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A special word of gratitude should be dedicated to my parents and family members for their unfailing encouragement and moral support. Without them, the task of completing this project would be impossible.

POE YI SHIN
May, 2006

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LIST OF ABBREVIATIONS

Abbreviations	Caption
RVA	Rapid Visco Analyzer
RVU	Rapid Visco Unit
DSC	Differential Scanning Calorimetry
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
SAXS	Small-angle X-ray scattering
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
HCl	Hydrochloric acid
I_2	Iodine
KI	Potassium iodide
PV	Peak viscosity
PT	Pasting temperature
Pt	Peak time
HPV	Hot paste viscosity
FV	Final viscosity
BD	Breakdown
SB	Setback
T_o	Onset temperature
T_p	Peak temperature
T_c	Concluding temperature
T_g	Glass transition temperature
T_m	Melting temperature

ΔH	Gelatinization enthalpy
SF	Swelling factor
DP	Degree of polymerization
CL	Chain length
σ_{eng}	Engineering stress
ε_{eng}	Engineering strain
σ_c	Corrected stress
ε_h	Hencky's strain
σ_f	Failure stress
ε_f	Failure strain
E	Young's modulus

KESAN PENGOLAHAN HABA-LEMBAPAN KE ATAS SIFAT-SIFAT FIZIKOKIMIA KANJI SAGU (*Metroxylon sagu*).

ABSTRAK

Kesan pengolahan haba-lembapan terhadap sifat-sifat fizikokimia kanji sagu telah dilakukan pada kandungan lembapan 13%, 18% dan 30%. Beberapa sampel telah diolahkan di dalam oven-udara pada suhu 62°C dan 110°C selama 8, 16 dan 32 jam manakala sampel yang lain diolah selama sejam dalam autoklaf. Analisis yang dilakukan adalah seperti pemerhatian morfologi granul, pembelauan sinar-X, amilosa terlarut resap, kesan pembengkakan, keterlarutan, sifat termal, sifat pempesan, kestabilan sejukbeku-nyahbeku, tekstur gel dan hidrolisis asid. Analisis mikroskopi menunjukkan pengolahan haba-lembapan tidak menukarkan bentuk dan saiz granul kanji. Walau bagaimanapun, granul bagi sampel yang diolah pada kandungan lembapan 30% pada suhu 110°C dan sampel yang diautoklafkan menunjukkan aglomerasi. Corak pembelauan sinar-X bagi kanji sagu telah ditukarkan dari jenis C ke jenis A selepas pengolahan. Intensiti bagi corak ini meningkat apabila keadaan pengolahan ditingkatkan. Berbanding dengan kanji natif, amaun amilosa yang melarut resap apabila kanji terolah haba-lembapan digelatinisasikan menurun. Apabila dipanaskan pada julat suhu 65-95°C, kesan pembengkakan dan keterlarutan kanji natif dan kanji yang telah dilakukan pengolahan meningkat dengan peningkatan suhu. Kajian Kalorimetri Penskanan Pembezaan (DSC) menunjukkan pengolahan haba-lembapan telah meningkatkan suhu permulaan (T_o), suhu gelatinisasi (T_p) dan suhu

pengakhiran (T_c). Namun begitu, julat gelatinisasi bagi sampel yang diolahkan pada 62°C telah dikurangkan manakala yang lain telah dilebarkan. Entalpi gelatinisasi bagi kanji yang diolahkan pada 110°C dan 121°C adalah sama atau lebih rendah daripada kanji natif manakala kanji yang diolahkan pada 62°C menunjukkan peningkatan. Suhu pempesan, kelikatan pes panas, kelikatan akhir dan “setback” meningkat manakala kelikatan puncak dan “breakdown” menurun selepas pengolahan haba-lembapan. Semua sampel yang diolahkan pada 110°C dan 121°C menunjukkan sineresis yang tinggi pada kitaran pertama berbanding kanji natif. Sampel yang diolahkan pada 62°C pula hanya menunjukkan peningkatan sineresis yang sedikit sahaja. Keteguhan gel bertambah selepas kanji dilakukan pengolahan haba-lembapan. Keteguhan gel juga meningkat selepas penstoran pada suhu 4°C selama 7 hari. Hidrolisis asid bagi kanji natif dan kanji terolah haba-lembapan adalah lebih tinggi pada tujuh hari yang pertama berbanding dengan tujuh hari yang seterusnya. Secara keseluruhannya, kesan pengalohan haba-lembapan ke atas hidrolisis asid adalah tidak begitu ketara. Pada hari pertama, hanya empat sampel mempunyai nilai hidrolisis yang lebih rendah daripada kanji natif manakala sampel yang telah mengalami aglomerasi menunjukkan nilai yang jauh lebih tinggi berbanding kanji natif. Sampel yang diolahkan pada suhu yang lebih tinggi daripada suhu gelatinisasi kanji natif sagu (110°C dan 121°C) menunjukkan perubahan konformasi molekul yang lebih besar berbanding dengan sampel yang diolahkan pada suhu bawah suhu gelatinisasi (62°C). Daripada kajian ini, ternyata pengolahan haba-lembapan dapat mengubah sifat-sifat fizikokimia kanji sago terutama dalam sifat gelatinisasi, pempesan dan retrogradasi.

THE EFFECTS OF HEAT-MOISTURE TREATMENT ON THE PHYSICOCHEMICAL PROPERTIES OF SAGO (*Metroxylon sagu*) STARCH.

ABSTRACT

Sago starch was subjected to heat-moisture treatment at 13%, 18% and 30% moisture content. Some samples were treated in an air oven at 62°C and 110°C for 8, 16 and 32 hours while some were autoclaved for one hour. The samples were analyzed for granule morphology, X-ray diffraction, amylose leaching, swelling factor, solubility, pasting properties, thermal properties, freeze-thaw stability, gel texture and acid hydrolysis. Microscopy studies revealed no change in granular shapes and sizes between native and heat-moisture treated samples, except for samples that were treated at 30% moisture content at 110°C and autoclave, where some of the granules were agglomerated. The X-ray pattern of the C-type, which is typical for sago starch, was altered to A-type pattern after treatment. The intensities of the pattern were slightly increased, as the conditions for the treatment were more extreme. Upon gelatinization, the amounts of amylose leached from treated samples were lower than that of native starch. When heated in the temperature range of 65-95°C, the swelling factor and solubility of native and heat-moisture-treated starches increased with increasing temperatures. Differential Scanning Calorimetry (DSC) studies revealed that heat-moisture treatment increased onset temperature (T_o), gelatinization temperature (T_p) and concluding temperature (T_c). However, the gelatinization range was narrowed for samples treated at 62°C while others were broadened. The gelatinization enthalpy for samples that were treated at

110°C and 121°C were similar or lower than that of native starch whereas starches that were treated at 62°C showed marked increase. Pasting temperature, hot paste viscosity, final viscosity and setback were increased after heat-moisture treatment whereas peak viscosity and breakdown were decreased. All samples treated at 110°C and 121°C showed very high syneresis on the first cycle compared to native starch. Samples treated at 62°C showed slightly higher syneresis than native. The firmness of starch gels was increased after heat-moisture treatment. The firmness also increased after seven days of storage at 4°C. Acid hydrolysis for native and heat-moisture treated starches on the first seven days were much higher compared to the next seven days. On the whole, the effects of heat-moisture treatment on the acid hydrolysis of starch were not that pronounced. On the first day, only four heat-moisture treated samples showed slightly lower values than native starch while samples that were agglomerated showed much higher values. Samples that were treated at temperatures higher than the gelatinization temperature (110°C and 121°C) showed greater changes in its molecular conformation than starches treated at temperature below the gelatinization temperature (62°C). Heat-moisture treatment has a major effect on the physicochemical properties of sago starch especially in the gelatinization, pasting and retrogradation properties of starch.

CHAPTER 1

INTRODUCTION

1.1 Background

Native starches from various plant sources have their own unique properties. Starch is a highly valued raw material in the food industry because of its good thickening and gelling properties, which makes it an excellent ingredient for the manufacture of various food products. However, native starches lack the versatility to function adequately in the entire range of food products currently available in the marketplace. The diversity of the modern food industry and the enormous variety of food products require that starch be able to tolerate a wide range of processing techniques as well as various distribution, storage and final preparation conditions. In order to meet the requirements of specific industrial processes, starches are modified chemically by degradation, substitution or cross-linking. However, there is increasing awareness on the danger of chemically modified starches in food components (National Research Council, 1989). Therefore, it is necessary to find alternative ways of starch modification.

Hydrothermal treatment was used by Stute (1992) to describe physical modification of starch resulting from combinations of moisture and temperature conditions which affect its properties without visible changes in granule appearance. There are two types of hydrothermal treatments, namely annealing and heat-moisture treatment. Jacobs and Delcour (1998) defines annealing as a physical treatment that involves incubation of starch granules in excess water or

at intermediate water content (≥40% water, w/w) during a certain period of time, at a temperature above the glass transition temperature (T_g) but below the gelatinization temperature, while heat-moisture treatment includes incubation of starch granules at low moisture levels (<35% water, w/w) during a certain period of time at a temperature greater than T_g but lower than gelatinization temperature. Nevertheless many studies have been conducted at temperatures above the gelatinization temperature (Kulp & Lorenz, 1981; Stute, 1992; Abraham, 1993; Hoover & Vasanthan, 1994a, 1994c; Hoover & Manuel, 1996). The general effects of hydrothermal treatments are increased gelatinization temperature, changes in gelatinization range (narrowing or broadening of the DSC endotherms), X-ray diffraction patterns, swelling volume and solubility, amylose leaching with consequent changes in functionality.

Early work on hydrothermal treatments was done on potato starch intended to replace corn in times of shortage (Stute, 1992). Lorenz and Kulp (1981) found heat-moisture treatment improved the bread and cake baking quality of potato starch but decreased that of wheat starch. The modified starches can be beneficial for nutritional purposes in view of the decreased digestibility as a result of heat-moisture treatment. Abraham (1993) noted that heat-moisture treated cassava starch had excellent freeze-thaw stability and could be used in pie filling with good organoleptic properties. Anderson and Guraya (2006) suggested that heat-moisture treatment could be used to produce resistant starch, which are formed as a result of food processing. Foods containing resistant starch, which is digested and absorbed slowly, may

be useful in the control of diabetes and obesity, by reducing the increase in blood glucose levels after a meal.

Sago starch was chosen as the raw material in this study as it is considered to be a potential cash crop in Malaysia. Nothing of significant commercial value can be grown in the extensive peat swamps of Sarawak, the land on which sago can be grown has very little value. The crop requires no fertilizer and demands very little husbandry. No crop rotation appears to be necessary (Cecil *et al*., 1982). Historically, sago starch found its most important industrial outlets in the cotton textile manufacturing areas of the United Kingdom. In addition to low cost, sago starch offers the advantages of relatively low viscosity, reasonable stability and fairly good weaving results. Among its drawbacks, however, are a bad coloration and enormous variability (Knight, 1969).

Until today, the basic knowledge of the physicochemical and functional properties of sago starch is limited. Consequently, studies on the physical and chemical modifications of sago starch are scanty. It is hope that by further exploring the potential of sago starch as a raw material, it can be applied in various applications especially in food processing that will produce high valued products.

1.2 Objectives

The objectives of this research were to study the effects of heat-moisture treatment on some of the physicochemical properties (granule morphology,

amylose leaching, swelling factor, solubility, pasting properties, thermal properties, freeze-thaw stability, gel texture, acid hydrolysis) of sago starch and the effects of the parameters used (moisture content, temperature and time) on the treated starch. It is hoped that the data generated from the studies will provide an efficient utilization route of the starch.

CHAPTER 2

LITERATURE REVIEW

2.1 Molecular Structure of Starch

Starch is basically a polymer made up from the six-carbon sugar D-glucose, which is often referred as the building block of starch. The structure of this monosaccharide can be depicted in either an open-chain or a ring form (Figure 2.1). The ring configuration is known as a pyranose, i.e., D-glucopyranose and can be in either the α or β form. The pyranose is the most thermodynamically stable configuration (Thomas & Atwell, 1999).

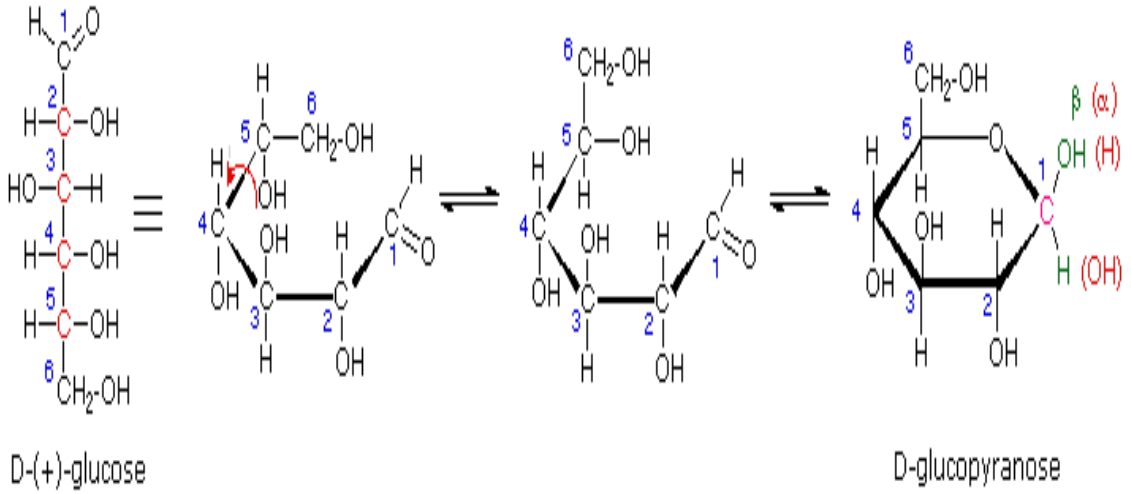

Figure 2.1 Open-chain and pyranose ring structures of the hexose sugar, D-glucose (Thomas & Atwell, 1999).

Starch consists primarily of D-glucopyranose polymers linked together by α-1,4 and α-1,6 glycosidic bonds (Figure 2.2). To form these bonds, carbon number 1 (C1) on a D-glucopyranose molecule reacts with carbon number 4 (C4) or carbon number 6 (C6) from another D-glucopyranose molecule. The

aldehyde group on one end of a starch polymer is always free, thus starch polymers always have one reducing end. The other end of the polymer is called the non-reducing end. The amount of non-reducing ends depends on the number of polymeric branches present in a starch molecule (Thomas & Atwell, 1999).

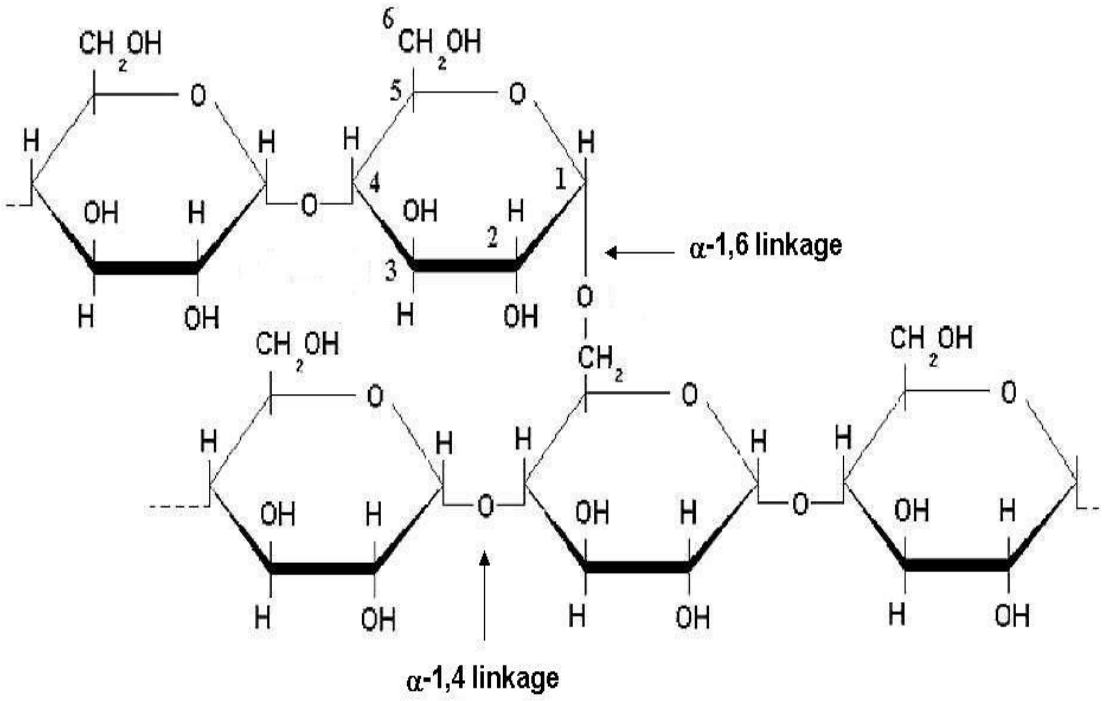

Figure 2.2 α-1,4 and α-1,6 glycosidic bonds of starch (Thomas & Atwell, 1999).

Glucose polymerization in starch results in two types of polymers, amylose and amylopectin. Although both composed of D-glucopyranose molecules, dissimilarities between these two polymers result in major differences in physical and functional properties (Thomas & Atwell, 1999). Some characteristics of amylose and amylopectin are listed in Table 2.1.

Table 2.1 Characteristics of amylose and amylopectin.

Characteristic	Amylose	Amylopectin
Shape	Essentially linear	Branched
Linkage	α-1,4 (some α-1,6)	α-1,4 and α-1,6
Molecular weight	Typically <0.5 million	50-500 million
Films	Strong	Weak
Gel formation	Firm	Non-gelling to soft
Colour with iodine	Blue	Reddish brown

(Thomas & Atwell, 1999)

2.1.1 Amylose

Amylose is considered to be an essentially linear polymer composed almost entirely of α-1,4-linked D-glucopyranose. However recent study has suggested that some branches are actually present on the amylose polymer (Curá *et al.*, 1995). Although often illustrated as a straight chain structure, amylose is mostly helical (Figure 2.3). The interior of the helix contains hydrogen atoms and is therefore hydrophobic, allowing amylose to form a clathrate complex with free fatty acids, fatty acid components of glycerides, some alcohols and iodine (Fennema, 1985). The resulting “inclusion complex” (Figure 2.3) can alter the properties of the starch.

Amylose is also well known for its ability to form a gel after the starch has been cooked, i.e., gelatinized and pasted. Gel formation is primarily the result of the reassociation of solubilized starch polymers after cooking and can occur quite rapidly with linear amylose.

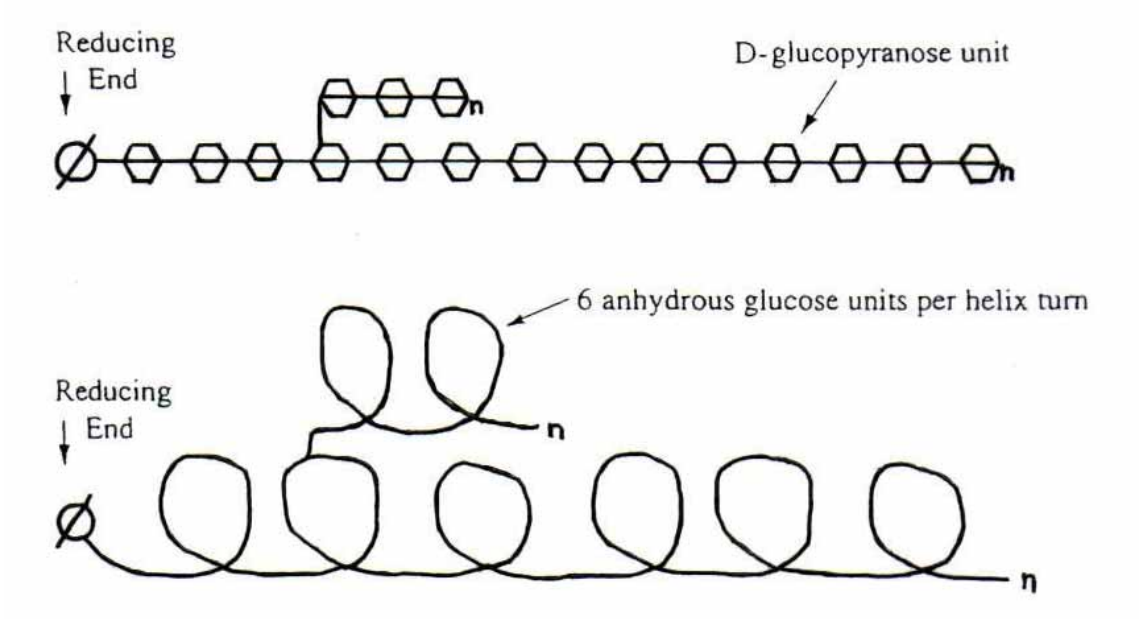

Figure 2.3 Amylose model. Amylose can be depicted as either a straight chain or a helix (Thomas & Atwell, 1999).

2.1.2 Amylopectin

Amylopectin, typically the predominant molecule in most of the starches, is a branched polymer and is much larger than amylose. It is composed of α-1,4-linked glucose units connected by α-1,6-linked branch points. The average molecule has more than 20000 branches but the branches themselves are not large. Because of its highly branched nature, its properties differ from those of amylose. For example, given the size of the molecule and its “tumbleweed-like” structure, retrogradation is slowed and gel formation can be delayed or prevented. Thus pastes from starches that contain mainly of amylopectin, i.e., waxy starches, are non-gelling but have a cohesive and gummy texture.

Three model structures have been proposed for amylopectin. There are the laminated structure of Haworth, the herringbone structure of Staudinger and the randomly branched structure of Meyer (Greenwood, 1976). However, the

clustered branching model of Nikuni (1969) and French (1972) was adapted soon after it appeared. The model by Hizukuri (1986) is now generally accepted cluster structure of amylopectin. The major feature of this model is a division of the unit chains into groups defined on the basis of a certain periodicity in length found among amylopectin samples. The most peripheral chains are A-chains that are linked to the molecule only by the potential reducing group, forming α-1,6 branch. B-chains carry A-chains or other B-chains. The C-chain has a reducing end, thus there is only one C-chain per amylopectin molecule. Figure 2.4 and 2.5 show the structures of amylopectin proposed by various investigators.

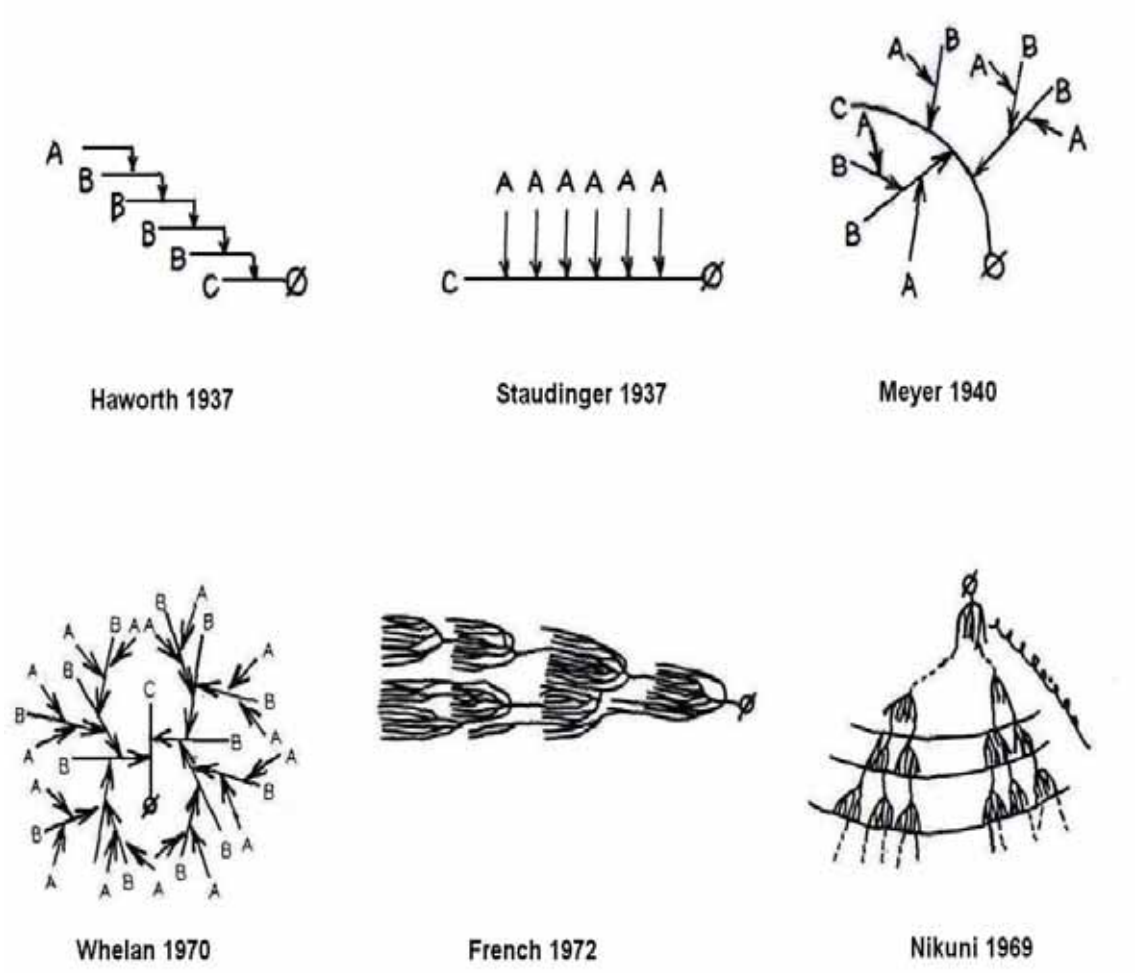

Figure 2.4 Structures of amylopectin proposed by various investigators (Hizukuri, 1996).

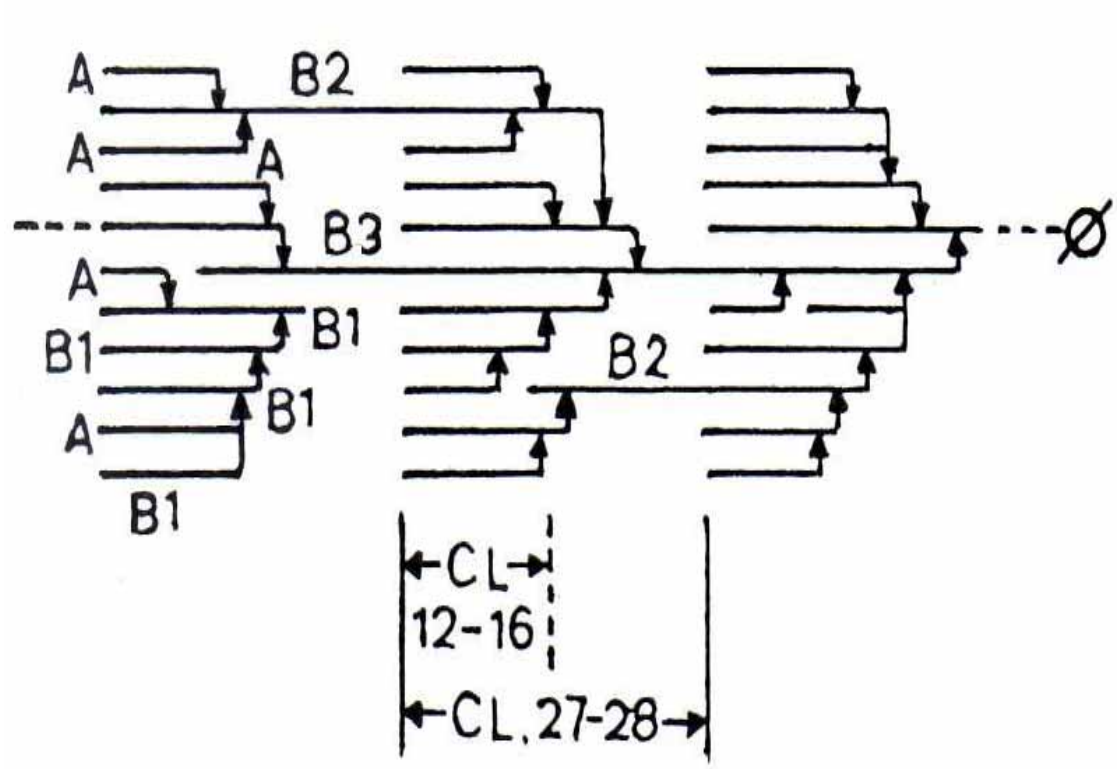

Figure 2.5 Structure of amylopectin proposed by Hizukuri 1986 (Hizukuri, 1996).

2.2 Granular Structure of Starch

Amylose and amylopectin do not exist free in nature, but as components of discrete, semicrystalline aggregates called starch granules. The size, shape and structure of these granules vary among botanical origins. The diameters of the granules range from less than 1 μm to more than 100 μm. The shapes can be regular (e.g., spherical, ovoid or angular) or quite irregular. Although the major components of all types of starch granules consist of amylose and amylopectin polymers, there is great diversity in the structure and characteristics of native starch granules (Thomas & Atwell, 1999).

Starch appears as a white, powdery material to the naked eye. Thus, light microscopy is often used to identify the type of starch. The general size and shape of starch granules from different sources can be observed with this technique. When viewed with a microscope under polarized light, all native starch granules exhibit a dark cross that centres through the hilum, which is called the “Maltese cross”. This is a typical feature of spherulitic type of organization. The fact that starch is birefringent implies that there is a high degree of molecular orientation in the granule. However, crystallinity is not a prerequisite of birefringence. Another well-known microscopic technique is iodine staining, which can provide information about the amylose and amylopectin content. Starches stain blue or reddish brown in the presence of a solution of iodine and potassium iodide. The resultant colour is dependent upon the complex formed when iodine is enclosed in helical starch chains within the granular structure. Long helix will produce a blue complex whereas shorter chains will produce a purple or reddish brown complex. Branch points in amylopectin disrupt this helical structure. Therefore, amylopectin produces reddish brown complex (Thomas & Atwell, 1999).

Figure 2.6 shows that the backbone of starch has numerous hydroxyl (-OH) groups projecting into its surrounding space. Hydroxyl groups have an affinity for other hydroxyl groups and can serve as a driving force in bringing starch chains together in an ordered manner through hydrogen bonding. When such ordering occurs, crystalline regions are deposited in the granule. The remaining regions of unordered starch are referred to as amorphous. It is the

crystalline regions that give the granule its structure and facilitate identification of raw (uncooked) starch.

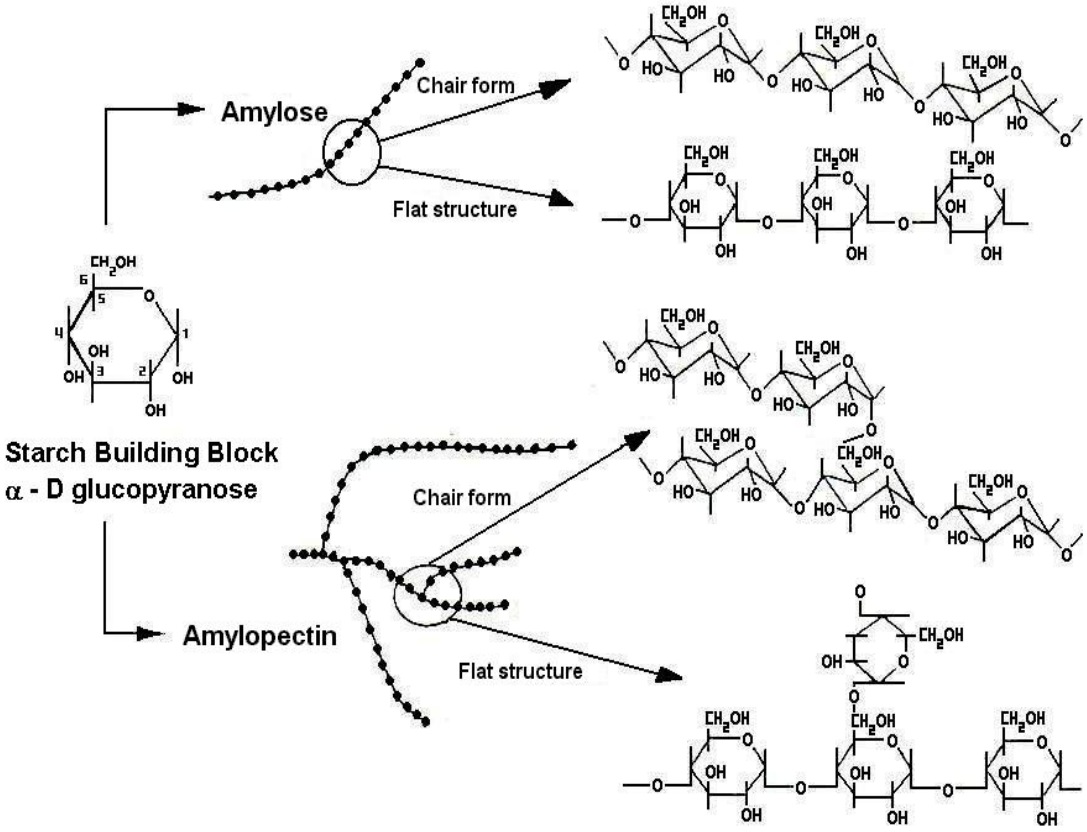

Figure 2.6 Linear and branched starch polymers (Murphy, 2000).

Although the amorphous material constitutes a major portion of granular starch, it has received very little attention until recently. The amorphous phase is less dense and more susceptible to chemical and enzymic modification (French, 1984; Biliaderis, 1982). At temperatures below gelatinization, it absorbs water readily and undergoes reversible swelling. The conformation of chains in the amorphous regions appears to be mainly a single helix or random coil (Biliaderis, 1998).

The distribution and arrangement of amylose and amylopectin within the starch granule remains a question. As the amylose content increases with grain maturation and the granule grows by apposition, it is assume that the outer parts of the granules have a higher proportion of amylose. Jane and Shen (1993) observed that amylose was more concentrated at the periphery and had smaller molecular size than that at the core of the granule. In addition, Jane *et al*. (1992) and Kasemsuwan and Jane (1994) suggested that in granular starch, amylose molecules do not exist in the form of bundles at amorphous regions but are interspersed among the amylopectin molecules. It is also plausible that some amylose molecules participate in double helices with amylopectin and thus become less prone to aqueous leaching or complexation with other components, e.g. iodine.

Numerous studies have been done over the years utilizing various forms of scattering to unravel the internal structure of starch. The well-defined characteristic peak seen in small angle X-ray scattering has been related to alternating stacks of crystalline and amorphous lamellae. Figure 2.7 shows a schematic diagram of the structure of a starch granule; (a) a single granule with alternating amorphous and semicrystalline layers, representing growth rings; (b) expanded view of the semicrystalline layer of a growth ring, consisting of alternating amorphous and crystalline lamellae; (c) chains of amylopectin arranged in a cluster structure within the semicrystalline layer of the growth ring (Jenkins *et al*., 1994).

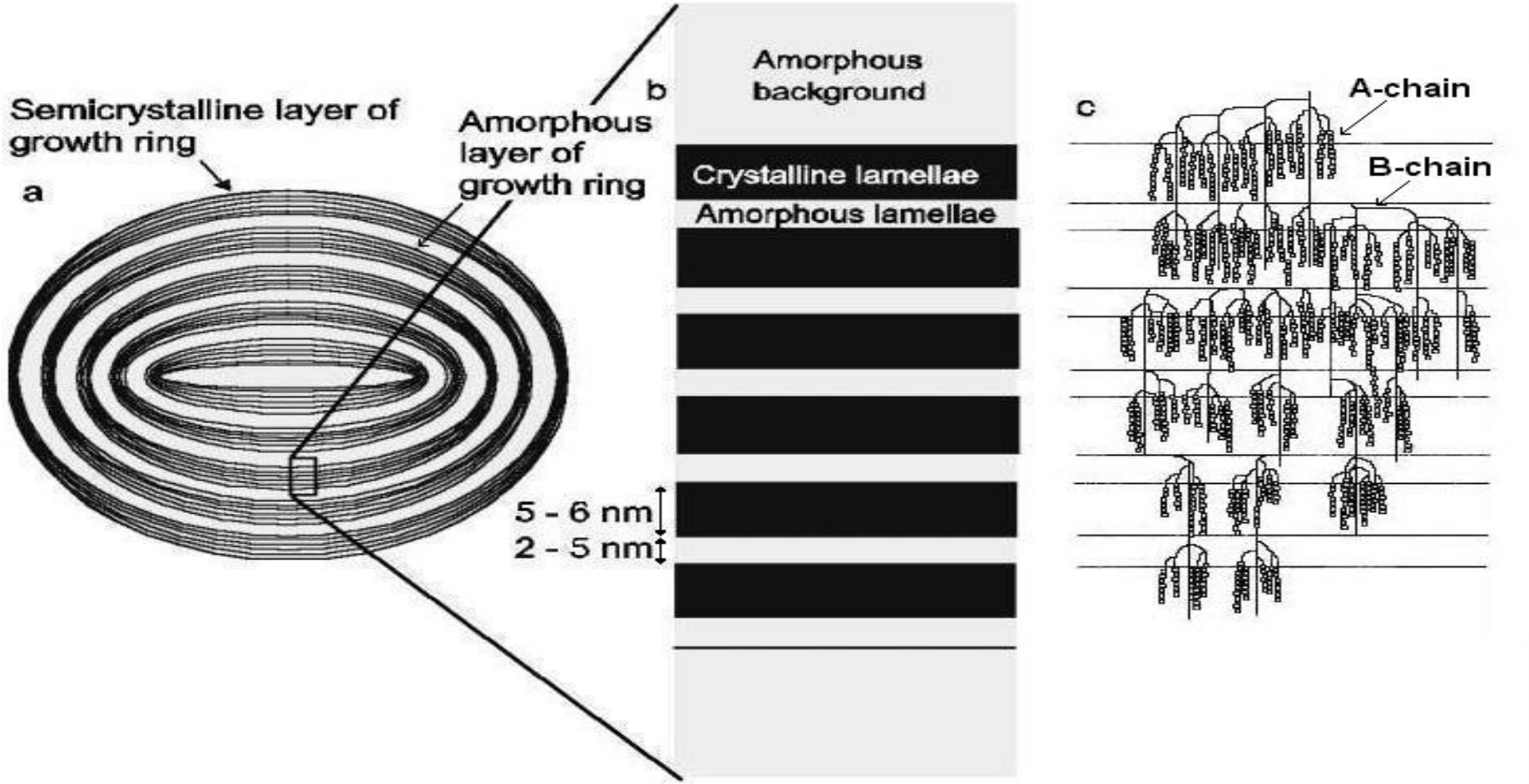

Figure 2.7 Schematic representation of starch granule structure (Jenkins *et al*., 1994).

X-ray crystallography has been used to study starch's crystalline nature. Native starch generally can be identified by three X-ray patterns, as shown in Figure 2.8. Native cereal starches such as wheat, rice and corn yield an A pattern, and tuber starches such as potato, fruit and high-amylose corn starches yield a B pattern. Smooth pea and bean starches give a C pattern, an intermediate form that probably results from mixtures of A and B types. According to Gidley and Bulpin (1987) and Gidley (1987), the A polymorph (the most thermodynamically stable form) is favored over the B structure (kinetically preferred form) under conditions of: (1) shorter α-D-glucan chain length, (2) higher crystallization temperature, (3) higher polymer concentration, (4) slower crystallization conditions and (5) the presence of alcohol. An additional pattern, known as V-type crystallinity corresponds to structures of helical inclusion complexes of amylose occurs in swollen granules. The V-type structure has not been found in native starches, but it may form as starch recrystallizes in the presence of a fatty acid or long-chain alcohol (Hoseney, 1994).

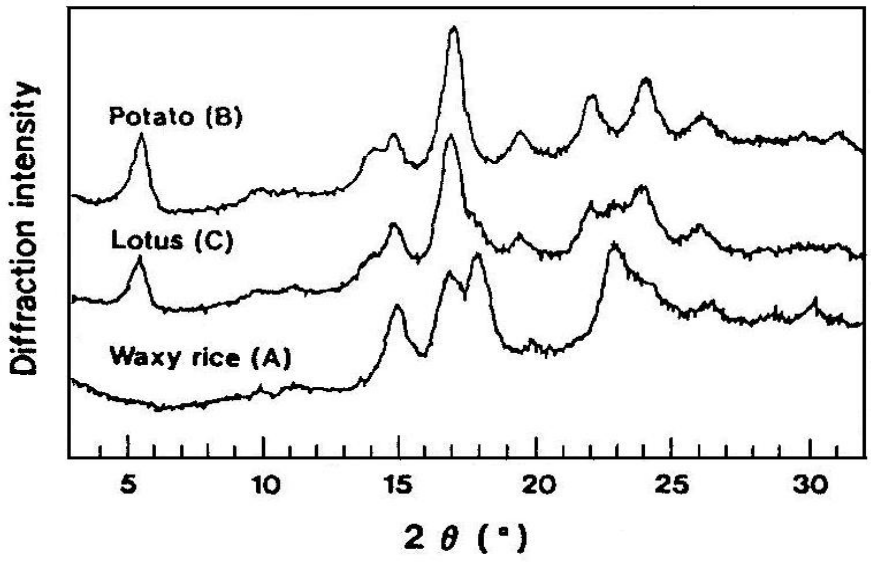

Figure 2.8 X-ray diffraction patterns of A, B and C type (Hizukuri, 1996).

The most detailed analysis of the A and B polymorphs has been based on X-ray and electron diffraction data from crystalline amylose and modeling studies (French, 1984; French and Murphy, 1977; Wu and Sarko, 1978a; Wu and Sarko, 1978b; Imberty *et al*., 1988; Imberty and Perez, 1988). Imberty *et al*. (1991) showed that in crystallites of both A and B starches double helices are found in pairs and all chains are packed in parallel arrays. The pairing of double helices is the same in both polymorphs and corresponds to the interaction between double helices that have the lowest energy. The double helical nature of starch chains in the crystallines explains their insolubility in cold water and their resistance to acid treatment (glycosidic oxygens are buried in the interior of the helix and thus are less accessible to hydrolysis by H_3O^+). Starches exhibiting A and B X-ray diffraction patterns differ in their water content and the manner in which the pairs of double helices are packed within their respective crystals (Figure 2.9). In B starches there are 36 water molecules present in a channel in the centre of a hexagonal arrangements of sixfold double helices packed parallel in the crystalline lattice and containing 12 AGUs (anhydroglucose units) per unit cell; each strand contributes three out of six residues per helix turn. Whereas in A starches there are only four water molecules present (Imberty *et al*., 1991). In addition, the centre of A starches is occupied by an amylosic helix rather than a column of water. It has been suggested that adjacent double helices within crystallites of A starches are mainly linked by direct hydrogen bonding (Imberty *et al*., 1991; Leach *et al*., 1959). However, in crystallites of B starches, adjacent double helices are mainly linked by hydrate water bridges and to limited extent by direct hydrogen bonding

(Leach *et al*., 1959). These structural models are consistent with the cluster-type molecular structure of amylopectin.

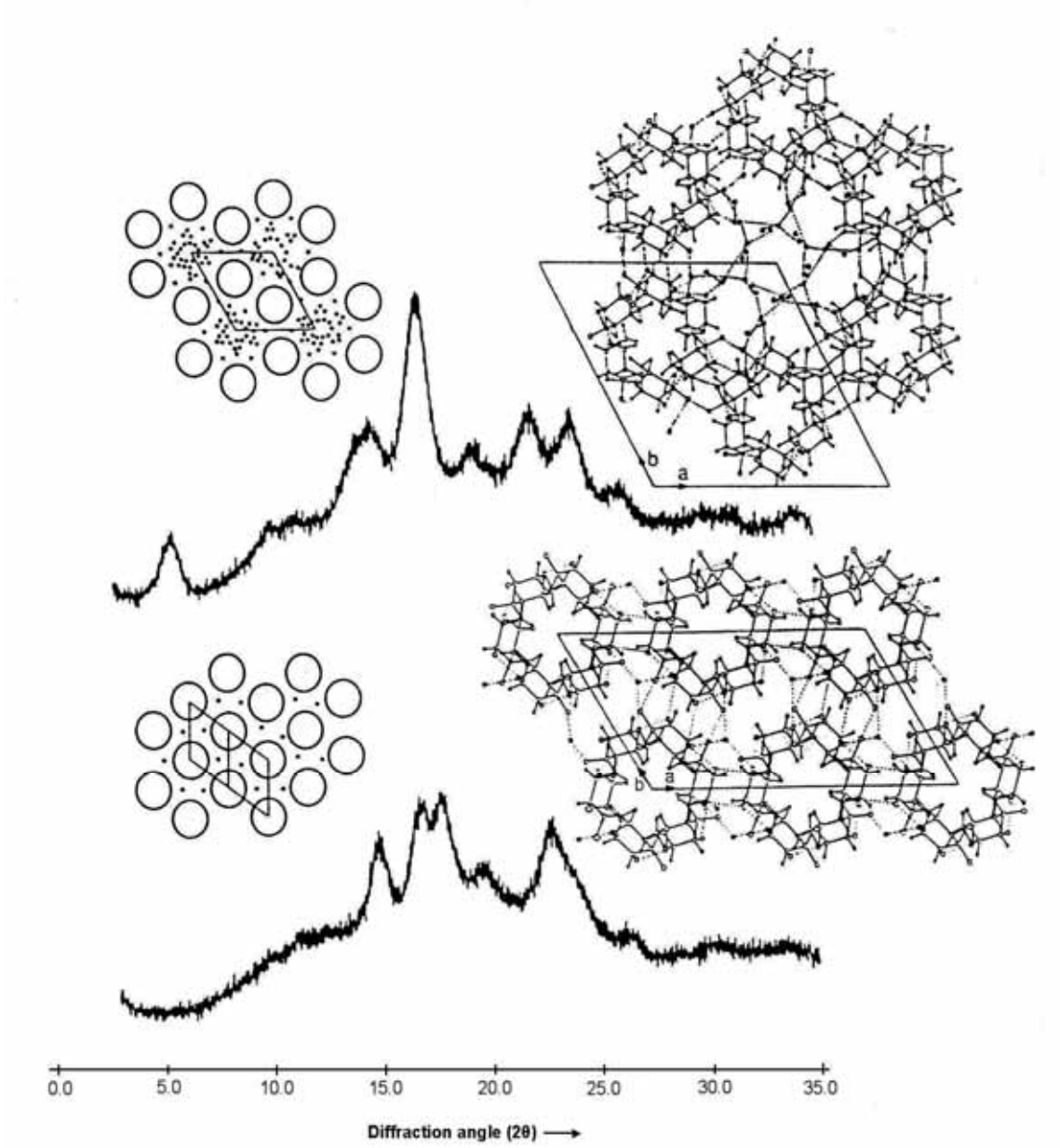

Figure 2.9 Typical X-ray diffraction patterns of A-type granular starches (bottom) and B-type granular starches (top) and of (*a*, *b*)-plane projections for their crystalline structure, showing the packing arrangements of double helices, water molecules and hydrogen bonding (Imberty *et al*., 1988; Imberty & Perez, 1988).

Recently, Gallant *et al.* (1997) proposed the “blocklet concept” as a new level of starch granule structural organization (between that of lamellae and the growth rings). They claimed that the crystalline and amorphous lamellae of amylopectin are organized into larger, more or less spherical “blocklet”. The diameter ranged from 20 to 500 nm (depending on their location in the granule and the botanical source of starch) and contains between 5 to 50 amylopectin short DP (degree of polymerization) chain clusters. In this type of granule organization, amorphous may exist in different regions: (a) in each lamellae (branching zone of amylopectin); (b) between clusters of side chains within each lamellae; (c) around each blocklet of side-chain clusters, and (d) in radially arranged channels in granules through which amylose can exit during gelatinization. They suggested that the size of blocklets and their arrangement in native starch might be important determinants of the granule resistance to enzymatic attack. The blocklets might be viewed as the structural elements of the alternating crystalline and partially crystalline shells of the starch granules often observed in scanning electron microscopy (SEM) micrographs of granular starches corroded by α-amylases.

Figure 2.10 shows an overview of the starch granule structure as suggested by Gallant *et al.* (1997). At the lowest level of granule organization (upper left), the alternating crystalline (hard) and semi-crystalline (soft) shells are shown in dark and light colours, respectively. The shells are thinner towards the granule exterior, due to increasing surface area to be added to by constant growth rate, and the hilum is shown off centre.

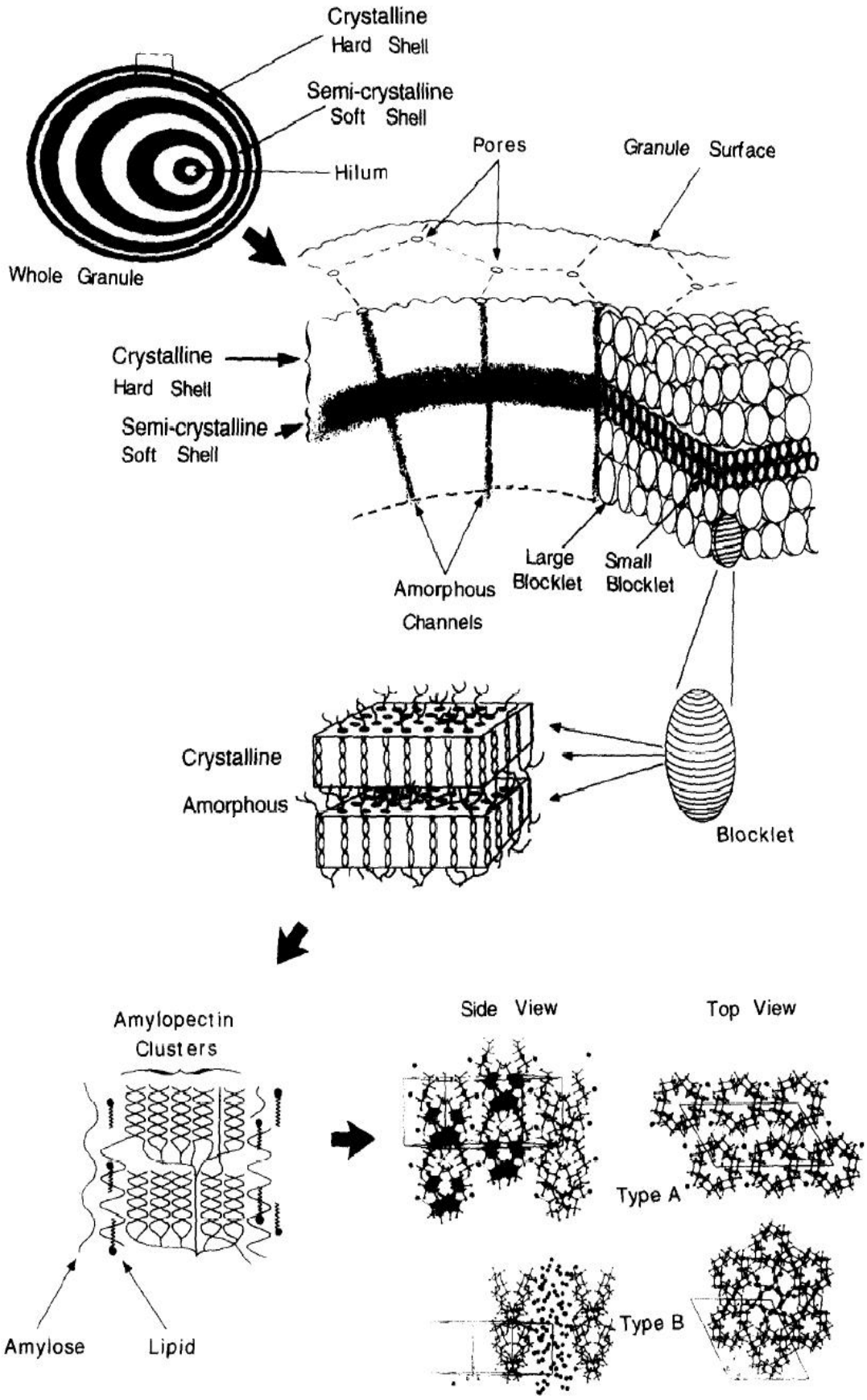

Figure 2.10 Overview of starch granule structure (Gallant *et al.*, 1997).

At a higher level of structure, the blocklet structure is shown in association with amorphous radial channels. Blocklet size is smaller in the semi-crystalline shells than in the crystalline shells. At the next highest level of structure, one blocklet is shown containing several amorphous crystalline lamellae. The next diagram shows the starch amylopectin polymer in the lamellae while the next image shows amylose-lipid (and protein) feature in the organization of the amylopectin chains. At the highest level of order, the crystal structures of the starch polymers are shown.

2.3 Sources of Starch

Starch is a major reserve polysaccharide of green plants and probably the second most abundant carbohydrate in nature next to cellulose. It is formed in the leaves and green parts of the plant from atmospheric water and carbon dioxide, through the agency of chlorophyll and sunlight. During the hours of darkness, the starch is broken down into sugars that are transported to other parts of the plant. Some of the sugars are reconverted into starch. Thus, starch is built up in the fruits, bulbs and tubers of the various plants. When digested, the starch is broken down through hydrolysis to its constituent glucose molecules and further down to the original component of carbon dioxide and water while energy is released.

Starch is the principal source of dietary calories to the world's human population. The most important sources of starch fall into three categories, namely seeds, stems and tubers. Wheat, corn and rice are examples of cereal seeds that contribute a major portion of the common starches produced. The

starch is found in the endosperm of the grains, normally interspersed in a matrix of protein. Thus, extraction of the starch has to be done by separating the external fibrous materials and protein. The most common example of stem starch is sago starch. The starch is found in the pith of the sago tree trunk and loosely held by fibrous materials. A large portion of the world starch supply comes from tubers. The most common sources of tuber starches are potato, sweet potato and tapioca. The starch is found among fibrous materials in the tuber and can be easily extracted by pulping and washing. Starches from others sources, such as pea and lentil, are also commercially available.

Maize and wheat are mostly grown in America and Europe whilst rice originates mainly from Asia. Potato is largely derived from the cooler climates of northern Europe. Tapioca is the exports of Brazil, Thailand and Indonesia. In fact, a very high proportion of the world's food energy intake is starch and over 80% of all food crops are composed of cereals and starch root crops.

2.3.1 Sago starch

Sago starch is isolated from sago palm (*Metroxylon spp*.), which is better known as "rumbia". Some of the important species widely used in sago starch production includes *M. longispinum*, *M. sylrestre*, *M. microcanthum*, *M. sagu* and *M. rumphii*. Most of the production of sago starch occurs in Sarawak and New Guinea. Trees of eight or more years old are used. Cut palm trunks are split and the pith are removed and kneaded in water to release the starch, which is later screened to remove fibre, then filtered and dried. A single mature palm trunk can yield 100 to 550 kg sago flour.

Sago palm is an important resource especially to the people in the rural areas because it has various uses mainly in the production of sago flour or sago pearl. Sago starch was used for many years in South East Asia in the food industry for the production of vermicelli, bread, crackers, biscuits, custard powder, confections, gravy powder and sauce mixes. Sago starch is important in the making of adhesives, particularly those for the laminated paperboard industry. In the pharmaceutical industry, sago starch is used to make bland, odourless and easily digested filler for drugs and medications. In the petroleum industry, pregelatinized sago starch is excellent as additives to coolant and lubricant used in well-drilling operations due to its viscosity and water-holding capacity (Knight, 1969).

Sago can compete economically on yield and price compared to other crops. The yield of sago starch is 2000-3000 kg/HaYr compared to cassava 2000 kg/HaYr and maize 1000 kg/HaYr (Stantan, 1992). It is estimated that 60 million tonnes of sago starch are produced annually in South East Asia (Wang *et al*., 1996).

The biggest sago area in Malaysia is in Sarawak. Sarawak is now the world's biggest exporter of sago, exporting annually about 25000 to 40000 tonnes of sago products to Peninsular Malaysia, Japan, Taiwan, Singapore and other countries. Currently, sago exports ranks as the fourth biggest agricultural revenue earner for Sarawak, after oil palm, pepper and cocoa. Sago brings in RM23.15 million in export earnings in 1993, overtaking the export of rubber in value terms in that particular year. The present area under sago in Sarawak is

19720 hectares. There are about 1.69 million hectares of peat soil in Sarawak, which are suitable for sago cultivation. Hence, the scope for the expansion of sago cultivation appears to be bright.

Besides the fact that sago starch is cheap, it has some other important properties that should be noted such as its low gelatinization temperature, its high viscosity if properly extracted and the ease with which it can be moulded. It has also been reported to undergo less syneresis than other starches (Takahashi, 1986). Some properties of sago and other starches are tabulated in Table 2.2.

Table 2.2 Properties of sago and other starches.

	Origin of starch				
	Sago	Maize	Wheat	Rice	Tapioca
Granule shape	Oval, truncated	Round, polygonal	Round	Polygonal	Oval with indentation
Granule size, μm	20-60	15	2-10 and 20-35	3-8	5-35
Amylose, %	27	26	25	17	17
Swelling power, %	97	24	21	19	71
Initial pasting temperature, °C	69	62	65	66	58

(Cecil *et al*., 1982)

2.4 Gelatinization, Pasting and Retrogradation

Native starch granules are insoluble in cold water. Thus, many unique characteristics of our foods, such as the mouth-feel of gravies, are the results of the changes native granules undergo when they are heated with water and not because of their inherent properties or behaviours.

The first change native granules undergo is gelatinization and pasting. They are irreversible and dependent on the amount of heat and water available to the system. These changes render all or part of the granule soluble and consequently able to contribute to food properties such as texture, viscosity and moisture retention. The last change is retrogradation, which involves reassociation of the molecules after the application of heat. The rate and extent of retrogradation are also dependent on temperature (Thomas & Atwell, 1999).

2.4.1 Gelatinization

Researchers have tried to define starch gelatinization for many years but still could not define the term accurately. According to Thomas and Atwell (1999), the critical points to make are that gelatinization:

- is the disruption of molecular order
- is temperature and moisture dependent
- is irreversible
- initially increases the size of granules (i.e., causes granular swelling)
- results in increased solution or suspension viscosity
- differs with respect to cooking conditions (e.g., pH and solids)
- differs with respect to granule type (botanical source)