

Physicochemical properties of sweet potato starches and their application in noodle products

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ABSTRACT

Starches isolated from 3 Chinese sweet potato varieties (XuShu18, SuShu2, and SuShu8) differed in granule size and particle size distribution as well as in protein, lipid and phosphorus contents but the amylose contents were similar for these starches (19.3-20.0%). The pasting behavior, swelling pattern, and syneresis properties were investigated and found to vary. On comparison, the physicochemical properties of the sweet potato starches rather differ from those of potato and mung bean starches.

The quality of the starch noodle made from SuShu8 starch was well comparable to that made from mung bean starch, and better than that made from SuShu2 and XuShu18 starches as evaluated by both instrumental and sensory analysis. Correlation between starch noodle quality and gel properties of the original starches was established in order to be able to predict the suitability of a starch for starch noodle manufacture. It was found that differently sized granule fractions showed a difference in ash, amylose and phosphorus content, as well as in gel firmness and freeze-thaw stability. The small size (<20 μm) granule fractions were found to be more suitable for starch noodle making and the qualities of both dried and cooked starch noodles made from these fractions were significantly better than those made from their original starches and much better than those made from the large size granule fractions.

Sweet potato and potato starches and their derivatives (acetylated and hydroxypropylated) were also evaluated for the ability to manufacture high quality White Salted Noodle (WSN) by replacing the commonly used wheat flour up to 20%. It was found that only the use of acetylated starches could significantly improve WSN quality resulting in decreasing cooking loss, and increasing softness, stretchability and slipperiness. The cold peak breakdown (CPBD) of the composite flour, as measured in 1.5% NaCl solution, showed a significant correlation with the cooking loss, stretch stiffness and stretchability of WSN.

Moreover, acetylated starch from potato and sweet potatoes were studied with respect to the degree of substitution (DS) and acetyl group distribution in differently sized granule fractions. The DS of the fractionated starches increased with decreasing starch granule size dimension. The DS of the amylopectin populations of differently sized granule fractions showed the same trends as the original starches, while the DS of the amylose populations were quite constant. It was confirmed that the acetylation only occurred in the outer lamellae of the crystalline region, but took place in all amorphous regions of starch granules. The acetyl group distribution is more heterogeneous in the amylose populations isolated from small size granule fractions.

Key words: Sweet potato, starch, noodle, granule, acetyl distribution

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CHAPTER 1

General Introduction

Aim of this research

This project was aimed at a better use of abundantly produced sweet potato starches in China. China produces more than 85% of the whole world sweet potato crop. However, this abundant resource is still poorly utilized, in spite of the fact that it is cheaper than other crops. The industrial utilization of sweet potatoes is mainly based on the starch which can be isolated from this crop and which can be used as ingredients for food products.

Noodles are important foods consumed in Asian countries. It is estimated that about 30-40 % of total wheat flour consumption is as noodle products in most Asian countries (Miskelly 1993). Starch noodle and Japanese White Salted Noodle (WSN) are the two most popular types, which qualities are mainly affected by starch properties. Starch noodles are made from starch only and the ideal raw material is mung bean starch. High quality WSN is typically made from wheat flour which is imported from Australia. The aim of this research is to evaluate the use of sweet potato starches or their derivatives in the manufacture of high quality starch noodles in order to replace mung bean starch and in the manufacture of high quality WSN by partially replacing commonly used wheat flour.

Starch

General introduction

Starch is a biopolymer composed of anhydroglucose units and is the major storage energy in various plants in nature. It can be widely found in cereal grain seeds (e.g. corn, wheat, rice, sorghum), tubers (e.g. potato), roots (e.g. cassava, sweet potato, arrowroot), legume seeds (e.g. peas, beans, lentils), fruits (e.g. green bananas, unripe apples, green tomatoes), trunks (e.g. sago palm) and leaves (e.g. tobacco). In Europe, about 7.7×10^6 t of starch is produced annually. It consists of corn starch (49%), wheat starch (29%) and potato starch (22%) (Röper 2002); the global situation is shown in figure 1 and is quite different from the situation in Europe.

Starch can be simply manufactured by the combination of grinding the starch-rich crop followed by wet separation techniques. The starch granules will sediment in water due to their higher density. Native starch is a white powder with bland taste and flavor, and insoluble in cold water. In general, cereal starches (e.g. corn, wheat, rice) contain relatively high levels of lipids (0.2-0.8%) and protein (0.2-0.5%) resulting in a lower paste transparency and a pronounced and persistent “raw cereal flavor” of the starch gels. Tuber (e.g. potato) and root (e.g. tapioca) starches have lower levels of lipids (0.1-0.2%) and protein contents (0.1-0.2%). Potato starch is the only native starch containing significant amounts of chemically bound phosphate ester groups (degree of substitution = 0.003 ~ 0.005) located in amylopectin

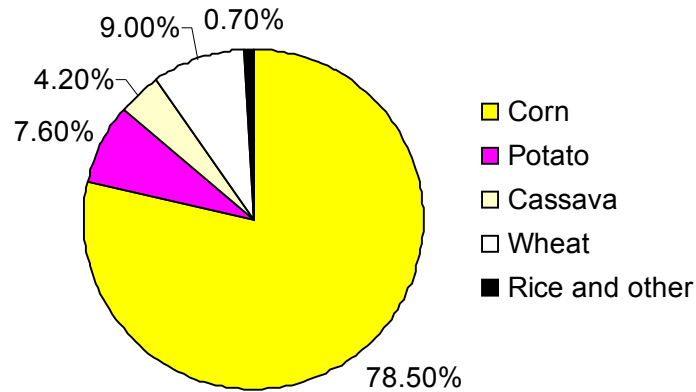


Figure 1-Starch production world wide basis on raw material (International Starch Institute, 1997)

Table 1-Chemical characteristics of starches obtained from various sources

Starch	Amylose (%)	Lipids (%)	Protein (%)	Phosphorus (%)
Corn ^a	28	0.8	0.35	0.00
Waxy corn ^a	<2	0.2	0.25	0.00
High-amylose corn ^a	50-70	nd	0.5	0.00
Wheat ^a	28	0.9	0.4	0.00
Potato ^a	21	0.1	0.1	0.08
Tapioca ^a	17	0.1	0.1	0.00
Mung bean ^b	39	0.3	0.3	nd

a: from BeMiller and Whistler, 1996; b: from Hoover and others, 1997. nd: not determined.

molecules (Table 1).

Starch granules are composed of two major polymers: amylose and amylopectin. Their structures and the relative amount of both populations play an important role in determining starch properties. The amylose content and degree of polymerization (DP) of amylose are important for the physical, chemical and technological properties of starch. Most starches contain ca 25% amylose. For waxy starches (e.g. waxy corn, waxy potato) the amylose content

can be less than 2%, while the amylose content of high amylose corn starch can be up to 70% (Table 1).

Amylose

Amylose is primarily a linear chain of D-glucose units linked by α -1 \rightarrow 4 linkages. However, some amylose molecules have about 0.3-0.5% of α -1 \rightarrow 6 linkages (branches) (Takeda and others 1990). The DP of amylose is around 1500-6000. DP is the total number of anhydroglucose residues present divided by the number of reducing ends. The total content of carbohydrate generally can be determined by the phenol-sulphuric acid method, while reducing residues can be determined by the Park-Johnson's colorimetric procedure for glucose (Hizukuri and others 1981). Amylose can form complexes with iodine and various organic compounds such as butanol and fatty acids. The complexing agents are incorporated within the amylose helices. These complexes are essentially insoluble in water. Amylose is easily leached out from swollen granules just above the gelatinization temperature. The amylose fraction usually can be isolated by such aqueous leaching procedures (Hizukuri 1996), by dispersion and precipitation (Adkins and Greenwood 1969; Ceh and others 1985; Banks and others 1971) and by ultracentrifugation methods (Montgomery and others 1961; Majzoobi and others 2003). Vorwerk and others (2002) reported a combined method using an enzyme to debranch amylopectin followed by butanol-1 complexing of the amylose. Amylose could be produced by this method at kg scale. The general properties and functionalities of amylose are described in table 2.

Table 2-Some important physicochemical characteristics of amylose and amylopectin

Property	Amylose	Amylopectin
Molecular structure ^a	Linear (α -1,4)	Branched (α -1,4; α -1,6)
Molecular weight ^b	$\sim 10^6$ Daltons	$\sim 10^8$ Daltons
Degree of polymerization ^a	1500-6000	3×10^5 - 3×10^6
Helical complex ^b	Strong	Weak
Iodine color ^a	Blue	Red-purple
Dilute solutions ^a	Unstable	Stable
Retrogradation ^b	Rapidly	Slowly
Gel property ^a	Stiff, irreversible	Soft, reversible
Film property ^b	Strong	Weak and brittle

a: from Jane (2000); b: from Zobel (1988a).

Amylopectin

Amylopectin is one of the largest molecules in nature. The molecular weight of amylopectin is 100 times higher than that of amylose. As compared to amylose, the amylopectin structure is more complex since 4-5% of the total linkages form branches. Due to its general dominance in granule composition, structure and properties, amylopectin has been studied extensively in the aspects of molecular size and structure.

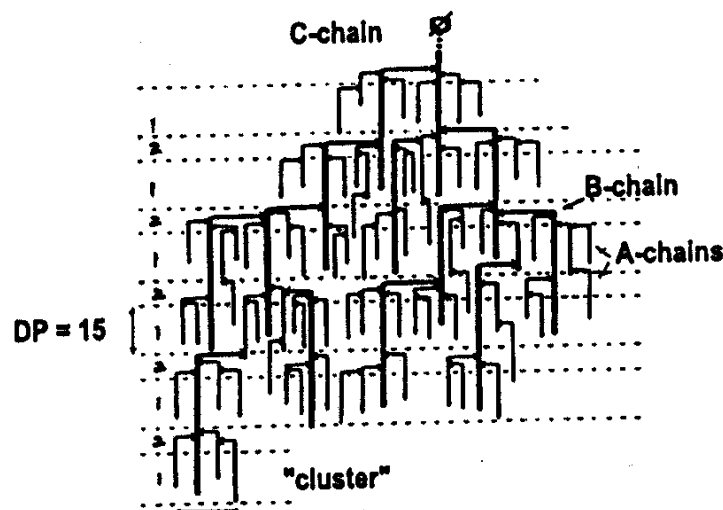


Figure 2-Proposed structure for amylopectin (1: crystalline region; 2: amorphous region; Ø: reducing end group. Robin and others 1974)

Amylopectin structure consists of three type chains (Figure 2). The C chain carries the sole reducing group in the molecule to which the B chains are attached, while the terminal A chain is attached to B chain (Manners 1989). Because the polymer molecules exist as heterogeneous mixtures, they are usually characterized by the average values of DP and “chain length” (CL). CL is the total amount of carbohydrate divided by the number of non-reducing end groups. HPLC is generally employed to estimate the CL distribution. The CL distribution can be determined by size-exclusion chromatography (SEC) and high performance anion-exchange chromatography (HPAEC) with pulsed amperometric detection after debranching of amylopectin with isoamylase or pullulanase (Hizukuri 1996). The average CL of most amylopectins is in the range 18-24 (Hizukuri 1996). The A chain is shorter than the B chain.

The ratio of A chain to B chain is the key parameter in amylopectin characterization. The most acceptable value of A/B ratio appears to be 1.0-1.4:1. A high proportion of A chain gives a low tendency to retrogradation of amylopectin (Hizukuri 1996). The characteristics of amylopectin are described in table 2.

Starch granule

Starch granules naturally exist in different ranges of size distribution, in different shapes and dimensions which depends on their botanical source, growing and harvest conditions. The granule size varies from the tiny granules in rice and oat starches (1.5-9 μm) to the large ones in potato starch (up to 100 μm). Mung bean starch has a relatively narrow size distribution while the broadest distribution is found for potato starch. Some cereal starches such as wheat, rye and barley show a bimodal size distribution. The small granules (called B-granules) are spherically shaped with a diameter below 10 μm and the large granules (called A-granules) are lenticular with a diameter around 20 μm (Eliasson and Gudmundsson 1996). The granule dimensions and shape descriptions of some starches are given in table 3. Since the morphological characteristics show significant difference, most starches can be identified from their appearance under a light microscope (Fitt and Snyder 1984).

Table 3-Characteristics of some starch granules

Starch	Diameter range (μm)	Average diameter (μm)	Shape
Corn ^a	2-30	10	Round, polygonal
Waxy Corn ^a	3-26	10	Round, polygonal
Wheat ^a	1-45	8	Round, lenticular
Potato ^a	5-100	28	Oval, spherical
Tapioca ^a	4-35	15	Oval, truncated
Mung bean ^b	7-26	NA	Oval round

a: from Swinkels; b: from Hoover and others, 1997. NA: not available.

A native starch granule consists of a semi-crystalline structure. The radial arrangement of the starch molecule displaying birefringence with the “Maltese cross” can be seen under a polarizing light microscope. The branches of amylopectin form double helices which are arranged in crystalline domains. Contrarily, amylose largely makes up the amorphous regions which are randomly distributed between the amylopectin clusters (Blanshard 1987; Zobel 1988b). The branching regions are constituted of the amorphous layer that separates the

crystallites from each other (Eliasson and Gudmundsson 1996). X-ray diffraction showed that the crystallinity of wheat, maize, potato, waxy maize, and tapioca was in the range of 20-28% (Cooke and Gidley 1992) pointing out that the major part of the starch granule was amorphous. According to the X-ray diffraction pattern, native starch granules can be classified as A, B and C type (see figure 3). Most cereal starches (e.g. normal corn, rice, wheat and oats) display the A type, while tuber starches (e.g. potato, lily, canna and tulip) exhibit the B type. The C type is the mixture of A and B types. Several rhizome and bean starches belong to the C type (Hizukuri 1996). It is believed that amylopectin is constituted of crystalline domains with the double helices arranged in the A, B or C pattern (Eliasson and Gudmundsson 1996). Starches with amylopectin of short average branch chains display the A pattern, whereas those with long branches give the B pattern. The average chain length in between forms the C pattern (Hizukuri and others 1983).

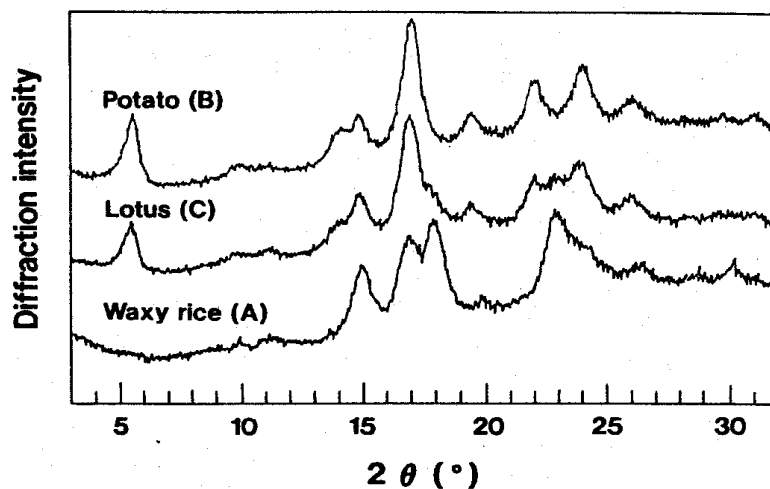


Figure 3-X-ray diffraction patterns of A (Waxy rice), B (Potato) and C (Lotus) types of starches (Hizukuri 1996)

Gelatinization and pasting behavior of starches

Native starch granule swelling in water is a reversible process at temperatures below the gelatinization temperature due to its stable semi-crystalline structure. The water absorption is usually less than 40%. When the temperature of a suspension of starch granules in excess of water increases to the gelatinization temperature, the starch granule will lose its birefringence and crystallinity, with concurrent swelling. This change is irreversible and called

“gelatinization”. The total gelatinization usually occurs over a temperature range (10-15 °C) (Evans and Haisman 1982).

Gelatinization is the process of granule swelling followed by disruption of granule structure in which the loss of crystalline order can be observed in the disappearance of the X-ray diffraction. Before granule disruption some materials (mainly amylose) already start to leach out from the granule. The leached material increases in molecular weight and more branched material leaches out with increasing temperature (Doublier 1987; Prentice and others 1992). However, not all amylose leaches out during gelatinization (Ellis and others 1988). The morphological change of the granules during swelling depends on the origin of the starch. For some starches, such as potato and corn, the granules swell in all directions, whereas for wheat, barley and rye starch granules the swelling is restricted in one dimension, resulting in complicated folding of the granules (Bowler and others 1980). The granule swelling ability is usually quantified by swelling power (the weight of sedimented swollen granules per gram of dry starch) or swelling volume (the volume of sedimented swollen granules per gram of dry starch) at the corresponding temperature (Konik and others 1993; Pinnavaia and Pizzirani 1998; Konik and others 2001). Starch swelling behavior not only depends on starch origin but also depends on amylose content. Normally potato starch gives a large swelling volume in native starches while waxy potato starch (<2% amylose level) shows a higher value for the swelling volume (Colonna and Mercier 1985; Tester and Morrison 1990).

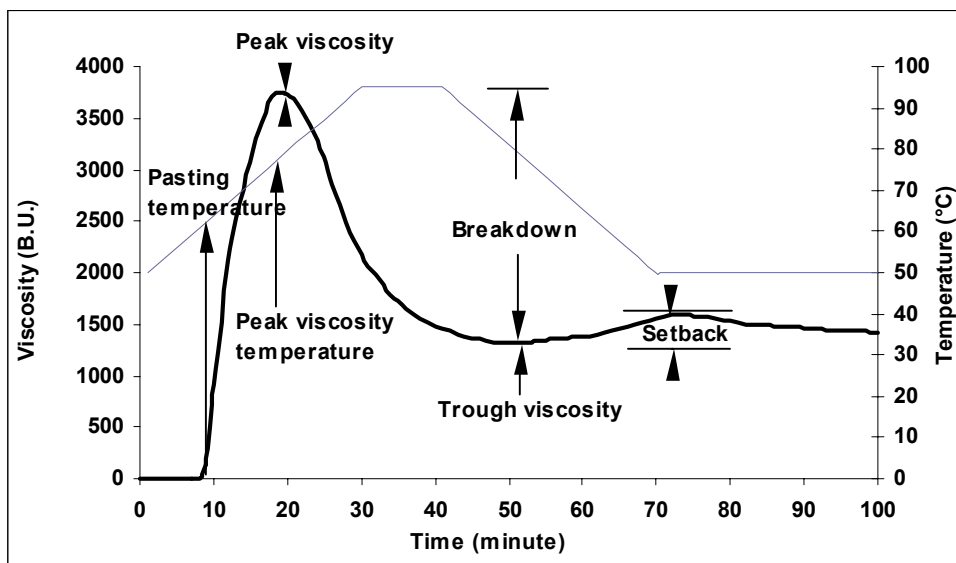


Figure 5-Brabender amylogram of potato starch (4%, w/v)

The pasting behavior of starches is very important for starch characterization and their applications. Useful information such as pasting temperature, peak viscosity, breakdown and setback values can be obtained from the profiles determined with Brabender amylograph (Figure 5) or Rapid Visco Analyzer (RVA). The pasting profile is believed to be a very useful indicator for starch application.

Retrogradation

During storage starch pastes may become cloudy and eventually deposit an insoluble white precipitate. This is caused by the recrystallization of starch molecules; initially the amylose forms double helical chain segments followed by helix-helix aggregation (Biliaderis 1992). This phenomenon is termed “retrogradation”. Amylose is considered primarily responsible for the short-term retrogradation process due to the fact that the dissolved amylose molecules reorient in a parallel alignment. The long-term retrogradation is represented by the slow recrystallization of the outer branches of amylopectin (Miles and others 1985; Ring and others 1987; Daniel and Weaver 2000). The recrystallized amylopectin in the retrograded gel can be melted at 55 °C, whereas for the recrystallized amylose the melting temperature rises to 130 °C (Zhang and Jackson 1992).

Basically, the rate and the extent of retrogradation increase with an increased amount of amylose. In addition to the origin of starch, retrogradation also depends on starch concentration, storage temperature, pH, temperature procedure and the composition of the starch paste. Retrogradation is generally stimulated by a high starch concentration, low storage temperature and pH values between 5 and 7. The salts of monovalent anions and cations can retard starch retrogradation (Swinkels).

Sweet potato starches

Since sweet potato starches are the major materials used in this research, their properties will be discussed in more detail. Sweet potato (*Ipomea batatas*) is an important crop in many developing countries. Although sweet potato originated from Central America, its ability to adapt to a wide variety of climatic conditions allow them to grow both in tropical and in moderate temperature regions of Africa, Asia and the Americas (Woolfe 1992). Total world sweet potato production in 2002 was 136 million tons, of which 114 million tons was produced in China (FAO 2002).

Sweet potatoes are rich in starch (6.9-30.7% on wet basis, Tian and others 1991) and starch production is the main industrial utilization of sweet potatoes. Sweet potato starch granules are reported as round, oval and polygonal shapes with sizes ranging between 2-42 µm (Tian and others 1991; Hoover 2001). Both A types and C types of X-ray patterns have been found for

sweet potato starches (Gallant and others 1982; Zobel 1988b; Lauzon and others 1995; McPherson and Jane 1999). Amylose contents of sweet potato starches vary between 8.5% and 38% (Tian and others 1991; Takeda and others 1987). The DP of sweet potato amylose has been reported in the range 3025 to 4100, while for amylopectin the average CL of 21-29 is reported (Hizukuri 1985; Takeda and others 1986; Ong and others 1994). Swelling and solubility of sweet potato starches are less than those of potato and cassava starches. Both single- and two-stage swelling patterns are found for sweet potato starches of different varieties (Rasper 1969; Delpuch and Favier 1980). Gelatinization temperatures of sweet potato starches are reported in the range of 58 to 84 °C and the gelatinization enthalpy is between 10.0 to 16.3 J/g (Takeda and others 1986; Zobel 1988a; Tian and others 1991; Garcia and Walter 1998; Collado and others 1999). The pasting behaviors of sweet potato starches exhibit a high peak viscosity and they become thinner rapidly with prolonged cooking before thickening on cooling (Tian and others 1991). However, for some sweet potato varieties no peak viscosity in the viscosity curves (Brabender amylogram) were observed (Seog and others 1987). Sweet potato starches have been reported to retrograde more slowly than wheat and corn starches but similar to potato starch (Del Rosario and Pontiveros 1983; Takeda and others 1986). Takeda and others (1986) found that sweet potato amylose appeared to retrograde at the same rate as tapioca amylose but it retrograded more slowly than potato amylose. Contrarily, Rasper (1969) showed that sweet potato amylose retrograded at a slower rate than that of tapioca and also that sweet potato amylopectin retrograded at a greater rate than tapioca amylopectin. Since there are many varieties of sweet potato grown in different field conditions, large variations in starch physicochemical properties are not really surprising.

Starches and derivatives in food application

Starch has always been an important item in the human diet. Except for its nutritional value, starch is usually added to foods as thickener, binder, adhesive, gelling agent, encapsulating agent, film former, stabilizer, texturizer, fat-replacer, or processing aid. Due to the sub-optimal behavior of native starch, modification of starch is the efficient way to provide starch products with suitable properties to meet the needs for specific uses. The commonly used modifications for starches are shown in table 4. Starches or their derivatives can be used in food as a major ingredient or as an additive to optimize processing efficiency, product quality or shelf life. In food industry, the application of starches or starch derivatives is in bakery products, desserts, confectionery, puddings (Sudhakar and others 1995), jams (Hall 1972), soups, sauces, dressings, beverages, meat products, dairy products (Yackel and Cox 1992), and coating

(Kroger and Igoe 1971). The proper selection depend on the behavioral characteristics and the cost of the starch (derivative) with respect to the achieved application goal.

Table 4-The commonly used modifications of starch in food application

No.	Type of modification	Main objectives	Treatments
1	Pregelatinized starch	Cold water dispersibility	Drum-drying, Extrusion
2	low-viscosity starches	Lower viscosity	
	a. Dextrins	Lower viscosity Range of viscosity stability	Dry heat treatment with acid
	b. Acid-modified starch	Lower viscosity High gel tendency	Acid hydrolysis (suspension)
	c. Oxidized starch	Lower viscosity Improved viscosity stability	Oxidation (in suspension or paste)
	d. Enzymatically modified starch	Lower viscosity	Alpha-amylase (paste)
3	Crosslinked starch	Modification of cooking characteristics	Crosslinking in suspension
4	Stabilized starch	Improved viscosity stability	Esterification, Etherification
5	Combinations of modifications 1, 2, 3 and/or 4	Combinations of objectives 1, 2, 3 and/or 4	Combinations of treatments 1, 2, 3 and/or 4
6	Starch sugars	Sweet saccharides	Acid and/or enzymes

(From Swinkels)

Noodle products

Since this research project is mainly focused on the application of sweet potato starches (derivatives) in starch noodle and Japanese White Salted Noodle (WSN) manufacture, more information will be given about noodle production in general.

Noodles are important foods throughout the world. Noodles originate from China and can be dated back over 6000 years to northern China (Hatcher 2001). During the Eastern Han Dynasty (25-220AD), the technique of Chinese noodle production was introduced to Japan by the Japanese envoy, and gradually noodles were spread out from China to other Asian countries such as Korea, Thailand, Philippines and Malaysia (Nagao 1981). When the Italian explorer and traveler Marco Polo visited China in 13th century he introduced the Chinese noodle-making technology to Europe, where noodle appearance gradually developed into current pasta products (Hou 2001). The instant noodle was firstly produced by the Nissin Foods company

and sold in Japan in 1957 (Miskelly 1993; Kubomura 1998). Nowadays, instant noodles can be found everywhere in the world.

Many varieties of noodles exist as a result of differences in composition, method of preparation and presentation depending on regional preference (Edwards and others 1996). Noodles can be generally classified into Chinese type wheat noodles, Japanese type wheat noodles, buck wheat noodles (Soba), Naengmyon noodles (Korean type noodles), rice noodles, starch noodles, and pasta according to their main raw materials and other ingredients used. In general, Chinese type wheat noodles are made from hard wheat flour. Yellow alkaline noodles contain alkaline salts (sodium carbonate or potassium carbonate) as an ingredient which produces the yellow color and a special flavor. White salted noodles only contain sodium chloride. The Japanese White Salted Noodles are made from soft wheat flour and sodium chloride (Nagao 1996; Nagao 1998; Crosbie and others 1999). The Chinese type noodles require a firm texture, while the soft and elastic textures are the preferable attributes for Japanese type noodles. Both the Chinese and the Japanese wheat noodle can be made by hand or by machine. In industrial manufacture, the dough is blended and sheeted to a certain thickness before being cut into noodle strands. Soba noodles are made from the mixture of wheat flour and buck wheat flour. Typically it contains 70% of hard wheat flour and 30% of buckwheat flour without adding salt. Naengmyon noodles are made from the mixture of wheat flour, buck wheat flour and selected potato starch, and salt. Naengmyon noodles are made by extrusion and the cooked noodles have a rubbery texture. Rice noodles are traditionally made from the whole rice flour by spreading the slurry on a cloth and steamed and then cut into noodle strands. Starch noodles are made from starches only. The starch dough containing 5% of pregelatinized starch paste and 95% of native starch is extruded by gravity through a cylindrical extruder with holes directly into hot water (95-98 °C) and cooked, cooled, frozen, and then dried (detailed description see chapter 3). Unlike the Oriental noodles, pastas are the western type noodles which are made from durum wheat semolina, or common wheat farina (Marchylo and Dexter 2001) by extrusion.

The processibility and the noodle quality are the main important aspects in noodle production. Both of them are determined by raw materials, ingredients and process technology in which starch and protein play the major roles.

Aim and outline of this thesis

The aim of this research is to systematically study the physicochemical properties of starches and starch derivatives made from 3 typical Chinese sweet potato varieties and to compare these properties with those of potato and mung bean starches. According to their physicochemical

properties, sweet potato starches will be compared with the relatively expensive mung bean starch used nowadays in high-quality starch noodle production in order to establishing if they can replace mung bean starch. Sweet potato starches and their derivatives will also be studied for their ability to improve White Salted Noodle (WSN) quality by replacing wheat flour.

The physicochemical properties of starches isolated from the 3 selected typical types of Chinese sweet potato varieties are described in Chapter 2. Starch noodles made from the 3 types of sweet potato starches were compared with mung bean starch noodle. The quality of the starch noodles is evaluated by sensorial and instrumental analysis. The correlation between starch noodle quality and the gel firmness of raw starch is established. SuShu8 starch is found to be more suitable for starch noodle making. The quality of the starch noodle made from SuShu8 starch is well comparable to that of mung bean starch noodle (Chapter 3). Since the average size of SuShu8 starch granules is smaller and its particle size distribution is narrower than those of the other two sweet potato varieties, the effect of starch granule on starch noodle processibility and quality is studied in Chapter 4. The starch granule size is found to play an important role in the processibility and quality of starch noodles.

It has been recognized that the quality of WSN is mainly affected by the starch property of wheat flour. Although many efforts have been directed towards the selection of wheat varieties which contain suitable starch for WSN production, it is also worthwhile to try to (partly) substitute commonly used wheat flour with starches or starch derivatives for improving WSN quality. The 3 sweet potato (SuShu2, SuShu8 and XuShu18) starches and potato starch, and their derivatives (hydroxypropylated and acetylated) were tested to substitute commonly used wheat flour in WSN production. The WSN quality and the effects of the replacement with sweet potato (potato) starch derivatives on the composite flours are described in Chapter 5. All acetylated starches can be used in replacing part of commonly used wheat flour to improve WSN quality. The physicochemical and functional properties of acetylated starches mainly depend on the degree of substitution (DS) and acetyl group distribution. Moreover, differently sized granule fractions were found to have significantly different physicochemical properties and show different functionality in starch noodle production. The DS of differently sized granule fractions of the acetylated starches and their corresponding amylose and amylopectin populations are determined. A model for the acetylation process of starch granules is presented and the acetyl group distribution in the amylose populations is studied (Chapter 6). Finally, in the concluding remarks an overview of this research work and further discussion is given (Chapter 7). Ways to apply starches and derivatives in future noodle production is suggested.

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CHAPTER 2

Physicochemical Properties of Starches Obtained from Three Different Varieties of Chinese Sweet Potatoes

ABSTRACT

Starches isolated from 3 typical types of Chinese sweet potato varieties (XuShu18, SuShu2, and SuShu8) were characterized and compared with starches isolated from potato and mung bean. The 3 sweet potato starches differed in granule size and particle size distribution, and protein, lipid and phosphorus contents, and pasting behaviors, swelling patterns, and syneresis. The retrogradation tendencies measured both by setback ratio and by syneresis differed for the 3 starches although the amylose content was quite similar (19.3-20.0%). Physicochemical properties of all 3 types of starches are evidently different from each other and from those of potato and mung bean starches.

Keywords: sweet potato, starch, gelatinization, retrogradation, swelling, syneresis

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Introduction

Sweet potatoes (*Ipomoea batatas*) originated from Central America; now most of the production is in China (>80%; about 115×10^6 Metric tons) (Woolf 1992; FAO 2001). Sweet potato has been cultivated in large parts of China partly due to its wide adaptability to climatic and soil conditions. There are more than 2000 varieties of sweet potatoes in China, which can be roughly divided into a “general type”, a “high-starch type” and a “food consumption type”. It is known that the starch content of the fresh roots can vary between 6.9-30.7% (Tian and others 1991).

Starch manufacture is the main industrial utilization of sweet potatoes which has been broadly used in starch noodles, bakery foods, snack foods (Palomar and others 1981; Wanjekeche and Keya 1995), confectionery products (Suzuki 1978), in the textile industry (Radley 1976), and by the alcohol production and brewing industries (Palomar and others 1981; Wanjekeche and Keya 1995). The use of sweet potato starch is primarily determined by its physicochemical properties. Starches isolated from sweet potato roots grown in Japan, India, Indonesia, Philippines, Peru, and Ghana have been studied. The purity of the starch isolates was found to vary between 88.1-99.8%; and the amylose content ranges from 8.5 to 37.4% (Takeda and others 1986; Tian and others 1991; Madhusudhan and others 1992; Collado and Corke 1997; Garcia and Walter 1998; Oduro and others 2000). Phosphate content varies significantly from 1.3 to 222 ppm (Tian and others 1991; Oduro and others 2000). The granule size is within the range of 2.1-30.7 μm and the mean is from 9.2 to 11.3 μm (Zhang and Oates 1999). Swelling and solubility properties were reported from a single to a two-stage pattern (Tian and others 1991, Garcia and Walter 1998). Crystalline structure, gelatinization, pasting behavior, and retrogradation have been investigated by X-ray diffraction, DSC, Brabender amylography and Rapid Visco Analyzer (RVA) by several scientists (Takeda and others 1986; Noda and others 1992, 1995; Collado and Corke 1997; Garcia and Walter 1998; Zhang and Oates 1999; Oduro and others 2000). Unfortunately, there is only very limited information available on the physicochemical properties of Chinese sweet potato starches (Lin and others 1996). Since China is by far the major producer in the world of sweet potatoes with the most varieties, a systematic study on physicochemical properties of their starches would be useful and aid in the utilization of Chinese sweet potato starches. Here we report physicochemical properties on 3 established and typical types of Chinese sweet potato starches.

Materials and Methods

Materials

Three typical types of sweet potatoes, XuShu18, SuShu2, and SuShu8, were obtained 1 week after harvest from the Sweet Potato Research Group, Nanjing Agricultural Institute, JiangSu, P.R. China. Potato and mung bean starches were used as reference and were kindly supplied by AVEBE R&D, Foxhol, The Netherlands.

Starch isolation

Starches were isolated according to the method of Collado and Corke (1997). The roots were washed thoroughly, immersed in ice-cold water for 1 h, peeled, sliced, macerated and washed extensively with ice-cold water. The isolated starches were then dried in an oven at 40 °C overnight.

Moisture content

Fresh sweet potato roots were washed, wiped, and sliced into fine pieces. The moisture contents of both raw material and isolated starch were determined by the official German method: 5 g of sample was heated for 1 h at 50 °C and then for 3 h at 120 °C to constant weight (Lyne 1976a).

Protein and starch contents

The protein content was determined by the Kjeldahl method ($N \times 6.25$; Garcia and Walter 1998). The starch content of raw roots was determined by the method of Noda and others (1992) using the phenol-sulfuric acid method instead of the anthrone-sulfuric acid method. The starch content of isolated starches was determined enzymatically using a test kit (Boehringer, Mannheim, Germany).

Amylose content

Amylose contents of isolated starches were measured by iodine complex formation according to the method of Bates and others (1943).

Lipid, ash, crude fiber and phosphorus

Lipids were Soxhlet-extracted with petroleum ether (40 °C-60 °C) according to the method of Vasanthan and Hoover (1992). Ash and fiber contents were determined following the AOAC methods (Lane 1990; Padmore 1990). The phosphorus content was measured spectrophotometrically by the method of the Corn Industries Research Foundation (Lyne 1976b).

Light microscopy

Starch granule shapes were observed and photographed using a BX 50 microscope (Olympus, Tokyo, Japan). Granule size was measured using a microscope fitted with a calibrated eyepiece to calculate the average and range of the granular size.

Size distribution

Particle size distribution was measured with a Coulter Multisizer (Coulter Multisizer II, Luton, UK) using isotonic water as an electrolyte. Samples were dispersed in demineralized water, then diluted in isotonic water and put in an ultrasonic bath (max. 2 min.). Results given are the average of 2 measurements.

Pasting behavior and gelatinization

Pasting behavior of starch suspension (4% or 6%, w/v) was measured using a Brabender Amylograph (model VS5-S; Duisburg, Germany) having 500-cmg sensitivity cartridge. The operation was at a bowl speed of 75 rpm. The temperature rose from 50 °C to 95 °C at a rate of 1.5 °C/min, held at 95 °C for 10 min and decline to 50 °C at the same rate, then held at 50 °C for 30 min. All data were recalculated to 250-cmg sensitivity. Alternatively, a Rapid Visco Analyzer (RVA) (model 3 C, Newport Scientific Pty. Ltd., Warriewood, NSW, Australia) was used in a defined program: 28 g of starch suspensions (4%, 6%, and 8%, w/v) were sheared at a paddle speed of 160 rpm/min heated from 45 °C to 90 °C at 14 °C/min, held at 90 °C for 5 min, cooled to 30 °C at 14 °C/min, and held at 30 °C for 5 min. The temperature range of gelatinization was measured by using a Kofler hot-stage polarizing microscope, according to Schoch and Maywald (1956).

Swelling volume

Swelling volume was determined by weighing 0.50 g (dry substance) starch into a 50-mL centrifuge tube to which 45 mL of distilled water was added. The sample was equilibrated at 25 °C for 5 min, then heated for 30 min at a given temperature (range 55-95 °C) under continuous mixing. The sample was cooled down to room temperature (25 °C) and then centrifuged at $1000 \times g$ for 15 min. The height of the gel was measured and converted to volume of gel per unit dry weight of the sample (Collado and Corke 1999).

Syneresis

Freeze-thaw stability was evaluated as follows: starch suspension (5%, w/v) was heated for 20 min at 100 °C (keeping the volume constant) and transferred directly into plastic cups (for triplicates), which then were sealed tightly with parafilm. The sample was cooled at room

temperature for 30 min and then stored at 4 °C for 16 h, frozen at -16 °C for 24 h, and thawed at 25 °C for 4 h. Then the starch gel was placed into a glass funnel allowing the water to drip out for 2 h by gravity which was measured by weighing. Subsequently the gel was refrozen in its plastic cup at -16 °C for 24 h. Five freeze-thaw cycles were performed.

Syneresis of starch gel without freezing and thawing treatment was measured by storing the gel at 2 °C. Starch paste treated as described above was weighed directly into conical centrifuge tubes (50 mL), which were then tightly sealed. These tubes were placed in a refrigerator at 2 °C for several days. With a one-day interval, the exuded water was measured after the starch gel was centrifuged at $1000 \times g$ for 20 min.

The syneresis was calculated as the amount of exuded water as a percentage of the original paste weight.

Results and Discussion

Characteristics of sweet potato roots

Three typical types of Chinese sweet potato varieties were selected. XuShu18, a “general type”, is the most popular variety in China which is grown in at least 9 provinces. SuShu2 is one of the most promising sweet potato varieties of the “high-starch type”. SuShu8 represents the “food consumption type” of sweet potatoes; it is popularly used as a kind of roasted snack food.

Table 1 shows that the starch content of fresh SuShu2 root is higher than that of XuShu18 root and much higher than that found in SuShu8. The starch contents (dry basis) of all the 3 varieties of sweet potato are higher than that of mung beans but similar to that of Irish potato tubers. The protein contents (dry basis) of the 3 sweet potato roots are rather similar but lower than that of Irish potatoes and much lower than that of mung beans. The high protein content of mung beans is one of the main factors for the tedious processing of starch isolation resulting in a rather expensive bean starch preparation (Kasemsuwan and others 1998). The lipid content of SuShu2 (dry basis) was lower than that of XuShu18 and SuShu8. All of them are much higher in lipid content than Irish potatoes, but not much different from mung beans. SuShu8 roots have the highest fiber content (on dry basis) followed by SuShu2 and XuShu18. The fiber content (on dry basis) for Irish potato tubers and mung beans are 2% and 4.5%, respectively. A lower fiber content is beneficial for efficient starch isolation.

During starch isolation the starch slurry of sweet potatoes readily undergoes browning. This is mainly related to the high level of polyphenol oxidase (PPO) and phenolic compounds present in sweet potato roots (Walter and Purcell 1980). A dark color not only affects the starch quality but also affects its commercial value. Vitamin C (V_c) and citric acid are reported as

common inhibitors of PPO during sweet potato starch isolation (Jing 1991). In our study, 4 different treatments (tap water, ice-cold water, 0.2% V_c , and 0.2% citric acid) were used during immersing, peeling, slicing and macerating. Although there were differences in color of the starch slurries during processing, after rinsing 5 times with tap water the colors of the 4 differently treated starches were nearly the same. This indicates that the brown color of sweet potato starch can be removed simply by rinsing with water.

Table 1-The chemical composition of 3 varieties of Chinese sweet potato roots and potato and mung bean (w/w, %)

Source	Moisture	Dry matter	Starch	Protein	Lipid	Ash	Fiber
Xushu18	68.1 ± 1.92	31.9	21.9 ± 1.35 (68.5)	1.6 ± 0.05 (4.9)	0.5 ± 0.03 (1.5)	0.7 ± 0.04 (2.2)	0.6 ± 0.04 (1.9)
Sushu2	63.3 ± 1.21	36.7	27.8 ± 1.47 (75.9)	2.0 ± 0.08 (5.5)	0.4 ± 0.03 (1.0)	0.9 ± 0.07 (2.5)	1.0 ± 0.10 (2.7)
Sushu8	81.4 ± 1.78	18.6	10.7 ± 0.92 (57.8)	1.0 ± 0.10 (5.5)	0.3 ± 0.03 (1.5)	0.6 ± 0.04 (3.1)	0.8 ± 0.05 (4.4)
Potato ¹	NA	NA	(75)	(10)	(0.3)	(2)	(2)
Mung bean ²	NA	NA	(56.3)	(25.8)	(1.3)	(3.8)	(4.5)

Values based on dry weight are given within parenthesis. 1) Values for potato are from Treadway (1967).

2) Values for mung bean are from Singh and others (1989). NA: value not available. N=3.

Chemical composition of isolated sweet potato starches

The chemical composition of the isolated starches is shown in table 2. The moisture contents were about 9% and the purity of all isolated sweet potato starches was reasonably high. The moisture contents of all the 3 sweet potato starches were slightly lower than that of mung bean starch and much lower than that of potato starch. This may be due to the starch granule structures of the sweet potato starches which are less hydrated as compared to potato starch. However the difference in moisture content will also depend on the extent of drying. It was also found that there was almost no difference in the amylose contents of the 3 sweet potato starches although it has been reported before that the amylose content may range from 8.5% to 37.4% for starches from different sweet potato varieties (Takeda and others 1986; Tian and others 1991; Madhusudhan and others 1992; Collado and Corke 1997; Garcia and Walter 1998; Oduro and others 2000). The amylose contents of the 3 sweet potato starches were slightly lower than that of Irish potato starch and much lower than that of mung bean starch

and these levels may be of importance since amylose content is one of the important factors affecting starch pasting and retrogradation behaviors. The protein content of XuShu18 starch was higher than that of SuShu2 and SuShu8 starches. Protein content of the 3 sweet potato starches were higher than that found for Irish potato starch but lower than that found for mung bean starch. This shows that the removal of protein present in the starting material is less complete for sweet potato as compared to Irish potato tuber but much better than for mung bean starch. The lipid content of XuShu18 starch was higher than that of SuShu2 and SuShu8 starches. The lipid content of the sweet potato starches was slightly higher than that found for Irish potato starch but lower than that found for mung bean starch. High lipid contents may result in low clarity of the starch paste (as with cereal starches) and repressing starch granule swelling (Kasemsuwan and others 1998). The phosphorus content of SuShu2 starch was lower than that of XuShu18 and SuShu8 starches, while these values were much lower than found for Irish potato starch which generally contains high phosphorus in native starches. Like potato starch the amylose of sweet potato starch contains less phosphate than the amylopectin (Takeda and others 1986). High levels of phosphate ester groups give amylopectin of potato starch a slight negative charge, resulting in some coulombic repulsion that may contribute to the rapid swelling of potato starch granules in warm water and to several properties of potato starch pastes like high viscosity, high clarity, and low rate of retrogradation (BeMiller and Whistler 1996).

Table 2-Chemical composition of isolated starches from 3 varieties of Chinese sweet potatoes compared with potato and mung bean starches (w/w %)

Source	Moisture	Starch(db)	Amylose(db)	Protein(db)	Lipids(db)	Phosphorus(db)
XuShu18	8.7 ± 0.13	96.3 ± 1.26	20.0	0.23 ± 0.021	0.21 ± 0.021	0.022 ± 0.0023
SuShu2	8.6 ± 0.14	97.5 ± 1.28	19.3	0.14 ± 0.012	0.14 ± 0.015	0.014 ± 0.0017
SuShu8	9.4 ± 0.32	97.4 ± 1.19	19.6	0.17 ± 0.012	0.16 ± 0.012	0.021 ± 0.0021
Potato	18.9 ± 0.48	99.3 ± 0.58	22.3	0.10 ± 0.012	0.10 ± 0.010	0.080 ± 0.0036
Mung bean	11.6 ± 0.52	96.8 ± 1.75	31.5	0.30 ± 0.012	0.27 ± 0.012	/

N=3.

Characteristics of sweet potato starch granules

Figure 1 and table 3 show that the starch granule shapes of all the 3 sweet potato varieties were heterogeneous. They were present in different shapes, but there were no obvious differences among the 3 varieties. The granule size range of XuShu18 starch was slightly

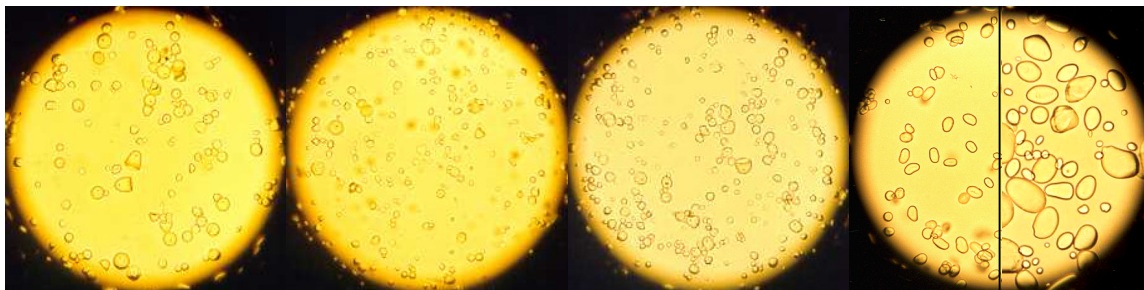


Figure 1-Light microscopy of starch granules from 3 Chinese sweet potato varieties as compared with mung bean and potato starches ($\times 200$)

Table 3-Characteristics of starch granules from 3 Chinese sweet potato varieties compared with mung bean and potato starches

Starch	Shape description	Size(μm)		Gelatinization temperature ($^{\circ}\text{C}$)*			
		Range	Mean	Initiation	Midpoint	Endpoint	Range
XuShu18	Round polygonal, polygonal, spherical, oval round	4.1-27.5	11.6 ± 0.42 (11.5)	69 ± 0.3	75 ± 1.3	82 ± 0.7	13
SuShu2	Round polygonal, polygonal, spherical, oval round	3.4-22.0	8.5 ± 0.64 (9.4)	59 ± 0.3	69 ± 1.1	79 ± 0.4	20
SuShu8	Round polygonal, polygonal, spherical, oval round	3.4-24.1	8.4 ± 0.42 (9.3)	58 ± 0.3	67 ± 1.0	77 ± 0.4	19
Potato	Oval, spherical, round polygonal	5.5-72.2	25.8 ± 0.99 (21.2)	56 ± 0.5	61 ± 1.4	67 ± 0.4	11
Mung bean	Oval, round	5.5-24.1	15.1 ± 0.42 (14.3)	65 ± 0.4	68 ± 1.1	74 ± 0.2	9

* Values measured with hot stage polarizing microscope. Values measured by Multisizer (number average) are given within parenthesis. Values of granule size are the average of 2 measurements. Values of gelatinization temperature are the average of 3 measurements.

broader than that of the SuShu2 and SuShu8 starches. The mean dimension of starch granule size measured by microscopy of XuShu18 starch was higher than that of SuShu2 and SuShu8 starches. These results were in good agreement with the results obtained by the Multisizer

(number average). Although there was no difference in the mean dimension of the starch granule size found for SuShu2 and SuShu8 starches, the particle size distribution of the 2 starches showed a clear difference (Figure 2). The particle size distribution of SuShu8 starch was the most homogeneous, while that of SuShu2 starch was the most heterogeneous of the 3 sweet potato starches.

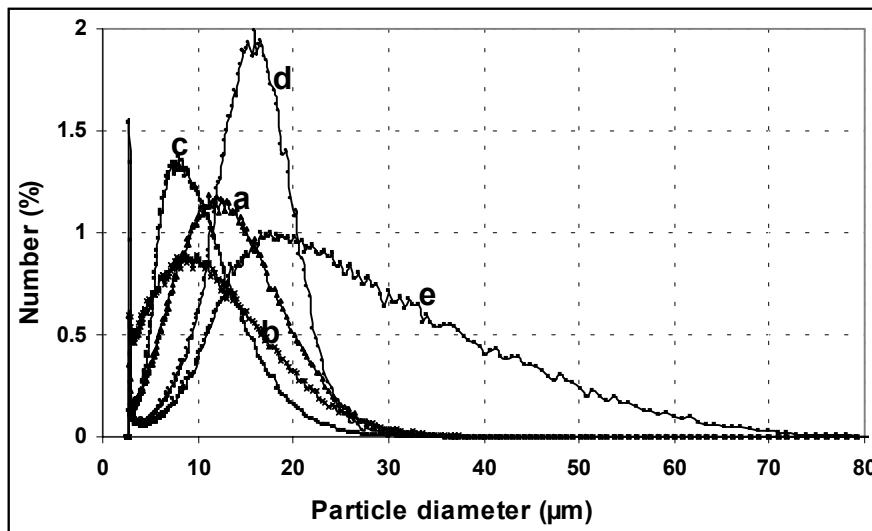


Figure 2-Starch particle size distribution from 3 Chinese sweet potato varieties as compared with potato and mung bean starches (a. XuShu18; b. SuShu2; c. SuShu8; d. Mung bean; e. Potato)

The starch granule shapes of the 3 sweet potato varieties were slightly less homogeneous than that of potato and much less homogeneous than that of mung bean. Granule size and particle size distribution are characteristics that markedly influence the functional properties of starch granules (Rasper 1971). The size range of the 3 sweet potato starches was not clearly different from that of mung bean starch but was obviously different from that of potato starch. The mean dimensions of starch granule sizes of the 3 sweet potatoes were lower than those of mung bean and potato. Particle size distributions of the 3 sweet potato starches were less homogeneous than that of mung bean starch. All of them were more homogeneous than potato starch which has the broadest particle size distribution in native starches.

Gelatinization and pasting behavior of sweet potato starches

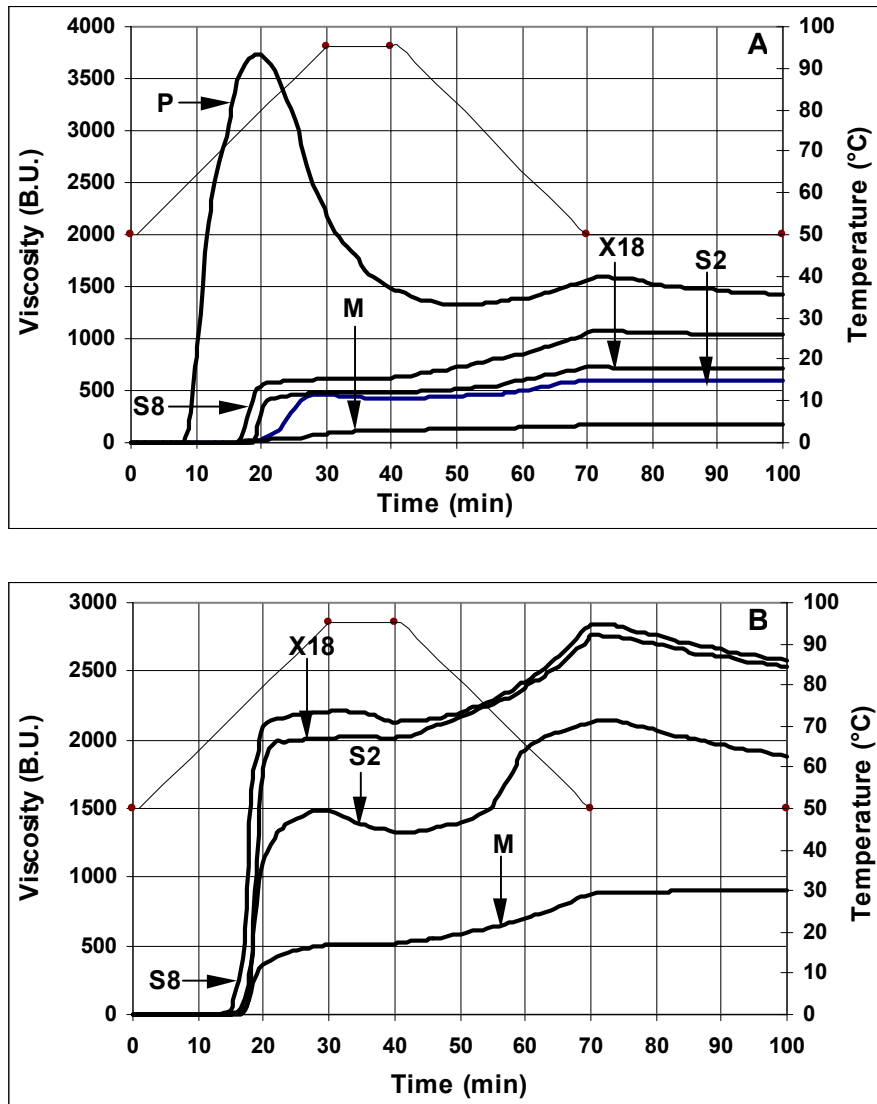


Figure 3-Brabender amylograms of 3 Chinese sweet potato starches as compared with potato and mung bean starches at concentration of 4% (A) and 6% (B) (X18: XuShu18; S2: SuShu2; S8: SuShu8; M: Mung bean; P = Potato)

Gelatinization temperature (measured by microscopy) of XuShu18 starch was higher than that of SuShu2 and SuShu8 starches (Table 3). While the gelatinization temperature range (between initiation and endpoint) of XuShu18 starch was narrower for than that of SuShu8 and SuShu2 starches. There was no clear relationship between the gelatinization temperature range and the homogeneity of particle size distribution in the 3 sweet potato starches. The Brabender amylogram showed that, at concentration of 4% and 6% (w/v), the starch pasting temperature of XuShu18 was the highest of the 3 sweet potato varieties, followed by SuShu2 and SuShu8 (Figure 3). The order in the pasting temperatures was independent of starch concentration and

was in agreement with the gelatinization temperature order measured by microscopy. It was also found that the larger the granule size the higher the gelatinization temperature in the 3 sweet potato starches. At the concentration of 4% the peak viscosity of SuShu2 starch (460 B.U.) was close to that of XuShu18 starch (484 B.U.) while SuShu8 starch did not show peak viscosity at all at this concentration. At the concentration of 6%, the peak viscosities of the starches of SuShu8 (2212 B.U.) and XuShu18 (2008 B.U.) were much higher than that of SuShu2 (1488 B.U.), although Collado and Corke (1997) reported that peak viscosity was significantly negatively correlated with amylose content. But it seems that there was no obvious relationship between the peak viscosity and amylose content of the 3 sweet potato starches studied since their amylose content was similar. The differences of the peak viscosities of the 3 sweet potato starches may partly result from the different phosphorus contents. According to Schoch and Maywald (1968), the starch paste viscosity patterns can be classified into 4 types: type A, which shows a high pasting peak followed by rapid and major thinning during cooking; type B, which shows a lower pasting peak and much less thinning during cooking; type C, which shows no pasting peak but rather a very high viscosity which remains constant or else increases during cooking; and type D, in which the amount of starch must be increased two- or three-fold to give a significant hot-paste viscosity of type C. All the amylograms of the 3 sweet potato starches showed type B behaviors, except SuShu8 at a concentration of 4% showing a type C behavior. The setback ratio is defined as the ratio of the viscosity at the completion of cooling to the viscosity at the onset of cooling (Kim and others 1996) and is usually used to predict the retrogradation tendency of starch (Karim and others 2000). At the lower concentration of 4% the setback ratio of SuShu8 starch (1.67) was the highest, followed by XuShu18 (1.51) and SuShu2 (1.40) starches, although the differences were not very clear. In contrast, the setback ratio of SuShu8 starch at a higher concentration of 6% was the lowest and SuShu2 starch was the highest of the 3 sweet potato starches. It seems the setback ratios were not strongly dependent on the amylose content of the starches but were more affected by starch concentration. RVA profiles also showed the same tendency both on pasting temperature and peak viscosity of all the samples (Figure 4). The setback ratios of the 3 sweet potato starches derived from the RVA profile at the concentrations of 4% and 8% showed the same order as seen in the Brabender amylogram at the corresponding concentrations of 4% and 6%.

The gelatinization temperature range of the 3 sweet potato starches was obviously higher than those of potato starch and mung bean starches. The gelatinization temperature and pasting temperature (measured both by Brabender amylograph and RVA) of the 3 sweet potato starches were slightly higher than those of mung bean starch and much higher than those of

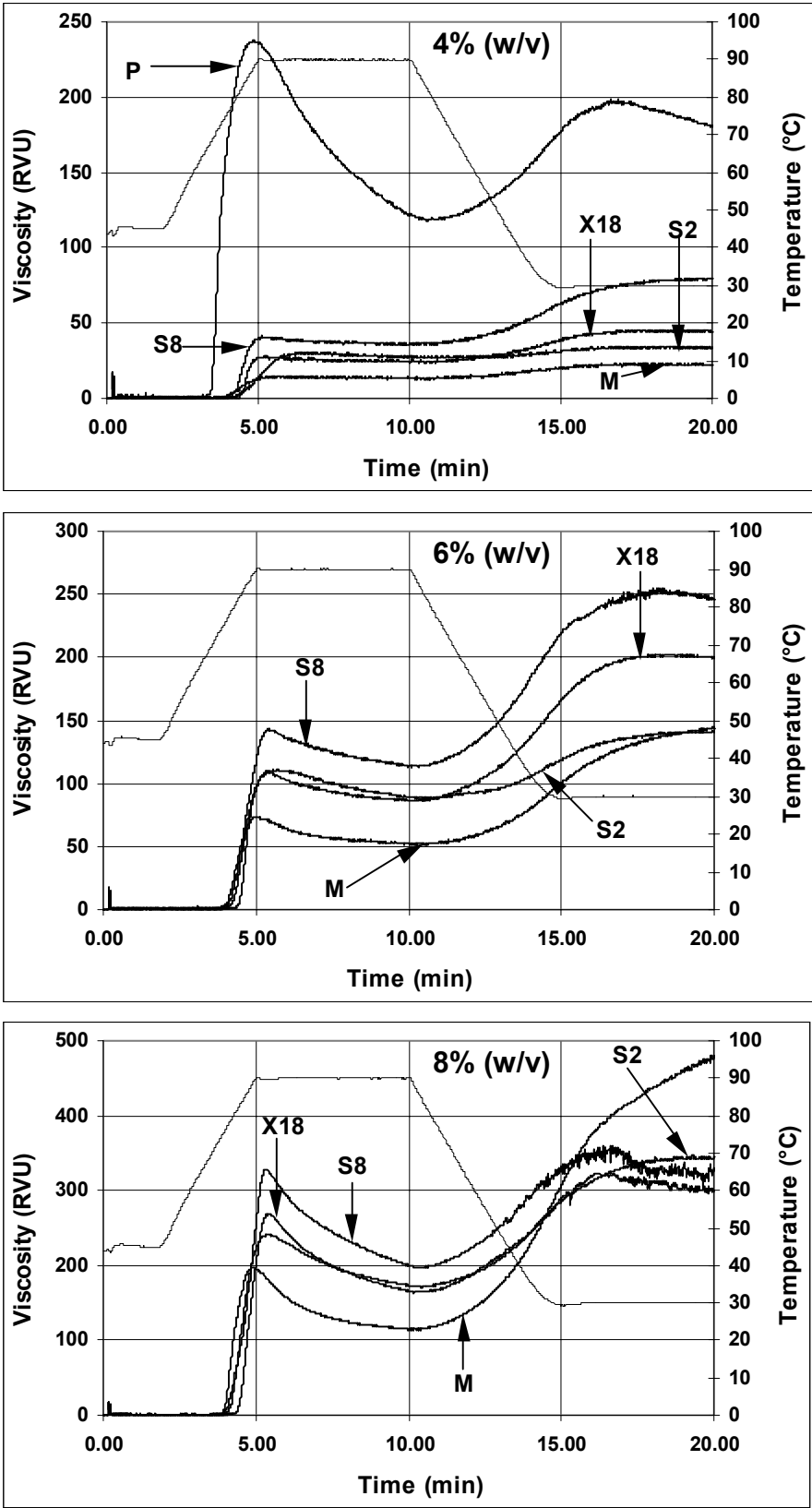


Figure 4-RVA viscosity profiles of 3 Chinese sweet potato starches as compared with potato and mung bean starches (X18 = XuShu18; S2 = SuShu2; S8 = SuShu8; M = Mung bean; P = Potato)

potato starch. At the concentration of 4% and 6% the pasting temperatures of all samples measured with RVA were slightly higher than those measured with the Brabender amylograph. At all concentrations the peak viscosity (both in the Brabender amylogram and RVA profile) of the 3 sweet potato starches are higher than that of mung bean starch but much lower than that of potato starch. In this study mung bean starch showed a typical C type in the Brabender amylogram but a B type in the RVA profile at the concentration of 6% and 8%. Potato starch showed the typical A type in both the Brabender amylograms and RVA profiles. The viscosity pattern not only depends on starch itself but is also influenced by the starch concentration. The setback ratios of all samples measured using Brabender amylograph were not consistent with the setback ratios measured using the RVA. Only at the higher concentration of 6% in Brabender amylogram and 8% in RVA profile the setback ratios of all the samples showed the same order. At these higher concentrations (6% in Brabender amylograph and 8% in RVA) the setback ratio of the starch of mung bean (1.76 and 4.19) was the highest followed by SuShu2 (1.42 and 1.99), XuShu18 (1.26 and 1.81), SuShu8 (1.21 and 1.63) and potato (1.06 and 1.38). In general, high amylose content results in high retrogradation tendency and, consequently, in high setback ratio (Collado and Corke 1997). Our results indicate that there is no obvious relationship between the setback ratio and amylose content of the starches. The setback ratio not only depends on starch properties, such as amylose content, lipid content, phosphorus content, and molecular weight, but is also affected by the starch concentration and the measuring method.

Swelling behavior of sweet potato starches

Swelling power indicates the water holding capacity of starch and has generally been used to demonstrate differences between various types of starches, such as potato, sorghum, tapioca, wheat, waxy maize and normal maize, and to examine the effects of starch modification (Crosbie 1991). Figure 5 shows that the swelling volume of SuShu2 was lower than that found for XuShu18 and SuShu8 starches. All the values found for sweet potato starches were higher than those found for mung bean starch but much lower than that found for potato starch. Both sweet potato and mung bean starches showed a two-stage swelling pattern. This type of swelling has been mentioned to be the typical swelling pattern of legume starches (Oates 1991). This is indicative for different mechanisms of interaction forces within the sweet potato starch granules. A first association was relaxed from 65-75 °C, which was again followed by a strong interaction from 80-95 °C, which was in agreement with the results on mung bean starch reported by Schoch and Maywald (1968) and Singh and others (1989). Swelling power is affected by the extent of chemical cross-bonding within the granules (Schoch 1964) and noncarbohydrate substances such as lipid or phosphate (Leach and others 1959). A high

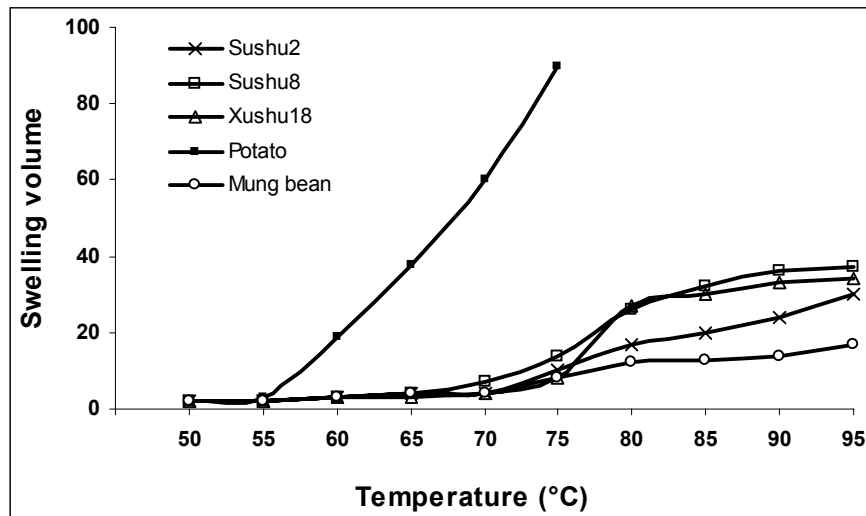


Figure 5-The swelling behavior of 3 Chinese sweet potato starches and potato and mung bean starches as influenced by temperature

amylose content as well as the presence of higher numbers of stronger intermolecular bonds may also reduce swelling (Delpeuch and Favier 1980). The swelling behavior of the 3 sweet potato starches may mainly be affected by the presence of ionizable phosphate ester groups which assist swelling by way of mutual electrical repulsion since their amylose contents were similar and the lipid content of SuShu2 was even lower than that of SuShu8 and XuShu18. In comparison with potato and mung bean starches the results suggest that sweet potato starch may have a higher degree of intermolecular association in its starch granules than potato starch but lower than mung bean starch.

Syneresis of sweet potato starches

Syneresis, in general, is related to “freeze-thaw” stability and the latter can be used as an indicator of the tendency of starch to retrograde (Eliasson and Kim 1992; Hoover and others 1997). The syneresis as a result of the 5 freeze-thaw cycles is generally measured for the excluded water by centrifugation (Karim and others 2000). It was found in our research that after the first cycle of freeze-thaw all the starch gels became sponge-like. This sponge structure made it difficult to measure the excluded water, for example, after centrifugation the sponge-like gel reabsorbed most of the separated liquid which led to misleading results. Similarly, Yuan and Thompson (1998) also found the same problem in their research. They suggested that it might be appropriate to define the first appearance of free liquid above the paste after

centrifugation. This is why we measured freeze-thaw stability as described in Materials and Methods.

Freeze-thaw stability (Figure 6a) shows that the syneresis of SuShu2 was higher than that of SuShu8 and XuShu18. Generally high syneresis indicates high retrogradation tendency of starch (Karim and others 2000). Mung bean starch showed the highest syneresis of all the samples while the syneresis of potato starch was as low as that found for SuShu8 and XuShu18 starches.

The syneresis measured without a freeze-thaw treatment (Figure 6b) shows that the retrogradation tendency of SuShu8 starch was lower than those of SuShu2 and XuShu18 starches, while that of SuShu2 starch is only slightly higher than that of XuShu18 starch. The syneresis values (without a freeze-thaw treatment) of all the 3 sweet potato starches were lower than that of mung bean starch but higher than that of potato starch.

The retrogradation tendency measured by the syneresis of freeze-thaw stability and by the syneresis without a freeze-thaw treatment (stored at 2 °C) was not in agreement with each other. Hoover and others (1997) stated the amount of water excluded in the freeze-thaw phase would be the result of increased intermolecular and intermolecular hydrogen bonding due to interaction between starch chains (amylose-amylose, amylose-amylopectin, and amylopectin-amylopectin) during frozen storage. Yuan and Thompson (1998) found that the extent of phase separation increases with an increase in the number of freeze-thaw cycles due to an increase in amylopectin retrogradation in the starch-rich phase. In fact, all starches in frozen state are hardly in the process of retrogradation while only during the freezing and thawing process the branched chains of starch may also undergo retrogradation effects. The syneresis without a freeze-thaw treatment (stored at 2°C) mainly exhibits the tendency of amylose retrogradation as amylose is more readily recrystallized at this temperature. In addition syneresis as stimulated by a freeze-thaw cycle may also reflect interactions between amylose and amylopectin.

The retrogradation tendency as measured by setback ratio of paste viscosity at the higher starch concentration (6% in Brabender amylogram and 8% in RVA profile) was in good agreement with the results measured by the syneresis without the freeze-thaw treatment (stored at 2 °C). Although setback has been generally used to predict starch retrogradation tendency (Karim and others 2000; Shelton 2000), the relatively short time (30-60 min) at higher temperature (50 °C) does not allow a very precise observation. This is why in this study only at high starch concentration the setback ratio is in agreement with the retrogradation tendency measured by the syneresis without the freeze-thaw treatment method which mainly exhibits amylose retrogradation tendency. It may suggest that the setback measured at higher

concentration of starch suspensions (>8%, w/v) from 95 °C cooling to 25 °C for a longer holding time may improve the prediction of the retrogradation tendency.

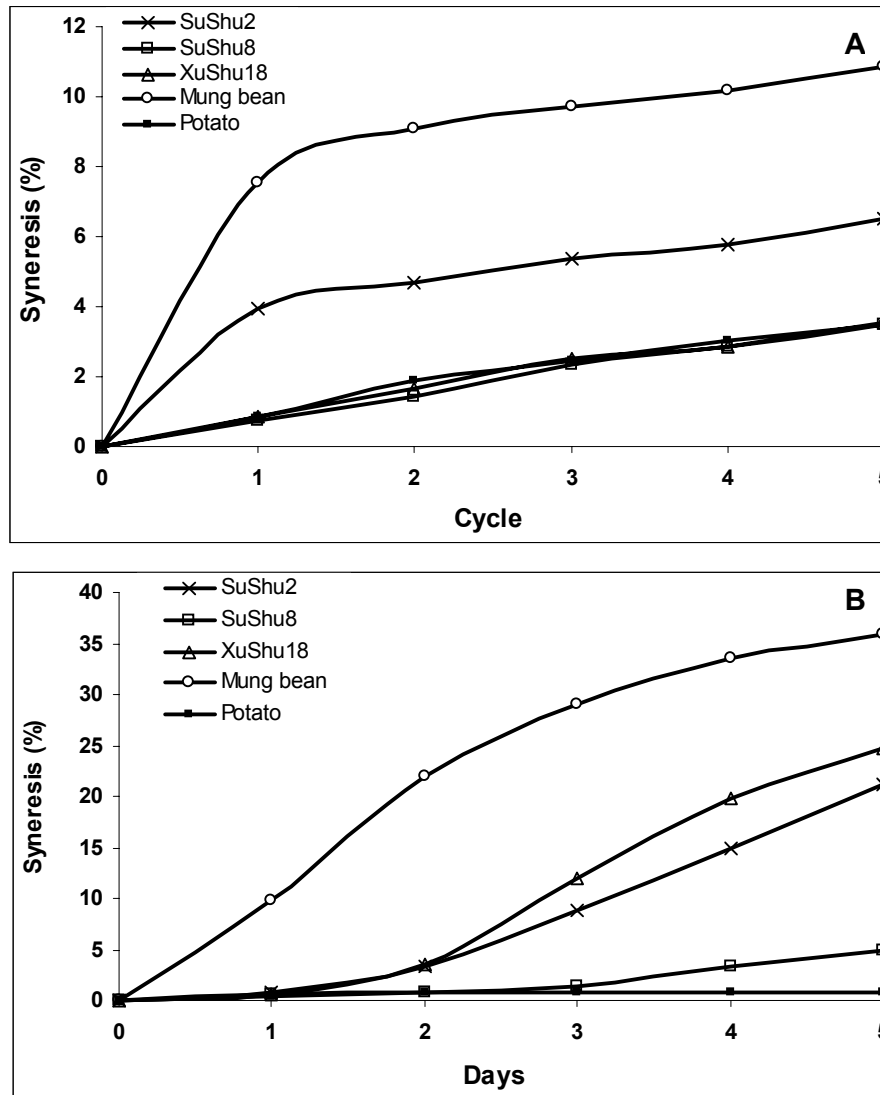


Figure 6- Syneresis of 3 Chinese sweet potato starches as compared with potato and mung bean starches (A: freeze-thaw stability; B: stored at 2 °C)

Conclusions

The “high-starch type” sweet potato root of SuShu2 contained the highest dry matter and starch. The isolated starch of SuShu2 also had the highest purity of starch. It seems that of the 3 sweet potatoes the SuShu2 root is the best raw material for starch isolation. The granule size

of XuShu18 starch was the largest, while SuShu8 starch exhibited the most homogeneous particle size distribution. SuShu8 starch showed a C type Brabender amylogram at 4% concentration and showed the highest peak viscosity at all concentrations measured in this study. SuShu2 starch presented the lowest swelling volume and the highest syneresis although the amylose content was quite similar for all sweet potato starches. The physicochemical properties of the 3 typical types of Chinese sweet potato starches are obviously different from those of Irish potato and mung bean starches. The application of the 3 sweet potato starches in starch noodle preparations will be studied in our next research.

Acknowledgment

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CHAPTER 3

Evaluation of Starch Noodles Made from Three Typical Chinese Sweet Potato Starches

ABSTRACT

The physical properties of starches from 3 typical Chinese sweet potato varieties (SuShu2, SuShu8, and XuShu18) were studied in relation to their noodle-making performance. The starch gel properties of SuShu2 differed from those of SuShu8 and XuShu18. As determined by both instrumental and sensory analysis the use of SuShu8 starch resulted in better noodle quality compared to XuShu18 and SuShu2 starches. The gel properties and noodle quality of the 3 sweet potato starches were clearly different from those of mung bean starch. Correlation between starch noodle quality and gel properties of the original starches was established.

Keywords: sweet potato, starch, gel, noodle

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Introduction

Starch noodle, also named glass noodle, clear noodle, transparent noodle, vermicelli, starch thread, FenShi, DongFen, bihon, or harusame is one of the traditional oriental foods which is popularly consumed both as a noodle food and in dishes throughout Asian countries (Takahashi and others 1985; Mestres and others 1988; Miskelly 1993; Galvez and others 1994; Kasemsuwan and others 1998; Collado and others 2001). It originates from the mainland of China and dates from at least 400 years ago (Cheng 1985). The starch noodle is obviously different from other types of noodles, such as pasta and wheat flour noodles, since it is made from gluten-free starch. The specific starch noodle dough is made from 5% of pregelatinized starch (acting as the “gluten” in wheat flour dough) mixed with 95% of the remaining (native) starch and water to a dough. Thus the starch itself plays an essential role in both starch noodle processing and the final starch noodle quality. Traditionally, mung bean starch is considered to be the most suitable raw material for starch noodle making, and the mung bean starch noodle is, consequently, regarded as the best of all kinds of starch noodles (Kim and Wiesenborn 1996; Kim and others 1996; Kasemsuwan and others 1998; Muhammad and others 1999). Due to the relatively high price of mung bean starch and the broad availability of cheaper starches, such as cereal, root and tuber starches, many efforts have been carried out to partially or totally substitute mung bean starch in high-quality starch noodles with starches of other origins (Lii and Chang 1981; Kawabata and others 1984; Takahashi and others 1985; Mestres and others 1988; Xu and Seib 1993; Kim and Wiesenborn 1996; Kim and others 1996; Kasemsuwan and others 1998; Muhammad and others 1999). Sweet potato starch is one of the promising substitutes, which is quite cheap and abundantly available. The quality of the starch noodles made from starches isolated from several varieties of sweet potatoes were reported to be inferior to mung bean starch noodles (Chang 1983). However, there are more than 2000 varieties of sweet potatoes present in China and it is known that sweet potato starch noodles are quite popular in some regions of China for many years. Unfortunately, no literature is available on the study of starch noodle preparation using the starches isolated from Chinese sweet potato varieties. Since up till now no systematic study on the processing of sweet potato starch noodles and noodle products has been performed, our study was meant to evaluate the starch noodles made from starches isolated from 3 typical Chinese sweet potato varieties using instrumental and sensory techniques. A comparison was made with high-quality mung bean starch noodles. The possibilities to predict starch noodle quality from known gel properties are discussed.

Materials and Methods

Starches

Sweet potato starches were isolated from 3 typical varieties of Chinese sweet potato, XuShu18, SuShu2, and SuShu8, which were obtained 1 week after harvest from the Sweet Potato Research Group, Nanjing Agricultural Institute, P. R. China. XuShu18, a “general type”, is the most popular variety in China, cultivated in many provinces, while SuShu2 is one of the most promising sweet potato varieties of the “high starch type”. SuShu8 represents the “roasted type” of sweet potato which is popularly used as a snack food. Mung bean starch was kindly supplied by AVEBE R&D, Foxhol, The Netherlands. The isolation of sweet potato starches has been described previously (Chen and others 2003).

Color of starches

The color of the starches was measured using a tricolor colorimeter (model LFM3, Dr. Lange, Berlin, Germany) as L, A, and B values. The L value states the position on the white/black axis, the A value the position on the red/green axis, and the B value the position on the yellow/blue axis.

Clarity of starch pastes

A 2% (w/v) starch suspension was prepared in distilled water and gelatinized in screw-cup tubes in a boiling water bath for 30 min, and then cooled to room temperature. The turbidity of the starch paste was measured with a portable turbidimeter (2100P, model 46500, Hach Company, Loveland, Colorado, U.S.A.).

Starch gel properties

A 5% (w/v) starch suspension was prepared in distilled water, gelatinized as described above, and transferred into a CVO (Creep, Viscometry and Oscillatory, Bohlin Instruments Limited, Cirencester, UK). The paste was covered with paraffin oil, cooled to 4 °C, and stored overnight. After heating the gel to 25 °C, a stress sweep profile was recorded. The oscillation frequency was 0.1 Hz. Start stress was 1 Pa, and end stress was 500 Pa. The geometry was a coaxial cylinder C 25 ($\phi = 25$ mm). The storage modulus (G'), the loss tangent ($\tan \delta = G''/G'$, G'' is the loss modulus), and the maximum strain were obtained from the profile.

Starch noodle preparation

Part of the starch (5%) was pregelatinized in distilled water (1:9 w/v) and then mixed with the remaining 95% of the starch. The mixture was kneaded with water to dough consistency “au bain-marie” at 40 °C. The uniform dough with moisture content of 55% was “extruded”

by a self-made lab-scale cylindrical extruder (100-500 g dough capacity). The dough was extruded through the holes (1.5-cm diameter) of the stainless steel cylinder by gravity, using a well fitted 2.25-kg stainless steel piston, directly into hot water (95-98 °C), and heated for 50-70 s at this temperature before transferring into cold water. The noodles were pre-cooled at 4 °C for 6 h, subsequently frozen at -5 °C for 8 h, and then dried by air. The dried noodles were equilibrated at room temperature for 4 h and then packed in polyethylene bags and stored at room temperature prior to analysis.

Texture analysis of starch noodles

The fresh starch noodles (before cooling), the noodles after freezing/thawing and cooked noodles (after boiling for 10 min in excess of water) were brought to room temperature and hung for 3 min in order to remove the water from the noodle surface.

Cohesiveness of starch noodles

The cohesiveness of starch noodles was determined by attaching 2 noodle strands to each other and pulling them apart using a texture analyzer (TA, model XT2i, Godalming, UK) as shown in Figure 1-a. The test speed was 1.00 mm/s and the 5-kg force transducer was used.

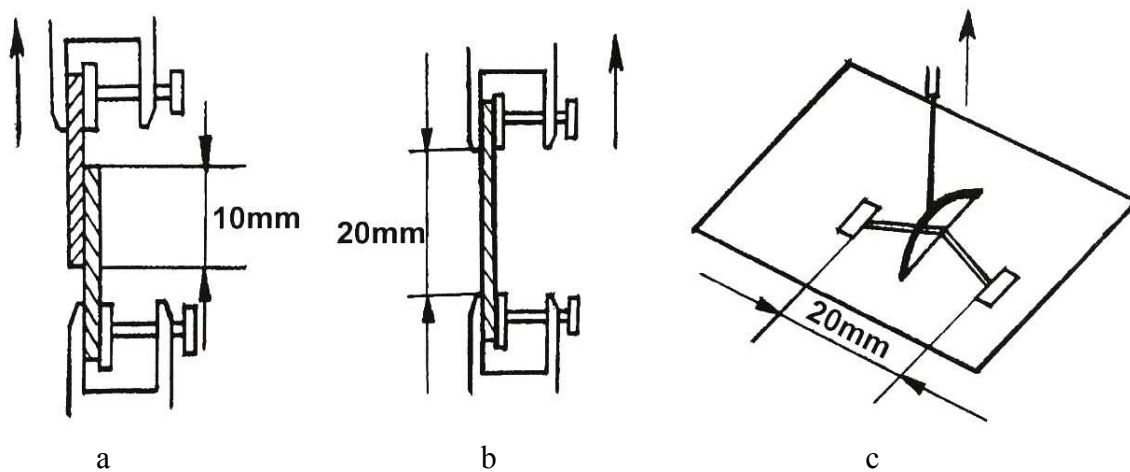


Figure 1-Schematic description of texture measurements of starch noodles

- a: Cohesiveness measurement;
- b: Extension measurement;
- c: Cutting behavior measurement.

Extension of starch noodles

The extension of dried and cooked starch noodles (a single strand) was measured by using 25-kg and 5-kg force transducers, respectively, using the texture analyzer, as shown in figure 1-b. The extension modulus (E) and the relative extension (r_e) were calculated from the following equations: $E = (F / \Delta L)(L/A)$ and $r_e = \Delta L/L$. Here F is the extension force, and A is the cross-sectional area of starch noodle. ΔL is the increased length, while L is the original length of starch noodle. The test speed was 1.00 mm/s.

Cutting behavior of starch noodles

Cutting behavior was measured using a 0.3-mm-diameter wire cutting probe to cut a single noodle strand, stabilized on the platform at 2 sides as shown in figure 1-c. Force transducers of 25kg and 5kg were used for dried and cooked starch noodle measurements, respectively. The test speed was 1.00 mm/s.

Cooking loss and swelling index

Cooking loss and the swelling index were measured according to Mestres and others (1988).

Sensory evaluation of starch noodles

A taste panel performed a quantitative descriptive analysis (QDA) to evaluate both the dried and cooked starch noodles in separate sessions. The attributes evaluated for the dried starch noodles were color, glossiness, transparency, and flexibility. For the cooked starch noodles, color, transparency, glossiness, elasticity, slipperiness, firmness, and chewiness were evaluated by the panel. Perceived intensities were scored on a 15-cm-interval scale (Kim and others 1996). The left ends of the scales corresponded to weak while the right ends corresponded to strong. Before scaling, panelists were requested to rank the samples on intensity. The panel consisted of 12 selected Chinese volunteers present in Wageningen (5 female and 7 male, of age 20 to 42, and from different regions of China) having experience with starch noodle consumption. Before the sensory evaluation was conducted the panel was trained twice by using commercial starch noodles to get familiar with the rating method and the terminology of the attributes used.

Statistical analysis

SPSS 10.0 for Windows was used for statistical analysis. Differences between noodles in sensory characteristics were tested using multivariate and Student's t-tests. The data of physical properties of the starches, sensory evaluation, and texture analysis of the starch

noodles were subjected to Pearson's product-moment correlation coefficient tests. A significance level of $p < 0.05$ was used throughout the study.

Results and Discussion

Starch color and starch paste clarity

In order to study the relationship of starch noodle color and transparency with its native starch, the starch color and its paste clarity were determined (Table 1). There was no difference in whiteness of the 3 sweet potato starches. The starch of SuShu2 was only slightly greener than that of SuSh8 and XuShu18, whereas the starches of SuShu2 and SuShu8 were more yellow than that of XuShu18. In comparison with mung bean starch all 3 types of sweet potato starch were only slightly less white. The clarity of the starch paste (2%, w/v) of SuShu8 was higher than that of XuShu18 or SuShu2. However, the paste clarity of all 3 sweet potato starches was much lower than that of mung bean starch. No correlation was found between the clarity of the starch pastes and the color of their starches. Craig and others (1989) concluded from their studies that the clarity of starch pastes depends mainly on the degree of granular integrity and the association of the chains after pasting.

Table 1-Starch color and paste clarity (2%, w/v) of 3 Chinese sweet potato varieties as compared with those of mung bean

Sample	Color			Turbidity (NTU)
	L	A	B	
SuShu2	93.25	- 0.55	3.96	784
SuShu8	93.66	- 0.35	4.27	678
XuShu18	93.63	- 0.39	2.91	778
Mung bean	95.32	0.52	1.71	486

All values were the mean of 3 measurements and coefficients of variations were less than 5%.

*NTU: Nephelometric Turbidity Unit.

Starch gel properties

The storage modulus (G') represents the firmness of the starch gel, while the loss tangent ($\tan \delta$) is a measure for the elasticity of the starch gel. It can be seen from table 2 that the starch gels of SuShu8 and XuShu18 were significantly firmer than that of SuShu2, while the elasticity

and the maximum strain were not significantly different. The starch gel of mung bean is significantly firmer and more elastic than those of the 3 sweet potatoes.

The maximum strain of mung bean starch gel was almost equal to that of the 3 sweet potato starch gels. The high gel strength of mung bean starch could be attributed to its high amylose content and longer side chains of amylopectin (Kasemsuwan and others 1998). However, the gel strength of the 3 sweet potato starches did not show any correlation with their amylose contents because the amylose contents of the 3 sweet potato starches are similar (19-20%) (Chen and others 2003).

Table 2-Stress sweep of 3 Chinese sweet potato starch gels compared with that of mung bean starch gel

Sample	G' (Pa)	tan δ	Max strain
SuShu2	160c \pm 10	0.034a \pm 0.004	0.35a \pm 0.03
SuShu8	300b \pm 17	0.030a \pm 0.003	0.35a \pm 0.05
XuShu18	320b \pm 30	0.027a \pm 0.004	0.33a \pm 0.04
Mung bean	820a \pm 27	0.007b \pm 0.001	0.38a \pm 0.03

N=3. Sample means with different letters in the same column are significantly different at $p < 0.05$.

Cohesiveness of starch noodles

One of the important factors in starch noodle production, also influencing the quality of the final product, is stickiness. Fresh mung bean starch noodles are known to have a low degree of stickiness and are easy to separate from each other during the drying process. Noodles made from other starches, including sweet potato starches, stick strongly to each other, thus causing more difficult separation during drying. Therefore, the cohesiveness of starch noodles at various stages of the preparation process may not only provide information on the separation ability of different kinds of starch noodles, but also exhibit the effects of treatments in the noodle making process, such as freezing. Several researchers have discussed this based on measuring the stickiness between the texture analyzer probe and stabilized noodle strands (Kim and Wiesenborn 1996; Kim and others 1996; Collado and Corke 1997; Collado and others 2001). Strictly speaking, this measurement is not the cohesiveness between starch noodles, but the adhesiveness between the instrument probe and the starch noodles. In this study the cohesiveness of starch noodles was determined by attaching 2 noodle strands together and the cohesive force (F_{co}) was then measured more objectively. The diameter of the fresh noodle, the noodle after freezing, and the cooked noodle were 1.7 mm, 1.6 mm, and 1.7 mm, respectively.

The cohesiveness of the fresh starch noodle of SuShu2 was the highest followed by SuShu8 and XuShu18 and the differences between them were significant (Table 3). After precooling and freezing/thawing the cohesiveness of the starch noodle of SuShu2 was still the highest, while that of SuShu8 and XuShu18 were rather similar. The cohesiveness of the sweet potato starch noodles decreased significantly by the freezing treatment. This confirms that freezing is an important step in starch noodle manufacture. A better separation of the noodles at this stage is not only due to the ice crystal formation between the starch noodle strands but also due to cohesiveness reduction of the starch noodle strands themselves. The cohesiveness of the cooked noodle of SuShu2 was significantly higher than that of SuShu8 and XuShu18, whereas the latter 2 were almost the same. The cohesiveness of cooked starch noodle not only affects the cooking property but also affects the mouthfeel of the starch noodle, such as slipperiness.

Table 3-Cohesiveness (F_{co} (N)) of starch noodles at different stages in the noodle preparation process

Sample	Noodles		
	Fresh	After freezing	Cooked
SuShu2	0.043a \pm 0.005	0.0106a \pm 0.0019	0.0075a \pm 0.0018
SuShu8	0.033b \pm 0.005	0.0068b \pm 0.0023	0.0049b \pm 0.0015
XuShu18	0.024c \pm 0.006	0.0065b \pm 0.0023	0.0050b \pm 0.0011
Mung bean	0.019c \pm 0.004	0.0044b \pm 0.0015	0.0046b \pm 0.0014

N=8. Sample means with different letters in the same column are significantly different at $p < 0.05$.

The cohesiveness of the fresh mung bean starch noodle was significantly lower than that of SuShu2 and SuShu8 fresh starch noodles, while it was quite similar to that of XuShu18 fresh noodle. This indicated that the separation of fresh mung bean starch noodles was easier than that of the noodles made from the sweet potato starches, but the starch noodles made from the different types of sweet potato also differed greatly. This is in accordance with the observation that mung bean starch noodles can be separated even without freezing, while such a freezing treatment is essential to obtain good noodles from sweet potato starches. The separation of SuShu2 fresh noodle was the most difficult one of all 3 sweet potato starch noodles. After freezing and cooking the cohesiveness of SuShu8 and XuShu18 starch noodles was not significantly higher than that of mung bean starch noodle.

Extension of starch noodles

The extension modulus (E) represents the stretch stiffness of starch noodles, while the relative extension (r_e) of the noodle strand is a measure for the stretchability of the starch noodle. Table 4 shows that the stretch stiffness (E) of dried starch noodle of XuShu18 was nearly as low as that of SuShu2, which was significantly lower than that of SuShu8. The stretchability (r_e) of SuShu8 was significantly higher than those of Sushu2 and XuShu18. The stretch stiffness of the dried mung bean starch noodle was significantly higher than the dried noodles made from SuShu2 and XuShu18, but not significantly different from that of SuShu8. The stretchability of dried mung bean starch noodle was not significantly different from that of dried SuShu2 and XuShu18 starch noodles, but was significantly less stretchable than dried SuShu8 starch noodle. Considering both the stretch stiffness and the stretchability of the cooked starch noodle, SuShu2 was performing the worst of the sweet potato starches tested. The stretch stiffness and stretchability of the cooked starch noodle of XuShu18 were not significantly different from that of SuShu8. The stretch stiffness of the cooked sweet potato starch noodles was significantly lower than that of cooked mung bean starch noodle, whereas there was no significant difference of the stretchability between the cooked SuShu8, XuShu18, and mung bean starch noodles. No clear correlation was found for the stretch stiffness and stretchability between dried and cooked stages.

Cutting behavior of starch noodles

Table 4-Texture characteristics of noodles prepared from starches of 3 Chinese sweet potato varieties and mung bean

Sample	Dried noodles				Cooked noodles		
	E (Pa)	r_e	F_c (N)	r_c	E(Pa)	r_e	F_c (N)
Sushu2	4.74×10^8 c (0.38×10^8)	9.70×10^{-2} b (0.81×10^{-2})	10.40c (1.39)	7.45×10^{-2} b (1.95×10^{-2})	2.62×10^5 c (0.55×10^5)	1.23×10^{-1} b (0.20×10^{-1})	1.13×10^{-1} c (0.24×10^{-1})
SuShu8	5.60×10^8 ab (0.44×10^8)	2.15×10^{-1} a (0.33×10^{-1})	19.69a (2.22)	1.13×10^{-1} a (0.19×10^{-1})	4.32×10^5 b (0.67×10^5)	2.59×10^{-1} a (0.72×10^{-1})	1.58×10^{-1} b (0.28×10^{-1})
XuShu18	4.95×10^8 bc (0.73×10^8)	1.11×10^{-1} b (0.26×10^{-1})	15.16b (2.32)	8.95×10^{-2} ab (1.72×10^{-2})	4.13×10^5 b (0.64×10^5)	2.16×10^{-1} a (0.36×10^{-1})	1.50×10^{-1} b (0.21×10^{-1})
Mungbean	6.10×10^8 a (1.22×10^8)	1.15×10^{-1} b (2.41×10^{-2})	19.79a (2.06)	9.86×10^{-2} a (1.39×10^{-2})	1.18×10^6 a (1.65×10^5)	1.99×10^{-1} a (2.93×10^{-2})	2.94×10^{-1} a (4.41×10^{-2})

N=8. Sample means with different letters in the same column are significantly different at $p < 0.05$. Standard deviations are given within parenthesis.

The cutting behavior is usually measured by using a cutting probe to cut the noodle strands placed on a metal platform (Galvez and others 1994; Kim and others 1996; Collado and Corke 1997; Collado and others 2001). During the study we found that it was difficult for the cutting probe to cut the noodle strands completely without inevitably touching the platform. Thus, the platform also gave a force to the cutting probe which made it rather difficult to measure values for the real cutting force of noodle strands. The results obtained from the measurements, described in Materials and Methods above, are more objective. The cutting force (F_c) and the increased length ratio (r_c) of dried noodles is a measure of the cutting firmness and the flexibility of the dried noodle strands. For the cooked noodles the cutting force (F_c) exhibits the firmness of the noodle strands which mimics the bite behavior during consumption. Table 4 shows that the dried starch noodle of SuShu8 was significantly firmer than that of XuShu18 and SuShu2 and significantly more flexible than that of SuShu2. The firmness of the dried noodle made from XuShu18 and SuShu2 starches was significantly lower as compared with that made from mung bean starch. The flexibility of dried mung bean starch noodle was only significantly higher than that of dried SuShu2 starch noodle. The firmness of the cooked starch noodles of SuShu8 and XuShu18 was significantly higher than that of SuShu2; however, all of them were significantly lower than the cooked noodle made from mung bean starch.

Cooking loss and swelling index of the starch noodles

At the cooking stage, small parts of the starch noodles will be separated from the noodle itself and suspended into the water. The noodle becomes weaker and less slippery while the cooking water becomes cloudy and thick. This is usually quantitatively described by the term “cooking loss”. During cooking or keeping in water the starch noodles will also absorb water constantly and the starch noodle will become more and more swollen and less textured. This is normally quantified by “swelling index”.

The cooking loss of the starch noodle of Sushu2 was considerably higher than that of SuShu8 and XuShu18 (Figure 2). Although the cooking loss of the starch noodle of mung bean is the lowest, both SuShu8 and XuShu18 seem to perform well with respect to this characteristic.

The swelling index of the starch noodle of SuShu2 was slightly higher than both SuShu8 and XuShu18 (Figure 3). The swelling indexes of all the 3 sweet potato starch noodles increased steadily during the first 0.5 h in hot water but were almost stable afterwards. The swelling indexes of all sweet potato starch noodles were higher than that of mung bean starch noodle, which showed a more favorable behavior. Mung bean starch noodle absorbed water slowly in the first 0.5 h but more rapidly during the period of 0.5-1 h. This characteristic gives the cooked mung bean starch noodle a good eating quality as the cooked noodles usually will be

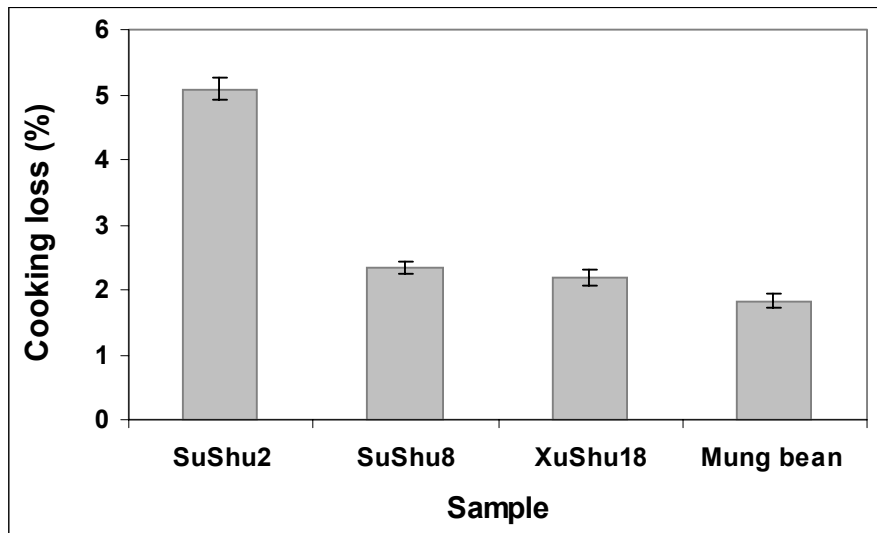


Figure 2- Cooking loss of the starch noodles made from 3 Chinese sweet potato varieties and mung bean

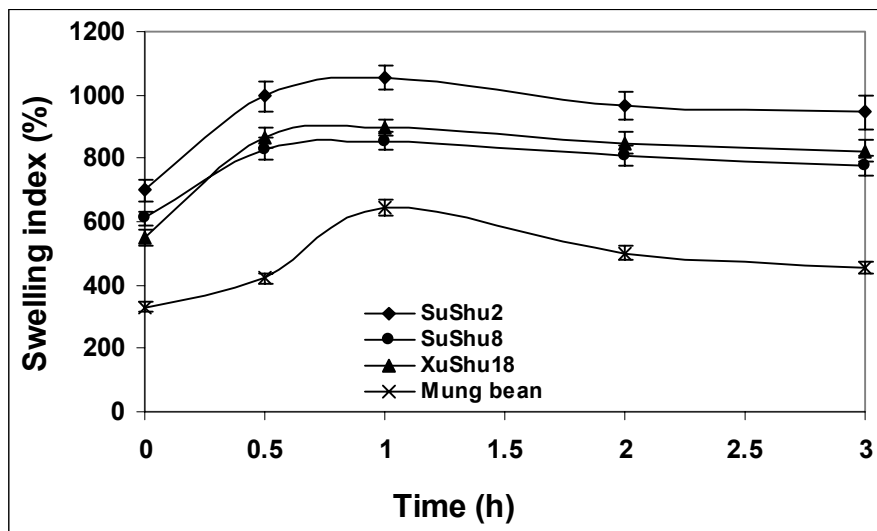


Figure 3-Swelling index of the starch noodles soaked in hot distilled water (90 °C)

consumed within 0.5 h. All the starch noodles were saturated after soaking for 1 h. All the swelling indexes showed a slight decrease in time after saturation due to the increased loss of small pieces or particles released from the saturated noodles.

Correlation between starch gel properties and cooking qualities of starch noodles

Cooking loss and swelling index are affected by recrystallization of the starch (Mestres and others 1988; Kim and Wiesenborn 1996) which also influences starch gel properties. It was found that the swelling index was significantly correlated with the G' (-0.985 , $p < 0.05$). The high firmness of the starch gel can predict low swelling index of the starch noodle made from such a starch. This suggests that the stress sweep measurement of the starch gel can be a useful method to predict the cooking quality of the starch noodles.

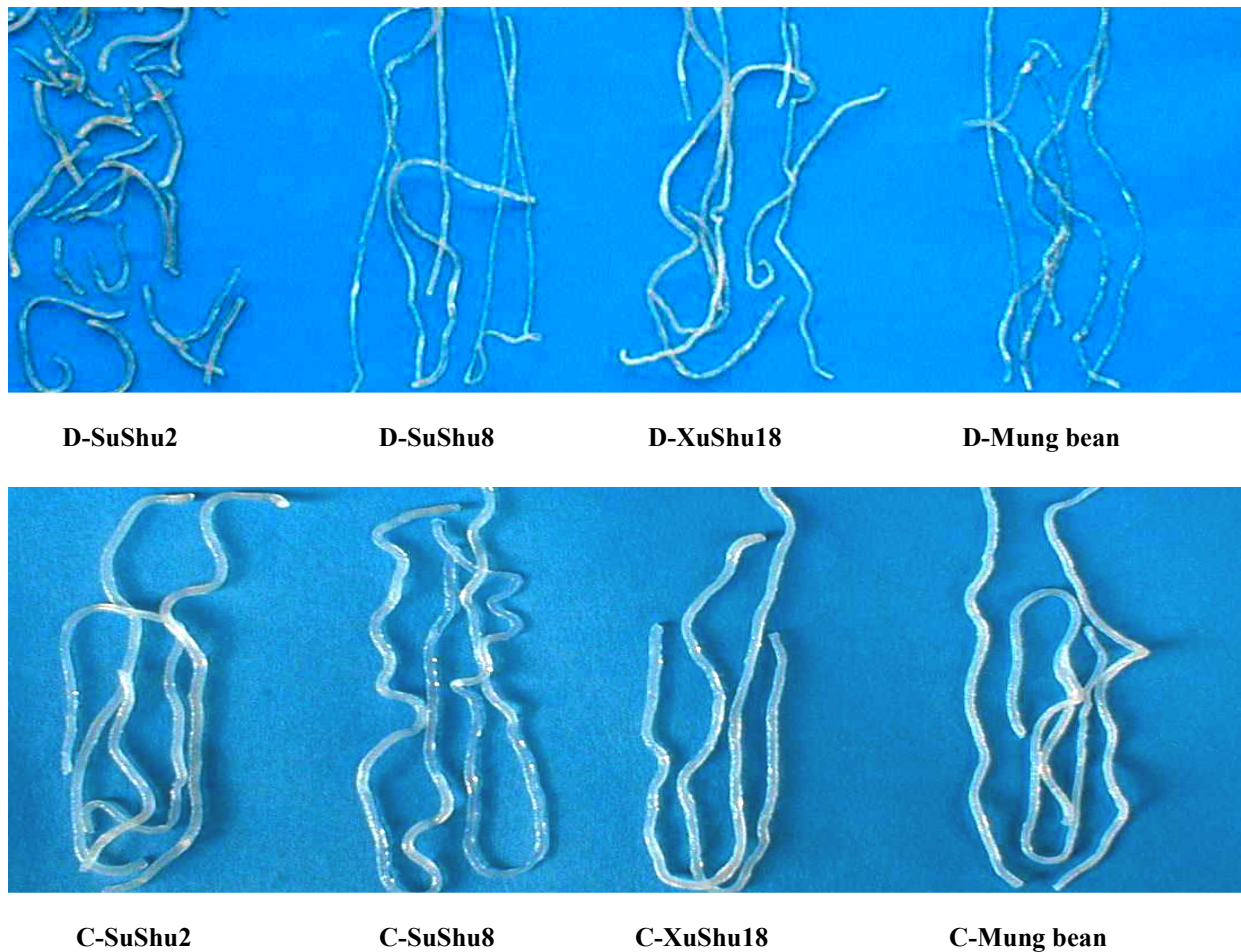


Figure 4-The appearance of the dried (D-) and cooked (C-) noodles made from 3 sweet potato and mung bean starches

Dried noodle sensory evaluation

Appearance of dried noodles is an important factor; it usually influences the purchasing behavior of customers. The appearances of the dried starch noodles are shown in figure 4. The perceived color of the dried starch noodles of SuShu8 and XuShu18 were significantly lighter than that of SuShu2 (Table 5). No significant difference in color was found by the panel between the dried noodles made from SuShu8 and mung bean starches, while mung bean noodle was significantly lighter than SuShu2 and XuShu18 noodles. The transparency of dried starch noodle of SuShu8 was the highest followed by XuShu18 and SuShu2 and the differences between them were significant. The dried mung bean starch noodle was significantly more transparent than SuShu2 and XuShu18, but not significantly different from SuShu8. The glossiness of the dried starch noodle of SuShu2 was significantly lower than that of SuShu8 and XuShu18. The glossiness of the dried starch noodle of mung bean was significantly higher than that of SuShu2 and XuShu18. The dried starch noodle of SuShu8 was as flexible as that of mung bean and both of them were significantly more flexible than SuShu2 and XuShu18. The preference test showed that the dried starch noodle of SuShu8 was nearly as preferable as dried mung bean starch noodle, and both were significantly more preferable than that of XuShu18 and SuShu2.

Table 5-Mean scale length values of sensory attributes and preference of dried noodles made from 3 Chinese sweet potato and mung bean starches

Samples	Attributes				Preference
	Color	Transparency	Glossiness	Flexibility	
SuShu2	10.9 ± 2.0a	5.6 ± 3.2c	5.0 ± 2.5c	6.2 ± 3.4b	5.3 ± 2.1c
SuShu8	6.9b ± 2.1c	9.6 ± 2.9a	8.9 ± 3.2ab	10.3 ± 2.3a	10.1 ± 2.6a
XuShu18	8.7 ± 1.6b	6.9 ± 2.1b	7.5 ± 2.3b	7.8 ± 2.7b	8.1 ± 2.6b
Mung bean	5.5 ± 2.2c	10.5 ± 3.1a	11.1 ± 3.2a	10.5 ± 2.5a	11.7 ± 1.4a

N=12. Sample means with different letters in the same column are significantly different at $p < 0.05$.

The preference of the dried starch noodle correlated significantly with the attributes of the color (-0.993 , $p < 0.01$), transparency (0.973 , $p < 0.05$), glossiness (0.991 , $p < 0.01$), and flexibility (0.972 , $p < 0.05$). All 4 attributes affected the preference significantly. Glossiness and color even showed a significant correlation with preference at $p < 0.01$.

Cooked noodle sensory evaluation

The appearances of the cooked starch noodles are shown in figure 4. There were no significant differences found between the scores of the attributes of color, transparency, glossiness, and slipperiness (Table 6). The elasticity of the cooked noodle of SuShu8 was the highest and was significantly different from that of SuShu2 and XuShu18. The firmness of the cooked starch noodle of SuShu8 was significantly higher than that of SuShu2 but was not significantly different from XuShu18 and mung bean. The chewiness of the cooked starch noodle of SuShu2 was significantly lower than that of SuShu8, XuShu18, and mung bean. The preference for the cooked starch noodle of SuShu8 was significantly higher than for the others including cooked mung bean starch noodle. This indicates the starch noodles made from some sweet potato varieties can probably compete for human consumption with mung bean starch noodle (which is generally regarded as the best quality) in the cooked state. No significant correlation was found between the attributes and the preference of the cooked starch noodles.

Table 6-Mean scale length values of sensory attributes and preference of the cooked noodles made from 3 Chinese sweet potato and mung bean starches

Samples	Attributes							Preference
	Color	Transparency	Glossiness	Elasticity	Slipperiness	Firmness	Chewiness	
SuShu2	6.8 ± 3.4a	6.1 ± 3.5a	7.7 ± 3.1a	6.1 ± 3.5b	9.4 ± 3.1a	4.8 ± 2.0c	5.9 ± 2.1b	6.3 ± 3.1b
SuShu8	5.4 ± 3.7a	7.3 ± 4.3a	9.4 ± 1.8a	11.5 ± 2.1a	11.0 ± 1.9a	8.3 ± 3.0ab	9.8 ± 2.0a	11.8 ± 2.6a
XuShu18	6.3 ± 2.9a	6.2 ± 2.8a	8.1 ± 2.5a	7.9 ± 3.5b	9.6 ± 2.0a	6.6 ± 2.2b	8.7 ± 2.8a	7.6 ± 2.6b
Mung bean	6.0 ± 4.2a	5.1 ± 2.6a	9.2 ± 2.7 a	8.8 ± 4.5ab	11.0 ± 2.2a	10.0 ± 2.7a	10.3 ± 2.6a	8.5 ± 3.0b

N=12. Sample means with different letters in the same column are significantly different at $p < 0.05$.

Correlation between the physical properties of starch and the results of texture analysis and sensory evaluation of the starch noodles

The characteristics of both the dried and cooked starch noodles are affected by the properties of the original starch itself. However, no significant correlation of either the preference or the attributes (color, transparency, and glossiness) between the dried and cooked starch noodles was found in this study.

The color, transparency, and glossiness are attributes that play important roles in the appearance of both dried and cooked starch noodles. However, no statistically significant correlation was found between the color, transparency, and glossiness of starch noodles

(evaluated by the sensory panel), and their starch color and paste clarity. The transparency of the starch noodle is not affected by its starch paste clarity but is at least partly affected by the degree of starch retrogradation. This will be dealt with in our future research.

Since no correlation was found between the noodle quality and the physicochemical properties described previously (Chen and others 2003), the starch gel properties appear to be more suitable for predicting final noodle quality. It was found that the G' of the starch gel had a significant correlation with E (0.997, $p < 0.01$) and F_c (0.998, $p < 0.01$) of the cooked starch noodles; whereas $\tan \delta$ had a significant correlation with E (-0.960, $p < 0.05$) of the cooked starch noodles. This suggested that high firmness and elasticity of the starch gel can predict high stretch stiffness and bite firmness of the cooked starch noodles. This result confirms that the starch gel properties can be used to predict the cooked noodle quality. The poor property of SuShu2 starch noodle may result from its much weaker gel structure. Cooking loss was significantly correlated with cohesiveness (0.997, $p < 0.01$), while swelling index was significantly correlated with stretch stiffness (-0.969, $p < 0.05$) and bite firmness (-0.974, $p < 0.05$) of the cooked starch noodles.

Comparing sensory evaluation results with texture analysis results, only a significant correlation between flexibility (0.990, $p < 0.05$) and preference (0.975, $p < 0.05$) of sensory evaluation and the cutting force of texture instrumental measurement of the dried starch noodles, and a significant correlation (-0.973, $p < 0.05$) between sensory chewiness and instrumental cohesiveness of the cooked starch noodles, were found. This result also shows that the attempt to use instrumental results to objectively quantify sensory attributes for foods is not easy. For the time being, both methods of sensory (subjective) evaluation and instrumental (objective) measurement are necessary and important to measure food appreciation.

Conclusions

The differences in the starch physical properties and their noodle qualities for 3 Chinese sweet potato varieties were obvious. The quality of both dried and cooked starch noodle of Sushu8 was the best, while that of SuShu2 was the worst of the 3 sweet potato starch noodles. Starch with high firmness and elasticity of its gel will result in good-quality starch noodle. Starch noodle quality can be predicted by starch gel properties. The qualities of dried and cooked starch noodles made from the 3 Chinese sweet potato varieties determined by both texture analyzer and sensory evaluation showed some difference. It can be said that dried starch noodle made from SuShu8 sweet potato had a final quality well comparable to the noodle made from mung bean starch. This was surely not the case for SuShu2 and XuShu18. For cooked noodles, the quality of SuShu8 was even better than that of cooked mung bean

starch noodle. Therefore, the statement in the literature cited that sweet potato starch is not very suitable for starch noodle making is generally incorrect. Obviously this depends on variety. The best performing sweet potato variety in our study is usually used for preparing roasted sweet potato food and may not have yet been tested for starch noodle preparation.

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CHAPTER 4

Starch Granule Size Strongly Determines Starch Noodle Processing and Noodle Quality

ABSTRACT

Chemical compositions, physical properties, and suitability for starch noodle making of different granule size fractions from potato and sweet potato starches were studied. The ash content, amylose content, phosphorus content, gel firmness, and freeze-thaw stability of small-size granule fractions (<20 μm) were significantly different from those of the large-size granule fractions. The processibility and the qualities evaluated by objective and subjective methods of both dried and cooked starch noodles made from small-size granule fractions were significantly better than those made from their initial starch preparations and much better than those made from the large-size granule fractions.

Keywords: sweet potato, potato, starch, granule size, starch noodle

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Introduction

It is well known that starch granules exist within a broad range of size distributions in nature. Physicochemical properties and structures of differently sized granule fractions of wheat, corn, barley, potato, amaranth and quinoa starches have been characterized (Appolonia and Gilles 1971; Kulp 1973; Goering and DeHaas 1974; Kainuma and others 1978; Ghiasi and others 1982; Soulaka and Morrison 1985; Jane and others 1992; Vasanthan and Bhatta 1995; Wilhelm and others 1998; Takeda and others 1999; Fortuna and others 2000; Tang and others 2001a; 2001b). Large-size granule fractions were found to be more susceptible to chemical and enzymatic hydrolysis (Farmakis and others 2000). Small-size granule fractions of barley had lower amylose contents than their larger fractions (Takeda and others 1999; Tang and others 2001b). However, no significant difference in amylose content was found for large- and small-size granule fractions of potato starch; the small-size granule fraction of potato starch had a higher phosphorus content (Kainuma and others 1978). Fortuna and others (2000) observed that large-size granule fractions of potato and wheat starches produced solutions having higher viscosity than small-size granule fractions; the difference was explained by the higher swelling capability of large granules and the higher resistance of small granules to external factors. However, for corn starch no significant difference in viscosity were noticed in pasting curves between its initial and fractionated starches. Small-size granule fraction starches have been reported in the applications of fat substitutes, starch-filled degradable plastic films, face (dusting) powders, stabilizers in baking powder and laundry-stiffening agents (Jane 1992; Jane and others 1992). In our previous studies of the physicochemical properties of sweet potato starches and their application in starch noodle production (Chen and others 2002; 2003) we reported a significant correlation between starch gel firmness and starch noodle qualities. In addition, starch granule size also was shown to have a relationship with starch noodle processing and final noodle quality. In order to understand that either granule size dimension or homogeneity of the granule size distribution affects starch noodle preparation, the characteristics of differently sized granule fractions of sweet potato and potato starches were investigated in relation to starch noodle preparation. The results are described in this paper.

Materials and Methods

Starch granule fraction separation

Potato starch (granule size: 6-75 μm ; measured with a Coulter Multisizer) was obtained from AVEBE R&D, Foxhol, the Netherlands. Sweet potato starches, SuShu2 (granule size: 4-30 μm ; Coulter Multisizer) and XuShu18 (granule size: 4-30 μm ; Coulter Multisizer), have been

described previously (Chen and others 2003). Starches were fractionated by sieving (model AS200 digit; F. Kurt Retsch GmbH & Co., Haan, Germany) with tap water, and then air-dried at 40 °C. Potato starch was separated into 4 fractions: larger than 53 µm, 36-53 µm, 20-36 µm and smaller than 20 µm, while sweet potato starches were separated only into 2 fractions: larger than 20 µm and smaller than 20 µm.

Analytical methods

Moisture, ash, amylose content, phosphorus content and swelling power were determined respectively, by the official German method (Lyne 1976a), AOAC method (Lane 1990), the method of Bates and others (1943), the method of Corn Industries Research Foundation (Lyne 1976b), and the method of Konik and others (1993) (for original and fractionated potato starches 0.50 g of sample was used instead of 1.00 g for swelling power determination). Protein content ($6.26 \times N$) was determined by using the Dumas combustion method apparatus (model NA 2100; ThermoQuest CE Instruments, Rodano, Italy). The measurements of gelatinization temperature using a Kofler hot-stage polarizing microscope, pasting behavior using RVA (4% w/w), starch color using a tricolor colorimeter, sweep stress of starch gel (6%, w/v) using a CVO, (Bohlin Instrument), freeze-thaw stability (5%, w/v), cooking loss and swelling index of starch noodle, and starch noodle texture using a texture analyzer, were described previously (Chen and others 2002; 2003).

Starch noodle preparation

Part of the starch (5%) was pregelatinized in distilled water (1:9 w/v) and then mixed with the remaining 95% of the starch. The mixture was kneaded with water to dough consistency “au bain-marie” at 40 °C. The uniform dough with moisture content of 55% was “extruded” by a self-made lab-scale cylindrical extruder (100-500 g dough capacity). The dough was “extruded” through the holes (1.5-cm diameter) of the stainless steel cylinder by gravity, using a well fitted 2.25-kg stainless steel piston, directly into hot water (95-98 °C), and heated for 50-70 s at this temperature before transferring into cold water. The noodles were pre-cooled at 4 °C for 6 h, subsequently frozen at -5 °C for 8 h, and then dried by air. The dried noodles were equilibrated at room temperature for 4 h and then packed in polyethylene bags and stored at room temperature prior to analysis (Chen and others 2002).

Statistical analysis

SPSS 10.0 for Windows was used for statistical analysis. Differences between samples of

different fractions were tested using general linear model univariate tests. A significance level of $p < 0.05$ was used throughout the study.

Results and Discussion

Chemical components of different granule size fractions

Table 1-Chemical composition of different granule size fractions of potato and sweet potato starches

Sample	Yield (%)	Moisture (%)	Ash (db, %)	Protein (db, %)	Amylose (db, %)	Phosphorus (db,%)
Potato	100	8.9	0.30 ± 0.01b	0.09 ± 0.03a	22.8 ± 0.17b	0.69c
Potato >53 μm	36	9.0	0.23 ± 0.02c	0.08 ± 0.04a	23.6 ± 0.15a	0.60d
Potato 36-53 μm	42	8.6	0.28 ± 0.02bc	0.09 ± 0.03a	22.9 ± 0.10b	0.69c
Potato 20-36 μm	17	8.6	0.33 ± 0.02b	0.08 ± 0.04a	22.1 ± 0.25c	0.75b
Potato <20 μm	5	8.2	0.45 ± 0.02a	0.10 ± 0.04a	21.3 ± 0.12d	0.98a
SuShu2	100	7.4	0.11 ± 0.01ab	0.13 ± 0.03a	19.4 ± 0.10ab	nd
ShShu2 >20 μm	42	7.8	0.13 ± 0.01a	0.12 ± 0.03a	19.7 ± 0.21a	nd
SuShu2 <20 μm	58	7.6	0.08 ± 0.02b	0.10 ± 0.04a	19.2 ± 0.20b	nd
XuShu18	100	7.9	0.21 ± 0.02b	0.22 ± 0.02a	20.5 ± 0.20b	nd
XuShu18 >20 μm	33	7.6	0.46 ± 0.02a	0.24 ± 0.01a	22.5 ± 0.15a	nd
XuShu18 <20 μm	67	7.7	0.09 ± 0.03c	0.23 ± 0.02a	19.7 ± 0.15c	nd

All values were the mean of 3 measurements. The coefficients of variations of yield, moisture, and phosphorus content are less than 10%. Values with different letters in the same column of same variety are significantly different at $p < 0.05$. nd: value was not determined.

In general, potato starches have the broadest granule size distributions (range of 5-100 μm) of all varieties of native starches. Table 1 shows that nearly 80% of potato starch granules were larger than 36 μm, while only 5% were smaller than 20 μm. The yield of the small-size granule fraction (<20 μm) of XuShu18 was higher than that for SuShu2. The relative amounts of the different granule size fractions obtained by sieving were in agreement with granule size distributions (measured with a Coulter Multisizer) of their initial starches (Chen and other 2003). Combining the method used (sieving) and data on size distribution of initial starches it can be concluded that the separated fractions are much more uniform than their corresponding

initial starches. The ash content of the small-size granule fraction (<20 μm) of potato starch was significantly higher than that of larger-size granule fractions, while the opposite results were found in SuShu2 and XuShu18 sweet potato starches. The protein content was not significantly different for the different fractions of both potato and sweet potato starches. All fractions of potato and sweet potato starches showed significantly lower amylose levels in the small-size granules. Similar results have also been found for wheat starches (Soulaka and Morrison 1985) and barley starches (Takeda and others 1999; Tang and others 2001b), although Kainuma and others (1978) reported no difference in amylose content between large and small-size granule fractions of potato starch. The phosphorus content was significantly different between different granule fractions of potato starch: the smaller the granule size, the higher the phosphorus content. This is in agreement with the result found by Kainuma and others (1978). However, the phosphorus content showed a clear negative correlation with amylose content in our study.

Physical properties of different granule size fractions

Table 2- Physical properties of different granule size fractions of potato and sweet potato starches

Sample	Color			Gelatinization temperature ($^{\circ}\text{C}$)				SP(%)
	L	A	B	Initiation	Midpoint	Endpoint	Range	
Potato	94.32	0.66	0.41	57.6	62.9	69.2	11.6	60.5
Potato >53 μm	93.33	-0.98	2.73	58.2	63.4	68.7	10.5	50.0
Potato 36-53 μm	93.44	-0.34	1.24	58.4	62.4	67.1	8.7	48.6
Potato 20-36 μm	93.78	-0.07	0.71	57.2	61.8	66.8	9.6	59.7
Potato <20 μm	93.17	-0.06	0.16	57.8	62.4	67.3	9.5	77.9
SuShu2	93.48	-0.53	3.92	59.1	68.8	78.8	19.7	21.5
ShShu2 >20 μm	90.63	-1.31	8.01	60.9	67.9	77.8	16.9	21.7
SuShu2 <20 μm	93.19	-0.70	4.47	61.0	68.0	78.2	17.2	24.3
XuShu18	93.62	-0.42	2.93	68.8	75.3	82.2	13.4	26.7
XuShu18 >20 μm	91.73	-1.38	6.12	68.6	73.6	78.8	10.2	26.4
XuShu18 <20 μm	92.86	-1.01	4.27	67.2	71.4	78.6	11.4	26.8

All values are the means of 3 measurements and the coefficient of variations are less than 10%.

SP: swelling power; L: white/black value; A: red/green value; B: yellow/blue value.

The larger-size granule fractions ($>20\ \mu\text{m}$) of potato starch had a slightly different color when compared to the small-size granule fraction ($<20\ \mu\text{m}$). Quantification of these changes using L, A and B values (Table 2) showed that the larger-size granule size fractions of potato starch were slightly more white, green and yellow than the small-size granule fraction. However, the large-size granule fractions ($>20\ \mu\text{m}$) of SuShu2 and XuShu18 starches were less white but more green and yellow than their small-size granule fractions ($<20\ \mu\text{m}$).

The initiation, midpoint and endpoint of gelatinization temperatures of the different granule size fractions of potato and sweet potato starches and their initial starches were rather similar. The gelatinization temperature range (from initiation to endpoint) for the different granule size fractions were only slightly narrower than those of their initial starches. This suggests that gelatinization temperature was more affected by the origin of the starch than by starch granule size or homogeneity in granule size distribution.

The swelling power of the small-size granule fractions ($<20\ \mu\text{m}$) of potato and SuShu2 sweet potato starches was higher than that of their large-size granule fractions. This is in agreement with the lower amylose contents measured in the small-size granule fractions. Consequently, the higher content of amylopectin, which dominantly forms the sedimentary gel of the heated starch slurry after centrifugation, resulted in higher swelling power. However, the swelling powers of different granule size fractions of XuShu18 starch were rather similar despite of the difference in amylose content. So, the origin of starch seems to be quite important in addition to granule size and amylose content.

Stress sweep results showed that all the gels made from small-size granule fractions ($<20\ \mu\text{m}$) of potato and sweet potato starches were significantly firmer (G' ; the higher G' the firmer the starch gel) than those made from their large-size granule fractions (Table 3). The elasticity ($\tan \delta$; the lower $\tan \delta$, the more elastic the starch gel) and maximum strain of gels prepared from the different granule size fractions were not significantly different. This result also confirmed our previous conclusion that the firmness of starch gels was not significantly correlated with amylose content (Chen and others 2002). However, comparing some of the gels of potato and sweet potato starches shows that similar size granule fractions strongly differ in starch gel firmness.

As found for the initial starches (Chen and others 2003), all the fractions obtained showed a B type of RVA profile (Figure 1). The small-size granule fraction ($<20\ \mu\text{m}$) of potato starch showed a typical 2-step swelling pattern. Kainuma and others (1978) explained this observation by high phosphate contents. They found that there was no difference in iodine binding capacity, beta-amylolysis limit, chain length distribution, and amylose content between large ($>50\ \mu\text{m}$) and small ($<10\ \mu\text{m}$) granule potato starch, although the phosphate content

Table 3-Stress sweep of different granule size fractions of potato and sweet potato starches

Sample	G' (Pa)	tan δ	Max strain
Potato	307 \pm 6b	0.038 \pm 0.004a	0.76 \pm 0.03a
Potato >53 μ m	260 \pm 10c	0.039 \pm 0.004a	0.80 \pm 0.02a
Potato 36-53 μ m	270 \pm 10c	0.038 \pm 0.003a	0.74 \pm 0.04a
Potato 20-36 μ m	297 \pm 6b	0.037 \pm 0.004a	0.75 \pm 0.02a
Potato <20 μ m	347 \pm 6a	0.036 \pm 0.003a	0.78 \pm 0.03a
SuShu2	230 \pm 10b	0.038 \pm 0.004a	0.65 \pm 0.04a
ShShu2 >20 μ m	223 \pm 6b	0.039 \pm 0.002a	0.70 \pm 0.03a
SuShu2 <20 μ m	260 \pm 10a	0.038 \pm 0.003a	0.70 \pm 0.03a
XuShu18	413 \pm 12b	0.024 \pm 0.004a	0.68 \pm 0.04a
XuShu18 >20 μ m	310 \pm 10c	0.026 \pm 0.002a	0.74 \pm 0.03a
XuShu18 <20 μ m	547 \pm 6a	0.020 \pm 0.004a	0.70 \pm 0.04a

N=3. Sample means with different letters in the same column of same variety are significantly different at $p < 0.05$.

differed greatly. The pasting temperature of the small-size granule fraction (<20 μ m) of potato starch was slightly lower than that of large-size granule fraction (>53 μ m). No difference was found in pasting temperature between large, small-size granule fractions and their initial sweet potato starches. The peak viscosity of the different granule size fractions of potato starches was quite similar (89-96 RVU), but all of them were lower than that of initial potato starch (117 RVU). However, Fortuna and others (2000) found that the lowest viscosity was obtained for the initial potato and wheat starches. This may be due to the different potato variety used, since we also observed quite some differences for both sweet potato starches having the same granule size. No clear difference was found for SuShu2 and XuShu18 sweet potato starches and their corresponding fractions (28-33 and 37-42 RVU, respectively). The breakdown values (the difference between peak viscosity and trough viscosity) for the different granule size fractions and their initial starches of both potato and sweet potatoes were not obviously different. This indicates that the hot paste stability is neither affected by starch granule size dimension nor by the homogeneity of the granule size distribution but by the origin of starch. The setback ratios of small-size granule fractions (<20 μ m) of potato (1.85) and SuShu2 (1.63) were slightly higher than those found for the larger granule fractions (1.70-1.82 and 1.60, respectively). All the isolated granule fractions of potato and SuShu2 showed higher setback ratios than their initial starches (1.70-1.85 versus 1.59 and 1.60-1.63 versus 1.28). However, there was no difference in setback ratio between large-size (1.80) and small-size (1.80) granule

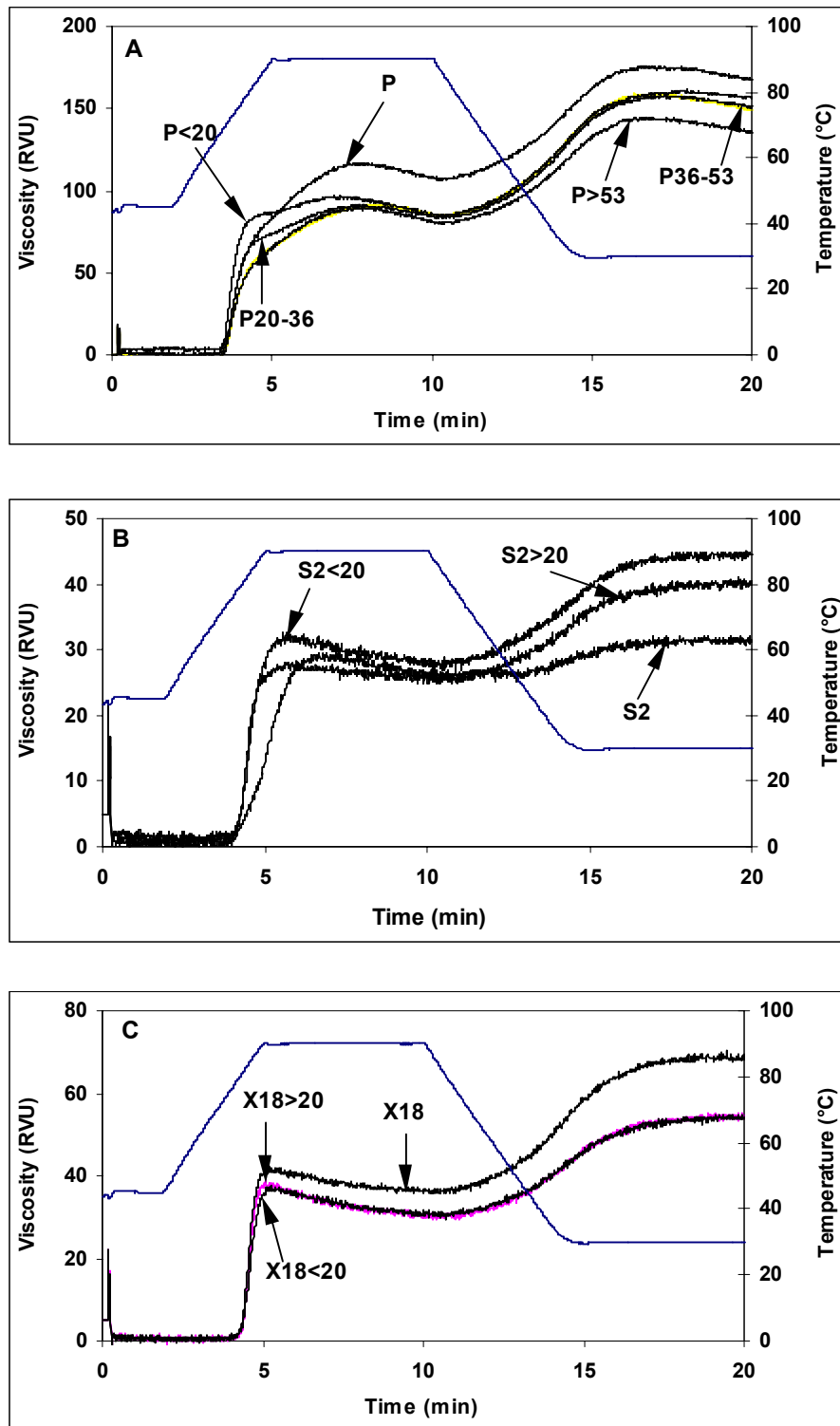


Figure 1-RVA profiles of different granule size fractions of potato (A) and sweet potato SuShu2 (B) and XuShu18 (C) starches (P: Potato; P >53: Potato >53 μm ; P 36-53: Potato 36-53 μm ; P 20-36: Potato 20-36 μm ; P <20: Potato <20 μm ; S2: SuShu2; S2 >20: SuShu2 >20 μm ; S2 <20 μm : SuShu2 <20 μm ; X18: XuShu18; X18 >20: XuShu18 >20 μm ; X18 <20: XuShu18 <20 μm).

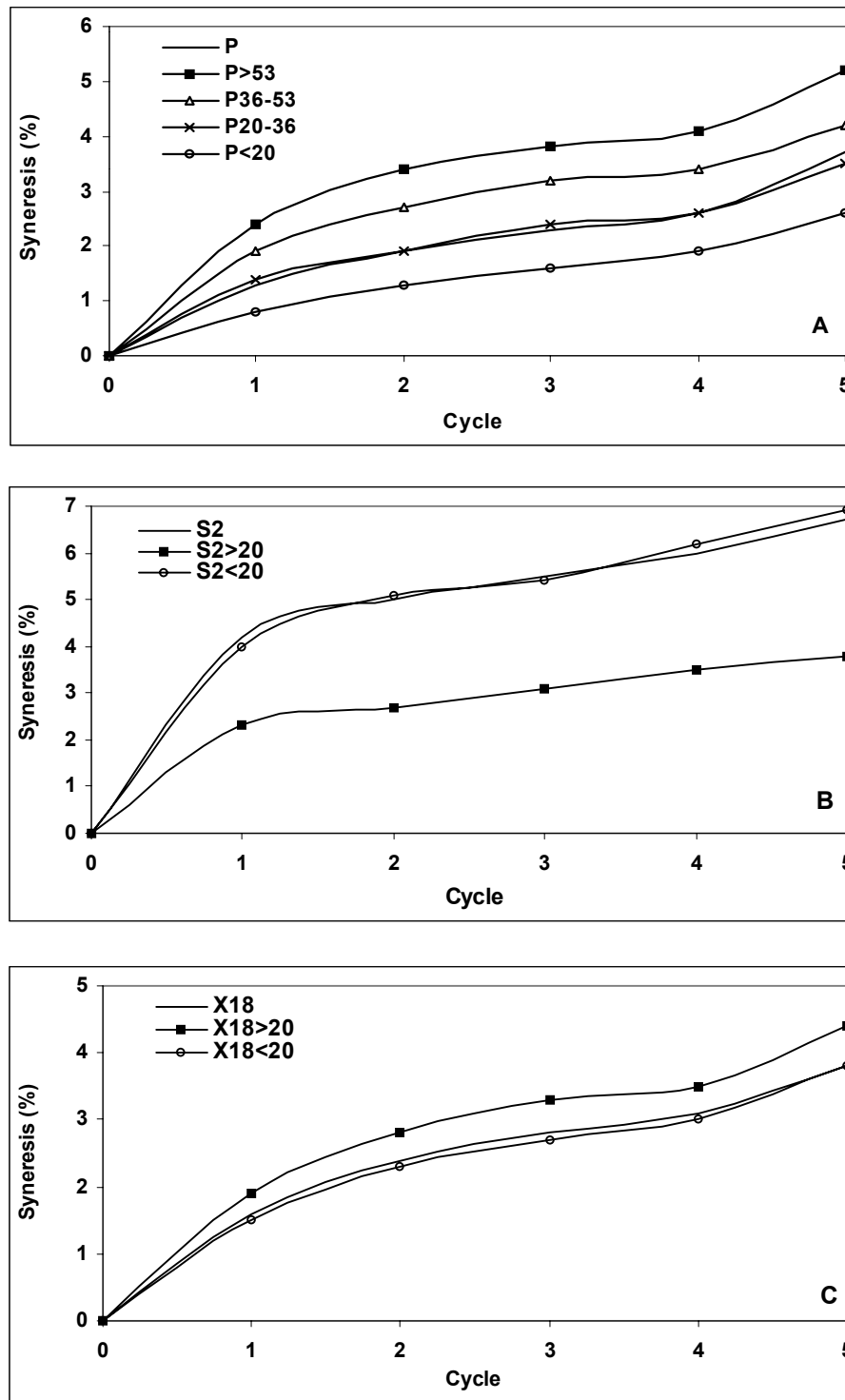


Figure 2-Freeze-thaw stability of different granule size fractions of potato (A) and sweet potato SuShu2 (B) and XuShu18 (C) starches (P: Potato; P >53: Potato >53 μm ; P 36-53: Potato 36-53 μm ; P 20-36: Potato 20-36 μm ; P <20: Potato <20 μm ; S2: SuShu2; S2 >20: SuShu2 >20 μm ; S2 <20 μm : SuShu2 <20 μm ; X18: XuShu18; X18 >20: XuShu18 >20 μm ; X18 <20: XuShu18 <20 μm).

fractions of XuShu18 starch, but both of them were slightly lower than that of the initial XuShu18 starch (1.89). The setback ratios did not show any correlation with the amylose content. This is in agreement with our previous study on different varieties of sweet potato starches (Chen and others 2003).

The freeze-thaw stability of 5 cycles is shown in figure 2. Syneresis of small-size granule fractions of potato and XuShu18 starches was lower than that of the large-size granule fractions. In other words, small-size granule fractions of potato and XuShu18 starches exhibited higher freeze-thaw stability, whereas the opposite results were found for the different granule size fractions of SuShu2 starch. Freeze-thaw stability did not show a correlation with amylose content.

Starch noodle preparation and evaluation

Table 4-Description of dough suitability for noodle making, and cooking loss and swelling index of starch noodles made from different granule size fractions of potato and sweet potato starches

Sample	Observation	Cooking loss (%)	Swelling index (%)
Potato	Lack of fluidity; Can't make noodle strands at all.	8.8	932
Potato >53 μm	Lack of fluidity; Can't make noodle strands at all.	9.3	973
Potato 36-53 μm	Lack of fluidity; Can't make consistent noodle strands.	4.3	865
Potato 20-36 μm	Lack of fluidity; Can't make consistent noodle strands.	6.1	892
Potato <20 μm	Can make consistent long noodle strands.	2.2	756
SuShu2	Lack of fluidity; Can't make consistent noodle strands.	5.2	714
ShShu2 >20 μm	Lack of fluidity; Can't make noodle strands at all.	8.3	742
SuShu2 <20 μm	Can make consistent long noodle strands.	1.9	617
XuShu18	Can make consistent long noodle strands.	2.1	552
XuShu18 >20 μm	Can make consistent long noodle strands; worse than initial XuShu18.	2.4	759
XuShu18 <20 μm	Can make consistent long noodle strands; better than initial XuShu18.	1.6	531

All values are the mean of 3 measurements and the coefficient of variations are less than 10%.

As mentioned previously, the dough for starch noodle making is composed of “gluten free” pure starch (Chen and others 2002). The dough should have good fluidity in order to make consistently long noodle strands. Table 4 showed that the dough rheological properties of small-size granule fractions (<20 μm) of both potato and sweet potato starches in noodle processing were better than that of the larger-size granule fractions and the initial starches. The large-size granule fractions (>53 μm for potato starch; >20 μm for sweet potato starches)

performed worse than the initial starches. All small-size granule fractions ($<20\ \mu\text{m}$) could make consistently long noodle strands. However, the initial and the large-size granule fraction ($>53\ \mu\text{m}$) of potato starch and the large-size granule fraction ($>20\ \mu\text{m}$) of SuShu2 could not make any noodle strand at all. So potato starch is not suitable for starch noodle preparation; however, the small-size granule fraction ($<20\ \mu\text{m}$) obtained from it gives good noodles. The dough properties were greatly influenced by starch granule size dimension and also the origin of starch. This is confirmed by the fact that the fraction of potato starch ($20\text{-}36\ \mu\text{m}$) can not be used for starch noodle preparation where the corresponding size of XuShu18 sweet potato starch can. The results of cooking loss and swelling index also showed that the cooking properties of starch noodles made from small-size granule fractions ($<20\ \mu\text{m}$) were better than those made from their initial starches and much better than those made from their large-size granule fractions. The cooking loss of the noodle made from small-size granule fraction ($<20\ \mu\text{m}$) of XuShu18 starch was even less than that of mung bean starch noodle leading to a higher quality noodle (Chen and others 2002).

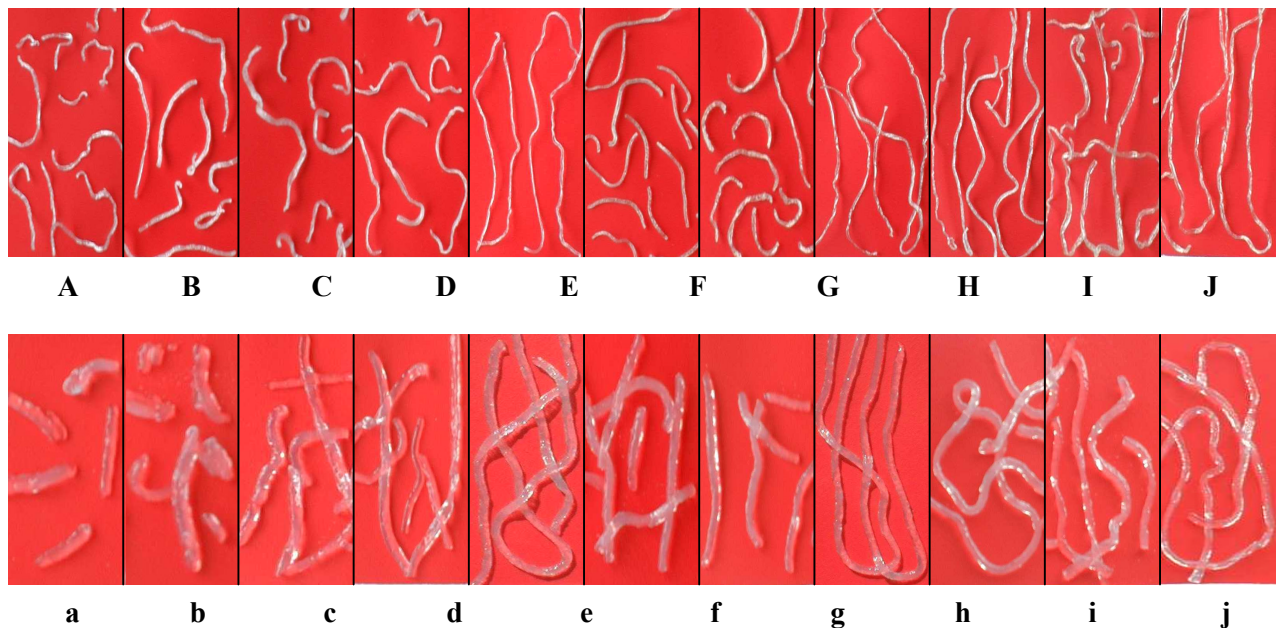


Figure 3-Appearances of dried (A-K) and cooked (a-k) starch noodles made from different granule size fractions of potato and sweet potato starches (A, a: Potato; B, b: Potato $>53\ \mu\text{m}$; C, c: Potato $36\text{-}53\ \mu\text{m}$; D, d: Potato $20\text{-}36$; E, e: Potato $<20\ \mu\text{m}$; F, f: SuShu2; G, g: SuShu2 $>20\ \mu\text{m}$; H, h: SuShu2 $<20\ \mu\text{m}$; I, i: XuSh18; J, j: XuShu18 $>20\ \mu\text{m}$; K, k: XuShu18 $<20\ \mu\text{m}$).

The appearances of dried and cooked starch noodles made from different granule size fractions are shown in figure 3. Only short fractional strands of the noodles made from large-size granule fractions ($>20 \mu\text{m}$) of potato and SuShu2 starches were available, while noodles made from small-size granule fractions ($<20 \mu\text{m}$) were consistently long strands. The noodle made from small-size granule fraction of XuShu18 was more transparent than that made from its initial and large-size granule fractions, however long noodle strands were also available for the initial and large-size granule starch fractions. Cooked noodles made from small-size granule fractions ($<20 \mu\text{m}$) of both potato and sweet potato starches were shown to be less swollen than those made from the large-size granule fractions.

Table 5-Texture characteristics of starch noodles made from different granule size fractions of potato and sweet potato starches

Sample	Dried noodles				Cooked noodles			
	E (Pa)	r_e	F_c (N)	r_c	E (Pa)	r_e	F_c (N)	F_{co} (N)
PotatoS	4.51×10^8 (0.23×10^8)	9.88×10^{-2} (0.17×10^{-2})	10.25 (1.67)	6.38×10^{-2} (0.92×10^{-2})	2.25×10^5 (0.26×10^5)	1.28×10^{-1} (0.22×10^{-1})	1.08×10^{-1} (0.19×10^{-1})	5.13×10^{-3} (0.99×10^{-3})
SuShu2	4.71×10^8 b (0.39×10^8)	9.73×10^{-2} b (0.79×10^{-2})	10.38 b (1.37)	7.47×10^{-2} b (1.92×10^{-2})	2.60×10^5 b (0.54×10^5)	1.21×10^{-1} b (0.20×10^{-1})	1.14×10^{-1} a (0.23×10^{-1})	7.43×10^{-3} a (1.54×10^{-3})
SuShu2S	5.67×10^8 a (0.23×10^8)	1.44×10^{-1} a (1.05×10^{-2})	14.88 a (1.25)	1.36×10^{-1} a (0.13×10^{-1})	3.94×10^5 a (0.19×10^5)	1.48×10^{-1} a (0.23×10^{-1})	1.26×10^{-1} a (0.25×10^{-1})	4.20×10^{-3} b (0.68×10^{-3})
XuShu18	4.92×10^8 b (0.71×10^8)	1.12×10^{-1} b (2.25×10^{-2})	15.13 b (2.26)	9.02×10^{-2} b (1.70×10^{-2})	4.11×10^5 b (0.65×10^5)	2.17×10^{-1} b (0.34×10^{-1})	1.53×10^{-1} a (0.20×10^{-1})	4.93×10^{-3} b (0.88×10^{-3})
XuShu18L	3.64×10^8 c (0.30×10^8)	1.01×10^{-1} b (2.29×10^{-2})	12.87 c (1.55)	6.25×10^{-2} c (1.04×10^{-2})	3.20×10^5 c (0.26×10^5)	1.65×10^{-1} c (0.17×10^{-1})	1.24×10^{-1} b (0.14×10^{-1})	6.27×10^{-3} a (0.88×10^{-3})
XuShu18S	7.55×10^8 a (0.27×10^8)	1.71×10^{-1} a (1.96×10^{-2})	19.25 a (3.11)	1.91×10^{-1} a (0.21×10^{-1})	5.48×10^5 a (0.35×10^5)	2.70×10^{-1} a (0.25×10^{-1})	1.69×10^{-1} a (0.20×10^{-1})	2.33×10^{-3} c (0.62×10^{-3})

N=8. Sample means with different letters in the same column of same variety are significantly different at $p < 0.05$. Standard deviations are given within parenthesis. S: Small-size granule fraction; L: Large-size granule fraction. E: Extension modulus; r_e : Relative extension; F_c : Cutting force; r_c : Increased ratio during cutting; F_{co} : Cohesive force.

The texture of starch noodles was analyzed by the texture analyzer (Table 5). Noodles made from initial and larger-size granule fractions ($>20\ \mu\text{m}$) of potato starch, and large-size granule fraction ($>20\ \mu\text{m}$) of SuShu2 starch, were not analyzed for texture because no long noodle strand was available. Stretch stiffness (E), stretchability (r_e), cutting firmness (F_c) and flexibility (r_c) of dried noodles made from small-size granule fractions of SuShu2 and XuShu18 were significantly higher than those made from their initial starches. While stretch stiffness (E), cutting firmness (F_c), and flexibility (r_c) of dried noodle made from large-size granule fraction of XuShu18 were significantly lower than those made from its initial starch. The flexibility of dried noodles made from small-size granule fractions of SuShu2 and XuShu18 increased with a factor 2, as compared with that made from their initial starches. Stretch stiffness (E) and stretchability (r_e) of cooked small-size granule fraction ($<20\ \mu\text{m}$) noodles made from SuShu2 and XuShu18 sweet potato starches were significantly higher when compared with those made from their initial starches. No significant difference was observed in the bite firmness (F_c) between the cooked noodles made from small-size granule fractions and their initial starches. Stretch stiffness (E), stretchability (r_e) and bite firmness (F_c) of cooked noodle made from large-size granule fraction of XuShu18 were significantly lower than those made from the small-size granule fraction and initial starches. The cohesiveness (F_{co}) of cooked noodle made from small-size granule fraction of XuShu18 was significantly lower (factor 2.1 and 2.7, respectively) than that for its large-size granule fraction and initial starch noodles. The cohesiveness of cooked small-size granule fraction noodle of SuShu2 decreased 1.8 times as compared with that made from its initial starch. This is in agreement with the result of cooking loss. Based on the above-mentioned characteristics of noodle textures, the starch noodle made from XuShu18 small-size granule fraction performed better than that made from small-size granule fractions of SuShu2 and potato starches.

Starch noodle textures were significantly affected by starch granule size dimension, however, they also depended on the origin of starch.

Conclusions

Our findings point out that a simple fractionation method on starch granule size is sufficient to use potato starch (fraction) for starch noodle preparation, while sweet potato starches can perform better with decreasing granule size. Granule size dimension plays a very important role in starch noodle making and noodle quality. The results also confirm our previous finding that high amylose content and C type of viscoamylogram pasting profile of starches are not necessary for making good-quality starch noodles, although several earlier publications stressed that these are necessities of ideal starches for starch noodle preparation. Starch gel firmness showed a significant correlation with starch noodle quality. Better processibility

(fluidity of starch dough for noodle making) and better quality of dried and cooked noodles made from small-size granule fractions ($<20 \mu\text{m}$) may mainly be attributed to their larger specific surface area of granules.

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CHAPTER 5

Improvement of White Salted Noodle Quality by Using Modified Potato and Sweet Potato Starches

ABSTRACT

Potato and sweet potato starches and their derivatives were applied in White Salted Noodle (WSN) manufacture in combination with partially substituted wheat flour. It was found that acetylated potato starch and acetylated sweet potato starches improve the cooking properties (cooking loss decreases) and eating quality (softness, stretchability and slipperiness increase) of WSN significantly. The color of the WSN made from all composite flours was whiter than the WSN made from wheat flour only. Replacement of wheat flour with all starches tested led to better dough properties. The physical properties of the starches and the composite flours made of them were different from those of wheat starch and wheat flour. The cold peak breakdown (CPBD) of the composite flour measured in 1.5% NaCl solution was found to have significant correlation with cooking loss, stretch stiffness, and stretchability of WSN.

Keywords: white salted noodle, potato starch, sweet potato starch, modified starch

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Introduction

White salted noodle (WSN), a Japanese-style wheat flour noodle, is a low-cost popular food in many Asian areas. A good-quality WSN should be slippery, soft, and elastic in texture with a clean, light, and bright appearance (Konik and Miskelly 1992). Only a few varieties of wheat, such as Australian Eradu and Cadoux (Hatcher 2001), meet the requirements for making high-quality WSN. Many earlier studies have been devoted to selecting new wheat varieties which are suitable for WSN manufacture. These studies indicated that both the protein and the starch present in wheat flour play important roles in WSN quality. Although protein in wheat flour was identified to be an important constituent contributing to Oriental wheat noodle texture (Oh and others 1985a, 1985b), Toyokawa and others (1989) reported that starch, rather than gluten, is the most important factor determining the quality of Japanese-style noodle (WSN). It has been reported that WSN quality has a significant positive correlation with swelling power, paste peak viscosity, and breakdown of wheat starch or wheat flour, but is significantly negatively correlated with setback and final viscosity (Nagao and others 1977; Moss 1980; Oda and others 1980; Rho and others 1988; Crosbie 1991; McCormick and others 1991; Crosbie and others 1992; Konik and Miskelly 1992; Konik and Moss 1992; Panozzo and McCormick 1993; Konik and others 1993; Bhattacharya and Corke 1996; Wang and Seib 1996; Batey and others 1997). The establishment of these correlations has been widely used for testing WSN quality and also in wheat breeding programs.

The use of sweet potato, potato, or waxy corn starches to improve eating quality of WSN is a common practice in Japan (Collado and Corke 1996). However, only a few studies have been devoted to the effect of the use of starches of other origin on noodle quality (Collado and Corke 1996; Lee and others 1998). Collado and Corke (1996) explored the application of sweet potato flours in WSN and yellow alkaline noodles to partially substitute wheat flour in order to extend the utilization of sweet potato and decrease the cost of noodle products. But the addition of sweet potato flours resulted in higher cooking loss and darker color than WSN made from wheat flour only. Since starch plays an important role in WSN performance and quality, and starch functionality often can be improved by suitable modifications (BeMiller and Whistler 1996), replacement of the commonly applied wheat flour with appropriately modified starches might have potential to improve WSN quality. If successful, the replacement with modified starches would be an easy way to improve WSN quality rather than wheat variety selection. In this study, starches isolated from normal potato and 3 typical sweet potato varieties, and modifications of them, were evaluated in WSN application.

Materials and Methods

Materials

Wheat flour was purchased from a local supermarket in Wageningen (The Netherlands) and was of unknown origin. Native sweet potato starches were isolated from 3 typical Chinese sweet potato varieties: SuShu2, SuShu8, and XuShu18 as previously (Chen and others 2003). Native potato starch, acetylated potato starch (DS=0.088), hydroxypropylated potato starches (DS=0.080 and DS=0.160), and acetylated SuShu2 (DS=0.088), SuShu8 (DS=0.088), and XuShu18 (DS=0.088) sweet potato starches were supplied by AVEBE R&D, Foxhol, the Netherlands. Wheat starch was isolated by the gluten hand-washing method (Baik and others 1994). Defatted wheat flour was prepared by washing the flour with 20% H₂O in methanol (ratio 1:4) at 40 °C for 30 min. After centrifugation (1000 × g), the sediment was treated 2 more times and air-dried.

Methods

White salted noodle (WSN) preparation

WSN was made according to Baik and others (1994) using a Marcato (Campodarsego, Italy) pasta machine. The dough was prepared from 300 g flour composed of 80% wheat flour and 20% starch or modified starch by adding 100 mL of 4.5% (w/v) NaCl solution. The dough was shaped into sheets by passing it through sheeting rolls at a final gap setting of 2.00 mm; the sheets were cut by cutting rolls into strips with 1.60 × 1.92 mm cross-section. The noodle sheet thickness was measured immediately and after storage in a plastic bag at room temperature for 2 h.

Dough and WSN quality analysis

The mixogram of the composite flour was determined using a 10-g Mixograph (National Manufacturing Division of TMCO, Inc., Lincoln, Nebraska, U.S.A.) at a spring setting of 8, and the optimum absorption of water by the dough was calculated according to AACC (1995b) method 54-40A. The mixing time, peak dough resistance, and breakdown (the change of resistance value between the peak and the point 8 min after the peak) were derived from the mixogram. The color of wheat flour, the various starches, and of the fresh WSN sheets were measured using a Tricolor Colorimeter (model LFM3; Dr. Lange, Berlin, Germany) as L (white/black), A (red/green), and B (yellow/blue) values (Chen and others 2002). Gelatinization temperature (initiation, midpoint, and endpoint) were determined using a Kofler hot stage polarizing microscope, according to Schoch and Maywald (1956). Swelling power of the starches and composite flours were measured both in distilled water and in 1.5% NaCl

solution using the method of Konik and others (1994). The optimum cooking time of freshly made WSN was measured by pressing test noodle strands between 2 glass plates. These strands were taken during noodle cooking in distilled water with intervals of 30 s until the core of the noodle strand was completely gelatinized (method 16-50; AACC, 1995a). Since not enough materials of the tested starches were present, the pasting behavior of the starches was recorded using a Rapid Visco Analyzer (RVA). The pasting behavior of the composite flours was examined using a Brabender Amylograph according to Chen and others (2003). All the pasting behavior measurements were conducted both in distilled water and in 1.5% NaCl solution, respectively. Cooking loss and swelling index were measured by the method as described previously (Chen and others 2002). Due to the higher cooking loss of wheat noodle products as compared to that of starch noodles (Chen and others 2002), the swelling index for wheat noodle products was calculated according to the following formula:

$$\text{swelling index (\%)} = (w_1 - w_2) \times 100 / w_2$$

where w_1 is the weight (g) of freshly cooked noodle and w_2 is the weight (g) of the tested cooked noodle after drying to completeness in an oven.

The texture of the cooked noodles was analyzed using a texture analyzer (TA; model XT2I; Godalming, UK). The extension modulus E (representing stretch stiffness), increased extension length ratio r_e (representing stretchability), cutting force F_c (representing bite firmness which was measured using a 0.3-mm-diameter wire cutting probe to cut a single noodle strand, stabilized on the platform at 2 sides), and cohesive force F_{co} (representing cohesiveness which was determined by attaching 2 noodle strands to each other and pulling them apart using a texture analyzer) of cooked noodle were measured using previously described methods (Chen and others 2002).

Statistical analysis

SPSS 10.0 for WindowsTM was used for statistical analysis. Differences between samples in each item were tested using General Linear Model, and the Tukey as a Post Hoc test. The data of the starch properties and noodle qualities were subjected to Pearson's product-moment correlation coefficient tests. A significance level of $p < 0.05$ was used throughout the study.

Results and Discussion

Evaluation of the quality of WSN made from wheat flours fortified with native or modified potato or sweet potato starches

In order to find starches suitable to improve the production and final quality of WSN, native potato starch, acetylated potato starch, and hydroxypropylated potato starches (DS=0.08 and

DS=0.16) were applied to substitute 20% of wheat flour in the WSN preparation. The wheat flour purchased is a commonly used wheat flour in The Netherlands. Its moisture, gluten, and ash contents were 15.0%, 11.9% and 0.45%, respectively. It is assumed that the effect of starch (derivative) fortification of the wheat flour used in our study on WSN quality also will occur with flours of other wheat varieties.

From table 1 it can be seen that the optimum cooking times of WSN made from the composite flours containing potato starch and its derivatives were halved when compared with WSN made from wheat flour only.

Table 1-Cooking properties and textures of WSN made from the composite flours containing potato and sweet potato starches as compared with those made from wheat flour only

Sample	Cooking property*			Texture of cooked WSN**			
	T _{oc} (min)	Cooking loss (%)	Swelling index (%)	E	r _e	F _c (N)	F _{co} (N)
WF	8.5a	8.9b	333c	20857a	0.86b	0.152a	0.0113b
PF	4.2b	10.6a	378b	19566b	0.79bc	0.124b	0.0094bc
APF	3.7c	6.7c	338c	14522c	1.11a	0.119b	0.0041d
HPLF	3.8bc	10.8a	410a	17366bc	0.61c	0.107c	0.0188a
HPHF	3.8bc	10.4a	377b	18827b	0.74bc	0.122b	0.0171a
S2F	4.2b	9.7ab	344c	20231ab	0.84b	0.129b	0.0081c
AS2F	3.8bc	7.4c	348c	14937c	1.06a	0.121b	0.0032d

Values shown are the means of 3 measurements (*) or 8 measurements (**).

Sample means with different letters in the same column are significantly different.

WF: Wheat flour; PF: Composite flour containing potato starch; APF: Composite flour containing acetylated potato starch; HPLF: Composite flour containing low-substituted hydroxypropylated potato starch (DS=0.08); HPHF: Composite flour containing high-substituted hydroxypropylated potato starch (DS=0.16); S2F: Composite flour containing SuShu2 sweet potato starch; AS2F: Composite flour containing acetylated SuShu2 sweet potato starch; T_{oc}: Optimum cooking time; E: Extension modulus of cooked WSN; r_e: Increased length ratio of extension of cooked WSN; F_c: Cutting force of cooked WSN; F_{co}: Cohesive force of cooked WSN.

The cooking loss and the swelling index are also important properties of noodle products with respect to noodle cooking and noodle consumption (Chen and others 2002). Low values for both the cooking loss and swelling index are preferred. It was found (Table 1) that the cooking loss of WSN could only be reduced when a composite flour containing acetylated potato starch was used. The swelling index of WSN made from the composite flour containing

acetylated potato starch was rather similar to that made from wheat flour only, whereas the replacement with native and hydroxypropylated potato starches increased the swelling index of WSN significantly. With respect to cooking loss and swelling index, only acetylated potato starch replacing 20% of the flour resulted in WSN having better properties when compared to the WSN made from wheat flour only.

The desired texture of cooked WSN should be soft, stretchable, and slippery, and these characteristics can be quantified by stretch stiffness (E), cutting force (F_c), stretchability (r_e), and cohesive force (F_{co}) which were measured by the texture analyzer according to Chen and others (2002). Characterization of the texture of cooked WSN showed that the stretch stiffness (E) of cooked WSN decreased significantly by the fortification with modified potato starches (Table 1). The bite firmness, represented by cutting force (F_c), was decreased significantly by the replacement with all the potato starches. This indicates that the replacement with potato starches improves the softness of cooked WSN significantly. The stretchability (r_e) of cooked WSN was increased only when replaced with acetylated but not with hydroxypropylated potato starches. The cohesive force (F_{co}) of cooked noodles provides information about the mouthfeel slipperiness during noodle consumption and the separation between noodle strands during cooking. A lower cohesive force represents a higher slipperiness. The cohesive force of cooked WSN was decreased significantly only by the replacement with acetylated potato starch.

The stretchability and slipperiness of cooked WSN were improved significantly by replacement with acetylated potato starch, but not by replacement with hydroxypropylated potato starches. Native potato starch did not show improvement in stretchability and slipperiness of cooked WSN.

Evaluation of the results obtained for WSN made by replacement of wheat flours with potato starch and its derivatives indicates that only acetylated potato starch could significantly improve the cooking properties and textures of WSN. Although acetylated and hydroxypropylated starches have rather similar hydrophobic interaction due to their functional groups (Van der Burgt 1999), it is assumed that the acetylation occurs exclusively in certain parts of the starch granules, whereas hydroxypropylation was more uniform through out the starch granules (Biliaderis 1982). The observation of the iodine binding capacity of hydroxypropylated starch is much lower than that of acetylated starch (data not shown), which explain the different behaviors in the fortification of WSN.

In our previous studies, some sweet potato starches showed good performance in starch noodle preparation. The question arises whether acetylated sweet potato starches can also improve WSN quality. To answer this question, 3 sweet potato starches (SuShu2, SuShu8, and XuShu18) in native and acetylated form were evaluated in WSN application. It was found that the optimum cooking time of WSN was shortened significantly by the replacement with all the

native and acetylated sweet potato starches (Table 1; For sweet potato starches only the data of one variety are shown in this paper). The cooking losses of WSN made from composite flours containing the acetylated sweet potato starches were significantly lower than those made from wheat flour only, while the cooking losses of WSN made from composite flours containing native sweet potato starches were rather similar to that, or higher than that, made from wheat flour only. The swelling indexes of WSN made from composite flours containing either native or acetylated sweet potato starches were not significantly different from those made from wheat flour. The stretch stiffness (E) of cooked WSN made from composite flours containing acetylated sweet potato starches was significantly lower, while the stretch stiffness of cooked WSN made from composite flours containing native sweet potato starches were similar when compared to WSN made from wheat flour only. The bite firmness (F_c) of cooked WSN made from composite flours containing either native or acetylated sweet potato starches were significantly lower than that made from wheat flour. The stretchability (r_e) of cooked WSN was increased significantly by the replacement with acetylated sweet potato starches. Native sweet potato starches did not show significant improvement of the stretchability of cooked WSN. The cohesive force (F_{co}) of cooked WSN was decreased significantly by the replacement with acetylated as well as native sweet potato starches.

Characteristics of fresh WSN made from the composite flours

The appearance of fresh WSN is an important attribute. Table 2 shows that fresh WSN made from all composite flours were significantly whiter and less yellow than those made from wheat flour. This might be due to the lower protein content in the final dough and also to the dilution of wheat flour with less colored starches.

The thickness of fresh WSN sheet, measured immediately (T_0) after preparation and after storing for 2 h (T_2), was significantly decreased by replacement with all starches and derivatives tested, while no significant difference was found between the fortified fresh WSN (Table 2). The increased thickness (the difference between T_0 and T_2) of fresh WSN sheets was also decreased by the replacements. This indicates that both the immediate swelling (springiness) and slow swelling of fresh WSN decreased by the replacement with native and modified starches. This might be due to the lower level of protein (gluten) content which is mainly responsible for the elasticity of dough. It appeared that the shapes of fresh WSN made from the composite flours were more constant during processing than those made from wheat flour only.

Physical properties of native and modified starches and of their composite flours

In general, it can be stated that replacement of wheat flour with acetylated sweet potato

Table 2-Some important properties of fresh WSN made from composite flours containing native and modified potato and sweet potato starches and from wheat flour only

Sample	Color			Thickness	
	L	A	B	T ₀ (mm)	T ₂ (mm)
WF	81.99e	-1.20ab	17.96a	2.03a	2.13a
PF	87.75bc	-2.57c	11.76c	1.95b	1.97b
APF	88.43b	-1.99b	12.29bc	1.93b	1.95b
HPLF	88.38b	-1.20ab	11.94c	1.95b	1.97b
HPHF	89.33a	-0.98a	11.45d	1.95b	1.96b
S2F	86.19d	-2.39c	12.77b	1.93b	1.96b
AS2F	87.51c	-2.59c	11.71c	1.96b	1.97b

Values shown are the means of 3 measurements.

Sample means with different letters in the same column are significantly different.

WF: Wheat flour; PF: Composite flour containing potato starch; APF: Composite flour containing acetylated potato starch; HPLF: Composite flour containing low-substituted hydroxypropylated potato starch (DS=0.08); HPHF: Composite flour containing high-substituted hydroxypropylated potato starch (DS=0.16); S2F: Composite flour containing SuShu2 sweet potato starch; AS2F: Composite flour containing acetylated SuShu2 sweet potato starch; T₀: Thickness of wet fresh WSN sheet measured immediately after preparation; T₂: Thickness of wet fresh WSN sheet measured after storing for 2h.

starches improves the cooking properties of WSN and the texture of cooked WSN significantly, quite similar to acetylated potato starches. The replacement with the other starch derivatives, however, leads to unfavorable WSN properties. To obtain a better understanding of the underlying mechanism for these phenomena, the physical properties of the various starches and the composite flours made from them were also investigated. Because the dough of WSN contains 1.5% NaCl, these properties were measured in distilled water and in 1.5% NaCl solution as well.

It is clear that the color of the isolated wheat starch was significantly whiter and more yellow, but less red, than that of wheat flour (Table 3). This indicates that components in wheat flour other than starch, such as fiber and protein, contribute to the darkness of color. Since all other starches were also significantly whiter than wheat flour, the replacement of flours resulted in improved color characteristics.

The gelatinization temperatures measured by the hot-stage polarizing microscope (initial, midpoint, and endpoint) of all acetylated potato and sweet potato starches were significantly

Table 3-Physical properties of native and modified potato and sweet potato starches compared with those of isolated wheat starch

Sample	Color			Gelatinization temperature (°C)			Swelling power (g/g)	
	L	A	B	Initiation	Midpoint	Endpoint	in Water	in 1.5% NaCl
WS	93.43d	0.63a	4.79b	56.7b	58.8c	63.0e	8.90f	7.38e
WF	92.01e	0.36b	11.25a					
P	96.87a	-0.04c	2.74f	55.8bc	61.4b	67.4c	60.23c	22.57d
AP	95.24bc	0.14b	3.13ef	51.3e	57.9c	63.8de	68.53b	31.43c
HPL	95.02c	0.18b	3.44e	55.4c	61.0b	66.1cd	70.93a	34.13b
HPH	95.29b	0.18b	3.49de	53.6d	57.6c	62.9e	69.20ab	42.67a
S2	93.27d	-0.54e	4.02c	59.2a	68.8a	78.7a	21.10e	14.79f
AS2	93.21d	-0.26d	3.68dc	53.9d	59.1bc	72.6b	30.20d	23.30d

Values shown are the means of 3 measurements.

Sample means with different letters in the same column are significantly different.

WS: Wheat starch; WF: Wheat flour; P: Potato starch; AP: Acetylated potato starch; HPL: Low-substituted hydroxypropylated potato starch (DS=0.08); HPH: High-substituted hydroxypropylated potato starch (DS=0.16); S2: SuShu2 sweet potato starch; AS2: Acetylated SuShu2 sweet potato starch.

lower than those of their corresponding native starches. The average gelatinization temperature (midpoint) of wheat starch is similar to that of acetylated potato starch, high-substituted hydroxypropylated potato starch, and acetylated SuShu2 starch, but significantly lower than that of the other starches. However, no correlation seems to be present between gelatinization temperature and optimal cooking time as reported above.

The swelling powers of the modified potato and modified sweet potato starches were significantly higher than those of their corresponding native starches when measured both in distilled water and in 1.5% NaCl solution. The substituent groups (such as the acetyl group) in starch facilitate the access of water to the amorphous region, due to an intragranular structural disorganization caused by steric effects and disruption of hydrogen bonds in the starch granules (González and Pérez 2002). This results in a lower gelatinization temperature and a higher swelling power. However, wheat starch showed a markedly lower swelling power than all other starches. Swelling power of all samples tested was lower when measured in 1.5% NaCl solution as compared to that measured in distilled water. The ratios of reduction were higher for the native starches than for the modified starches. This suggests that the swelling behavior of the native starches was more restricted by NaCl. This could be explained by the fact that native starch is weakly acidic and is negatively charged. According to Lii and Lee (1993) some

protons of alcohol groups in the starch granule may be exchanged by the sodium ions in the presence of a swelling inhibitor (such as sodium chloride). These alcoholates will better dissociate and cause a rise in the Donnan potential and to retard gelatinization and the swelling of starch. Acetyl and hydroxypropyl groups, on the other hand, decrease the negative charge in starch granule and the modified starch is consequently less affected by NaCl when compared to the native starch.

Table 4 illustrates that the swelling power of wheat flour is higher measured in 1.5% NaCl solution than when measured in distilled water. Unlike the pure starches, the swelling power of the composite flours containing these starches was rather similar when measured in distilled water or in 1.5% NaCl solution.

Table 4-Physical properties of the composite flours containing native and modified potato and sweet potato starches compared to those of wheat flour

Sample	Swelling power (g/g)		Value of mixogram		
	In water	In 1.5% NaCl	Mixing time (min)	PDR (MU)	Breakdown (MU)
WF	8.30f	10.31f	3.0a	7.0a	1.2a
PF	14.00c	13.47c	2.7b	5.0c	0.5cd
APF	11.00e	12.54d	2.0c	5.0c	0.3d
HPLF	17.63a	15.37b	2.3c	5.0c	0.3d
HPHF	16.47b	16.26a	2.6b	5.0c	0.3d
S2F	11.56de	11.77e	2.5b	6.0b	1.0b
AS2F	12.50d	11.94e	2.5b	6.0b	0.8bc

Values shown are the means of 3 measurements.

Sample means with different letters in the same column are significantly different.

WF: Wheat flour; PF: Composite flour containing potato starch; APF: Composite flour containing acetylated potato starch; HPLF: Composite flour containing low-substituted hydroxypropylated potato starch (DS=0.08); HPHF: Composite flour containing high-substituted hydroxypropylated potato starch (DS=0.16); S2F: Composite flour containing SuShu2 sweet potato starch; AS2F: Composite flour containing acetylated SuShu2 sweet potato starch; PDR: Peak dough resistance.

The mixograms showed that the mixing time, peak dough resistance (PDR), and breakdown of the composite flours were significantly lower than those for wheat flour only (Table 4). The composite flours fortified with native and modified potato and sweet potato starches apparently were more tolerant to mixing and able to form the optimal dough more easily.

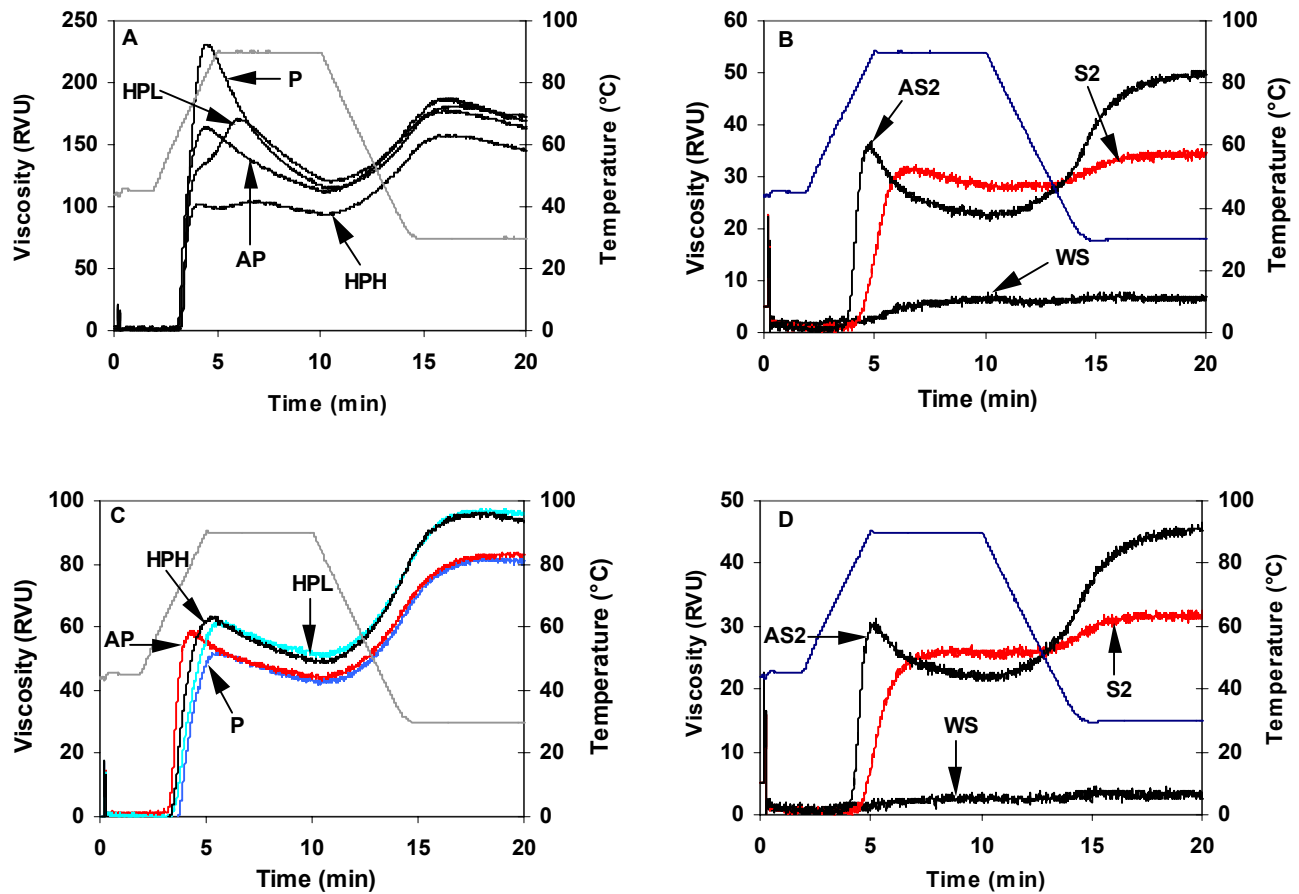


Figure 1-RVA profiles of potato and sweet potato starches compared to those of wheat starch (4%, w/w).

A and B as measured in distilled water. C and D as measured in 1.5% of NaCl solution.

P: Potato starch; AP: Acetylated potato starch; HPL: Low-substituted hydroxypropylated potato starch (DS=0.08); HPH: High-substituted hydroxypropylated potato starch (DS=0.16); S2: SuShu2 sweet potato starch; AS2: Acetylated SuShu2 sweet potato starch; WS: Wheat starch.

Pasting behavior of the starches was recorded with RVA (Figure 1). The pasting temperatures of both modified potato and sweet potato starches measured in distilled water were lower than those of their native starches. This is in agreement with the gelatinization temperatures measured with the hot-stage polarizing microscope. The peak viscosity of native potato starch was higher than that of its acetylated and hydroxypropylated forms, while the peak viscosity of native sweet potato starch was lower than that of its acetylated form. The difference observed between potato and sweet potato starches may be due to the much higher

phosphate (negatively charged group) content in potato starch. Pasting profiles of hydroxypropylated potato starch (both high and low DS) showed a shoulder in the viscosity curve before the peak viscosity was reached. The shoulder might be due to the substitution with hydroxypropyl groups throughout the entire starch granule (Biliaderis 1982). The peak viscosity of potato and sweet potato starches and their derivatives was much higher than that of wheat.

When measured in 1.5% NaCl solution, the pasting temperatures of all samples tested were increased as compared to those measured in distilled water. NaCl present in solutions in a concentration <7% was found to retard starch gelatinization (Chiotelli and others 2002). The pasting temperature of modified potato and sweet potato starches were lower than those of their native starches and the difference was clearer than those measured in distilled water. When measured in 1.5% NaCl solution, the peak viscosity of native potato starch was lower than that of its derivatives. This was not the case when measured in distilled water. The peak viscosity of acetylated sweet potato starch was still higher than that of native sweet potato starch. The peak viscosity of all starches tested was lower when measured in 1.5% NaCl solution as compared to that measured in distilled water due to the restriction effect of NaCl. The “shoulder”, which is present in the pasting profiles of hydroxypropylated potato starches when measured in distilled water, did not appear when measured in 1.5% NaCl solution. The restriction of NaCl on starch swelling might minimize this phenomenon.

Since large quantities of samples were available and better information could be obtained by using a Brabender amylograph (Limpisit and Jindal 2002), pasting behavior of the composite flours was analyzed using a Brabender amylograph (Figure 2). The pasting temperature of the composite flours containing modified potato or sweet potato starch, measured either in distilled water or in 1.5% NaCl solution, was always lower than that of the corresponding composite flours containing the native starches. The pasting temperature of all of them was lower than that of wheat flour. The peak viscosity of composite flour containing native potato starch as measured in distilled water or in 1.5% NaCl was higher than that of composite flours containing hydroxypropylated or acetylated potato starches, while the peak viscosity of composite flour containing acetylated potato starch was even lower than that of wheat flour. Peak viscosity of composite flour containing native sweet potato starches was higher than that of their corresponding composite flours containing acetylated sweet potato starches, but all of them were higher than that of wheat flour. Unlike the native and modified starches, the peak viscosity of all composite flours and wheat flour obviously increased by the presence of NaCl.

It was found that all composite flours containing modified starches showed a clear “shoulder” in the Brabender amylograms before peak viscosity was reached when measured in distilled water. The “shoulder” was also found when measured in 1.5% NaCl solution, but it

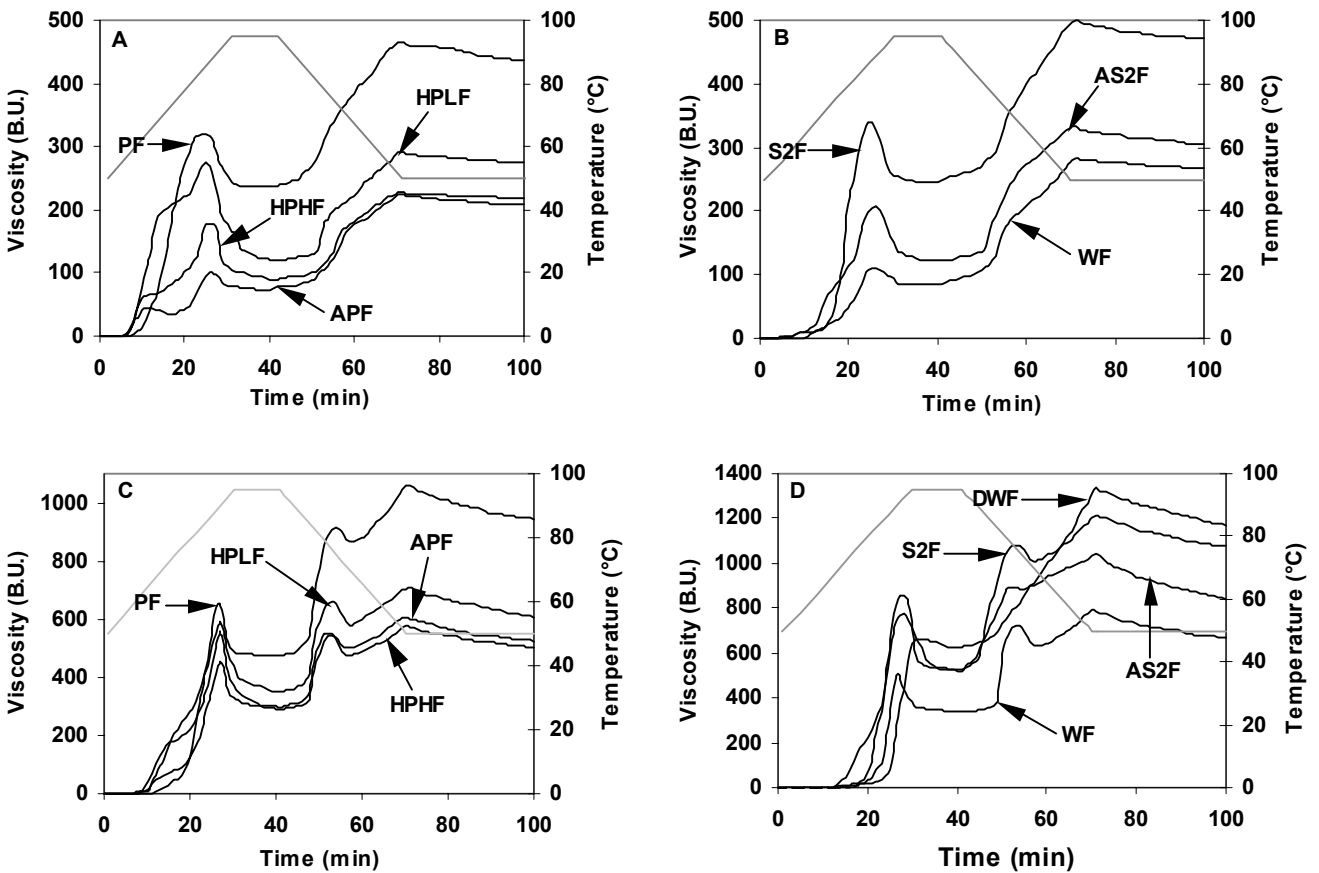


Figure 2-Brabender amylograms of composite flours containing potato or sweet potato starches compared to that of wheat flour (8%, w/v).

A and B as measured in distilled water; C and D as measured in 1.5% NaCl solution.

PF: Composite flour containing potato starch; APF: Composite flour containing acetylated potato starch; HPLF: Composite flour containing low-substituted hydroxypropylated potato starch (DS=0.08); HPHF: Composite flour containing high-substituted hydroxypropylated potato starch (DS=0.16); S2F: Composite flour containing SuShu2 sweet potato starch; AS2F: Composite flour containing acetylated SuShu2 sweet potato starch; WF: Wheat flour; DWF: Defatted wheat flour.

was less clear. This minimization of the shoulder might be due to the restriction effect of NaCl on starch. The presence of a shoulder was also observed in a blend of sweet potato flour and wheat flour (25:75, w/w) by Collado and Corke (1996). However, the shoulder did not appear in the Brabender amylograms of the composite flours containing native potato and sweet potato starches in this study.

When measured in 1.5% NaCl solution, the amylograms of wheat flour and all composite flours showed a “cold peak” before the highest viscosity was reached during the cooling cycle (from 95 °C to 50 °C). But such a “cold peak” could not be observed when measured in distilled water. The peak was explained due to the formation of amylose-monoacylglycerol complexes, which increase paste consistency. The role of sodium chloride, however, could not be explained by Kim and Seib (1993). Interestingly, the “cold peak” is neither present in the Brabender amylograms of defatted flour nor in the RVA profiles of isolated wheat starch when measured in 1.5% NaCl solution. These results support the view that the lipids present in wheat flour, but not in starch, cause the “cold peak” effect. It was also found that all composite flours containing acetylated potato or sweet potato starches exhibited a smaller “cold peak” as compared to the composite flours containing native or hydroxypropylated potato starches, or native sweet potato starches, or wheat flour. The acetyl substituents apparently hinder the complex formation of the lipid fraction with the starch in the wheat flour.

Correlation between properties of the starches and composite flours, and noodle quality attributes

Although a high swelling power of wheat flour and wheat starch was reported to be important for high-quality WSN (Nagao and others 1977; Moss 1980; Oda and others 1980; Rho and others 1988; Crosbie 1991; McCormick and others 1991; Crosbie and others 1992; Konik and others 1993; Wang and Seib 1996), our statistical evaluation shows that a high swelling power coincides with poorer cooking properties of WSN like high cooking loss and high swelling index (Table 5). This is in agreement with findings by Crosbie and others (1992) who stated that high-quality noodles are obtained from flours with moderate swelling power.

It has been reported that the peak viscosity and breakdown had a significant positive correlation, while setback had a significant negative correlation with WSN quality (Moss 1980; Oda and others 1980; Crosbie 1991; McCormick and others 1991; Crosbie and others 1992; Konik and Miskelly 1992; Konik and Moss 1992; Panozzo and McCormick 1993; Bhattacharya and Corke 1996; Batey and others 1997). We only found a significant correlation of the peak viscosity of the starches with cohesive force (0.635, $p < 0.05$) when the viscosity had been measured in 1.5% NaCl solution. The early establishment of the correlation between pasting behavior and WSN quality may be applicable only to wheat flour or wheat starch and not suitable for the composite flours fortified with the starches.

The cold peak breakdown (CPBD) has a significant correlation with cooking loss (0.702, $p < 0.05$), stretch firmness (0.860, $p < 0.01$), and stretchability (-0.736, $p < 0.01$) of WSN. A low value for the CPBD of composite flour resulted in the low cooking loss, soft texture (low E),

and high stretchability of WSN. Composite flours which show a low CPBD when measured in 1.5% NaCl solution are preferable for making high-quality WSN.

Conclusions

Acetylated potato and acetylated sweet potato starches can be used efficiently to fortify commonly used wheat flour for the manufacture of high quality WSN. The cooking properties and eating quality of WSN were improved significantly by the replacement with all acetylated potato and acetylated sweet potato starches compared to WSN made from wheat flour only.

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Table 5-Correlation coefficients between properties of starches and composite flours and WSN quality attributes

	Starches								Composite flours							
	In distilled water			In 1.5% NaCl solution					In distilled water				In 1.5% NaCl solution			
	SP	PT	BD	SP	PT	PV	BD	SB	SP	PT	BD	SB	SP	PT	SB	CPBD
OCT	-0.614*	0.670*	-0.219	-0.679*	0.570	0.284	-0.530	0.111	-0.658*	0.554	-0.485	0.393	-0.590	0.669*	0.183	0.371
CL	0.680*	-0.118	0.347	0.036	-0.115	0.232	-0.246	0.455	0.402	0.035	0.413	-0.276	0.331	0.132	-0.206	0.702*
SI	0.680*	-0.599	0.618*	0.546	-0.566	0.371	0.386	0.632*	0.880**	-0.524	0.688*	-0.732*	0.791**	-0.458	-0.482	0.140
E	-0.330	0.457	-0.057	-0.520	0.173	-0.377	0.190	-0.569	-0.221	0.577	0.002	0.356	-0.266	0.663*	0.176	0.860**
r _c	-0.298	0.151	-0.373	-0.089	0.173	-0.377	0.190	-0.569	-0.468	0.068	-0.436	0.434	-0.404	-0.015	0.389	-0.736**
F _c	-0.765**	0.766**	-0.436	-0.739**	0.707*	-0.010	-0.632*	-0.186	-0.797**	0.691*	-0.605*	0.656*	-0.709*	0.779**	0.376	0.284
F _{co}	0.446	-0.301	0.308	0.318	-0.370	0.635*	0.089	-0.724*	0.532	-0.291	0.359	-0.676*	0.572	-0.239	-0.665*	0.601

OCT: Optimum cooking time; CL: Cooking loss; SI: Swelling index; E: Extension modulus; r_c: Increased length ratio of extension; F_c: Cutting force; F_{co}: Cohesive force.

SP: Swelling power; PT: Pasting temperature; BD: Breakdown; PV: Peak viscosity; SB: Setback; CPBD: Cold peak breakdown.

* Correlation is significant at the 0.05 level. **Correlation is significant at the 0.01 level.

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CHAPTER 6

Differently sized granules from acetylated potato and sweet potato starches differ in the acetyl substitution pattern of their amylose population

ABSTRACT

Acetylated potato and sweet potato starches were fractionated according to granule size. From the fractions obtained amylose and amylopectin were isolated and characterized with respect to degree of substitution (DS) and degradability with α -amylase and amyloglucosidase. The DS of the amylopectin populations originating from the different size fractions increased with decreasing granule size. In contrast, the DS of the amylose populations of differently sized granule fractions were quite constant. The acetylation occurred in the amorphous regions, but only took place in the outer lamellae of crystalline regions of starch granules. The amylose populations isolated from small size granule fractions of the acetylated starches tested were less susceptible to digestion by α -amylase and amyloglucosidase than the amylose originating from the large granule fractions, even though the DS were similar. Acetyl group distribution in the amylose populations separated from small size granule fractions is more heterogeneous.

Keywords: acetyl group, degree of substitution, amylose, granule size

This chapter will be submitted by the authors Z. Chen, H.A. Schols and A.G.J. Voragen

Introduction

Acetylated starches with low degree of substitution (DS) are widely used in food industries for many years because of important characteristics such as low gelatinization temperature, high swelling and solubility, and good cooking and storage stability (de Graaf and others 1998; Liu and others 1999; Wang and Wang 2002). The acetylated starches are also less susceptible to retrogradation. It is thought that the amylose fraction which is mainly responsible for starch retrogradation, is modified and as a result is less susceptible to retrogradation (Jarowenko 1986). The physicochemical properties of acetylated starches depend on their chemical structures, DS and acetyl group distributions. Until now only a few publications are dealing with structure features of acetylated starches (Biliaderis 1982; Laignel and others 1997; Heins and others 1998; Wang and Wang 2002). Biliaderis (1982) reported that high substitution exists only in certain parts of the amylopectin of acetylated starch and he assumed that acetylation of smooth pea starch occurred exclusively in the outer lamella of the granules. Oestergard and others (1988) reported that substitution with acetyl groups reduced the degradability of acetylated starch by α -amylase. For highly acetylated starches NMR analysis showed that the glucose residues are equally substituted in O-2 and O-3 position, while for hydroxyethyl starches the position O-2 is highly preferred (Heins and others 1998).

In a previous study we reported that acetylated potato and sweet potato starches could significantly improve the quality of White Salted Noodle by replacing part of commonly used wheat flour (Chen and others 2003a). This in contrast to replacing of wheat flour with non-modified or hydroxypropylated starches. Starches from different sweet potato varieties differ in both average granule size and granule size distribution. The different size granule fractions of potato and sweet potato starches were found to differ greatly in chemical compositions (e.g. amylose, phosphorous), gel properties, and processibility to starch noodles (Chen and other 2003b). We assume that differently sized starch granules differ in their susceptibility to chemical reagents (acetic anhydride) which react with the hydroxyl groups of the glucose moieties of both amylose and amylopectin populations present. Since the amorphous regions are more easily accessible for chemical reagents and since amylose prevails in these amorphous regions we studied the extent of substitution with acetyl groups (DS) and distribution pattern of acetyl groups in amylose populations isolated from differently sized granule fractions of acetylated potato and sweet potato starches. We report here on these studies. Similar studies on the amylopectin fractions will be reported elsewhere.

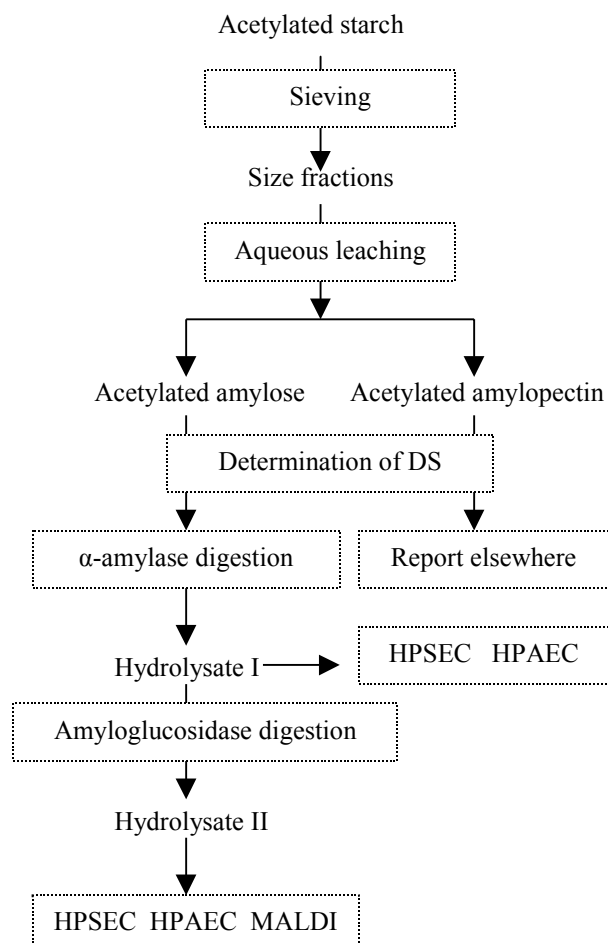


Figure 1-Schematic overview of methodology to reveal the acetyl group distribution of amyloses isolated from acetylated potato and sweet potato starches

Materials and Methods

Materials

Acetylated potato and sweet potato (SuShu2 and XuShu18; Chen and others, 2003b) starches were prepared by AVEBE R&D (Foxhol, the Netherlands). The starches were modified in an aqueous suspension by adding dropwise acetic anhydride in such amounts that a theoretical DS (mol acetyl group per mol glucose) of 0.08 is obtained for all the modified starches.

Alpha-amylase (10069, from *Bacillus subtilis*, 393 U/mg) and amyloglucosidase (A9268, from *Aspergillus oryzae*, 1400U/mL) were purchased from Fluka (Switzerland) and Sigma

(US), respectively. α -amylase was dissolved in distilled water while amyloglucosidase was diluted in acetate buffer (0.01M, pH 4.5), to yield dilutions containing 0.38 U/ μ L and 0.14 U/ μ L, respectively.

The acetylated starches were fractionated according to size by sieving according to Chen and others (2003b). Acetylated potato starch was separated into 4 fractions: larger than 53 μ m, between 36-53 μ m, between 20-36 μ m and smaller than 20 μ m, while acetylated sweet potato starches (ShuSu2 and XuSu18) were separated only into 2 fractions: larger than 20 μ m and smaller than 20 μ m.

Amylose and amylopectin separation

Amylose and amylopectin were separated using the aqueous leaching method of Shi and BeMiller (2002) with minor modification. Acetylated starch slurry (4 g starch in 100 mL distilled water) was gently stirred at the initial gelatinization temperature (measured with a Kofler hot-stage polarizing microscope) overnight and then centrifuged at $10,000 \times g$ for 20 min. The supernatant (amylose population) was separated and freeze dried. The residues were gently restired in 100 mL distilled water at 95 °C for 2h and then centrifuged at $10,000 \times g$ for 20 min. The supernatant was discarded and the procedure repeated 5 times for the residue. The purity of the separated amylose was checked with HPSEC using the equation (Purity (%) = Amylose peak area/Sum of all peak areas) according to Shi and BeMiller (2002), while the purity of the separated amylopectin was checked by iodine potentiometric method (Bates, 1943).

Degree of substitution (DS) assay

5 mg of samples were saponified with 0.01 M NaOH for 2 h and neutralized with 0.01 M citric acid. The released acetate was determined using Scil acetic acid assay kits (EnzytecTM, Scil Diagnostics GmbH Martinsried, Gemany). The DS is calculated as molar substitution (mol acetate / mol glucose).

Enzymatic digestions

5 mg of acetylated amylose was solubilized in 1 mL distilled water and incubated with 5 μ L of α -amylase solution at 25 °C for 8 h. After inactivation by boiling for 5 minutes, half of the hydrolysate was used for high-performance anion exchange chromatography (HPAEC) and high-performance size-exclusion chromatography (HPSEC) analysis. The remaining part was adjusted to pH 4.5 with 0.01M acetate buffer and then incubated with 5 μ L of amyloglucosidase at 55 °C for 8 h. The reaction was stopped by boiling for 5 minutes. The hydrolysates were submitted to HPSEC, HPAEC and matrix assisted laser

desorption/ionization time of flight-mass spectrometry (MALDI-TOF-MS) analysis as such and after saponification.

HPSEC

High-performance size-exclusion chromatography (HPSEC) was performed on a Thermo Quest AS3000 equipped with three TSK gel columns (each 300×7.5 mm) in series (PW_{XL} 4000, PW_{XL} 3000, and PW_{XL} 2500; Tosohaas) in combination with a TSK XL guard column (40×6 mm). Elution was at 30 °C using 0.2 M sodium acetate at a flow rate of 0.8 mL/min. The elute was monitored using a Shodex SE-61 Refractive Index detector. The system was calibrated with standards with molecular weights in the range 200-500000 (as determined by viscometry). The software was obtained from Thermo Quest.

HPAEC

For HPAEC analysis, a Thermo Quest HPLC is used which included a quaternary gradient pump and AS3000 autosampler completed with a He degassing unit and a PED detector in PAD mode (Dionex). A Thermo Quest PC 1000 data handling system was used. A CarboPac PA1 column (4×250 mm) with guard column (Dionex) was operated a flow rate of 1.0 mL/min at 20 °C. The gradient was obtained by mixing solutions of 0.1 M NaOH and M NaOAc in 0.1 M NaOH. After 15 min equilibration with 0.1 M NaOH, 20 μ L of the sample was injected and a linear gradient to 0.50 M NaOAc in 0.1 M NaOH within 30 minutes was followed by a linear gradient in 5 min to 1 M NaAc in 0.1 M NaOH. Finally, the column was washed for 5 min with 1 M NaOAc in 0.1 M NaOH.

MALDI-TOF-MS

The matrix solution was prepared by dissolving 10 mg of 2,5-dihydroxybenzoic acid in a 1 mL mixture of acetonitrile : water (2:1) containing 0.1% trifluoroacetic acid. For analysis, 10 μ L samples were added to 30 μ L of matrix solution and circa 50 mg Dowex 50 WX8 (H⁺) was added. Samples were thoroughly mixed and centrifuged ($8000 \times g$) for 30 sec to pellet the Dowex material. From the clear supernatants, aliquots of 1 μ L were applied to the target plate and dried in a gentle stream of air at room temperature. Samples were analyzed with a Voyager DE-RP™ (Perseptive biosystems) with a nitrogen laser of 337-nm wavelength and 3 ns-pulse width. The mass spectrometer was operating in the positive-ion mode with a delayed extraction time of 200 ns. Ions were accelerated to an energy of 12 kV before entering the TOF mass spectrometer. The minimum laser power required to obtain a good spectrum was used and 50-200 spectra were accumulated for each run. The mass spectrometer was calibrated externally with a mixture of glucose oligomers.

Results and Discussion

Differently sized granule fractions of the acetylated starches were obtained by sieving. The yields of the size fractions were well in agreement with the fractions obtained after sieving of the corresponding native starches (Chen and others 2003b) as shown in table 1. We previously showed that the amylose content decreases significantly with decreasing granule size dimension, while phosphorous content showed the opposite trend (Table 1; Chen and others 2003b). Protein contents are rather constant in different granule size fractions. Since acetylation would not significantly change the starch chemical composition, the chemical characteristics for the acetylated starch samples should be similar to those of their corresponding native starches.

Table 1-The yields and chemical compositions of the separated fractions (Chen and others 2003b)

Sample	Yield (%)	Amylose (%)	Protein (%)	Phosphorus(%)
P	100	22.8 ± 0.17b	0.09 ± 0.03a	0.69 ± 0.02c
P>53µm	36	23.6 ± 0.15a	0.08 ± 0.04a	0.60 ± 0.03d
P36-53µm	42	22.9 ± 0.10b	0.09 ± 0.03a	0.69 ± 0.02c
P20-36µm	17	22.1 ± 0.25c	0.08 ± 0.04a	0.75 ± 0.03b
P<20µm	5	21.3 ± 0.12d	0.10 ± 0.04a	0.98 ± 0.06a
S2	100	19.4 ± 0.10ab	0.13 ± 0.03a	nd
S>20µm	42	19.7 ± 0.21 a	0.12 ± 0.03a	nd
S<20µm	58	19.2 ± 0.20b	0.10 ± 0.04a	nd
X18	100	20.5 ± 0.20b	0.22 ± 0.02a	nd
X18>20µm	33	22.5 ± 0.15a	0.24 ± 0.01a	nd
X18<20µm	67	19.7 ± 0.15c	0.23 ± 0.02a	nd

P: potato starch; P>53: potato starch (granule size >53 µm); S2: SuShu2 starch; X18: XuShu18 starch; nd: Value was not determined. All values are the mean of 3 measurements. Values with different letters in the same column of same variety are significantly different at $p < 0.05$.

Although several methods have been used for the fractionation of starch in its components, it

is still difficult to separate amylose and amylopectin in a quantitative way without contamination with the other component (Schoch 1945; Banks and others 1959; Whistler and Doane 1961; Hizukuri 1996). Mua and Jackson (1995) suggested that the most efficient method for obtaining pure amylose was to leach the amylose from starch granules followed by centrifugation and crystallization using 1-butanol. They reported that corn amylose could be obtained in a high purity (>95%) by aqueous leaching at the gelatinization temperature range (60-80 °C) of corn starch. High purity (>90%) hydroxypropylated corn amylose was also obtained by leaching amylose in water followed by centrifugation (Shi and BeMiller 2002). The purity of the amylose populations isolated from differently sized granule fractions of acetylated potato and sweet potato starches were higher than 92%, while for the isolated amylopectin the purity was higher than 96% (Table 2). The recovery of acetyl groups after fractionation by sieving is between 88% and 96%. When further fractionated into amylose and amylopectin populations the recovery of the acetyl groups is between 76% to 96%. The loss of acetate is due to the fact that not all material was pooled after fractionation amylose and amylopectin.

It was found that in general the DS of the isolated amylose population was higher than that of the amylopectin populations (Table 2). The DS of the amylose populations were 40-200%, 25-54% and 27-82% higher than those of the amylopectin populations of acetylated potato, SuShu2 and XuShu18 starch fractions, respectively. The same phenomenon was observed in hydroxypropylated potato starch by Kavitha and BeMiller (1998) who found that at a molar substitution (MS) of hydroxypropylated whole starch is 0.099, of amylose, 0.113, and of amylopectin, 0.096. The difference of DS between amylose and amylopectin is slightly lower than that for acetylated starches in our study. This may be due to the fact that hydroxypropyl groups can randomly distribute throughout the amorphous regions of amylopectin part (Seib, 1997), and the hydroxypropyl substituent could be substituted by themselves. Although the DS of amylose population was 25-200% higher than that of the amylopectin population, it should be realized that due to the large proportion of amylopectin most acetyl groups were located in the amylopectin part. It was calculated that about 25% of all acetyl groups present in small starch granules (both acetylated potato and sweet potato) is present within the amylose population starches. However, this value ranges from 28% (for acetylated SuShu2 starch) to 49% (for acetylated potato starch) for large granules. It can be seen that the DS of amylose are constant in differently sized granule fractions, while the DS of amylopectin, similar to the DS of the total starch fraction, increases with decreasing granule size dimension. This suggests that the variation in DS of different granule size starches is due to the different DS of the corresponding amylopectin part, but not of the amylose part. It is known that amylose is mainly located in the amorphous regions while the branched chains of amylopectin make up

Table 2-Purity and molar substitution of amylose and amylopectin isolated from different size granule fractions of acetylated potato and sweet potato starches

Sample	Purity (%)		Degree of molar substitution (%)		
	Amylose	Amylopectin	Starch	Amylose	Amylopectin
ACP	93	97	0.0648c (0.0012)	0.0827a (0.0013)	0.0418b (0.0009)
ACP>53µm	94	96	0.0469e (0.0002)	0.0825a (0.0006)	0.0275d (0.0011)
ACP36-53µm	92	98	0.0596d (0.0013)	0.0812a (0.0014)	0.0349c (0.0008)
ACP20-36µm	96	96	0.0679b (0.0002)	0.0835a (0.0009)	0.0427b (0.0005)
ACP<20µm	93	97	0.0763a (0.0006)	0.0835a (0.0010)	0.0598a (0.0011)
ACS2	96	96	0.0578b (0.0009)	0.0641a (0.0004)	0.0431b (0.0008)
ACS>20µm	95	97	0.0471c (0.0003)	0.0631a (0.0004)	0.0411c (0.0009)
ACS<20µm	94	98	0.0598a (0.0007)	0.0635a (0.0009)	0.0509a (0.0004)
ACX18	95	97	0.0550b (0.0007)	0.0609a (0.0020)	0.0383b (0.0011)
ACX18>20µm	94	96	0.0406c (0.0007)	0.0608a (0.0019)	0.0335c (0.0010)
ACX18<20µm	95	97	0.0590a (0.0004)	0.0627a (0.0003)	0.0495a (0.0010)

ACP: acetylated potato starch; ACP>53: acetylated potato starch (granule size >53 µm); ACS2: acetylated SuShu2 starch; ACX18: acetylated XuShu18 starch. All values are the mean of 3 measurements. Values with different letters in the same column of same variety are significantly different at $p < 0.05$. Values in the parenthesis are the standard deviations.

the crystalline regions of starch granules. Our results indicate that amylose as present in the amorphous regions are equally acetylated whereas amylopectin in the crystalline regions is

selectively acetylated. With decreasing granule size dimension the amylopectin is even more favored. Since, in general, small granules have larger specific surface areas than the large ones (Morrison and Scott 1986), the crystalline regions in the outer lamellae of small granules have more space to react with the chemical reagent (acetic anhydride) resulting in higher DS in the amylopectin present. It can be concluded that the acetylation can not take place throughout the crystalline regions of the whole granule but only occur in the outer lamellae. This may be due to the poor penetrating ability of acetic anhydride in starch granules. Our result confirms the assumption of Biliaderis (1982) who reported that the acetylation of smooth pea starch occurred exclusively in certain parts of the granule, and that only part of the amylopectin is (highly) substituted. The model of acetylation in the starch granule is supposed in figure 2.

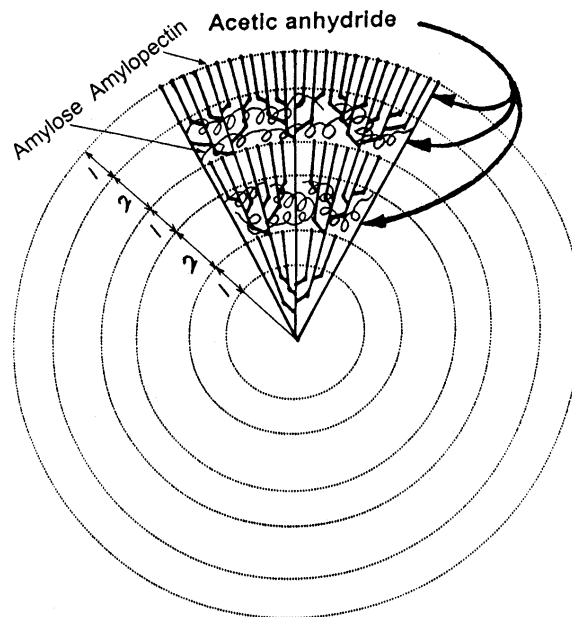


Figure 2-Proposed model for the starch granule acetylation (1. crystalline region; 2. amorphous region)

Distribution of acetyl groups over amylose revealed by enzyme digestion

α -amylase digestion

α -amylase is an endo-enzyme which hydrolyzes polysaccharides randomly at α -(1 \rightarrow 4) D-glucosidic linkages to produce glucose and oligosaccharides containing two to seven glucose

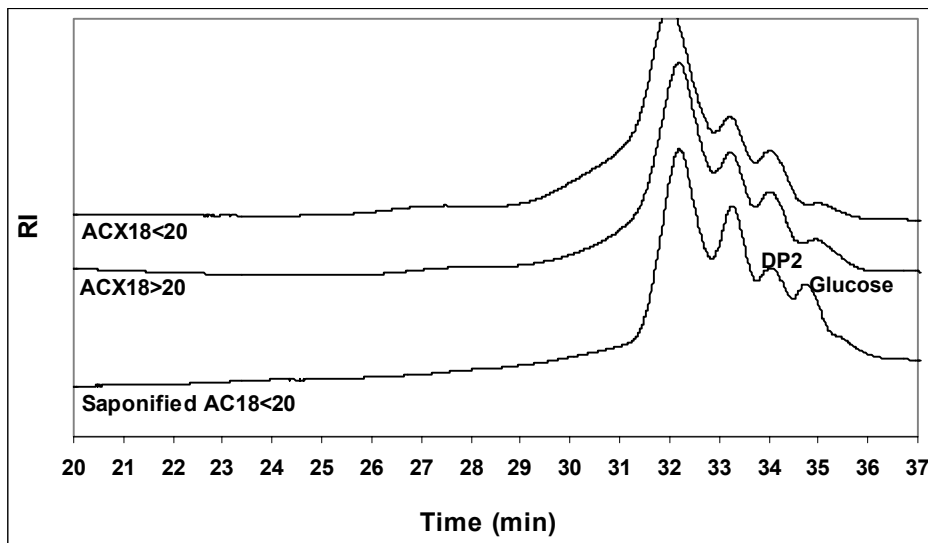


Figure 3-HPSEC elution profiles of the α -amylase hydrolysates of the amylose populations isolated from different size granule fractions of acetylated XuShu18 sweet potato starch (AC18>20: amylose isolated from large size granule fraction (>20 μm) of acetylated XuShu18 starch)

residues (Hizukuri 1996). Digestion by α -amylase may be hindered by substitution of the substrate and therefore analysis of the digest may give the information on the distribution of acetyl group over the acetylated amylose. The DS of the amylose population of differently sized granule fractions of acetylated potato, acetylated SuShu2 and acetylated XuShu18 are about 0.08, 0.06, and 0.06 corresponding to 2.1%, 1.5% and 1.5% of the introduced acetyl group, respectively. Although only small amount of acetyl groups were introduced, it appears from comparison of the HPSEC and HPAEC profiles of the acetylated amylose and their saponified samples (Figure 3 and Figure 4) that α -amylase digestion is hindered by acetyl substitution. This is in agreement with the result of Biliaderis (1982) that acetyl substituents exert a similar effect to hydroxyethyl groups which restrict α -amylase attack on adjacent α -(1 \rightarrow 4) glucosidic linkages. The HPSEC elution profile of the saponified samples digested with α -amylase showed them to be more degradable than the acetylated samples. The HPSEC elution profile of the acetylated amylose samples showed that the small granule fractions were less digested than for that from large granule fraction. It can be clearly seen from the HPAEC elution profile that the saponified sample was digested to oligomers degree of polymerization (DP) \leq 6, whereas oligomers with a DP $>$ 6 were found in the digests of all acetylated samples. It was also found that the components with higher DP were more present in the amylose isolated from small size granule fractions. Although the DS of the amylose populations of

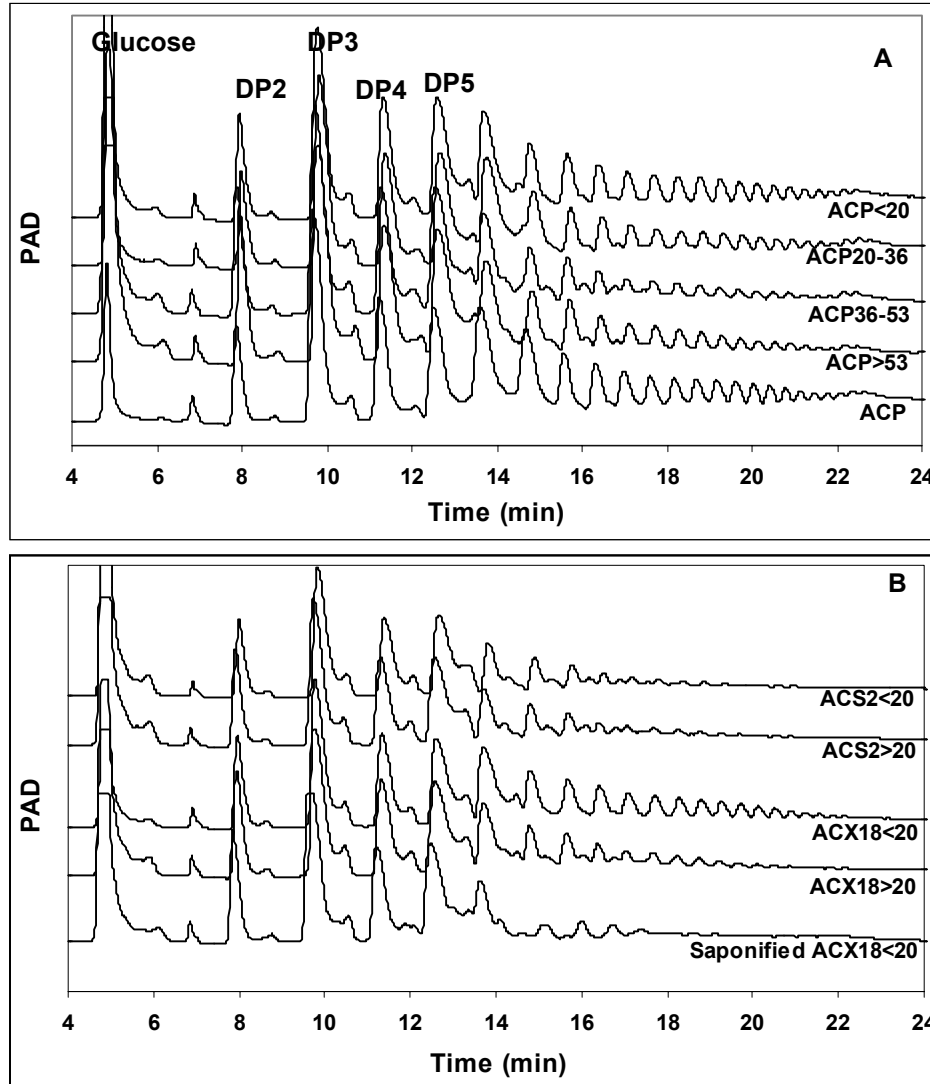


Figure 4-HPAEC elution profiles of the α -amylase hydrolysates of the amylose populations isolated from different size granule fractions of acetylated potato (A) and sweet potato (B) starches (ACP: amylose isolated from acetylated potato starch; ACS2<20: amylose isolated from small size granule fraction (<20 μm) of acetylated SuShu2 starch; AC18>20: amylose isolated from large size granule fraction (>20 μm) of acetylated XuShu18 starch)

differently sized granule fractions were quite similar, the susceptibility of the amylose populations of both acetylated potato and sweet potato (SuShu2 and XuShu18) starches to α -amylase degradation was obviously different. The susceptibility decreased with decreasing granule size dimension. This indicates that the acetyl groups were distributed in different patterns in the amylose populations of differently sized granules. The acetyl group distribution

patterns in the amylose populations of small size granule fractions are more difficult for α -amylase to digest suggesting a more heterogeneous acetyl group distribution. Moreover, it could also be observed that amylose from differently sized granule fractions of acetylated potato starch were less susceptible to α -amylase than that from acetylated sweet potato (SuShu2 and XuShu18) starches. This is partly due to the higher DS in the amylose of acetylated potato starch. The DS of amylose from differently sized granule fractions of acetylated SuShu2 and XuShu18 are similar, but the difference of the susceptibility to α -amylase between the amylose from large and small size granule fractions is more clear for acetylated XuShu18 starch than for acetylated SuShu2 starch. This suggests that acetyl group distribution not only depends on granule size but also depends on starch origin. Other properties of starch granules such as granule density may also influence the acetylation of starch granules.

Since all HPSEC and HPAEC elution patterns of acetylated potato, SuShu2 and XuShu18 digested with enzymes showed the same trends, we only showed the elution profiles of acetylated XuShu18.

Amyloglucosidase digestion

The α -amylase hydrolysates were further digested with amyloglucosidase. Amyloglucosidase is capable to hydrolyze completely both α -(1 \rightarrow 4) and α -(1 \rightarrow 6) linkage in polysaccharides through an exo-mechanism from the nonreducing terminal residues producing β -D-glucose (Hizukuri 1996). Simultaneous α -amylase and amyloglucosidase digestion of normal starches will result in a complete conversion into glucose. After amyloglucosidase digestion it could be observed from HPSEC profiles (Figure 5) that some oligomers remained in the digested acetylated amylose, while the saponified samples were digested completely to glucose. This indicates that amyloglucosidase is also hindered by acetyl groups. The susceptibility of the amylose of differently sized granule fractions of acetylated potato and sweet potato (SuShu2 and XuShu18) starches to amyloglucosidase digestion showed the same trends as to α -amylase digestion. The different susceptibility to enzyme digestion is probably due to the different acetyl group distribution in the amylose population of the differently sized granules. It is clearly seen from HPAEC elution profiles (Figure 6) that higher DP oligomers resistant to further digestion were present in the amylose population of small size granule fractions of acetylated starches. This suggest that acetyl groups were more heterogeneously distributed in the amylose of small size granules, since the chain of substituted enzyme resistant fragments will be longer when the acetyl substituents are more clustered. The smallest enzyme resistant oligomer was trimer. The concentration of trimer in the digests of acetylated potato, SuShu2 and XuShu18 starches were about 28%, 35% and 38%, respectively. Mass spectrometry results

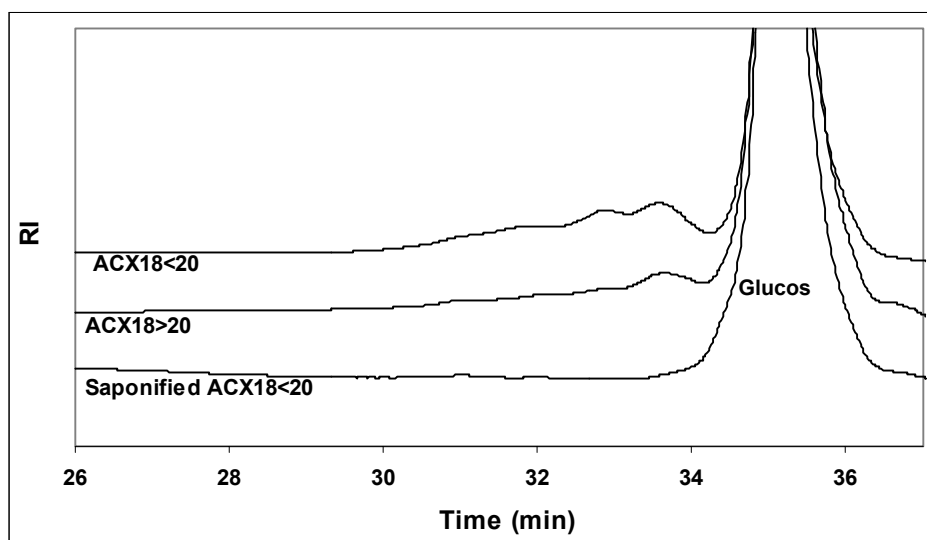


Figure 5-HPSEC elution profiles of the amyloglucosidase hydrolysates of amylose populations isolated from large and small size granule fractions of acetylated XuShu18 starch (AC18>20: amylose isolated from large size granule fraction (>20 μm) of acetylated XuShu18 starch)

of the enzyme digested hydrolysates (MALDI-TOF-MS) showed that the enzyme resistant component of DP3 contains 1 acetyl group, DP4 contains 1 and 2 acetyl groups, and DP5, DP6 and DP7 contains 2 and 3 acetyl groups, respectively (Figure 7). This result confirms that the enzyme resistant residues contain at least 1 acetyl group which causes the hindrance for α -amylase and amyloglucosidase digestion. Although the O-2 and O-3 position of the glucose residues were found to be equally substituted and the O-3 position has nearly no substituent in the relatively high DS (0.42-0.81) acetylated starches (Heins and others 1998), the presence of di/tri substituted glucose moieties in enzyme resistant oligomeric fragments and the precise location of acetyl with the oligomer will be investigated in future.

The DS of the amylose of acetylated potato and sweet potato starches are about 0.08 and 0.06 corresponding to, on average, 1 acetyl group on every 13 and 17 glucose units, respectively. The enzyme digestion clearly points out that the acetyl groups were unevenly distributed in amylose population as is indicated by the presence of DP 5-7 oligomers having 2-3 acetyl groups present. This distribution further depends on the granule size and on the starch origin as well.

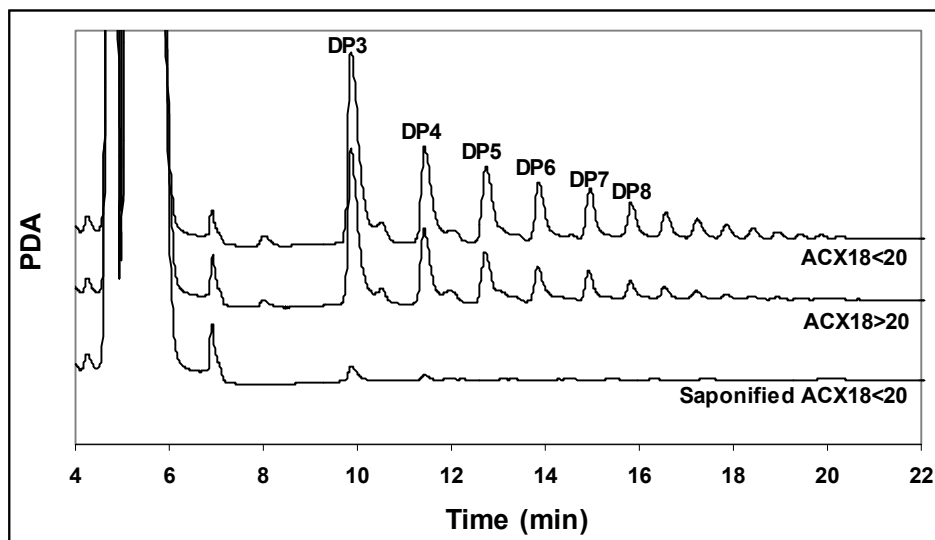


Figure 6-HPAEC elution profiles of the amyloglucosidase hydrolysates of amylose populations isolated from large and small size granule fractions of acetylated XuShu18 starch (AC18>20: amylose isolated from large size granule fraction (>20 μm) of acetylated XuShu18 starch)

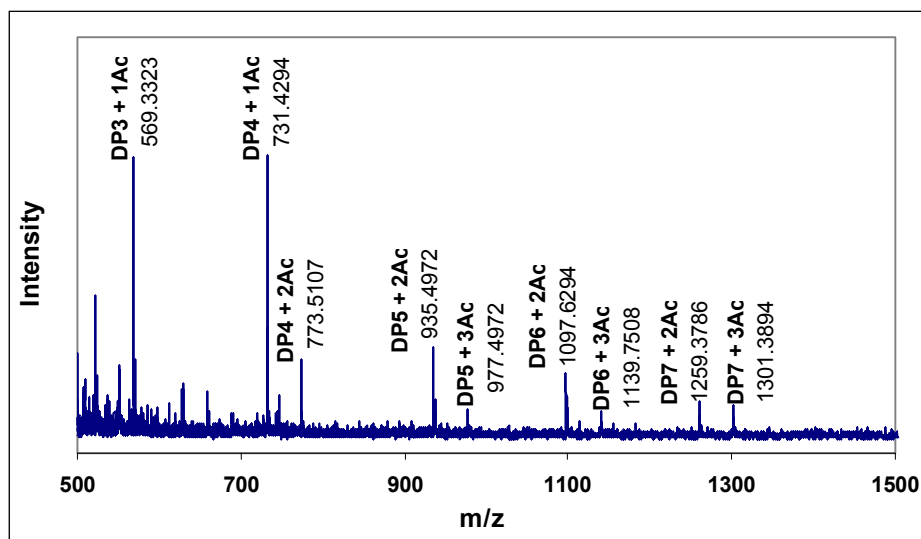


Figure 7-MALDI-TOF mass spectra of the enzyme (α -amylase and amyloglucosidase) hydrolysates of amylose population separated from small size granule fractions of acetylated XuShu18 starch (Ac: acetyl group)

Conclusion

The degree of acetylation of the starch isolated from differently sized granule fractions differed significantly: the DS increased with decreasing starch granule size dimension. The DS of the isolated amylose populations of differently sized granule fractions were constant while the DS of the isolated amylopectin populations showed the same trends as the original acetylated starch material: DS increased with decreasing granule size dimension. From the fact that amylose is mainly located in amorphous region and the branched chains of amylopectin are in crystalline region, and that the specific surface area of starch granule increases with decreasing starch granule dimension, we conclude that acetylation occurs in all amorphous regions and only in the outer lamella of crystalline regions. Our results are in the agreement with the assumption of Biliaderis (1982) for the acetylation in starch granules. Enzymatic digestion showed that both α -amylase and amyloglucosidase were hindered by acetyl group. Although the amylose populations isolated from differently sized granule fractions have similar DS, they clearly showed different susceptibility to enzymatic digestion. Enzyme resistant residues with higher DP were present in the amylose populations isolated from small size granule fractions. This indicates that the distribution of the acetyl group over the glucan backbone is more heterogeneous in the amylose populations isolated from small size granule fractions.

Acknowledgement

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CHAPTER 7

Concluding remarks

Introduction

Sweet potato (*Ipomoea batatas*) has been recognized as an important food crop having a high yield during a fairly short harvest season (about 3-5 months), and having a good adaptability to varying climatic and field conditions (Tain and others 1991; Woolfe 1992). Most of the sweet potatoes are consumed as simple food products (e.g. fresh, steamed, or roasted snacks) or used as an animal feed. There has been a strong desire from the sweet potato farmers and processors to increase their revenue by adding economic value to sweet potato products. Until now, starch is the main industrial product from sweet potatoes but its use is still limited (Jangchud and others 2003). The limited industrial application for sweet potato starch is considered to be partly due to impurities and lack of information about its properties (Narayana-Moorthy 2002). Although there are hundreds of publications dealing with the physicochemical properties of the starches from various varieties of sweet potatoes, only little information of Chinese sweet potato starches is available. In contrast, China is by far the major producer of sweet potatoes in the world (>85%) with more than 2000 varieties. This research is aimed at a systematic study on physicochemical properties of Chinese sweet potato starches from 3 selected varieties and their applications in 2 popular Asian noodle products as an approach to better use the abundant Chinese sweet potato starches.

Characteristics of typical Chinese sweet potato starches

Starches from 3 selected Chinese sweet potato varieties have been isolated and characterized. The chemical compositions of the three typical Chinese sweet potato starches were found to be similar to those from reported Indian, Japanese, and USA sweet potato varieties (Table 1). The data for amylose, protein, and lipid contents from Nigeria sweet potato varieties are extremely higher. This may be due to both the variety and the growing condition.

According to literature, the granule sizes of sweet potato starches are quite heterogeneous with a broad granule size distribution (Table 2). The granule sizes ranges of the Chinese sweet potato starches are narrower than those from Nigeria and USA varieties (Osundahunsi and others 2003; Walter and others 2002) but broader than those from Indian varieties (Madhusudhan and others 1992). The average granule size of SuShu8 is relatively small when compared to XuShu18 and SuShu2, and the starches from Japanese and USA varieties. Studies towards the characterization of sweet potato starches are usually directed to the high starch content varieties, while varieties not used for starch production, like for consumption in roasted form (SuShu8), with much lower starch content are generally ignored in these studies.

Other physical properties such as gelatinization temperature, pasting curve pattern and swelling behavior of the Chinese sweet potato starches are quite comparable with those found

Table 1-Chemical compositions of isolated starches from local sweet potato varieties from various countries (w/w %)

Source	Amylose(db)	Protein(db)	Lipids(db)	Phosphorus(db)
China (XuShu18)	20.0	0.23	0.21	0.022
China (SuShu2)	19.3	0.14	0.14	0.014
China (SuShu8)	19.6	0.17	0.16	0.021
India (local varieties) ¹	17.0-22.0	0.14-4.28	NA	0.045-0.053
Nigeria (TIS-1499) ²	32.2	4.38	2.21	NA
Nigeria (TIB-2) ²	34.2	5.56	2.28	NA
Japan (Koganesengan) ³	18.9	0.04	NA	0.013
Japan (Minamiyutaka) ³	17.2	0.05	NA	0.014
Japan (Norin-2) ³	19.0	0.05	NA	0.012
USA (local variety) ⁴	22.8	NA	NA	0.020

1. from Madhusudhan and others (1992); 2. from Osundahunsi OF and others (2003); 3. from Takeda and others (1986); 3. from Garcia and Walter (1998); 4. from McPherson and Jane (1999); NA: not available. db: dry base.

Table 2-Physical properties of isolated starches from local sweet potato varieties from various countries

Source	Size (μm)		Gelatinization temperature ($^{\circ}\text{C}$)	Pasting pattern	Swelling power (90°C)	Syneresis (%)
	Range	Mean				
China (XuShu18)	4-28	12	75	B	33	29
China (SuShu2)	3-28	9	69	B	24	26
China (SuShu8)	3-24	8	67	B	36	8
India ¹	2-13	NA	67-75	A	NA	NA
Nigeria ²	2-40	NA	66-75	B	56-58	NA
Japan	NA	8.6-11.0 ³	72-76 ³	B ⁴	NA	NA
USA	3-60 ⁵	13.3-21.3 ⁵	62.8-71.4 ⁵	B ⁶	32-38 ⁵	NA
Korea ⁷	NA	NA	74.7	NA	NA	75

1. from local varieties (Madhusudhan and others 1992); 2. from TIS-1499 and TIB-2 varieties (Osundahunsi and others 2003); 3. from Koganesengan and Shiroyutata varieties (Noda and others 1995); 4. from Koganesengan, Minamiyutaka and Norin-2 varieties (Takeda and others 1986); 5. from Jewel, Beauregard, NC10-28, NC2-26, NC6-30 and NC8-22 varieties (Walter and others 2000); 6. from local variety (McPherson and Jane 1999); 7. from an unknown Korean variety (Lee and others 2002); NA: not available.

for the varieties in other countries. However, the swelling power of SuShu2 starch was lower. For only one other source of sweet potato starch data is available on its syneresis behavior. This value for starch from an unknown Korean sweet potato variety differs significantly with our findings. Such a difference between our results and literature (Lee and others 2002) is probably due to the different methods used. Although syneresis data have been used as an indication for starch retrogradation tendency for many years, the results reported by different researchers were rather incomparable. Typically, syneresis is measured after “freeze-thaw” cycle which involves subjecting samples to repeated freezing and intermittent thawing to room temperature over a period of 2-4 h. After the thawing step in each cycle, the free water is separated (usually by centrifugation) and quantified according to Karim and others (2000). We found that after the first “freeze-thaw” cycle the sample became sponge-like. This spongy structure makes the measurement of free water in the following cycles impossible. After centrifugation the excluded water was instantaneously reabsorbed by the sponge-like samples. Moreover, many other parameters such as centrifugal force, freezing temperature, freezing and thawing rate, freezing duration also affect the results. This problem was also observed by Yuan and Thompson (1998) and they suggested that it might be appropriate to define freeze-thaw stability of starch pastes by the number of freeze-thaw cycle necessary to detect the first appearance of free liquid above the paste after centrifugation. But it is impossible to get the data of syneresis after the first “freeze-thaw” cycle by this suggested method. Recently, Lee and others (2002) used another method to measure syneresis. After thawing they transferred the gel onto a filter paper and then vacuum-filtered with an electric aspirator for 10 min. A 1 kg weight (stainless steel cylinder) was placed upon the gel to accelerate water release. Although this method could measure syneresis of starch gels throughout all the cycles, the applied force may damage the structure of starch gels. In order to be able to determine the syneresis throughout the whole cycles without damaging starch gel structures we developed a new method for measuring the syneresis based on the water excluded by gravity after thawing (see Chapter 2). The syneresis measured by this method is more close to the “freeze-thaw” situation of starchy food during storage and transportation.

Effect of starch characteristics on starch noodle preparation

The necessity of high amylose content and C type viscosity curve of starches for starch noodle manufacture

Starch noodle is one of the special products containing only starch and water. Obviously, starch properties determine the processibility and quality of starch noodle. Mung bean starch is traditionally regarded as the ideal raw material for starch noodle making and mung bean starch

noodle is the most favorable one of all starch noodle products. Mung bean starch is more expensive than other commonly used commercial starches such as corn, wheat, potato, tapioca starches due to the tedious starch isolation process and the low yield. Starch and starch noodle industries are very much interested in replacing mung bean starch totally or partially by a cheaper starch (derivative) without loss of quality. For this and other reasons, the physicochemical properties of mung bean starch and its noodle quality have been intensively studied (Lii and Chang 1981; Singh and others 1989). The previous studies concluded that suitable materials for starch noodle making should show a C-type Brabender viscosity curve (see the description in Chapter 2), should have a restricted swelling and should have a high amylose content. These conclusions stimulated other researchers to look for a starch (derivate) having these characteristics in order to substitute mung bean starch. Several studies have been carried out using cross-linked potato, sweet potato or tapioca starches, or by using the starch from selected potato or sweet potato genotypes, or using a mixture of cross-linked tapioca starch and high amylose maize starch (Xu and Seib 1993; Kim and others 1996; Kim and Wiesenborn 1996; Kasemsuwan and others 1998; Muhammad and others 1999). Although these efforts showed some positive results, none of the starches under investigation found application on a commercial scale. Contrarily to the statement that high amylose content is required for the starch to produce high quality starch noodle, some starches having high amylose content, such as high amylose corn starch, were found not to be suitable for starch noodle making. Also Kim and others (1996) found that there was not significant correlation between amylose content and the hardness of cooked starch noodle. They suggested that, with respect to noodle cooking quality, next to a certain threshold level of amylose, other starch properties are more important than amylose content.

A C-type Brabender viscosity curve of a starch has also been thought to be essential for starch when applied in starch noodle making. The C-type Brabender viscosity curve and restricted swelling behavior of starch can generally be achieved by chemically cross-linking. This may be the reason that cross-linked starches are preferably applied for starch noodle making. However, two commercial cross-linked potato starches showing C-type Brabender viscosity curves and restricted swelling were examined in our lab and were found unfit to make starch noodle at all. Although these cross-linked starches meet the requirements of showing a C-type Brabender viscosity curve and restricted swelling, they have increased resistance to gelationization, and decreased paste clarity (Wurzburg 1986) which are considered as deficiencies for starch noodle making. Viscosity curve patterns reported in literature can not be compared due to different starch concentrations or equipment (Brabender amylograph or RVA) used. The curve pattern is dependent on starch concentration. Even for mung bean starch, C-type Brabender viscosity curves are only obtained when the starch concentration is lower than

8% (w/v). When the concentration increase above 8% (w/v), mung bean starch will show a B-type Brabender viscosity curve. The viscosity curve pattern was originally classified by Schoch and Maywald (1968) according to Brabender amylogram. We noticed that mung bean starch at the concentration of 6% (w/v) showed a C-type in Brabender amylogram but exhibited a B-type in RVA viscosity curve. For Brabender amylograph 10-100 g of samples are used, the required time is between 90-160 min, and a bowl speed of 75 rpm is usually applied. Whereas, for RVA only 2-5 g samples are required and can be measured within 20 min. However, the much higher paddle speed (160-960 rpm) of RVA causes much more shearing on starch granules.

Some sweet potato starches have been used for starch noodle manufacture in China, Korea and Japan for many years. In Malaysia native potato starch has been used commercially to substitute part of mung bean starch in the production of starch noodle, however the cooked noodle quality decreased (Muhammad and others 1999). In our study the starch from SuShu8 (which is usually used for roasted sweet potato consumption), showing a B-type Brabender viscosity curve (at the concentration of 6-8%), a relatively high swelling power, and low amylose content, has fairly good processibility into noodles with a quality well comparable to noodles made from mung bean starch (see Chapter 3). Contrarily, SuShu2 starch having relatively higher restricted swelling and retrogradation tendency could not make long starch noodle strands and the quality is much worse than that made from SuShu8 starch. No correlation was found between amylose content, swelling power or types of viscosity curve, and starch noodle quality. A significant correlation between the starch noodle quality and the G' (storage modulus, representing the gel firmness) of the starch gel was observed (see Chapter 3).

Effect of retrogradation on the processing and quality of starch noodle

Retrogradation is generally regarded as an undesirable effect in starch-based products, responsible for, e.g. bread staling or syneresis of gel products. On the other hand, retrogradation sometimes can improve the quality of starch-based products, such as the quality of Japanese “harusame” noodle and Chinese rice vermicelli for which reduced stickiness and more desirable textures could be achieved (Watanabe 1981; Seow and others 1996). Also Mestres and others (1988) stated that commercial starch noodle products of good quality are obtained from starches exhibiting a high extent and high rate of retrogradation. In some regions of Asia starch noodle is traditionally called “Dong Feng” which means “winter noodle”. This refers to the time that cooling and freezing treatments, which are important steps in starch noodle manufacture, could only be carried out during the winter season. Unfortunately, most of the literature did not pay attention to these important steps. Unlike other types of noodles,

starch noodles are cooked and then dried (see Chapter 3). During the cooling stage the gelatinized starch of the noodle is undergoing recrystallization. This step can be considered as the short-term retrogradation in which mainly amylose is involved. During freezing amylopectin will also contribute to retrogradation. Therefore, the amylose content may not necessarily be the evaluation criteria for the raw material to describe its suitability for starch noodle making. Characteristics of amylose and amylopectin such as degree of polymerization (DP), length of A and B chains in amylopectin, and A/B chain ratio may be even more important. We observed that the dried noodle transparency increased with the increasing cooling and freezing treatment. The cohesiveness of the raw starch noodle decreased significantly by cooling and freezing treatments. In fact, the freezing treatment is the efficient way to separate the raw starch noodle strands automatically.

Effect of starch granule size on starch noodle processibility and quality

Processibility is as important as noodle quality in noodle manufacture. Many commercial starches can not be used for starch noodle making because they either lack the fluidity to form the constant long noodle strands or they form strands which are too sticky to separate of the fresh noodle strands. The proper processibility is an important prerequisite of the raw starch for starch noodle production. Unfortunately, not enough attention has been paid by food scientists towards the processibility of starch in starch noodle production till now.

Function of gelatinized starch in dough for starch noodle making

Unlike wheat flour dough, dough made from only starch does not contain gluten which forms a network to integrate other components (such as starches) to form a visco-elastic dough. The dough for starch noodle making is formed by pregelatinized starch paste (5% of total starch), native starch (95% of total starch) and some water. The optimum dough is obtained by kneading at 40 °C. The pregelatinized starch paste, which functions as gluten in wheat flour, integrates the native starch granules to form a special “dough”. This starch dough does not have elasticity but does have fluidity. Due to the low water holding capacity and the high granule density of the native starch, water is not homogeneously distributed in the dough. When the blending stops, the dough will spread by gravity and part of the water will exude to the surface. The spreadability and viscosity of the mixture of the native starch and the pregelatinized paste together provide the starch dough the special fluidity which allows the dough to be extruded by gravity to form the noodle strands. The proposed model of the starch dough is shown in figure 1.

The starch dough fluidity is affected by the properties of both pregelatinized starch paste and the native starch. The fluidity is sensitive to temperature but is reversible. When the

temperature is above 30 °C (but below gelatinization temperature) the starch dough exhibits a better fluidity, while below 30 °C the fluidity is too low to make starch noodle strands. The temperature may influence the pregelatinized starch paste in forming the network of the dough.

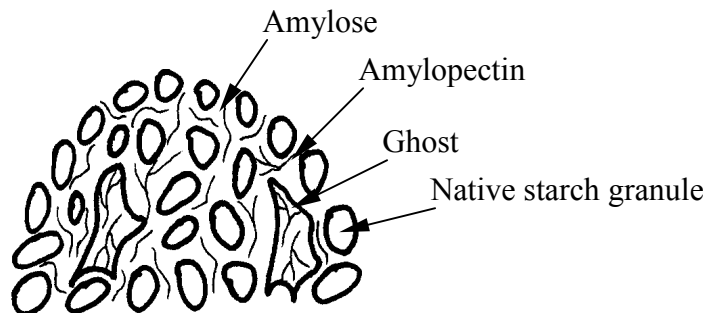


Figure 1-Proposed model of starch dough for starch noodle making (the native starch granule represented 95% of the dough)

Effect of granule size of native starch on dough for starch noodle making

The major part of the dough is formed by native starch granules. These starch granules may play an important role in the dough fluidity. It was found in our study that the sweet potato SuShu8 starch (having smaller granules) showed a better processibility and noodle quality than the other sweet potato starches. The processibility of SuShu8 starch is even better than mung bean starch. Contrarily, Sushu2 starch, having a high proportion of relatively large granules, exhibits a poor processibility and poor noodle quality. Potato starches which have very large granules could not make starch noodle at all. After separation by sieving, the small granule fractions of all starch sources (<20 μm) showed a better processibility and gave good quality starch noodles (see Chapter 4). From figure 2 it can be seen that the proportion of small granules (<20 μm) in Sushu8 starch is even higher than that of mung bean starch. This may explain why the processibility of SuShu8 starch is even better than that of mung bean starch.

The fact that small size granule starches have a better processibility into starch dough is partly due to the large specific surface areas of small granules compared to that of large size granules. The large specific surface areas of small granules provide more interaction areas to be glued together with the gelatinized starches in a more strong interaction between “efficiently” packed starch granules. Therefore, the starch dough made from small granules can

make long noodle strands consistently by gravity. The importance of starch granule size in products has been recognized by Sitohy and Ramadan (2001) who pointed out that the suitability of a starch for specific purposes in food or other application may well be dependent on the size and morphology of the native or swollen granule.

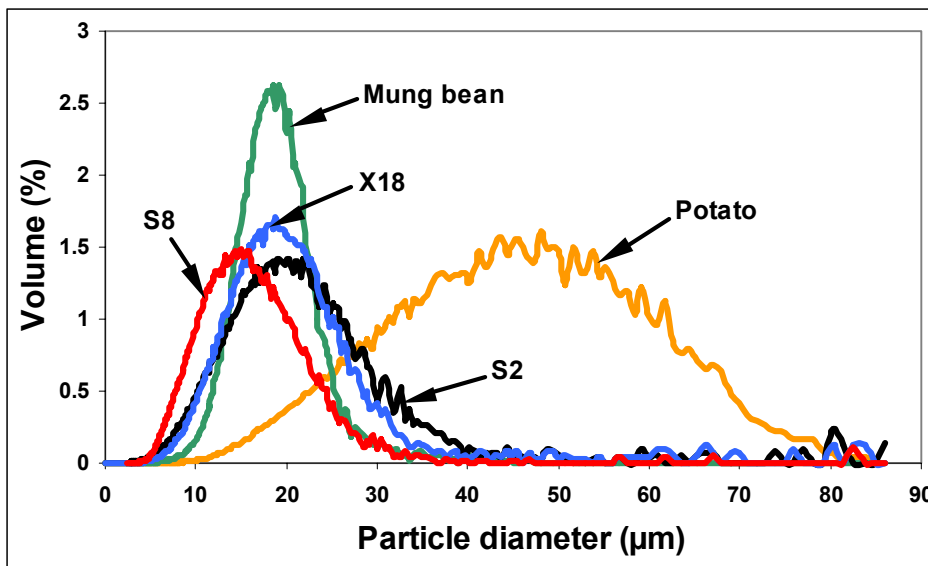


Figure 2-Particle size distribution of starches (S2: SuShu2; S8: SuShu8; X18: XuShu18)

Starch noodles are made by extruding noodle strands directly into hot water (95-98 °C) kept for about 1 min and then rinsed, pre-cooled, frozen and dried. Although differential scanning calorimetry (DSC) and X-ray diffraction determinations showed that nearly all the starches gelatinized, it is assumed that the starch granules might not be completely disrupted during the process. The granular remnants usually called the “ghosts” constitute a dispersed phase to introduce an interface which governs interactions between starch and other components through its hydrophobic-hydrophilic character, and through the components present at the interface (Eliasson and Gudmundsson 1996). The efficient packing of small granules (before gelatinization) together with the large specific surface areas of the granular remnants of the small granules provide strong integration between the various remnants, and between the remnants and leached materials resulting in a high compacted structure of the starch noodles. Therefore, noodles made from the small granule starches exhibit high transparency and flexibility of the dried noodles, low cooking loss, low swelling index, and high elasticity of the cooked noodles. However, it has been recognized that not all kinds of small granule starches

can make good quality starch noodle, as is the case for rice starch, wheat starch and corn starch. Obviously, the starch noodle quality also depends on the starch origin. Other properties of starch granules such as granule density, granule shape and the smoothness of the granule surface may affect the starch noodle quality as well.

Possibility for improving wheat noodle quality by using starch/derivative replacement

Classification of noodle products

Noodles are starch-rich products. Although noodles have many varieties with various ingredients, starch is always the major component. According to their main ingredients, noodles can be generally classified into various groups as shown in figure 3 and table 3. This overview is mainly based on an investigation of noodle markets and industries in China, since not enough information in this aspect can be found in literature.

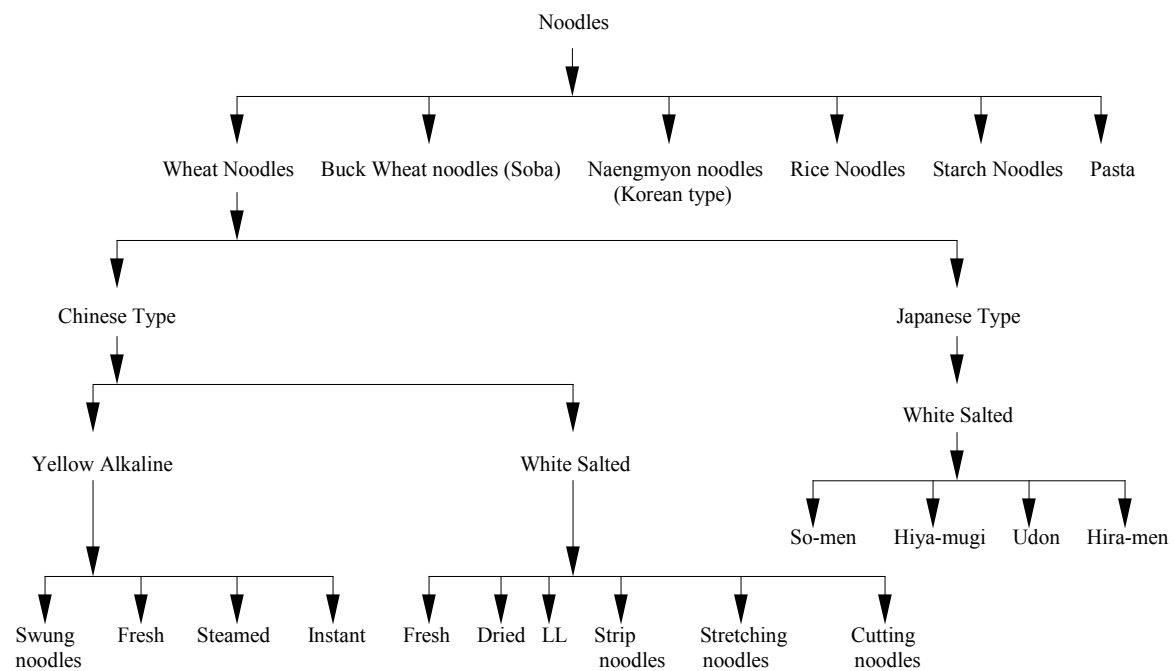


Figure 3-Classification of noodle products (Modified from Hou 2001)

Wheat noodles are generally made from wheat flours which include Chinese type and Japanese type. Buck wheat noodle (Soba) is another type of Japanese noodle which is made

from the composite flour of wheat flour and buckwheat flour (less than 50%) without adding any salt, having a special gray color and clear bite texture (Hatcher 2001). Soba is traditionally consumed in Japan and Korea. Naengmyon noodle is a Korean type noodles which are very popular during the summer season (Kim 1997). They are also called “Korean cold noodles” and made from a mixture of wheat flour, buckwheat flour and potato starch. Naengmyon noodles, unlike the Japanese Soba noodle, are made by extrusion. These noodles have a dark brown color and a rubbery texture. Rice noodles are made from rice flour slurry which is spread on a cloth and steamed and then cut into noodle strands, or made by extrusion (Luh 2001). Rice noodles have a white color, a clear bite and a smooth mouth-feel. These noodles are traditionally consumed in tropical and sub-tropical areas of Asian countries. Starch noodles are made from starch only, and the detailed description can be found in Chapter 3. Pastas such as spaghetti, macaroni, and others types of short goods with different shapes, are western type noodles and traditionally made from durum wheat semolina by extrusion (Marchylo and Dexter 2001).

Table 3-General description of noodles

Noodle	Materials	Marketing state	Quality requirement (cooked noodles)
Swung Noodles	Wheat flour, alkali	Fresh	Smooth, firm, chewy
YAN (machine made)	Wheat flour, alkali	Fresh, steamed, dried	Smooth, firm, chewy
Instant Noodles	Wheat flour, sodium chloride, alkali	Fried, air dried	Smooth, moderate firm, chewy, elastic
WSN (machine made)	Wheat flour, sodium chloride	Fresh, dried	Smooth, moderate firm, elastic
LL Noodles	Wheat flour, sodium chloride	Cooked	Smooth, moderate firm, elastic
Strip Noodles	Wheat flour, sodium chloride	Fresh	Smooth, moderate firm, elastic
Stretching Noodles	Wheat flour, sodium chloride	Dried	Smooth, soft, elastic
Cutting Noodles	Wheat flour, sodium chloride	Fresh	Smooth, moderate firm, elastic
So-men Noodles	Wheat flour, sodium chloride	Dried	Smooth, soft, elastic
Hiya-men Noodles	Wheat flour, sodium chloride	Dried	Smooth, soft, elastic
Udon Noodles	Wheat flour, sodium chloride	Fresh, boiled, dried	Smooth, soft, elastic
Hira-men Noodles	Wheat flour, sodium chloride	Dried	Smooth, soft, elastic
Soba Noodles	Buck wheat flour, wheat flour, sodium chloride	Fresh, dried	Smooth, soft
Naengmyon noodles	Wheat flour, buckwheat flour, potato starch, sodium chloride	Fresh, dried	smooth, rubbery
Rice Noodles	Rice flour	Fresh, dried	Smooth, soft
Starch Noodles	Starch	Dried	Smooth, soft, elastic, transparent
Pasta	Durum wheat semolina	Dried	Smooth, firm, elastic

YAN: Yellow Alkaline Noodles; WSN: White Salted Noodles; LL: Long Life noodle.

Wheat noodles are the major noodle products in Asian countries where about 30-40% of all wheat flour is consumed as part of wheat noodle products (Miskelly 1993). In general, according to the type of wheat flour used (hard versus soft wheat), wheat noodles can be classified into Chinese type and Japanese.

Chinese types of wheat noodles (usually made from hard wheat flour) can be further classified into: 1) yellow alkaline noodle (YAN) which contains sodium or potassium carbonate as an ingredient having a good slipperiness and a special color and flavor; and 2) white salted noodle which contains sodium chloride as an ingredient resulting in firm texture of the cooked noodles.

Yellow alkaline noodles can be made by hand and by machine. Swung noodle is a typical Chinese alkaline hand-made noodle. Its unique processing and favorable texture makes it difficult to produce these noodles on an industrial scale. While machine-made yellow alkaline noodles are usually sold as fresh, or as dried products after steaming. Instant noodles, in fact, contain both potassium carbonate and sodium chloride, and are the most popular noodles nowadays. The freshly made noodle strands are waved, steamed and then dehydrated either by deep fry in hot oil or by hot air. The noodles can be easily consumed after soaking in hot water or cooking for 3-5 min.

The hand-made Chinese white salted noodles including “strip noodle”, “stretching noodle” and “cutting noodle” differ from the manner of noodle making and noodle appearance. The machine-made Chinese white salted noodle usually sold both as fresh and as dried products. It is estimated that there are more than 2×10^6 t of dried white salted noodle products consumed in China per year. The LL (Long Life) noodle is a kind of new, ready-to-eat, noodle developed in 1990's. The freshly made noodles are cooked, rinsed with water, soaked in an acidic solution ($\text{pH} \approx 4$) and then packed and subjected to thermal processing to increase shelf life and cooling. The noodles can be kept at room temperature for 5-6 months. LL noodles are consumed just after being soaked in hot water.

In contrast, the Japanese types of wheat noodles are traditionally made from soft wheat flours. Sodium chloride is a necessary ingredient for these types of noodles. Japanese types of wheat noodles are usually called white slated noodles (WSN) and the soft and elastic textures are specially required for these types of cooked noodles. Japanese white salted noodles normally include 4 types which differ in noodle width: So-men noodles (0.7-1.2 mm), Hiya-mugi noodles (1.3-1.7 mm), Udon noodles (1.9-3.8 mm) and Hira-men noodles (5.0-6.0 mm) (Hou 2001).

Cooking loss of wheat noodle products

Cooking is a necessary step for noodle product consumption. The cooking and eating properties of wheat noodle products are mainly affected by the gelatinization process and the (incompletely) gelatinized starches. During cooking two major physical actions occur in wheat noodle products: 1) starch granules in noodle products will be gelatinized; and 2) the turbulence caused by boiling water will give a shear force on noodle surface. Although noodles are usually cooked in boiling water, the temperature at the beginning is not as high as 100 °C, since the ratio water : noodles in house-hold cooking is rather low. When the water temperature is below the starch gelatinization temperature, part of the starch granules will disintegrate from the noodle strands and disperse in water due to the lack of interaction. The shear force, caused by the boiling water, will even stimulate this effect. The amount of starch released will increase with increasing time necessary to have a complete gelatinization. On the other hand, even after gelatinization, part of the starch still will release into the water. The released materials will lead to cooking loss, and result in a decreasing of the texture and slipperiness of noodle products. Obviously, if the starch in noodle products can be gelatinized at a relatively low temperature and the gelatinized starch can provide enough interaction between the components of wheat noodle (such as ungelatinized starch granules, protein and “ghosts”), the cooking loss will be lower. Consequently, the texture and slipperiness of the cooked noodle products will be improved. Therefore, it is stated that the choice of (modified) starch to apply in wheat noodles could efficiently affect the performance of the noodle products.

It is known that starch derivatives such as acetylated and hydroxypropylated starches have the characteristics of a lower gelatinization temperature, a higher swelling behavior and higher viscosity, and a higher paste clarity than the original starches. However, when both types of starch derivatives are applied in WSN manufacture, we observed that only acetylated starches significantly improved WSN quality (see Chapter 5). During cooking the acetylated starch gelatinize at very low temperature (51-54 °C) and then act as a gluing agent to bind other materials, like ungelatinized starch granules and wheat protein, to prevent them to be released from the noodles into the water. The strong interaction of acetylated starch also result in a high elasticity of the cooked WSN. The high clarity of the acetylated starch paste produces a shiny appearance of cooked WSN. In fact, it has been recognized that wheat flours having high pasting and swelling behavior such as waxy wheat flour is preferable for WSN production (Crosbie 1991; Epstein and others 2002). This may also be due to the high interaction properties of the starches when gelatinized. Although it is not clearly understood why hydroxypropylated starches did not yield good quality WSN, the difference between the starches may be due to the type of substituent and its distribution over the starch (components).

Acetyl group distribution of acetylated starches

Acetylated starches have been known for more than 100 years (Jarowenko 1986). Low acetylated starches with a degree of substitution (DS) of 0.01-0.2 have been of commercial interest for many years with respect to the properties of film forming, binding, adhesivity, thickening, stabilising and texturing (de Graaf and others 1998). Generally, acetylated starches show a better paste and gel clarity, a better stability, an increased resistance to retrogradation, and an increased freeze-thaw stability when compared to the original starches (Agboola and others 1991). Food-grade starch acetates are limited to those prepared by esterifying granular starch with either acetic anhydride or vinyl acetate. By regulation of the Food and Drug Administration (FDA, USA) the acetyl content of the acetylated starch used for food application should not exceed 2.5% (w/w). This corresponds to a DS approaching 0.1 (Jarowenko 1986). The properties of acetylated starches not only depend on DS but also depend on the acetyl group distribution.

Unlike hydroxypropylated starches, only limited information is available on the structure of acetylated starches. Biliaderis (1982) compared the structures of acetylated smooth pea (DS 0.06) and hydroxypropylated waxy maize (DS 0.09) starches, and reported that a relatively high substitution exists only in certain parts of the amylopectin part of acetylated starch, while hydroxypropylated starch showed a more uniform distribution of the substituents in the starch macromolecular components. Moreover, he suggested that acetylation of the amylopectin of smooth pea starch occurred exclusively in certain parts of the granule, presumably the outer lamellae, while hydroxypropylation of waxy maize starch was more uniform throughout the granule. Heins and others (1998) determined the substitution position of seven acetylated starches having a DS of 0.42-0.82 by NMR and found that the frequency of substitution at the position O-2 and O-3 are similar. In contrast, for hydroxyethyl substitution the O-2 position is preferred and the O-3 position is almost not substituted (Heins and others 1998).

Different acetyl substitution of amylose and amylopectin

It has been reported in Chapter 6 that the degree of substitution (DS) differed significantly in differently sized granule fractions. Furthermore, the DS of the isolated amylopectin populations showed the same trends as that of acetylated starches: DS increases with decreasing granule size dimension. In contrast, the DS in the amylose populations of different granule fractions remain rather constant.

These difference in acetylation may be partly explained by the acetylation process where the reactive acetic anhydride is added into a slurry of granular starch. Furthermore, the physical structure (packing) of the granules seems to be very important as well. It was found, although the major part of the acetyl groups (in molar) were mainly distributed in the amylopectin parts

(51-77%) of differently sized granule fractions, the amylose populations have higher DS (20-67% higher than the DS in corresponding amylopectin populations) indicating a more concentrated acetyl substitution (see Chapter 6). This was also observed in hydroxypropylated potato starch. Kavitha and BeMiller (1998) found that the molar substitution of hydroxypropylated whole potato starch is 0.099, of amylose, 0.113, and of amylopectin, 0.096. Although the amylose content of the differently sized granule fraction is significantly different: amylose content decreases with decreasing granule size dimension, the DS of differently sized granule fraction is similar. Our results obtained on the DS of amylose and amylopectin populations isolated from differently sized granule fractions pointed out that the acetylation occurs in all amorphous regions resulting in similar DS of the amylose in differently sized granule fractions and only occurs in the outer lamellae of crystalline region resulting in a higher DS present in the amylopectin of the smaller granule fractions. The model of acetylation in starch granules proposed by determining the acetylation behavior over differently sized starch granules is shown in Chapter 6. Further research should be directed to the fractionation of the amylopectin populations of acetylated starches in a non-substituted part and a high-substituted part in order to confirm our statement.

Acetyl distribution patterns of amylose populations

Amylose is considered as the important factor that causes starch retrogradation (Jarowenko 1986). One of the important purposes to esterify starches with acetate is to increase the paste stability at low temperature. The introduced acetyl groups in amylose inhibit the retrogradation of starch efficiently. Not much information can be found in literature concerning the acetyl group distribution in amylose. In our study, it was found that amylose from differently sized granule fractions of acetylated potato and sweet potato starches have a similar DS showing that the mechanism of acetylation of amylose is not affected by the granule structure as was mentioned before. However, enzyme degradation studies of these amylose populations clearly showed that the acetyl distribution pattern was quite different (see Chapter 6). HPSEC and HPAEC elution profiles showed the presence of higher oligomeric degradation products in the α -amylase and amyloglucosidase digests of acetylated amylose isolated from small granules when compared to the same digests of acetylated amylose isolated from large granules. The enzymes (α -amylase and amyloglucosidase) were obviously hindered in their action by acetyl groups and could be successfully used in the elucidation of the fine structures of acetylated starch. The acetylation of the (higher) oligomers present in the digestion was confirmed by MALDI-TOF-MS spectrometry. The presence of 2-3 acetyl groups in maltopentaose-maltoheptaose showed that the distribution of acetyl groups are clearly clustered in certain part

of amylose, since, on average, every 13-17 glucose moieties only contain one acetyl group (see Chapter 6).

Preliminary studies on the degradability of the isolated acetylated amylopectin populations show that the acetyl group distribution patterns were also different. This indicates that acetyl distribution is different in both the amylose and the amylopectin parts of differently sized granule starches. The fine structures of amylopectin populations will be systematically studied in the future. It is clear that the DS and acetyl group distribution in differently sized granule fractions of acetylated starches will exhibit different physicochemical and functional properties. This may lead to a further innovation in the use of differently sized granule starch derivatives in some new application areas.

In conclusion, it may be stated that this PhD study contributes to bridge the gap between functional starch knowledge and food application. It is also demonstrated that a detailed knowledge of the chemical characteristics only is not sufficient to understand the suitability of the starches for a given food application.

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Summary

In addition to rice, wheat and corn, sweet potato (*Ipomea batatas*) is an important food crop in many developing countries. In 2002, the total sweet potato production of the world was 136 million tons, of which 114 million tons was produced in China, making China the major producer of sweet potatoes, that are grown in more than 2000 varieties. Starchy products are the major industrial use of sweet potatoes. Due to the limited information on the physicochemical and functional properties of Chinese sweet potato starches, their possible applications in food products are still not well orientated. In China as well as in other sweet potato producing countries the potential values of the abundant resources of sweet potato have not been sufficiently developed. One of the important food products in which sweet potato starch can be used is noodle. Noodles are the staple foods for many Asian people. The starch noodle is a very popular type of noodle which is consumed as pure noodle foods and in many dishes in most Asian countries. A rough estimation of the consumption ranges over 1 million tons of dry starch noodle products per year in China. Starch noodle is made from the isolated starch component, and its processibility and quality solely depend on starch properties and process conditions. Starch noodle made from mung bean starch is considered to have the highest noodle quality. However, due to its availability and production costs mung bean starch is much more expensive than most of the commercially available starches. Therefore, it is aimed by the starch and noodle industries to produce sufficiently high quality starch noodles by replacing part of the mung bean starch with cheaper starches or starch derivatives.

Wheat noodle is another type of important noodle product in Asia. In most Asian countries 30-40% of wheat flour is consumed as wheat noodle, of which White Salt Noodle (WSN) is a popular type. High quality WSN is generally made from the imported soft wheat flour (Australian Standard White). Therefore, it is of great interest to produce high quality WSN by using domestic wheat flours. Previous studies concluded that starch of the wheat flour is the most important component affecting the special requirement of WSN quality (softness and elasticity). Since starch properties play the major role in these two types of noodle products, this project is aimed at applying the abundant potential cheap starches: sweet potato starches or their derivatives in replacing mung bean starch for starch noodle production and in partially replacing wheat flour for WSN production.

In Chapter 1 general information of starches especially sweet potato starches is given together with the application of starches and starch derivatives in food products. The general descriptions of noodle products are also summarized.

Three typical types of Chinese sweet potato varieties were selected and their starches were isolated. The physicochemical properties of their starches were characterized and compared with those of potato and mung bean starches (Chapter 2). XuShu18, a “general type” of sweet potato, is the most popular variety in China. SuShu2 is one of the most promising sweet potato varieties of the “high-starch type”. SuShu8 represents the “food consumption type” of sweet potatoes; it is widely used as a kind of roasted snack food. The “high-starch type” sweet potato root of SuShu2 showed the highest dry matter and starch content while starch isolated from it had the highest purity of the starches isolated from the 3 varieties. The amylose contents of the 3 isolated sweet potato starches were similar (19.3-20.0%). The average granule size of XuShu18 starch was the largest, while SuShu8 starch had the smallest granule size and showed a very homogeneous particle size distribution. The particle size distributions of the 3 sweet potato starches are narrower than that of potato starch but broader than that of mung bean starch. The average granule size of SuShu8 starch is even smaller than that of mung bean starch. The pasting viscosity curves of the 3 sweet potato starches showed a B type pattern at concentration of 4-8% (w/v), except for SuShu8 starch which showed a C type Brabender amylogram at 4% concentration. SuShu8 starch showed the highest peak viscosity at all concentrations measured in this study. The Brabender amylogram of potato starch showed a typical A type pattern while that of mung bean starch showed a typical C type pattern. The peak viscosity of the 3 sweet potato starches is higher than that of mung bean starch but much lower than that of potato starch. SuShu2 starch presented the lowest swelling volume and the highest syneresis. The swelling volumes of the 3 sweet potato starches are higher than that of mung bean starch but much lower than that of potato starch. Both the sweet potato starches and mung bean starch showed a two-stage swelling pattern indicating 2 different mechanisms of interaction forces within the starch granules.

The 3 Chinese sweet potato starches were also tested for performance of starch noodle manufacture, and their noodle qualities were compared with that of mung bean starch (Chapter 3). Potato starch could not produce starch noodle at all. The differences in the starch physical properties and their noodle qualities determined by both texture analyzer and sensory evaluation for the 3 different sweet potato varieties were significant. The quality of both dried and cooked starch noodle of Sushu8 was the best, while that of SuShu2 was the worst of the 3 sweet potato starch noodles. The starch noodle quality can be predicted by starch gel properties because a firmer starch gel will result in a better cooking and eating qualities of the starch noodle. It appeared that starch noodle made from SuShu8 sweet potato starch had a quality well comparable to the noodle made from mung bean starch. This was surely not the case for SuShu2 and XuShu18. For cooked noodles, the quality of SuShu8 was even better than that of cooked mung bean starch noodle. Obviously, the suitability of sweet potato starch for starch

noodle making strongly depends on the variety used. The best performing sweet potato variety in our study is usually used for preparing roasted sweet potato food and may not have yet been tested for starch noodle preparation.

Chapter 4 points out that starch granule size dimension plays an important role in starch noodle making and noodle quality. Our findings show that a simple fractionation method to obtain starch differing in granule size is sufficient to use potato starch for starch noodle preparation, whereas sweet potato starches perform even better when smaller sized granule fractions were used. In the meantime, the results obtained from the differently sized granule fractions confirm our previous finding that high amylose content and C type of pasting viscosity curve pattern of starches are not necessary for the production of high-quality starch noodles. Dried and cooked noodles made from small-size granule fractions ($<20\ \mu\text{m}$) had a better processibility (fluidity of starch dough for noodle making), and a better cooking and eating quality.

Chapter 5 describes the application of potato and sweet potato starches, and their derivatives (hydroxypropylated and acetylated starches) in White Salted Noodle (WSN) production by partially replacing wheat flour. It was found that only acetylated potato and acetylated sweet potato starches could be used. Optimum cooking times of WSN made from the composite flours were drastically reduced to half of that required for pure wheat flour noodle. Replacement with native and modified potato starches as well as sweet potato starches decreased the dough mixing time, peak dough resistance and breakdown of dough during mixing which are all beneficial for WSN manufacture. The cold peak breakdown (CPBD) of the composite flour, as measured in 1.5% NaCl solution, exhibited a significant correlation with the cooking loss, stretch stiffness and stretchability of WSN. Cooking loss is a dominating cooking property of WSN, and stretch stiffness and stretchability are the important texture attributes of cooked WSN. Therefore, the general quality of WSN made from composite flour can be well predicted from the CPBD value.

Moreover, the acetylated starch samples were studied with respect to the degree of substitution (DS), acetyl group distribution and granule size. The results are described in Chapter 6. The DS of differently sized granule fractions differed significantly. The DS of the isolated amylose populations of differently sized granule fractions were constant while the DS of the isolated amylopectin populations showed the same trend as with the acetylated starches: DS increased with decreasing granule size dimension. Amylose is mainly located in amorphous region and the branched chains of amylopectin are in crystalline region. Because the specific surface area of starch granule increases with decreasing granule dimension, it is concluded that acetylation occurs in all amorphous regions but only takes place in the outer lamella of the crystalline regions. A model for starch granule acetylation is presented.

The acetyl group distributions of the various amylose populations were investigated. Although the amylose populations isolated from differently sized granule fractions have similar DS, they showed different susceptibility to enzymatic digestion. HPSEC and HPAEC elution profiles showed the presence of higher oligomeric degradation products in the α -amylase and amyloglucosidase digestion of acetylated amylose isolated from small granules when compared to the same digests of acetylated amylose isolated from large granules. The enzymes (α -amylase and amyloglucosidase) were obviously hindered by acetyl group and could be used in the elucidation of acetylated starch structures successfully. The acetylation of the (higher) oligomers present in the digestion was confirmed by MALDI-TOF-MS spectrometry. The acetyl group distributions of the amylose populations isolated from small size granule fractions were proved to be more heterogeneous.

Finally, an overview of the main results of this study, and the discussion of starch properties and the mechanism of starch and starch derivatives in starch noodle and WSN products are given in Chapter 7. A critical evaluation on some widely accepted requirements for starch noodle making (e.g. amylose content, viscosity curve pattern, retrogradation) is given. The possibility to use of starches and starch derivatives in other wheat noodle products is briefly presented.

Samenvatting

Naast rijst, tarwe en mais is zoete aardappel (*Ipomea batatas*) een belangrijk voedselgewas in veel subtropische landen, vooral in Azië. In 2002 bedroeg de totale wereldproductie van zoete aardappelen 136 miljoen ton; hiervan werd 114 miljoen ton geproduceerd in China. Met meer dan 2000 variëteiten is China 's werelds hoofdproducent van zoete aardappelen. Vanwege de nog beperkte kennis over de fysisch-chemische en functionele eigenschappen van zoete aardappelzetmelen zijn nog niet alle mogelijke toepassingen ervan in levensmiddelen en andere producten bekend. Ook zijn in China zowel als in andere zoete aardappel producerende landen de potentiële mogelijkheden van daar ruim aanwezige zoete aardappelen nog lang niet uitgeput.

Een der belangrijkste levensmiddelen waarin zoete aardappelen worden gebruikt is het deegwaarproduct noedel, dat een hoofdvoedingsmiddel is voor vele aziaten (in de nederlandse volksmond worden noedels en deegwaren ook wel 'pasta' genoemd). Zetmeelnoedels worden in allerlei aziatische gerechten gebruikt en consumptieschattingen in China belopen meer dan 1 miljoen ton droge noedels per jaar. Zetmeelnoedels worden bereid uit zetmeel dat uit de grondstof is geïsoleerd, en de verwerkbaarheid en eigenschappen van het noedelproduct hangen vooral af van de zetmeeleigenschappen en de toegepaste procescondities. Zetmeelnoedels gemaakt van mungbonzetmeel worden beschouwd als zijnde de topkwaliteit. Echter vanwege zijn beschikbaarheid en productiekosten is mungboonzetmeel veel duurder dan de meeste andere commerciële beschikbare zetmeelsoorten. Zetmeel- en noedelindustrieën trachten daarom zetmeelnoedels van voldoende hoge kwaliteit te produceren door een deel van het mungboonzetmeel in noedels te vervangen door goedkopere zetmelen of zetmeelderivaten (zetmelen waarin eigenschappen chemisch of fysisch zijn veranderd).

Tarwenoedel is een ander in Azië belangrijk noedelproduct. In de meeste aziatische landen wordt 30 – 40% van de tarwe geconsumeerd als noedels, vooral het type White Salt Noodle (WSN, witte gezouten tarwenoedel) vormt meer dan de helft van de geconsumeerde tarwenoedels. WSN van hoge kwaliteit wordt gemaakt van geïmporteerde zachte tarwebloem (in China meestal type Australian Standard White). Mede hierdoor is in Azië de interesse groot om WSN noedels te produceren van lokaal gegroeide tarwe. Eerdere studies concludeerden reeds dat het ook hier de zetmeelcomponent van tarwebloem is die bepalend is voor de kwaliteit van WSN noedels (zacht en elastisch).

Doordat het zetmeel uit de grondstof en de zetmeeleigenschappen de kwaliteit van noedels bepalen wil deze studie het potentieel onderzoeken van de relatief goedkope zoete aardappelzetmelen en hun derivaten voor de noedelproductie. Voorbeelden zijn de vervanging

van mungboonzetmeel voor de productie van zetmeelnoedels en het gedeeltelijk vervangen van tarwebloem voor de productie van WSN noedels.

Hoofdstuk 1 geeft algemene informatie over zetmelen, belang, productie, componenten en gedrag, in het bijzonder over zoete aardappelzetmeel. Verder worden de toepassingen van zetmelen en zetmeelderivaten in levensmiddelen, speciaal in noedels, behandeld.

Drie zoete aardappel variëteiten, representatief in China, werden geselecteerd en hun zetmelen gewonnen. Vervolgens werden de fysisch-chemische eigenschappen van deze zetmelen gekarakteriseerd en vergeleken met die van aardappel en mungboon. Dit staat beschreven in hoofdstuk 2. De drie variëteiten waren: XuShu 18, een “algemeen” type dat in China de grootste populariteit geniet; SuShu 2 is een “hoog zetmeel” type en één der meest veel belovende varianten; en SuShu 8 is een “voedselconsumptie” type dat in China wijd verbreid wordt gegeten als geroosterd snackvoedsel. Van de drie variëteiten vertoonde het “hoog zetmeel” type SuShu 2 de hoogste droge stof- en zetmeelgehalten, en het hieruit gewonnen zetmeel had de hoogste zuiverheid. De amylosegehalten van de drie zetmelen bleken vrijwel gelijk te zijn (19.3 – 20.0%). De gemiddelde deeltjesgrootte was het hoogst voor XuShu 18 zetmeel, terwijl die voor SuShu 8 het laagst was; ook had SuShu 8 een opvallend homogene deeltjesgrootteverdeling. Verder bleek dat zoete aardappelzetmelen een smallere deeltjesgrootteverdeling hadden dan gewone aardappelzetmeel heeft, maar een bredere verdeling dan zetmeel van mungboon laat zien. De gemiddelde deeltjesgrootte van SuShu 8 zetmeel bleek kleiner dan van mungboonzetmeel die, voor zover bekend, al een der kleinste deeltjesgroottes heeft.

De geleerviscositeitscurves van de drie zoete aardappelzetmelen, gemeten als Brabender amylogrammen bij 4% zetmeelconcentratie, vertoonden een B-type patroon behalve voor SuShu 8 die een C-type te zien gaf en een B-type bij hogere concentraties. SuShu 8 vertoonde ook de hoogste piekviscositeit bij alle onderzochte concentraties. In vergelijking vertonen de Brabender amylogrammen van gewone aardappelzetmeel een typisch A-patroon en mungboonzetmeel een typisch C-patroon. De piekviscositeit en het zwelvolume van zoete aardappelzetmeel zijn hoger dan die van mungboonzetmeel maar veel lager dan die van gewone aardappelzetmeel (die de hoogste piekviscositeit heeft van alle bekende zetmelen). Van de drie zoete aardappelvarianten vertoonde SuShu 2 het laagste zwelvolume en de grootste synerese. Zowel de zoete aardappelzetmelen als het mungboonzetmeel vertoonden een zwelpatroon in twee stadia, hetgeen wijst op twee verschillende interactiemechanismen binnen de zetmeelkorrels.

Hoofdstuk 3 beschrijft hoe de drie zoete aardappelzetmeelmonsters ook zijn getest op hun geschiktheid voor de bereiding van zetmeelnoedels, en hun noedeleigenschappen werden vergeleken met die van mungboonzetmeel. Gewone aardappelzetmeel bleek niet in staat om

noedels te produceren. Uit textuuranalyse en organoleptisch onderzoek kwam naar voren dat de verschillen in zetmeleeigenschappen en noedelkwaliteit tussen de drie zoete aardappelvarianten aanzienlijk waren. De kwaliteit van zowel de gedroogde als de gekookte noedel van SuShu 8 bleek het beste en die van SuShu 2 het minst van de drie. De kwaliteit van de zetmeelnoedel kan worden voorspeld vanuit de zetmeelgel-eigenschappen daar een steviger zetmeelgel zal resulteren in betere kook- en eeteigenschappen voor de zetmeelnoedel.

Ook bleek dat zetmeelnoedel afkomstig van de zoete aardappelvariëteit SuShu 8 een kwaliteit had welke goed vergelijkbaar is met die van mungboon zetmeelnoedel, hetgeen niet kon worden geconcludeerd voor de beide andere zoete aardappelvarianten. Wat de gekookte noedels betreft was de kwaliteit van SuShu 8 zelfs beter dan die van mungboon. Klaarblijkelijk hangt de geschiktheid van zoete aardappelzetmeel voor noedelproductie sterk af van de gebruikte variëteit. SuShu 8 wordt in China gewoonlijk angewend voor de bereiding van geroosterde zoete aardappelvoedsel, en wellicht is deze variëteit nog niet eerder getest voor de bereiding van zetmeelnoedels.

Hoofdstuk 4 werkt verder uit dat de zetmeelkorrelgrootte een belangrijke rol speelt in de bereiding van zetmeelnoedels en de noedelkwaliteit mede bepaalt. Onze bevindingen tonen tevens aan dat een simpele fractioneringsmethode, waarmee zetmeelfracties van verschillende deeltjesgroottes worden verkregen, voldoende is om gewone aardappelzetmeel geschikt te maken voor de bereiding van zetmeelnoedels. Ook zoete aardappelzetsmelen worden hiervoor meer geschikt naarmate fracties met kleinere zetmeelkorrels worden toegepast. Tegelijkertijd bevestigen deze resultaten met verschillende deeltjesgroottes onze vroegere bevindingen dat hogere amylosegehalten en C-type amylogrampatronen voor de zetmelen niet noodzakelijk zijn om zetmeelnoedels van hoge kwaliteit te produceren. Gedroogde en gekookte noedels, die zijn gemaakt van fracties kleine zetmeelkorrels ($< 20 \mu\text{m}$), bleken een betere bewerkbaarheid (met name een goede stroombaarheid van zetmeeldeel tijdens de noedelbereiding) en betere kook- en eeteigenschappen te vertonen.

Hoofdstuk 5 beschrijft resultaten van de toepassing van zoete aardappel- en aardappelzetsmelen en hun derivaten in de productie van WSN noedels, waarbij de grondstof tarwebloem tot maximaal 20% is vervangen door andere zetmelen. Het bleek dat alleen de geacetylerde zetmelen van aardappel en zoete aardappel de WSN noedelkwaliteit effectief kunnen verbeteren en significant betere kook- en eeteigenschappen werden verkregen. Vooral het effect op de optimale kooktijd was groot want deze bleek gereduceerd te worden tot de helft van de kooktijd die nodig is voor WSN noedel van alleen tarwebloem. Vervanging met natief en gemodificeerd aardappel- en zoete aardappelzetmeel verminderde de deegmengtijd, de piekdeegweerstand en de deegafbraak tijdens menging, allemaal effecten die gunstig zijn voor de WSN noedelbereiding. De koude piekafbraak (cold peak breakdown – CPBD) van de

samengestelde bloem, die wordt gemeten in 1.5% keukenzout-oplossing, vertoonde een significante correlatie met de kookeigenschappen, met name het kookverlies, en de textuureigenschappen stevigheid en strekbaarheid van de WSN noedel. Hierdoor kan de algemene kwaliteit van WSN noedels, die zijn geproduceerd uit deels vervangen tarwebloem, vooraf worden afgeleid uit de CPBD waarde.

Hoofdstuk 6 geeft de resultaten met geacetyeerde zetmeelmonsters weer, met name de effecten van distributiegraad, acetylgroepverdeling en deeltjesgrootte. De substitutiegraden (degree of substitution, DS) van zetmelen uit fracties met verschillende deeltjesgrootte bleken aanzienlijk te verschillen: DS neemt toe met afnemende deeltjesgrootte. Dit laatste bleek ook te gelden voor geïsoleerde amylopectine maar niet voor geïsoleerde amylosemonsters die een gelijkblijvende DS voor verschillende deeltjesgroottes vertoonden. Amylose bevindt zich voornamelijk in de amorfe gebieden van de zetmeelkorrel terwijl amylopectine vooral voorkomt in de kristallijne gebieden. Omdat fysisch het specifiek deeltjesoppervlak toeneemt met afnemende deeltjesgrootte, werd geconcludeerd dat acetylering plaatsheeft binnen de amorfe delen maar in de kristallijne gebieden alleen aan de randen. Een model voor de mogelijke acetylering van zetmeel is weergegeven.

Omdat de amylosemonsters een hoge DS te zien gaven en volgens de literatuur amylose verantwoordelijk is voor tal van fysisch-chemische eigenschappen van zetmeel, zoals retrogradatie en gelvorming, werd de verdeling van acetylgroepen in amylose verder onderzocht. Enzymatische behandeling toonde aan dat de enzymen α -amylase en amyloglucosidase beiden worden gehinderd door gesubstitueerde acetylgroepen. Alhoewel de amylosefracties met verschillende deeltjesgrootte een gelijke DS hadden, vertoonden ze toch verschillend gedrag tijdens enzymatische afbraak. In het na enzymatische behandeldeling overgebleven residu van de kleinkorrelige fracties werden componenten met een hoge polymerisatiegraad aangetroffen. Dit betekent dat de distributie van acetylgroepen meer heterogeen is in de amylose van kleine zetmeelkorrels.

Tenslotte wordt in hoofdstuk 7 een overzicht gegeven van de voornaamste resultaten van deze studie, samen met een discussie over relevante eigenschappen en mechanismen van zetmeel en zetmeelderivaten in zetmeelnoedels en WSN producten. De toekomstige mogelijkheden van het gebruik van zetmelen en hun derivaten voor de noedelproductie krijgen hierbij de aandacht.

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Curriculum vitae

Zhenghong Chen was born in Jin Zhai, P.R. China, on February 1, 1964. He graduated from Zhengzhou Grain College in 1986 and received a Bachelor's degree of Engineering in Grain Storage. After graduation, he worked as a teaching assistant in the Department of Food Science and Technology in Nanjing Agricultural University (NAU) and served as a technological director and senior advisor to several food companies. He obtained his MSc degree in Food Science from WuXi Light Industrial University in 1992. Thereafter, he became a lecturer in the Department of Food Science and Technology in NAU, and was promoted to associate professor in 1997. Subsequently, he was the head of Agrofood Technology Group, and the director of Food Engineering Department in NAU. Meanwhile, he was the director of Industrial Food Nutrition Branch, Jiangsu Province Society of Nutrition, and the vice secretary-general of Jiangsu Province Society of Nutrition, P. R. China. From March 1999 till October 2003, he was a PhD researcher working on the project of "Physicochemical properties of sweet potato starches and their application in noodle products" at the laboratory of Food Chemistry in Wageningen University.

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1. **Zhenghong Chen**, Henk A. Schols and Alphons G. J. Voragen. 2003. Differently sized granules from acetylated potato and sweet potato starches differ in the acetyl substitution pattern I. Amylose population. *Journal of Food Science* (Submitted).
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The cover includes:

1. MALDI-TOF mass spectra of the enzyme (α -amylase and amyloglucosidase) hydrolysates of amylase population separated from small size granule fraction of acetylated XuShu18 starch (Ac: acetyl group).
2. Particle size distribution of sweet potato (XuShu18, SuShu2 and SuShu8), potato and mung bean starches.
3. Light microscopy of sweet potato (XuShu18, SuShu2 and SuShu8), potato and mung bean starches ($\times 200$).

