the solubility of starch in DMSO can be an index of granular structure. Figure 1 shows the solubilities of native, cross-linked, and hydroxypropylated rice starches in DMSO. The solubility of native rice starch increased linearly with time. Cross-linking seemed to enhance the bonding between starch molecules and retain the integrity of starch granules. Thus, the solubilities of cross-linked starches (X351, X366) were reduced compared to that of native starch. However, two hydroxypropylated starches (Hop5 and Hop4) dissolved more in DMSO. Initially, the dissolution occurred rapidly; more than 80% starch dissolved in 8 hr. After that, the dissolution became slower. More than 95% of the hydroxypropylated starches were dissolved in 24 hr. The results are in agreement with Leach and Schoch (1962).

DSC Analysis

Figure 2 is a typical thermogram from DSC analysis. It is very similar to that reported by Biliaderis et al (1986) on rice starch. In Figure 2, onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and glass transition temperature (T_g) are shown. The corresponding heat of gelatinization (ΔH) was calculated. Biliaderis (1990) reported that T_g was about 68°C for rice starch when water content was higher than 30%. Levine and Slade (1992) found that T_g increased with molecular weight for a homologous series of amorphous linear polymers.

Native, cross-linked, hydroxypropylated, and dual-modified starches exhibited similar profiles on the DSC thermograms. Table II lists the values of T_g, T_o, T_p, T_c, and ΔH. Hydroxypropylation loosened the granular structure and thus lowered T_g, T_p, and ΔH. Hop5 had lower T_g, T_p, and ΔH than either Hop4 or native starch because of the higher level of hydroxypropylation achieved. This result is in agreement with the report of Wootton and Bamunuarachchi (1979).

The formation of cross-linkages retains the integrity of starch granules. Thus, more heat was needed for gelatinization (Rutenberg and Solarek 1984). ΔH increased with the degree of cross-linking in X322, X351, and X366 (Table II). However, T_g and T_p were not significantly affected. Starch granules could have been swollen or damaged due to alkali treatment or heating at 35°C during the cross-linking preparation. The degree of cross-linkage was low (on the order of 10^{-4}) in this investigation. Thus, the cross-linking did not significantly affect T_g and T_p. This is
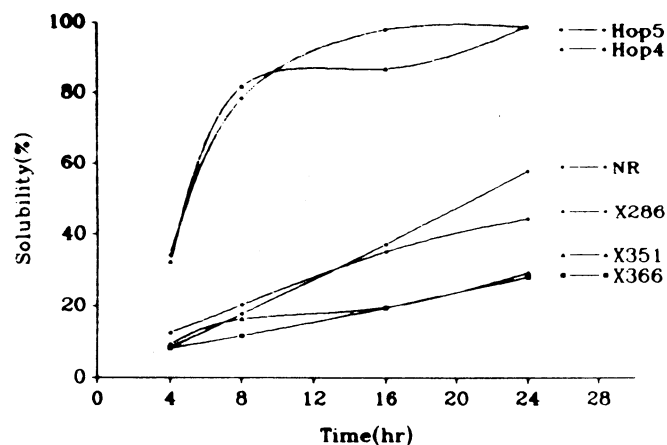

Fig. 1. Solubilities of starches in dimethyl sulfoxide. Starches include native rice starch (NR), cross-linked starches (X351, X366), and hydroxypropylated starches (Hop5, Hop4).

similar to the observation by Wootton and Bamunuarachchi (1979).

T_g is characteristic of a specified polymer (Levine and Slade 1992). Hydroxypropylation lowered T_g by 4–5°C (Table II). These results indicate that the structure of the amorphous region in the starch granule had been altered. This is another implication that hydroxypropylation had taken place inside starch granules. Cross-linking lowered T_g by only about 1°C. Thus, it is very difficult to verify where the cross-linking occurred. T_o and T_c were lowered by both modifications in a pattern similar to those of T_g and T_p.

Paste Viscosity

Figure 3 shows the Brabender amylographs of native and selected modified starches. Native rice starch started yielding viscosity at 71.4°C. They reached a peak viscosity (600 Brabender units [BU]) at 84.6°C. The viscosity decreased during holding at 95°C. Cross-linked starch (X351) possessed higher viscosity than that of native starch after reaching peak viscosity at 800 BU. Hydroxypropylated starch (Hop4) exhibited behavior different from that of cross-linked starch. It showed a slightly

higher peak viscosity (690 BU) than that of the native starch, but it was much less stable. Dual-modification resulted in starches with higher peak viscosity (about 700 BU) and more stability than that of native starch.

Stability value and average slope from the amylographs were used to quantify this stability comparison. Stability value was the viscosity difference between peak viscosity and the viscosity after 60 min of holding at 95°C (Wu and Seib 1990). Average slope was the mean slope of the viscosity curve during holding at 95°C. The lower the absolute value of stability, the more stable the starch paste was to shearing exerted by the agitator in the Brabender Viscograph. The higher the absolute value of the average slope, the more the viscosity dropped, and the less stable the starch paste was. Table III compares the values of stability and average slope from different starches. Table III also lists temperatures of initial pasting and peak viscosity. The variation of initial pasting temperature between different starches was only 2°C. Cross-linking raised the peak viscosity temperature (T_{pv}), whereas hydroxypropylation caused the drop of T_{pv}. Cross-linking increased the stability of paste from −300 to −200 BU for X351 during holding at 95°C. Hydroxypropylation had an opposite

TABLE II
Differential Scanning Calorimetry Temperatures (°C)[a] and Enthalpy (ΔH) of Native and Modified Rice Starches

Starch[b]	T_g[b]	T_o	T_p	T_c	ΔH (J/g)
NR	69.5	71.3	79.2	86.4	−10.40
X366	68.4	70.2	78.7	86.9	−13.45
X351	68.1	70.0	78.5	86.4	−12.80
X322	68.2	69.9	78.4	86.2	−10.95
Hop5	64.2	64.5	74.9	83.1	−8.20
Hop4	65.4	67.5	75.7	82.9	−9.40
DX351-H5	65.6	67.1	76.0	83.3	−10.55
DX351-H4	66.8	67.2	76.6	84.4	−11.35
DH5-X	64.2	63.9	74.8	83.4	−10.95
DH4-X	68.4	69.2	78.4	87.5	−12.35

[a] T_g = glass transition, T_o = onset, T_p = peak, T_c = conclusion.
[b] See Table I for abbreviations.

TABLE III
Brabender Amylograph Analysis

| Starch[a]	Temperature (°C)		Stability[d] at 95°C (BU)	Average[e] Slope at 95°C
	T_i[b]	T_{pv}[c]		
NR	71.4	84.6	−300	−0.1
X351	71.4	87.0	−200	−0.0
Hop5	69.0	78.6	−370	−0.19
Hop4	69.0	81.0	−425	−0.15
DH4-X	69.0	81.0	−325	−0.06
DX351-H4	69.0	83.4	−220	−0.06
DX351-H5	69.0	85.8	−150	−0.0

[a] See Table I for abbreviations.
[b] T_i = initial pasting temperature.
[c] T_{pv} = temperature at peak viscosity.
[d] Viscosity after holding at 95°C for 60 min − peak viscosity. BU = Brabender units.
[e] Average slope of viscosity curve at 95°C holding.
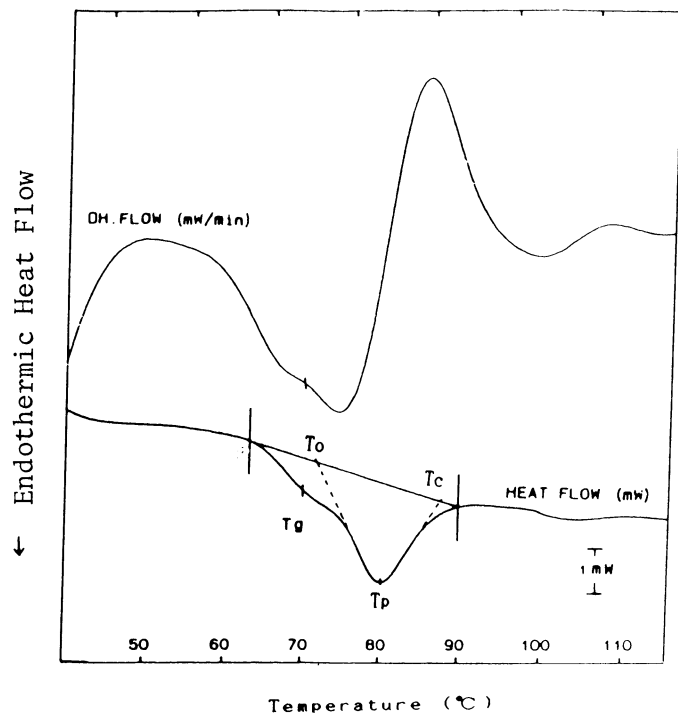
Fig. 2. Typical differential scanning calorimetry thermogram of rice starch. DH = first derivative of heat flow. T_o = onset temperature, T_g = glass transition temperature, T_p = peak temperature, T_c = conclusion temperature.
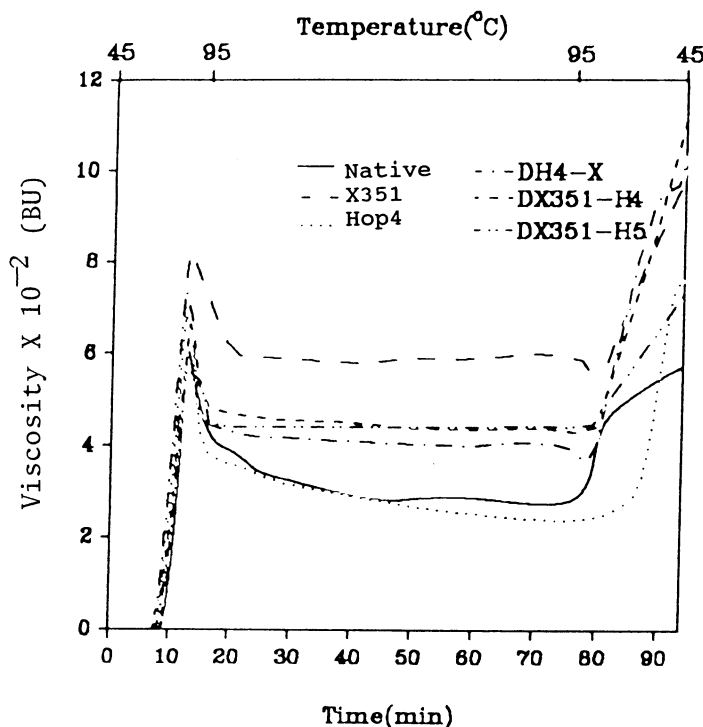
Fig. 3. Amylographs of native, cross-linked (X351), hydroxypropylated (Hop4), and dual-modified starches (DH4-X, DX351-H4, DX351-H5).

effect. This phenomenon was also observed in the changes of average slope values. The average slope for cross-linked starch was nearly zero, which was lower than that of native starch.

The data in Table III show that cross-linking done after hydroxypropylation raises the stability. But a dual-modified starch (such as DH4-X) is still much less stable than cross-linked starch (X351). However, hydroxypropylation done after cross-linking (i.e., DX351-H4 and DX351-H5) did not reduce the stability. This indicates that hydroxypropylation did not reduce the heat and shearing resistance exerted by cross-linking.

The effect of dual-modification depended upon the preparation procedure. Cross-linking followed by hydroxpropylation yielded starches (DX351-H4 and DX351-H5) that were more stable than native starch. However, when the hydroxypropylation was conducted first, the resulting starch (DH4-X) tended to be less stable than native starch. This may be due to the structural change of starch granules after the first modification. Thus, the degree of substitution in the second modification was affected. These interaction effects are illustrated in Figures 4 and 5. Figure 4 shows the effect of cross-linking on hydroxypropylation. Molar substitutions higher than 0.03 were obtained for Hop5 and Hop4 using native starch as the starting material. However, it was very difficult to achieve hydroxypropylation using cross-linked starch (X351). The molar substitution obtained was less than 0.005. Cross-linking enhanced the bonding between starch molecules and inhibited the reaction between starch molecules and propylene oxide. Therefore, the degree of hydroxypropylation was greatly reduced. Oppositely, hydroxypropylation enhanced cross-linking as shown in Figure 5. The enhancing effect depended on the degree of hydroxypropylation. The higher the degree of hydroxy-

propylation, the more cross-linking occurred. Hydroxypropylation loosened the bonding between starch molecules, and more $POCl_3$ could react with starch molecules. This is another indication that hydroxypropylation takes place inside starch granules.

Freeze-Thaw Stability

The resistance to freeze-thaw cycles depended on the variety of starch used. Juliano (1985) reported that the amylopectin in nonwaxy rice starch did not show syneresis in three to five freeze-thaw cycles. The amylopectin in waxy rice starch was stable for eight to 14 cycles. Schoch (1967) found that waxy rice starch was very stable at over 22 freeze-thaw cycles. However, barley and corn starch showed syneresis in one or two cycles (Wu and Seib 1990). Figure 6 shows the percentages of separated water from three starches during 20 freeze-thaw cycles. Although cross-linking enhanced the shearing stability of paste, it reduced the resistance to freeze-thaw cycles. After six cycles, cross-linked starch (X351) yielded more than 40% separated water. Native starch started yielding separated water after 11 cycles. After 20 cycles, hydroxypropylated starches not shown in the figure (Hop5, Hop4, DH5-X, and DH4-X) did not yield any separated water and were more freeze-thaw stable. Also, the dual-modified starch (DX351-H4) was more resistant to freeze-thaw cycles than was cross-linked starch (X-351), due to the added hydroxypropylation.

As discussed here, hydroxypropylation (done after cross-linking) did not reduce the heat and shearing resistance exerted by cross-linking. Figure 6 shows that hydroxypropylation could improve the freeze-thaw stability of cross-linked starch. Therefore, dual-modification (cross-linking first, followed by hydroxypropylation) could meet both requirements of heat resistance and cold-storage stability.
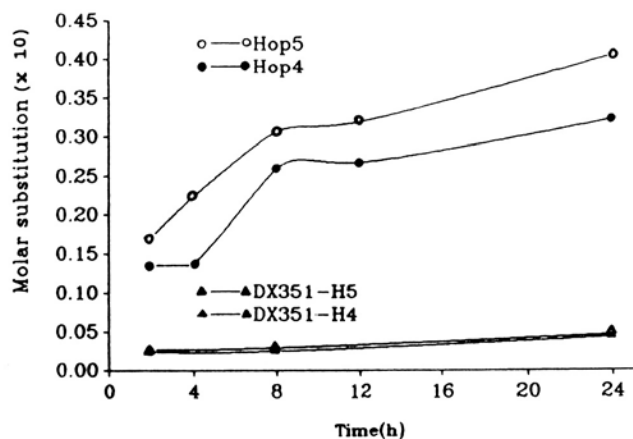

Fig. 4. Variation of molar substitution during the etherification of native and cross-linked starches. DX351-H4 and DX351-H5, dual-modified starches. Hop5 and Hop4, hydroxypropylated starches.
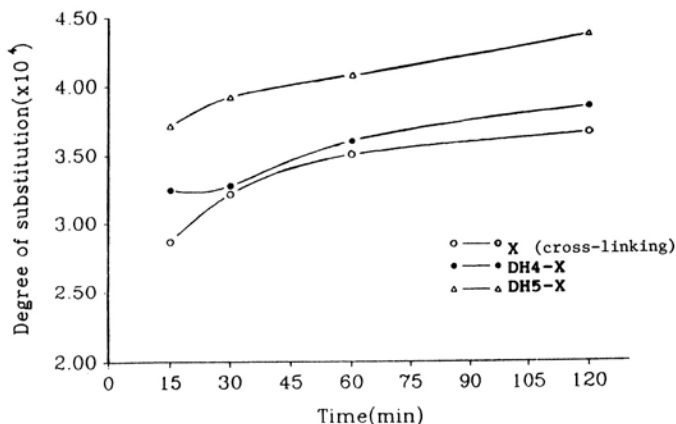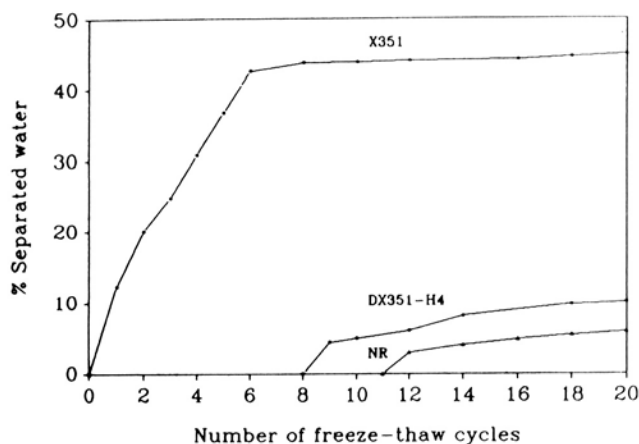

Fig. 6. Percentages of separated water during freeze-thaw cycles for native (NR), cross-linked (X351), and dual-modified (DX351-H4) starches.

Fig. 5. Variation of degree of substitution during cross-linking of native and hydroxypropylated starches (DH4-X and DH5-X).
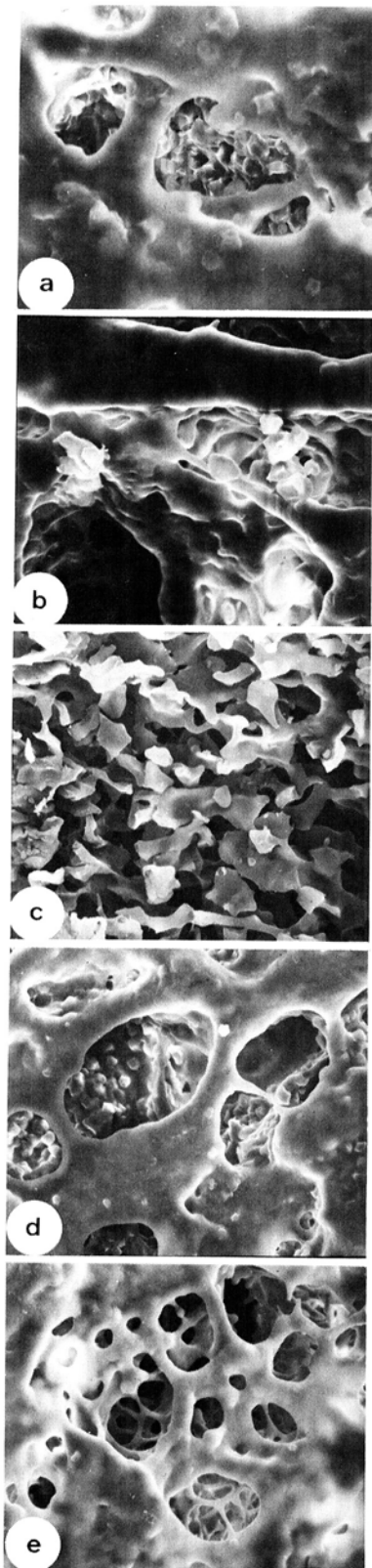

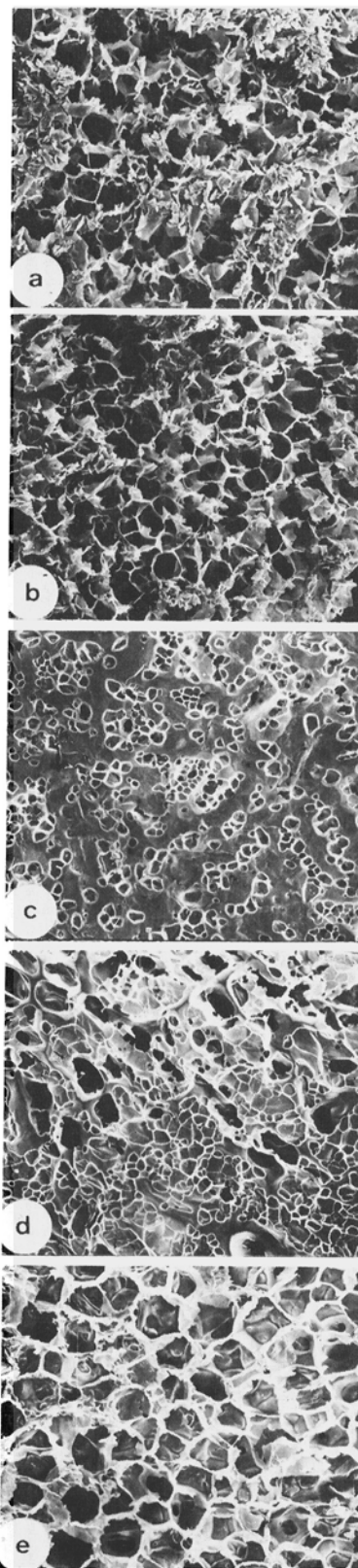Fig. 7. Scanning electron micrograph of native rice starch.

SEM

Using SEM, Williams and Bowler (1982) observed the swelling of starches during gelatinization. They found some planar swelling and some three-dimensional swelling. The type of swelling depended on the variety of starch. Varriano-Marston et al (1985)

pointed out that the preparation method affected the morphology of starch granules. Figure 7 shows the native starch granules under SEM. Modification did not noticeably change the appearance or size of starch granules as shown in this figure. However, the morphology of some starch pastes was altered. Figure 8 shows

Fig. 8. Scanning electron micrographs for different starch pastes heated at 60°C, 30 min. a, native starch. b, cross-linked starch (X351). c, hydroxypropylated starch (Hop5). d, dual-modified starch (DX351-H4). e, dual-modified starch (DH5-X).

Fig. 9. Scanning electron micrograph of different starch pastes heated at 90°C, 30 min. a, native starch. b, cross-linked starch (X351). c, hydroxypropylated starch (Hop5). d, dual-modified starch (DX351-H4). e, dual-modified starch (DH5-X).

the morphology of starch pastes heated at 60°C for 30 min. Native, cross-linked (X351), and dual-modified (DX351-H4) starches exhibited similar network structures with some intact starch granules. Hydroxypropylated starch (Hop5) did not show any network structures, but did show a planar structure (Fig. 8c). Dual-modified starch (DH5-X), however, exhibited a very good network structure. After heating 30 min at 90°C, no intact starch granules were observed in any SEM photographs (Fig. 9). Because hydroxypropylation alone tended to make a paste with a planar structure, and because cross-linking could enhance the three-dimensional network of a paste, the posttreatment cross-linking of Hop5 would restore its network structure, as observed for DH5-X.

The network structure is necessary for good texture (e.g., elasticity), which is especially desirable in some traditional Chinese desserts. SEM showed that a dual-modified rice starch (such as DX351-H4) exhibited the network structure. The combined information of viscosity stability, freeze-thaw stability, and SEM observation, indicated that a dual-modification (cross-linking first, followed by hydroxypropylation) was suitable for producing starches when both heat resistance and cold-storage stability are needed.

CONCLUSION

The results of this study indicate that hydroxypropylation of rice starch takes place inside starch granules. Cross-linking enhances the bonding of starch molecules and retains the integrity of starch granules. Thus, more heat of gelatinization is required by cross-linking, and the network structure of the paste is enhanced. Hydroxypropylation loosens the structure of starch granules, requiring less heat of gelatinization. The paste shows a planar structure. The preparation procedure for dual-modified starch affects the product properties. Cross-linking reduces the degree of subsequent hydroxypropylation, and hydroxypropylation increases the degree of subsequent cross-linking.

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