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Preparation of clear noodles with mixtures of tapioca and high-amylose starches[1]

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Abstract

Ways to simulate the making of clear noodles from mung bran starch were investigated by studying the molecular structures of mung bean and tapioca starches. Scanning electron micrographs showed that tapioca starch granules were smaller than those of mung bean starch. X-ray diffraction patterns of mung bean and tapioca starch were A- and C_A-patterns, respectively. Iodine affinity studies indicated that mung bean starch contained 37% of apparent amylose and tapioca starch contained 24%. Gel permeation chromatograms showed that mung bean amylopectin had longer peak chain-length of long-branch chains (DP 40) than that of tapioca starch (DP 35) but shorter peak chain-length of short-branch chains (DP 16) than that of tapioca starch (DP 21). P-31 n.m.r. spectroscopy showed that both starches contained phosphate monoesters, but only mung bean starch contained phospholipids. Physical properties, including pasting viscosity, gel strength, and thermal properties (gelatinization), were determined. The results of the molecular structure study and physical properties were used to develop acceptable products using mixtures of cross-linked tapioca and high-amylose maize starches. Tapioca starch was cross-linked by sodium trimetaphosphate (STMP) with various reaction times, pH values, and temperatures. The correlation between those parameters and the pasting viscosity were studied using a visco/amylograph. Starches, cross-linked with 0.1% STMP, pH 11.0, 3.5 h reaction time at 25, 35, and 45°C (reaction temperature), were used for making noodles. High-amylose maize starch (70% amylose) was mixed at varying ratios (9, 13, 17, 28, 37, and 44%) with the cross-linked tapioca starches. Analysis of the noodles included: tensile strength, water absorption, and soluble loss. Noodle sensory properties were evaluated using trained panelists. Noodles made from a mixture of cross-linked tapioca starch and 17% of a high-amylose starch were comparable to the clear noodles made from mung bean starch. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Mung bean; Starch noodle; Clear noodle; Mung bean starch; Tapioca starch; High-amylose maize starch; Starch structures

1. Introduction

Clear noodles made from mung bean starch are popular in Oriental food. The noodles are uniquely translucent and resilient after cooking and have a bland taste (Chiu and Chua, 1989). The clear noodles are expensive compared with other types of noodles because mung bean starch is expensive as a result of its low production supply and tedious processing methods (Zhu et al., 1990; Haase et al., 1991). The molecular structure of mung bean starch and its contribution to noodle quality have been previously reported (Mestres et al., 1988; Singh et al., 1989; Oates, 1990; Xu and Seib, 1993). Research has been conducted to produce clear noodles with other starches such as canna, red bean, sweet potato, pigeonpea, and modified starches (Lii and Chang, 1981; Chiu and Chua, 1989; Singh et al., 1989). Noodles prepared from unmodified tapioca starch were too soft and not acceptable as replacements for mung bean starch noodles (Chiu and Chua, 1989). Tapioca starch is a good candidate to manufacture clear noodles because of its low cost and the clarity of its starch paste.

The relation between starch structure and physical properties has been partly understood, such as high-amylose starch providing strong gel-strength (Hullinger et al., 1973) and the effect of amylose molecular size and amylopectin branch-chain length on paste properties (Jane and Chen, 1992). Characterization of the molecular structures and the physical properties of mung bean starch and tapioca starch could provide information necessary for revealing the relation between the starch molecular structure and noodle quality.

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The purposes of this study were: (1) to investigate and compare the molecular structures and the physical properties of mung bean starch and tapioca starch; and (2) to simulate physical properties of mung bean starch by using a mixture of chemically modified tapioca starch and high-amylose maize starch to make clear noodles.

2. Materials and methods

2.1. Materials

Tapioca and high-amylose maize starches were donated by National Starch and Chemical Company (Bridgewater, NJ). Mung bean starch was purchased from Srithinun Company (Bangkok, Thailand). All the chemicals were reagent grade and used without further treatment. Crystalline *Pseudomonas* isoamylase (EC 3.2.1.68) was purchased from Hayashibara Shoji, Inc. (Okayama, Japan).

2.2. Starch structure analyses

Scanning electron microscopy (SEM) followed the Jane et al. (1994) method. The micrographs were obtained with a JEOL JSM-35 scanning electron microscopy. X-ray diffraction patterns of starches were obtained with an X-ray diffractometer (D-500, Siemens, Madison, WI) following the method of Jane et al. (1992).

Apparent amylose contents were calculated from iodine affinities determined (after the starch was defatted with methanol for 24 h) by potentiometric titration (Schoch, 1964) using a potentiometric autotitrator (702 SM Titrino, Brinkmann Instruments, Westbury, NY). Absolute amylose contents were calculated following the Kasemsuwan et al. (1995) method. Analysis was replicated at least three times.

Molecular size distributions were determined by Sepharose CL-2B gel (Pharmacia LKB, Uppsala, Sweden) permeation chromatography (GPC), following the method of Jane and Chen (1992). Molecular size distributions were determined on the basis of total carbohydrate (anthrone–sulfuric acid reaction) measured at 630 nm. Blue values were used to identify locations of amylose and amylopectin in the chromatograms (measured at 640 nm). The chromatograms were done in duplicate.

Amylose was separated from amylopectin using the method of Schoch (1942) and Jane and Chen (1992). The amylopectin fraction was purified by recrystallization for at least four times to remove amylose residues. The amylopectin was debranched by isoamylase, following the method of Jane and Chen (1992). The amylopectin branch-chain length distributions were determined by Bio-gel P-6 (Bio-Rad Laboratories, Hercules, CA) gel permeation chromatography. Peak chain-lengths were also analyzed by following the Jane and Chen (1992) and Kasemsuwan et al. (1995) methods. Phosphorus structures and contents were determined by using P-31 n.m.r. spectroscopy (Bruker AC200, USA Bruker Instruments, Billerica) following the method of Kasemsuwan et al. (1995).

2.3. Starch physical properties analyses

Viscosity and pasting properties of starches were determined by using a visco/amylograph (model VA-5, 700 cm-g, Brabender, Hackensack, NJ), following the methods of Smith (1964) and Kasemsuwan and Jane (1994). The amylograms were replicated at least twice.

Gel strength was measured with a Voland texture analyzer (model TA, Scarsdale, NY) following the method of Takahashi et al. (1989). The starch paste (8%, from the visco/amylograph) was stored at 5°C for 24 h before analysis. A 2 mm diameter probe and a 3 mm distance of penetration were used throughout the analysis. The measurement was replicated 10 times.

Gel strength of the paste of modified tapioca starch and high-amylose starch (70% amylose content) mixture at the same ratios as that in the noodles was determined. The paste (10%, dry starch base, dsb) of the starch mixture was prepared by mixing the amylograph-cooked, modified tapioca starch with pressure reactor-cooked high-amylose starch, as described in noodle preparation. The gel strength was measured by using the same method as previously described.

Thermal properties of starches were determined following the methods of Wang et al. (1992) and Kasemsuwan et al. (1995). Gelatinization properties of starches were analyzed by using a Perkin-Elmer DSC-7 analyzer equipped with an Intra-Cooling II system and a thermal analysis data station (Perkin-Elmer Corp., Norwalk, CT). Onset temperature, peak temperature, temperature range, and enthalpy change were computed automatically; thermal analyses were repeated at least three times.

2.4. Starch cross-linking with sodium trimetaphosphate (STMP)

Tapioca starch (200 g, dsb) was suspended in distilled water (400 g). Sodium sulfate (4 g) was added into the starch slurry, and the slurry was adjusted to a designated pH (11.0 or 11.5) with 4.0 M NaOH. STMP (0.2 g in 5 ml of distilled water) was slowly added to the slurry. The mixture was mechanically stirred, and the pH was controlled by using a pH controller (Chemcadet, Cole Parmer Instrument Company, Chicago, IL). Temperature was controlled by using a water-bath at a designated temperature (25, 35, or 45°C). After a selected reaction time (1.5, 2.5, or 3.5 h), the slurry mixture was adjusted to pH 5.5 to stop the reaction. The treated starch was washed three times with distilled water and dried in a forced-air oven at 40°C. Cross-linked starches were analyzed by using the visco/amylograph to determine pasting temperature, peak viscosity, viscosity after shear-thinning, set-back viscosity (at 50°C), and gel strength.

Table 1
Comparison of the molecular structures between tapioca starch and mung bean starch

	Tapioca starch	Mung bean starch
Granular diameter (μm)	5–20	10–21
X-ray diffraction pattern	C_A-type	A-type
Apparent amylose[a] content (%)	24.3 ± 1.8	37.0 ± 0.5
(Iodine affinity)[a]	(4.9 ± 0.4)	(7.4 ± 0.1)
Absolute amylose content[a,b] (%)	19.6 ± 0.7	30.7 ± 0.5
Total phosphorus content (%, dsb)	0.008	0.012
Phospholipids content (%, dsb)	N/D[c]	0.0033
Phosphate monoester (%, dsb)	0.0065	0.0083
Amylopectin peak		
Short chain-length[a]	21.4 ± 2.7	15.9 ± 3.5
Long chain-length[a]	35.4 ± 4.3	40.0 ± 2.8
Ratio (w/w) of amylopectin long-chain/short-chain	0.77:1.0	0.56:1.0

[a] Data were reported in means ± standard deviation

[b] Absolute amylose contents were calculated following Kasemsuwan et al. (1995) method

[c] Not detected

2.5. Statistic design and analysis

Experiments included the study of the effect of three treatment factors: pH (11.0 and 11.5), reaction time (1.5, 2.5, and 3.5 h), and reaction temperature (25, 35, and 45°C). All combinations of these factors were used, resulting in a total of 18 treatment combinations. A split-plot experimental design (Steel and Torrie, 1980) was chosen with temperatures randomly allocated to the whole-plot. A randomized complete block design was used for the whole-plot treatment, with two replications. Reaction time and pH treatment combinations were randomly allocated to each temperature. Analysis of variance was carried out for all dependent variables (paste temperature, peak viscosity, viscosity after shear-thinning, setback viscosity, and gel strength).

2.6. Noodle preparation

The process for making mung bean noodles involves mixing dry and gelatinized starch paste to form a thick slurry at 25°C, extruding it directly into boiling water to cook, cooling the cooked noodles in cold water, holding them at refrigerated or freezing temperatures, washing them in cold water, and drying the washed noodles (Lii and Chang, 1981; Chiu and Chua, 1989; Galvez et al., 1994). In this study, high-amylose maize starch (70% amylose content) was gelatinized in a pressure reactor (model 4522) with a controller (model 4843, Parr Instrument Company, Moline, IL). The high-amylose starch slurry (10, 15, or 20%, dsb) was first heated on a hot plate with continuous stirring for 10 min, and the heated slurry was transferred to the pressure reactor. The starch slurry (in the pressure reactor) was stirred at 100 r.p.m., heated to 150°C, and held at 150°C for 10 min. The slurry was then cooled to 90°C and held at 90°C for 1 h. The dry tapioca starch (200 g, dsb) and gelatinized high-amylose starch pastes (200, 400, 600, or 800 g starch paste weight) were mixed for 10 min by using a dough hook and kitchen mixer at speed 3 (Model K5SS, Kitchen Aid Mixer, St. Joseph, MI). The thick slurry was extruded, by using an extruder attachment with hole openings of 2 mm diameter (Model SNPA, Kitchen Aid, St. Joseph, MI), into boiling water containing a small amount (≈0.001%) of soybean oil. The noodles were cooked in the boiling water for selected times (10, 20, 30, 40, 50, and 60 s) and were immediately transferred into ice-cold water and held for about 5–10 min. The noodles were then hung on racks and placed in a cold room (5°C) for approximately 24 h. After this, they were transferred into water and soaked at

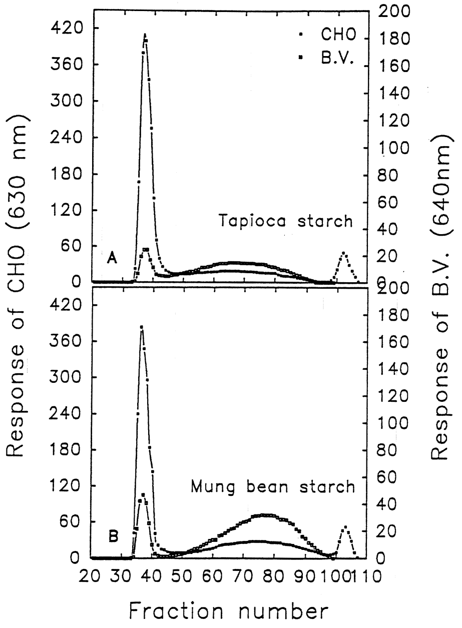

Fig. 1. Sepharose CL-2B column (2.6 I.D. × 90 cm) profiles of native starches: (A) tapioca starch, (B) mung bean starch. The column was eluted with 50 mM sodium chloride aqueous solution with 10 mM NaOH, and flow rate was 0.5 ml min^{-1}. Fractions (4.8 ml) were analyzed for total carbohydrate (anthrone–sulfuric acid procedure) (○) and blue value (amylose–iodine complex) (●). Glucose was used as the marker.

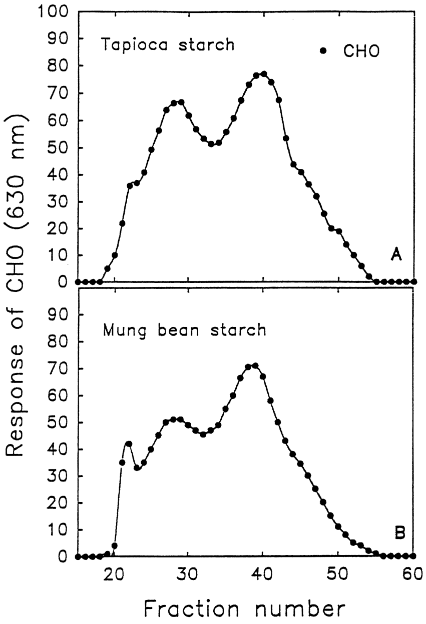

Fig. 2. Bio-Gel P-6 column (1.5 I.D. × 80 cm) profiles of debranched mylopectins: (A) tapioca starch, (B) mung bean starch. The column was eluted with distilled deionized water. Fractions (2.3 ml) were analyzed for total carbohydrate (anthrone–sulfuric acid procedure) (●). The first peak eluted at the void volume (peak fraction 22) represents very long chains (*B*3 and *B*4); the second peak (peak fractions 27–29) represents long chains (*B*2); and the third peak (peak fractions 39–40) represents short chains (*A* and *B*1).

(≈25°C for 24 h. Finally, they were air-dried on a rack at room temperature, and stored in plastic bags at room temperature.

2.7. Noodle analyses

2.7.1. Mechanical properties

The analyses followed the method of Lii and Chang (1981) with modification. The dried noodles were cut into 10–15 cm long segments. They were equilibrated for moisture content in a 54% RH humidity chamber (containing a saturated solution of calcium nitrate). Tensile strength was measured using an Instron Universal Testing System (UTM, model 4502) with a 100N load cell and pneumatic-action grips No. 2712-002 (Instron Corporation, Canton, MA). For each treatment, at least five specimens were tested (at a crosshead speed of 50 mm min^{-1} and a distance between the two grips of 50 mm), and the values were averaged.

2.7.2. Physical properties

Water absorption was determined following the method of Paetau et al. (1994) with modification. Noodles (approximately 2 g) were conditioned by drying in an oven at 110°C for 24 h and were then cooled in a desiccator and weighed. After this, the noodles were soaked in distilled water for 24 h at 25°C, surface water was wiped off, and the noodles were weighed. The 24 h water absorption was calculated as a percentage of the dry noodle weight.

Soluble loss was also determined following the method of Paetau et al. (1994) with modification. Noodles were weighed after soaking for 24 h and dried in the same manner (110°C, 24 h) before they were reweighed. The weight difference between before- and after-soaking was calculated as the percentage soluble loss of dry-weight noodles.

2.7.3. Sensory evaluation

Freshly cooked noodles were prepared by boiling them in water for 10 min and then cooling them in tap water (≈20°C). Products were evaluated by 10 trained panel members (the sensory properties were explained to the panel members before the evaluation) for firmness, chewiness, clarity, flavor, and general acceptability, using an unstructured 6 inch line-scale. Panelists tasted the noodles under red lights (to mask possible color differences). Noodles were evaluated in sets of five samples per plate and each set was replicated twice; scores of each characteristic were averaged.

3. Results and discussions

3.1. Scanning electron microscopy (SEM)

SEM micrographs of mung bean and tapioca starches indicated that mung bean starch granules were oval shaped with an indent in the middle, and the diameter ranged from 10 to 21 mm. Tapioca starch granules were irregularly shaped. The diameter ranged from 5 to 20 mm. SEM micrographs of the starches were reported by Jane et al. (1994). The diameter of tapioca starch was smaller than that of mung bean starch (Table 1).

3.2. X-ray diffraction pattern

The X-ray diffraction pattern of the mung bean starch showed an A-pattern, but that of tapioca starch showed a

Table 2
Comparison of the gelatinization property between tapioca starch and mung bean starch[a]

	Tapioca starch	Mung bean starch
Onset temperature, T_o (°C)	63.8 ± 0.2	68.0 ± 0.9
Gelatinization range, R (°C)	61.5 ± 0.8 to 82.2 ± 1.4	63.3 ± 0.1 to 85.5 ± 3.3
Gelatinization enthalpy, ΔH (cal g^{-1})	7.6 ± 0.3	8.0 ± 0.01

[a] Data were reported in means ± standard deviation

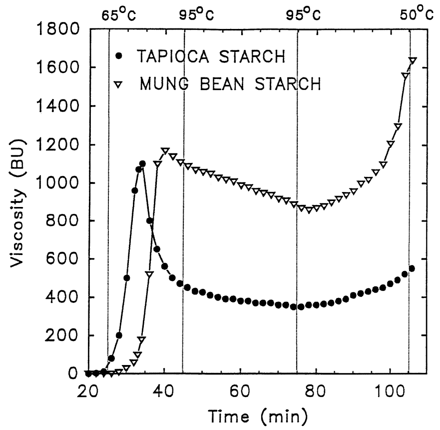

Fig. 3. Brabender amylogram of slurries (8% dsb) of mung bean starch (▽), tapioca starch (●).

C_A-pattern (Table 1). X-ray diffraction patterns also showed higher crystallinity of tapioca starch than that of mung bean starch which contained more amylose (Table 1).

3.3. Amylose contents

The potentiometric titration results showed that mung bean starch contained more apparent amylose (37.0%) than tapioca starch (24.3%, Table 1). Because long branch-chains of amylopectin bound significant iodine, which increased the apparent amylose content, the absolute amylose content needed to be determined. The absolute amylose content in mung bean starch was 30.7 ± 0.5%, significantly greater than that of tapioca starch (19.6 ± 0.7%) (Table 1). Tapioca starch showed less of a difference between the apparent amylose content and the absolute amylose content than mung bean starch. This could be attributed to mung bean starch having longer peak chain-length of long branch-chains than tapioca starch (DP 40 versus DP 35 at peak). The maximum extinction coefficient ($E_{\max}$) of the amylose–iodine complex is proportional to log DP of amylose up to DP 100 (Szejtli et al., 1967). Amylose is the most important factor affecting the starch gel-strength because of its prompt association and retrogradation and its interaction with lipids to form helical complex and with amylopectin to give strong gel networks (Jane and Chen, 1992).

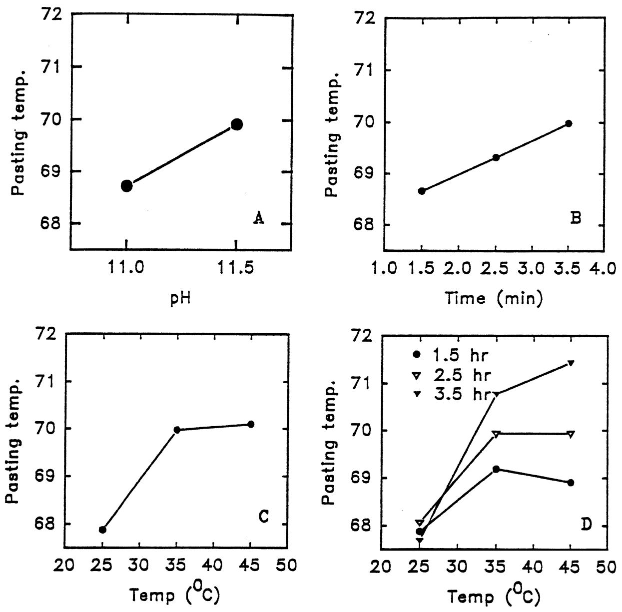

Fig. 4. Pasting temperatures of the modified tapioca starch (8%) were measured by using the visco/amylograph. (A) The effect of reaction pH (averaged over reaction times of 1.5, 2.5, and 3.5 h and reaction temperatures of 25, 35, and 45°C) on pasting temperature. (B) The effect of reaction time (averaged over reaction temperatures of 25, 35, and 45°C and pH values of 11.0 and 11.5) on pasting temperature. (C) The effect of reaction temperature (averaged over reaction times of 1.5, 2.5, and 3.5 h and pH values of 11.0 and 11.5) on pasting temperature. (D) The combined effect of reaction temperature and reaction time (average over pH values 11.0 and 11.5) on pasting temperature.

3.4. Gel permeation chromatography

The molecular-size distribution of starch molecules was determined by GPC. A chromatogram (Fig. 1) shows three

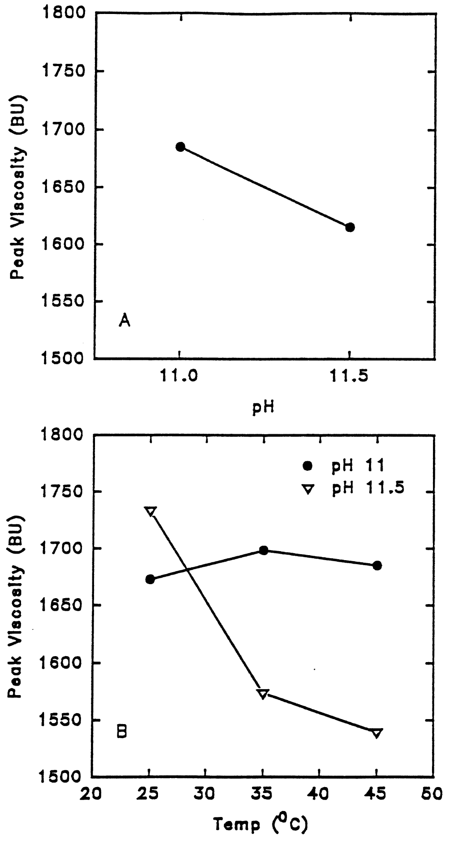

Fig. 5. Peak viscosity of the modified tapioca starch (8%) was measured by using the visco/amylograph. (A) The effect of reaction pH (averaged over reaction times of 1.5, 2.5, and 3.5 h and reaction temperatures of 25, 35, and 45°C) on peak viscosity. (B) The combined effect of reaction temperature and reaction pH (averaged over reaction times of 1.5, 2.5, and 3.5 h) on peak viscosity.

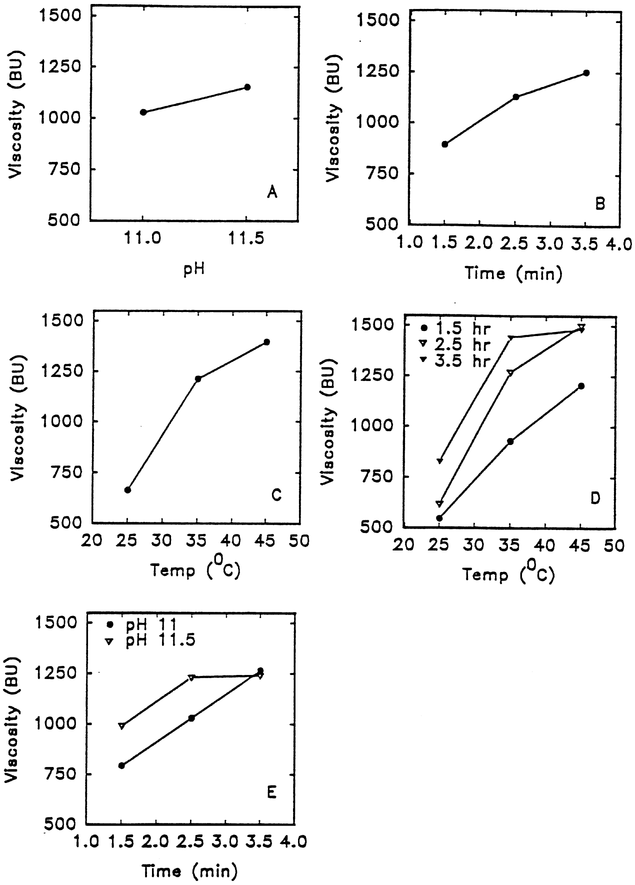

Fig. 6. Viscosity after shear thinning of the modified tapioca starch (8%) was measured by using the visco/amylograph. (A) The effect of reaction pH (averaged over reaction times of 1.5, 2.5, and 3.5 h and reaction temperatures of 25, 35, and 45°C) on shear viscosity. (B) The effect of reaction time (averaged over reaction temperatures of 25, 35, and 45°C and pH values of 11.0 and 11.5) on shear viscosity. (C) The effect of reaction temperature (averaged over reaction times of 1.5, 2.5, and 3.5 h and pH values of 11.0 and 11.5) on shear viscosity. (D) The combined effect of reaction temperature and reaction time (averaged over pH values 11.0 and 11.5) on shear viscosity. (E) The combined effect of reaction time and reaction pH (averaged over reaction temperatures of 25, 35, and 45°C) on shear viscosity.

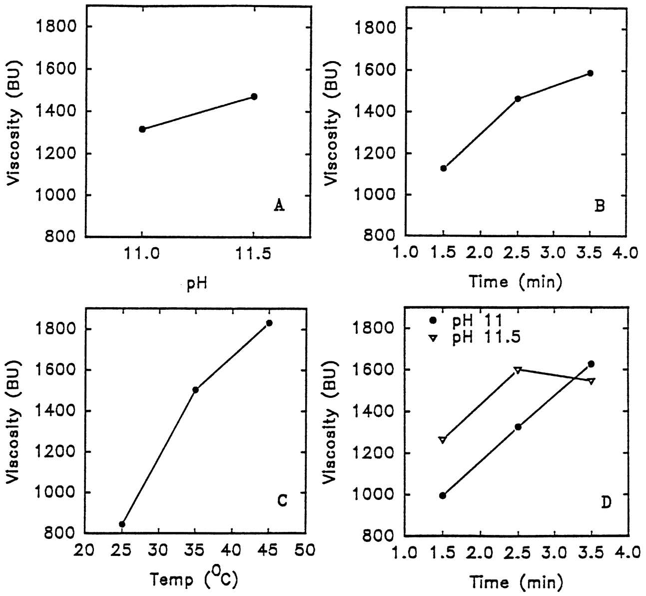

Fig. 7. Setback viscosities of the modified tapioca starch (8%) were measured by using the visco/amylograph. (A) The effect of reaction pH (averaged over reaction times of 1.5, 2.5, and 3.5 h and reaction temperatures of 25, 35, and 45°C) on the setback viscosity. (B) The effect of reaction time (averaged over reaction temperatures of 25, 35, and 45°C and pH values of 11.0 and 11.5) on setback viscosity. (C) The effect of reaction temperature (averaged over reaction times of 1.5, 2.5, and 3.5 h and pH values of 11.0 and 11.5) on setback viscosity. (D) The combined effect of reaction time and pH (averaged over reaction temperatures of 25, 35, and 45°C) on setback viscosity.

peaks: the first peak, eluted at the void volume, represents the amylopectin fraction; the second peak (broad peak) represents the amylose fraction; and the last peak is the glucose marker. The chromatogram also showed that mung bean starch contained smaller sized amylose than the tapioca starch; results agreed with those reported previously (Biliaderis et al., 1981; Takeda et al., 1987; Xu and Seib, 1993). The chromatograms showed no intermediate components in either starch.

3.5. Branch-chain length of amylopectin

Amylopectins were studied for their branch chain-length distribution (by GPC), chain lengths of the short and long branch-chains, and weight ratio between the long and short chains (Table 1). Chromatograms of debranched amylopectins isolated from both starches are shown in Fig. 2. They both contained more short chains (A and B1) than long chains (B2 and longer). The chromatogram of the debranched mung bean amylopectin also showed that it contained very long chains (possible B3, B4), which eluted out at the void volume. The chemical analysis indicated that the long chains of mung bean amylopectin (DP 40 at peak) were longer than that of tapioca starch (DP 35 at the peak), but the short chains of mung bean amylopectin (DP 16) were shorter than that of tapioca starch (DP 21). The ratio of long chains to short chains was greater in tapioca starch than in mung bean starch, indicating that tapioca starch contained more long chains than mung bean starch.

3.6. P-31 n.m.r. spectroscopy

P-31 n.m.r. spectra showed that mung bean starch contained more total phosphorus than tapioca starch (Kasemsuwan and Jane, 1996), and results are summarized in Table 1. The spectra also showed that mung bean starch contained phospholipids, whereas tapioca starch did not. The phospholipids in mung bean starch might affect the clarity of the starch paste. Tapioca starch paste was clearer than mung bean starch paste; however, both starches contained starch phosphate monoester, which enhanced the clarities and the viscosities of these starches. The repulsion of negatively charged phosphate groups in these starches

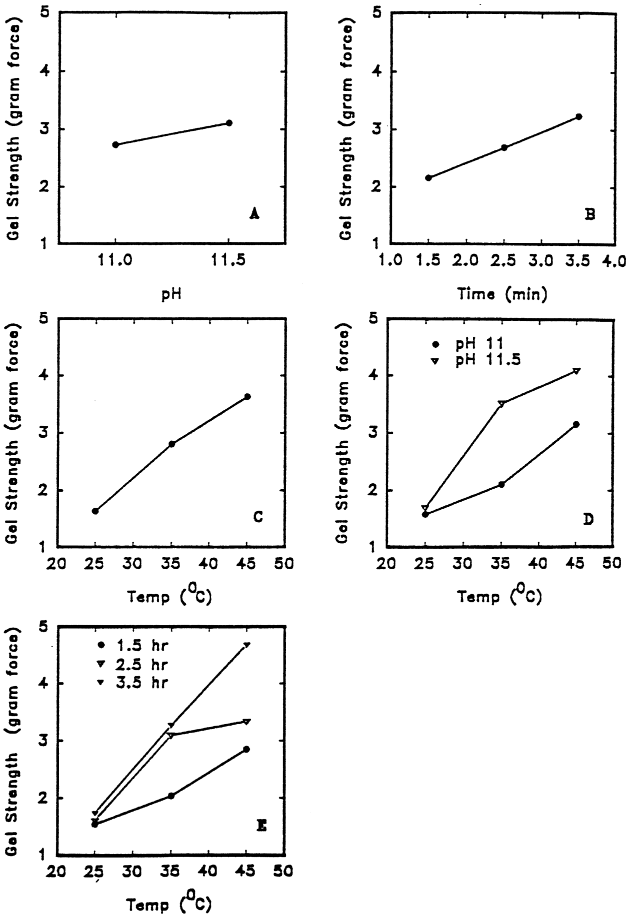

Fig. 8. Gel strength of 8% (dsb) modified tapioca starch paste kept at 5°C for 24 h was measured by using Voland Texture Analyzer. (A) The effect of reaction pH (averaged over reaction times of 1.5, 2.5, and 3.5 h and reaction temperatures of 25, 35, and 45°C) on gel strength. (B) The effect of reaction time (averaged over reaction temperatures of 25, 35, and 45°C and pH values of 11.0 and 11.5) on gel strength. (C) The effect of reaction temperature (averaged over reaction times of 1.5, 2.5, and 3.5 h and pH values of 11.0 and 11.5) on gel strength. (D) The combined effect of reaction temperature and pH (averaged over reaction times of 1.5, 2.5, and 3.5 h) on gel strength. (E) The combined effect of reaction temperature and reaction time (averaged over pH values of 11.0 and 11.5) on gel strength.

may account, in part, for the more rapid hydration and swelling and the greater viscosities of the starch pastes, compared with those starches that do not contain phosphate monoester, such as maize and wheat starches (Galliard and Bowler, 1987).

3.7. Thermal properties

Thermal properties determined by d.s.c. are shown in Table 2. The gelatinization peak of mung bean starch ranged from 63.3 to 83.5°C, and its amylose–lipid complex peak ranged from about 95 to 105°C. The gelatinization peak of the tapioca starch was similar to that of mung bean starch (61.5 to 82.2°C). No amylose–lipid complex transition peak was found in the tapioca thermogram. The onset gelatinization temperature of mung bean starch (68.0°C) was higher than that of tapioca starch (63.8°C). The enthalpy change of the mung bean starch (8.0 cal g^{-1}) was slightly greater than that of tapioca starch (7.6 cal g^{-1}).

3.8. Viscosity and pasting properties

Tapioca starch had a lower pasting temperature than mung bean starch (Fig. 3) as determined using a visco/amylograph (the temperature at which viscosity began to increase). The higher pasting temperature was primarily attributed to the lipid and higher amylose contents of the mung bean starch. Peak viscosities (the highest viscosity during heating) of both starches were similar. During the holding period, the tapioca starch underwent significant shear thinning (Fig. 3). The viscosity of the tapioca starch dropped from 1100 to 400 BU, whereas mung bean starch did not show much shear thinning. Mung bean starch paste showed a good shear resistance, similar to the pasting properties of cross-linked starches. The significant shear thinning of tapioca starch was attributed to the breakdown of swollen granules caused by high temperatures and shear forces. The swollen mung bean starch granules withstood the shear forces and high temperatures, which could be attributed primarily to its greater amylose and lipid contents. Amylose complexed with lipids holding the integrity of the granules and preventing the disruption. During cooling, mung bean starch paste showed a significant setback.

One way to increase shear resistance of tapioca starch is to cross-link the starch. In this study, we selected sodium trimetaphosphate as the cross-linking agent, which provided a more controlled reaction than phosphorus oxychloride. Cross-linking reaction was influenced by factors such as pH, starch concentration, reagent concentration, temperature, and reaction time. To select the optimum product, tapioca starch (50% suspension) was cross-linked with 0.1% sodium trimetaphosphate (w/w, STMP/starch) at various pH values, reaction times, and temperatures. We selected pH 11.0 and 11.5 for the study because the cross-linking reaction predominated at high alkalinity (Felton and Schopmeyer, 1943), and it was difficult to control the reaction of the pH above 11.5. The relations between the pasting temperature, peak viscosity, viscosity after shear thinning, setback viscosity, and gel strength (24 h at 5°C) with reaction time, reaction pH, and reaction temperature are shown in Figs. 4–8.

Pasting temperatures were affected by reaction pH (significant at $P \geq 0.0001$), reaction time (significant at $P \geq 0.0007$), reaction temperature (significant at $P \geq 0.033$), and the combinations of reaction temperature and three different reaction times (significant at 0.0118). The relationships between these factors are shown in Fig. 4a–d.

Peak viscosities were affected by reaction pH (significant at $P \geq 0.0237$) and the combinations of reaction temperature and reaction pH values (significant at 0.0155). The relationships between these factors are shown in Fig. 5a,b.

Viscosities after shear thinning were affected by reaction pH (significant at $P \geq 0.0033$), reaction time (significant at $P \geq 0.0001$), and reaction temperature (significant at $P \geq 0.025$). A significant relationship was demonstrated between reaction temperatures and three different reaction times (significant at 0.0452), and the combinations of reaction times and reaction pH values (significant at 0.0315). The relationships between these factors are shown in Fig. 6a–e.

Setback viscosities at 50°C were affected by reaction pH (significant at $P \geq 0.0011$), reaction time (significant at $P \geq 0.0001$), reaction temperature (significant at $P \geq 0.0124$), and the combinations of reaction times and reaction pH values (significant at 0.0120). The relationships between these factors are shown in Fig. 7a–d.

Gel strengths were affected by reaction pH (significant at $P \geq 0.0001$), reaction time (significant at $P \geq 0.0001$), reaction temperature (significant at $P \geq 0.0273$), the combinations of reaction temperatures and reaction pH values values (significant at 0.0009), and the combinations of reaction temperatures and reaction times (significant at 0.0009). The relationships between these factors are shown in Fig. 8a–e.

The gel strength of the mung bean starch paste after 24 h storage at 5°C was much greater than that of tapioca starch paste (Table 3). The mung bean starch gel was very strong and less sticky compared with tapioca starch gel, which was weak and very sticky. The high gel strength of mung bean starch could be attributed to its high amylose content and longer long branch-chains of amylopectin. Both starches were clear as pastes and gels, probably the result of their phosphate monoester derivatives. The gel strengths of the cross-linked tapioca starches, with different degrees of cross-linking, were still much lower than that of mung bean starch, but they were less sticky than the native tapioca starch. The gel strength of the cross-linked tapioca starch prepared at different conditions indicated that the starches having a greater degree of cross-linking exhibited greater gel strength. The greater amount of the high-amylose starch in the mixture of starch gel also increased the gel strength, which could be attributed to the gel network resulting from amylose retrogradation. A starch mixture, prepared by mixing 13% (dsb) high-amylose starch and 87% (dsb) tapioca starch, contained 30.2% apparent amylose, and the one prepared by mixing 17% high-amylose starch and 83% tapioca starch contained 32.1% apparent amylose. Both of the mixtures contained less apparent amylose than mung bean starch (37%) and displayed less gel strength than mung bean starch (Table 3).

3.9. Properties of mung bean starch noodles

Clear noodles were made from a thick slurry derived from different ratios of dry and gelatinized mung bean starch paste at ratios of 1:1, 2:3, and 1:2 (w/w). Lower and higher ratios of gelatinized starch were attempted, but the slurry either was too dry or too soft to extrude.

SEM micrographs of a clear noodle surface and cross-section are shown in Fig. 9. The cross-section of the noodle showed that the starch granules were gelatinized and ruptured. There were no intact starch granules. The micrograph of the cross-section also indicated that the starch formed networks, resulting from the retrogradation process. The pattern of the networks was similar to the retrograded amylose (at 5°C) micrographs reported by Lu et al. (1997).

Tensile strength of mung bean starch clear noodles prepared from the lower ratios of gelatinized starch was greater than that of noodles prepared from higher ratios of gelatinized starch (Table 4). Water absorption of the noodles after 24 h soaking in water at room temperature (25°C) increased slightly as the ratio of the gelatinized starch increased. The ratio of the gelatinized starch did not significantly affect the amount of soluble-matter loss (≈5%).

Table 3
Gel strength[a] (10% dsb) of tapioca starch, mung bean starch, cross-linked tapioca starches, and the mixture of the cross-linked starches and high amylose starch

Starches	Gel strength (gram force)
Native tapioca starch	1.5 ± 0.2
Native mung bean starch	49.1 ± 2.3
Cross-linked tapioca starch[b] at 25°C reaction temperature	1.6 ± 0.4
Cross-linked tapioca starch[b] at 35°C reaction temperature	2.6 ± 0.2
Cross-linked tapioca starch[b] at 45°C reaction temperature	4.8 ± 0.9
Mixture of native tapioca starch and 13% (w/w) high-amylose starch[c]	2.6 ± 0.5
Mixture of the cross-linked starch (25°C reaction temperature) and 13% high-amylose starch[c]	3.5 ± 0.8
Mixture of the cross-linked starch (35°C reaction temperature) and 13% high-amylose starch[c]	7.9 ± 1.5
Mixture of the cross-linked starch (45°C reaction temperature) and 13% high-amylose starch[c]	11.7 ± 1.4
Mixture of the native tapioca starch and 17% high-amylose starch[c]	3.2 ± 0.6
Mixture of the cross-linked starch (25°C reaction temperature) and 17% high-amylose starch[c]	3.9 ± 0.6
Mixture of the cross-linked starch (35°C reaction temperature) and 17% high-amylose starch[c]	10.8 ± 1.2
Mixture of the cross-linked starch (45°C reaction temperature) and 17% high-amylose starch[c]	15.2 ± 2.1

[a] Starch paste (10%, dsb) was stored at 5°C for 24 h before being measured with a Voland texture analyzer (Model TA, Scarsdale, NY). A 2 mm diameter probe and a 3 mm distance of penetration were used. The measurement was replicated at least 10 times and reported as means ± standard deviation

[b] Cross-linked tapioca starch with 0.1% sodium trimetaphosphate at pH 11.0, 3.5 h reaction time

[c] High-amylose maize starch, contained 70% amylose

3.10. Properties of clear noodles made from mixtures of tapioca and high-amylose starches

Many starch compositions were tested to make clear noodles. Native and cross-linked tapioca starch alone produced noodles which were too soft and could not be separated into single strands. Mixtures of tapioca starches (native or cross-linked starch) and high-amylose starch were more successful for making clear noodles. In the process, the high-amylose starch was gelatinized and pasted and the paste mixed with dry tapioca starch. Noodles were made by using mixtures of dry tapioca starch and the cooked high-amylose starch paste (15 and 20%) at ratio of 1:1 (w/w), which contained 13 and 17% high-amylose starch, equivalent to 30 and 32% apparent amylose content, respectively. Lower percentages of high-amylose starch content (9% and lower) were also tested, but the noodles were not consistent in diameter and broke into short strands during extrusion. Higher levels of high-amylose starch were also attempted, but we were unable to make stable high-amylose starch paste with a solid concentration above 20% (dsb).

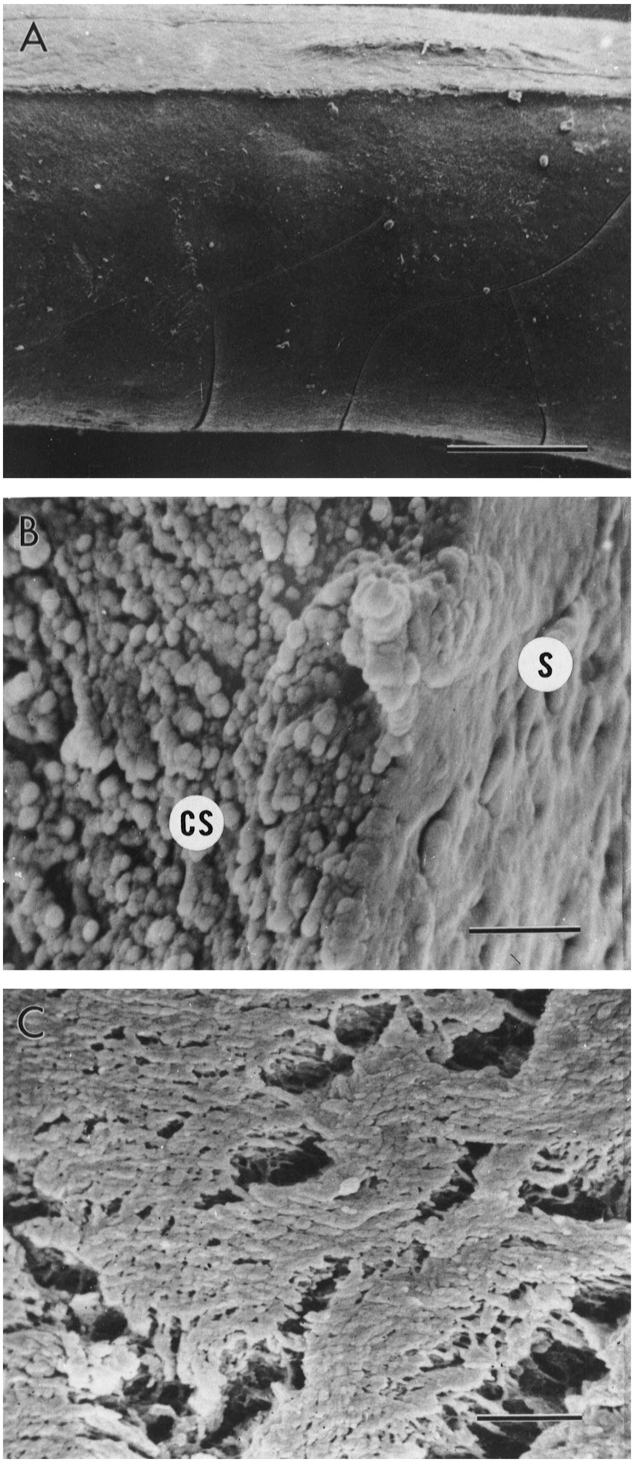

Fig. 9. Scanning electron micrograph: (A) noodle surface (bar = 300 mm), (B) noodle surface (S) and the cross-section (CS) (bar = 3 mm), and (C) noodle cross-section (bar = 8 mm).

Noodles were made by using mixtures of tapioca starch and the cooked high-amylose starch paste (20%) at ratios 1:2, 1:3, and 1:4 (w/w), which contained 29, 38, and 44% high-amylose starch, equivalent to 37.4, 41.4, and 44.6% apparent amylose content, respectively. Only were the thick slurry made from a ratio of tapioca starch and the high-amylose starch paste at 1:2 (contained 29% high-amylose starch, equivalent to 37.4% apparent amylose content) extrudable, but the noodles were more opaque than those that contained a lower amount of high-amylose starch. The noodles made from the higher ratios of cooked high-amylose starch were brittle and broke into small pieces.

The tensile strength, water absorption, and the soluble loss of the noodles made from mung bean starch and from mixtures of tapioca starch and high-amylose starch, boiled for the different lengths of time (10–60 s) after extrusion were all similar (data not shown). This indicated that the length of boiling time between 10 and 60 s after extrusion did not affect the tensile strength, water absorption, and the soluble loss of the noodles. The tensile strengths of noodles made from mixtures of tapioca starch (native or cross-linked starches) and high-amylose starch (13 or 17%, dsb) were also similar (Fig. 10). This indicated that the different mixtures of starch did not affect the tensile strength of the dry noodles. The tensile strengths of the dry noodles did not relate the eating property of the cooked noodles.

The water absorption (after soaking at 25°C for 24 h) of noodles made from mixtures of tapioca starch and high-amylose starch is shown in Fig. 11. Noodles made from mixtures of tapioca starches (87%) and high-amylose starch (13%) absorbed more water than the noodles made from mixtures of tapioca starches (83%) and high-amylose starch (17%). Noodles made from mixtures of cross-linked tapioca starches and high-amylose starch absorbed less water than those made from mixtures of native tapioca starch and high-amylose starch at the same ratio. Noodles made from tapioca starch with higher degrees of cross-linking (higher reaction temperature) also absorbed less water. Water absorption of the noodles could be used to predict the cooking quality of the noodles because the less water the noodles

Table 4
Properties of mung bean starch noodles prepared with different ratios of dry and gelatinized starches[a]

Ratio between dry: gelatinized starches[b] (moisture content, %[c])	Tensile strength (MPa)	Water absorption at 24 h (%)	Soluble loss (%)
1:1 (45%)	54.1 ± 4.0	127.7 ± 5.4	5.0 ± 0.3
2:3 (54%)	48.6 ± 4.1	133.5 ± 5.1	5.0 ± 0.4
1:2 (60%)	24.5 ± 1.8	138.4 ± 6.4	5.8 ± 0.8

[a] Data are reported in means ± standard deviation
[b] Dry starch base weight:starch paste weight (from 10%, dsb, slurry)
[c] Percentage based on the total weight of the starch thick slurry

absorbed, the stronger the texture of the noodles. Mung bean starch noodles absorbed a similar amount of water (127.7%, w/w) compared with noodles made from the mixtures of cross-linked tapioca starches (prepared at 35 and 45°C reaction temperature) and 17% high-amylose starch (133.2 and 126.1%, respectively).

The soluble losses of those noodles made from the mixtures of the cross-linked tapioca starches and 13% high-amylose starch were less than those made from the mixtures of 17% high-amylose starch counterparts (Fig. 12). The greater soluble loss of the noodles that contained greater proportions of high-amylose starch might have resulted from the leaching of amylose. The degree of cross-linking of tapioca starch in noodles did not affect the degree of soluble loss. The soluble loss of mung bean starch noodles (4.9%) was similar to that of the noodles made from mixtures of cross-linked tapioca starch and 13% high-amylose starch (4.9–5.3%).

Sensory evaluations (Fig. 13) indicated that the firmness of the cooked mung bean starch noodles was greater than that of cooked clear noodles made from the mixtures of tapioca starches (native or cross-linked) and high-amylose starch. The firmness increased as the degree of cross-linking increased. The noodles containing 13 and 17% high-amylose starch did not show significant differences in firmness. Chewiness also increased as the degree of cross-linking increased. The amount of high-amylose starch in noodles (13 and 17%) did not affect chewiness. The clarity of the noodles made from mixtures of tapioca starch and high-amylose starch was less than the mung bean starch noodles. The noodles made from mixtures of tapioca starch and high-amylose starch were more opaque because of the high-amylose starch. The noodles made from mixtures of high-amylose starch (13 and 17%) and tapioca starch did not differ in the clarity. The degree of cross-linking also did not affect the clarity of the noodles. The degree of off-flavor of mung bean starch noodles was the same as that of noodles made from mixtures of tapioca starch and high-amylose starch. Even though lower in firmness, chewiness, and clarity, the noodles made from mixtures of tapioca starch and high-amylose starch were ranked higher in general acceptability by the panelists than noodles made from mung bean starch. The greater acceptability of the noodles made from the mixtures of tapioca starch and high-amylose starch was due to the panelists' overall preference of the noodles.

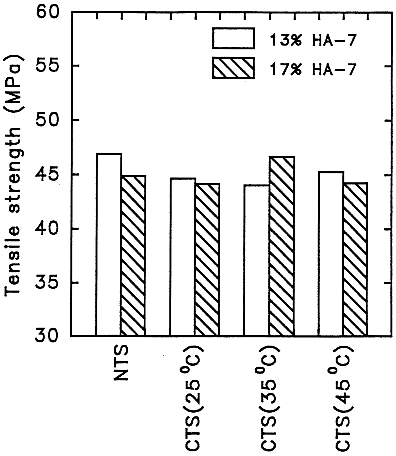

Fig. 10. Tensile strengths of noodles (54% moisture) prepared from the native tapioca starch (NTS) containing high-amylose starch (13 and 17%, dsb) and cross-linked tapioca starch (CTS) prepared at 25, 35, and 45°C reaction temperatures containing high amylose starch.

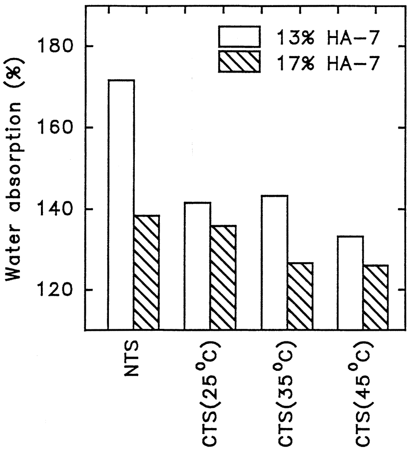

Fig. 11. Water absorptions of dry noodles after being soaked in water at 25°C for 24 h. Noodles prepared from mixtures of native tapioca starch (NTS) and high-amylose starch (13 and 17%, dsb) and cross-linked tapioca starch (CTS) prepared at 25, 35, and 45°C reaction temperatures and the same amount of high-amylose starch.

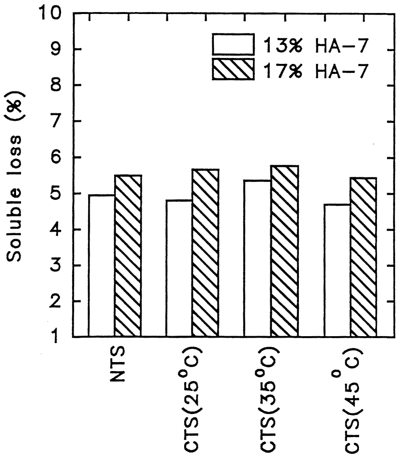

Fig. 12. Soluble loss of noodles prepared from mixtures of native tapioca starch (NTS) and high-amylose starch (13 and 17%, dsb), and cross-linked tapioca starch (CTS) prepared at 25, 35, and 45°C reaction temperature and high amylose starch (13 and 17%, dsb).

4. Conclusions

The results of this research on the fine molecular structures and physical properties of starch revealed relationships between these structures and properties. These relationships should help researchers understand starch behavior and utilization. Tapioca starch cross-linked by using STMP with varying reaction temperature, reaction time, and reaction pH, viscosities, and pasting properties indicated that the different cross-linked treatments affected the functional properties of starch. Native and cross-linked tapioca starch alone produced noodles that were unacceptable. The noodles prepared from mixtures of cross-linked tapioca starch and high-amylose starch indicated good quality at both the dry and cooked stages. The sensory evaluation indicated that panelists preferred the noodles made from the mixtures of tapioca and high-amylose starch rather than mung bean noodles.

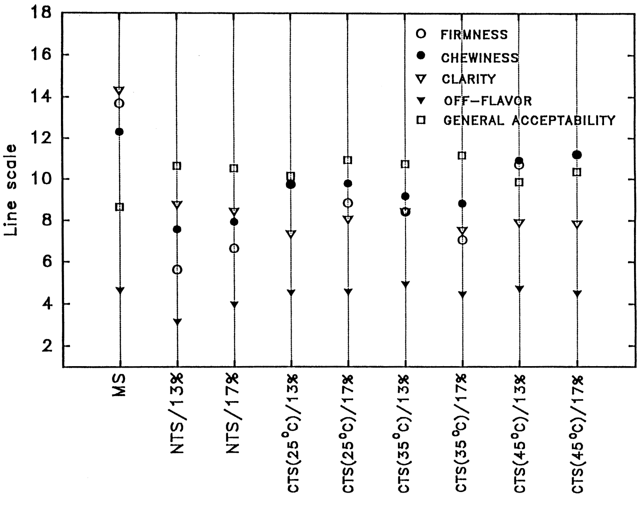

Fig. 13. Sensory evaluations determined by line scale: firmness (○), chewiness (●), clarity (▽), off-flavor (▼), and general acceptability (□). Line scale: 1, least, 18, most; MS, mung bean starch noodles; NTS, native tapioca starch; and CTS, cross-linked tapioca starch.

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