EFFECT OF SELECTED NON-STARCH POLYSACCHARIDES AND BULK SWEETENERS ON THE PROPERTIES OF ACID-THINNED STARCH JELLY CANDY

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by

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LIST OF SYMBOLS / ABBREVIATIONS

ALG = Alginates

CMC = Carboxymethyl cellulose

CPI = Isomalt

CPM = Maltitol

CPP = Palatinose

DP = Degree of polymerization

DS = Degree of substitution

G' = Storage modulus

G" = Loss modulus

GI = Glycemic Index

NSP = Non starch polysaccharide

PEC = Pectin

RVA = Rapid Visco Analyzer

RVU = Rapid Visco Unit

TPA = Texture Profile Analysis

KESAN-KESAN POLISAKARIDA BUKAN-KANJI DAN PEMANIS PUKAL TERPILIH KE ATAS SIFAT-SIFAT KANDI JELI KANJI DINIPIS ASID

ABSTRAK

Sampel-sampel kandi jeli berasaskan kanji dinipis asid telah diperkembangkan. Kesan-kesan polisakarida bukan-kanji yang terpilih (NSP: pectin, selulosa karboksimetil, dan alginat), dan pemanis pukal rendah kalori (isomalt, maltitol dan isomaltulose) ke atas sifat-sifat fizikal kandi jeli berasaskan kanji telah dikaji dari segi sifat-sifat pempesan, viskoelastik, pengaliran, tekstur, sensory, kestabilian penstoran dan indeks glisemik. Penambahan NSP terpilih didapati meningkatkan viskositi puncak pes kanji secara signifikan dan ini mencadangkan bahawa NSP ditambah mungkin meningkatkan beban kepekatan semasa pemasakan sluri kanji dinipis asid, khususnya benar apabila alginat dan selulosa karboksimetil ditambah. Kehadiran pectin didapati menambahbaik kebolehkerjaan sluri dan kandi jeli yang dihasilkan adalah lebih mudah dibentuk dan permukaannya lebih licin apabila dibanding dengan sampel yang lain. Kesan-kesan ini disebabkan oleh peningkatan dalam sifat pengaliran yang bergantung kepada masa dan sifat viskoelastik yang bertambahbaik. Apabila membandingkan kesan-kesan penggantian gula dengan isomalt, maltitol dan isomaltulose, nilai modulus penyimpanan (G’) didapati berkurang dengan peningkatan dalam tahap penggantian, dan kesan yang paling besar telah ditonjolkan oleh sample yang mengandungi isomalt dan isomaltulose. Selain itu, isomalt dan maltitol didapati adalah lebih berkesan dalam meningkatkan sifat pengaliran yang bergantung kepada masa, jika berbanding dengan isomaltulose. Untuk sifat-sifat tekstur, adalah didapati penggantian dengan maltitol telah menghasilkan kandi jeli dengan sifat-sifat seperti kekerasan yang stabil, *springiness* yang rendah, kegaman dan *resilience* yang tinggi sepanjang masa penstoran selama 180 hari. Tahap penggantian maltitol paling tinggi yang tercapai ialah 30%, lebih tinggi daripada itu didapati sampel menerima tahap penerimaan yang rendah daripada ahli-ahli sensori. Dengan 30% penggantian gula dengan maltitol, sampel menunjukkan indeks glisemik (GI) sebanayak 58.75, yang mana jatuh dalam kategori makanan GI sederhana (56>GI>69).

EFFECT OF SELECTED NON-STARCH POLYSACCHARIDES AND BULK SWEETENERS ON THE PROPERTIES OF ACID-THINNED STARCH JELLY CANDY

ABSTRACT

Jelly candy samples based on acid thinned starch were developed. The effects of selected anionic non-starch polysaccharides (NSP: pectin, carboxymethyl cellulose, and alginates), and low-calorie bulk sweeteners (isomalt, maltitol and isomaltulose) on the physical properties of starch-based jelly candy were studied for selected properties such as pasting properties, viscoelasticity, flow properties, textural properties, storage stability, sensory properties, and glycemic index. Addition of the selected NSP was found to significantly increased peak viscosity of starch paste and this suggests that NSP added may increase viscous load during cooking of acid thinned starch slurry, especially when alginates and carboxymethyl cellulose were added. Presence of pectin enhanced the workability of the slurry and the jelly candies produced were more regularly shaped and smoother when compared to the other samples. These effects were attributed to an increase in flow time dependency and an enhanced viscoelasticity. When comparing the effects of sugar substitution with isomalt, maltitol and isomaltulose, storage modulus (G’) value decreased with increase in substitution concentration, and greater effect was shown in isomalt and isomaltulose samples. Apart from this, isomalt and maltitol were found to be more effective in increasing time dependency of the candy slurry than isomaltulose. As for the textural properties, with maltitol substitute, the jelly candy samples showed stable hardness, lower springiness, higher gumminess and resilience properties over the storage period of 180 days. The highest possible substitution level of maltitol determined was 30%, above which the samples received very low acceptability by sensory panellists. With 30% sucrose substitution with maltitol, sample showed a glycemic index (GI) of 58.75, which falls in the category of medium GI food (56 > GI > 69).

CHAPTER 1
INTRODUCTION

1.1 Background and Rationale

One of the major nutritional problems faced today is the tendency to overly consume sweet and sugary foods, which many believe has been associated with health problems such as obesity, dental illness and other serious diseases (Zoulias, *et al.,* 2002). Among which, obesity is literally a growing problem worldwide and this epidemic is accelerating among children and the young age group. This group of consumers remains the heaviest snackers. Confectioneries appear to be the most popular snack among this group of consumer. Thus, there is no question that this group eats far more sugar than they need. In view of this, food manufacturers have been trying to formulate more savory 'healthy' snack attributing low-sugar, low-salt and low fat.

In this study, light has been shed on jelly candy. Acid thinned starch-based jelly candy was studied instead of gelatin due to the emerging and lucrative halal, kosher and vegetarian market. Acid-thinned starch is the basic ingredient of many jelly candy products. Starch-based jelly candy just like many other high-solid food products are regarded as being craft based. Therefore, literature reporting on all parts starting from the characteristics of starch during and after cooking in the presence of other ingredients, through rheological responses during pumping and deposition, and product quality during storage is relatively sparse. All these are of great importance to the confectionery industry for selecting the right ingredient and processing condition that may confer the right product quality.

Non-starch polysaccharides (NSP) are incorporated to enhance the gel properties. NSP is added in starch-based gel system to provide a wide range of properties such as texture, storage stability, processability, and control release (Yoshimura, Takaya, & Nishinari, 1998; Shi & BeMiller, 2002; Lubbers & Guichard, 2003; Al-Marhoobi & Kasapis, 2005; Savary, Lafarge, Doublier, & Cayot, 2007). A voluminous literature exists on studying the effects of NSP on starch-based products properties, among the NSPs tested are guar gum, pectin, alginates, kappa-carrageenan, xanthan, cellulose derivatives, just to name a few. In the present study, we focused on characterizing the effects of anionic NSP including high methoxyl pectin (PEC), carboxymethyl cellulose (CMC) and alginates (ALG) on acid-thinned starch system. To the best of our knowledge, effects of anionic gums on acid-thinned starch have not been studied in greater detail, especially in a high-solid system mimicking the industrial preparation. The use of NSP in materials containing high solid is significant, since the high solid contents always impart high viscosity and making the food system difficult to handle during processing. With the addition of NSP, the characteristics and workability of a high solid food can be enhanced. From the work of Al-Marhoobi and Kasapis (2005), it was suggested that the tendency for biopolymer to form progressively longer and, hence more thermally stable helices at high levels of co-solute should be increasingly counterbalanced by the inability to sustain those helices in the form of stable aggregates due to the scarcity of water molecules. The presence of anionic NSPs was believed to complicate more the complexity of the system and might cause greater phase separation, which could be of advantage or disadvantage to the system.

Low calorie bulk sweeteners, namely isomalt, maltitol and isomaltulose, were used to replace sugar in jelly candy. These sweeteners can be used as the same bulk as the traditional sugars. These bulk sweeteners taste just as natural and sweet as sugar. These sweeteners do not produced marked elevation in blood glucose and provide relatively lower calorie.

1.2 Objectives and Research Protocol

The general objective of the project was to develop and characterize acid-thinned starch-based jelly candy.

The specific objectives of this study were:

1) To determine the effects of selected anionic non-starch polysaccharides (namely pectin, carboxymethylcellulose and alginates) on the physical properties and storage stability of jelly candy.
2) To evaluate the suitability of different bulk sweeteners (i.e. isomalt, maltitol, and isomaltulose) to be used as sugar substitute that has low impact on the physical properties and storage stability, show low glycemic index and high sensorial acceptability of the jelly candy.

The research protocol of this project has been divided into three sub-sections. In the beginning, selected NSPs were screened. Effects of NSPs on acid-thinned starch pasting properties and paste rheological properties were studied. Jelly candy samples were prepared and characterized by textural properties as a function of storage time over a period of 180 days. The most suitable NSP was selected and added to the base materials for jelly candy making in the subsequent section.

In line with the second specific objectives, selected bulk sweeteners were used to substitute sucrose at two levels (25% and 50%). The effects of the sweeteners on the rheological properties of jelly candy slurry and the textural properties of jelly candy prepared were characterized.

In the final part of the project, jelly candy were prepared with the best sweetener identified in previous section and the substitution levels were varied to a greater range (10, 20, 30, 40, and 50%) in order to determine the highest possible substitution level, which provide relatively better and stable candy quality. Among the analyses carried out were rheological and textural properties determination, sensory evaluation and glycemic index determination.

CHAPTER 2

LITERATURE REVIEW

2.1 Starch

2.1.1 General description of starch

In nature, starch is available in abundance surpassed, only by cellulose as a naturally occurring organic compound (Huang & Rooney, 2001). Starch serves as a food reserve for plants and provides a mechanism by which nonphotosynthesizing organisms, such as man, can utilize the energy supplied by the sun (Bastioli, 2002). Starch is the major source of calories and dietary energy in most human food systems (Niba, 2006). Starch presents naturally in plants and is the storage polysaccharide of plants (Niba, 2006). Starch is deposited in granules in almost all green plants and in various types of plant tissues and organs, e.g., leaves, roots, shoots, fruits, grains, and stems (Preiss, 2004). It is found in all forms of green leafed plants, located in their roots, stems, seeds or fruits (National Starch and Chemical Company, 1996). Starch is obtained from various plant sources. The most common sources of dietary and industrial starch are grains, such as maize and wheat, and roots such as potato and cassava (tapioca) (Niba, 2006).

Starch has found widespread application in the food industry. Starch is totally biodegradable in a wide variety of environments and could permit the development of totally degradable products for specific market demands (Bastioli, 2002). Starch performs various functions in food systems. It is used as a carrier in various products, as a texture modifier, as a thickener, and as a raw material for the production of other valuable food ingredients and products (Niba, 2006). Starch is a member of the ‘polysaccharide’ group of polymers. It is laid down as insoluble, compact and microscopic semi-crystalline granules of size 1–100µm (Murphy, 2000). It occurs in the form of granules which are usually an irregular rounded shape, ranging in size from 2 to 100 µm. Both the shapes and sizes of the granules are characteristic of the species of plant and can be used to identify the origin of a starch or flour (Coultate, 2002). In the human dimension, for 1g of starch typically contains something of the order of 1,000,000,000 granules with each granule, in turn, containing about 10,000,000,000,000 starch molecules (Murphy, 2000). When starch is preferentially digested, the trapped energy is released as when the starch is broken down by hydrolysis back to its constituent glucose molecules and further back to the original carbon dioxide and water molecules (Niba, 2006; Murphy, 2000).

The glucose polymers that make up starch come in two molecular forms, linear and branched (Murphy, 2000). Starch is unique in the sense that amylose and amylopectin molecules are biosynthesized and assembled in the form of semi-crystalline aggregates, called granules, which vary in size (1–100 µm) and shape according to the botanical source (Niba, 2006). Starch is a heterogeneous polysaccharide composed of two high molecular weight entities called amylose, which is essentially linear α-D(1-4)- glucan, and amylopectin, which is α-D(1–6) –linked at the branch point (Bastioli, 2002;Coultate, 2002; Niba, 2006). Normal starches, such as normal maize, rice, wheat and potato, contain 70 – 80% amylopectin and 20 – 30% amylose (Jane, 2009).

2.1.2 Starch components

2.1.2.1 Amylose

The amylose structure is also of a smaller molecular size than amylopectin. Amylose is mainly found as linear chains of about 840 to 22,000 units of α-D-glucopyranosyl residues linked by α-(1->4) bonds (molecular weight around 136,000 to 3.5 x 10^6) (Preiss, 2004). Amylose consists of long chains of a-D-glucopyranosyl residues linked, as in maltose, between their 1- and 4-positions and has a molecular weight in the range of 30,000 to greater than 10^6, depending on source (Niba, 2006;Coultate, 2002). There are no certainty about the length of the chains, but they are generally believed to contain many thousands of glucose units so that typical, average molecular weights are between 2 x $10^5$and 2 x10^6 (Coultate, 2002). It is interesting to note that amylose and cellulose are very similar in structure with the single exception of the spatial arrangement of the bridging between the numbers 1 and 4 carbons (National Starch and Chemical Company, 1996). Low-amylose starches, when cooked, provide viscous pastes with a cohesive texture and a low tendency to retrograde, which is preferable for use as adhesives (Jane, 2009). It is becoming clear that amylose chains are not entirely linear; they do contain a very small amount of branching of the type which is characteristic of amylopectin (Coultate, 2002). Starches of higher amylose content have the disadvantage of more difficult rehydration, due to retrogradation in the noodle (Jane, 2009). In fact, the 'linear' amylose has a small degree of branching but it is predominantly regarded as a single chain. The chain length can vary with the botanical origin of the starch but will be of the order of 500 to 6000 glucose units. Because of its more simple polymeric structure, amylose has a greater propensity to deposit in a regular manner forming crystals (Murphy, 2000).

2.1.2.2 Amylopectin

Amylopectin is a larger molecule, having about $l0^6$ glucose units per molecule than amylose in most normal starches and their chains are classified as small chains, with an average degree of polymerization (DP) of about 15, and large chains, in which the DP is larger than 45 (Andréa, 2009; Gidley *et al*., 2001). Molecular size is relatively easily determined for low or intermediate weights (Andréa, 2009), but sample preparation and handling requirements may make it difficult to identify true molecular weights for some large amylopectins (Gidley *et al*., 2001). The multitude of branching in amylopectin gives it a molecular weight that is 1000 times that of amylose (Murphy, 2000). This is because above $l0^8$ Da, molecules may be sufficiently large that either they are mechanically unstable in solution or they are more colloidal than molecular in dimensions and consequently cannot be chromatographed or measured accurately by light scattering (Gidley *et al.,* 2001). While the amylopectin backbone exhibits a primary structure identical to that of amylose (Niba, 2006). Amylopectin, in contrast, which usually comprises about 70% of the starch granule, is more highly branched with about 4 to 5% of the glucosidic linkages being α-1->6 (Preiss, 2004). Amylopectin is a highly-branched polymer, consisting of three types of branch chains (Jane, 2009; Eliasson, 2004). A-chains are those linked to other chains (B- or C-) by their reducing ends through α -D-(1 → 6) linkages, but they are not branched themselves (Gidley *et al.,* 2001; Jane, 2009). B-chains are those linked to another B-chain or a C-chain, but B-chains are branched by A-chains or other B-chains at O-6 of a glucosyl unit (Jane, 2009). There is only one C chain per amylopectin molecule, which carries the sole reducing end of the molecule (Jane, 2009; Eliasson, 2004). The average branch chain length of amylopectin has a bimodal distribution that differs from the single modal distribution of that of glycogen. The average branch chain length of amylopectin varies with the origin and maturity of the starch and the location of molecules in the granule (Gidley *et al.*, 2001; Jane, 2009). This crystallinity reflects the organization of amylopectin molecules within the starch granules, whereas amylose makes up most of the amorphous materials that are randomly distributed among the amylopectin clusters (Andréa, 2009).

2.1.3 Functional properties of starch

2.1.3.1 Gelatinization

Gelatinization occurs when the ordered structure of the starch granule is disrupted and reorganized in the presence of heat and sufficient moisture (Niba, 2006). Starch gelatinization involves granule melting in an aqueous medium when the starch granule is heated in water, the weaker hydrogen bonds in the amorphous areas are ruptured and the granule swells with progressive hydration and granule swelling increases with temperature and it leads to a transfer of water in the suspension to water associated with starch components (amylose and amylopectin) at 40˚C. The more tightly bound micelles remain intact, holding the granule together. Birefringence is lost. As the granule continues to expand, more water is imbibed, clarity is improved, more space is occupied, movement is restricted and viscosity increased (National Starch and Chemical Company, 1996; Andréa, 2009; Copeland *et al.*, 2009). When starch temperature reaches about 140–160˚ F (60–71˚ C), insoluble granules are disrupted by the energy supplied breaking hydrogen bonds, leaking out amylose unit, resulting in a loss of molecular organization, consequently, and loss of its crystallinity (Andréa, 2009; Copeland *et al.*, 2009). The steps in the gelatinization process are as follows: Firstly, the gelatinization temperature is reached at approximately 140–160 ° F (60 –71 ° C), depending upon the starch type, and is completed at 190–194 ° F (88–90 ° C), or higher. Secondly, the kinetic energy of the hot water molecules breaks the hydrogen bonds between the starch molecules. Hydrogen bond interchange occurs as starch forms hydrogen bonds with water molecules instead of other starch molecules. As hydrogen bonds are formed, water is able to penetrate further into the starch granule and swelling takes place. Sufficient water must be present to enter and enlarge the starch granule. Thirdly, diffusion of some amylose chains occurs as they leach out of the starch granules. Fourthly, Birefringence and the ordered crystalline structure of the uncooked granule is lost. Increased translucency is apparent because the refractive index of the expanded granule is close to that of water. Fifthly, granule swelling increases as the temperature increases. The larger starch granules are the first to swell. Next, swollen granules take up more space and the mixture thickens as the enlarged granules leach amylose and possibly amylopectin. And the starch paste continues to become thicker, more viscous, and resistant to flow as it gelatinizes. The final step in the gelatinization involves the necessity of cooking the gelatinized starch mix—gravy, pie filling, and so forth—for 5 minutes or longer to develop flavor. Unnecessary over stirring thins the cooked starch mixture because the swollen starch granules implode, rupture, and lose some of the liquid held inside the enlarged granule (Vaclavik & Christian, 2007). Gelatinization temperatures are considered as ranges covering the temperatures at which loss of bi-refringence is first noticed and less than 10% remains and this temperature range is greatly influenced by the binding forces within the granule which vary with species (National Starch and Chemical Company, 1996). The gelatinization temperature is reached at approximately 140–160° F (60–71° C), depending upon the starch type, and is completed at 190–194° F (88–90° C), or higher (Vaclavik & Christian, 2007). High amylose corn has much greater bonding force than the other maize varieties due to the high degree of linearity within the granule. On the other hand, orthophosphate ester groups within the potato granule tend to weaken bonding and lower energy requirements to gelatinize (National Starch and Chemical Company, 1996). However, optimum gelatinization occurs at 90ºC and further heating decreases the viscosity (Vaclavik & Christian, 2007).

2.1.3.2 Retrogradation

The process of retrogradation happened during cooling of gelatinized starch results in the re-association of the leached amylose from gelatinized granules (Niba, 2006). Retrogradation is an ongoing process occurring over an extended period, to as setback, and occurs with re-crystallization of amylose (Hui, 2006; Copeland *et al.*, 2009). Retrogradation refers to the occurrence where starch reverts or retrogrades to a more crystalline structure upon cooling (Vaclavik & Christian, 2007) Amylose retrogrades over minutes to hours and amylopectin over hours to days, depending on the ability of the branched chains to form associations. The retrogradation of amylose in processed foods is considered to be important for properties relating to stickiness, ability to absorb water, and digestibility, whereas retrogradation of amylopectin is probably and more important determinant in the staling of cakes and bread (Copeland *et al.*, 2009). Amylose and amylopectin may participate in a textural change that makes starch based food products somewhat more “gritty” with time. Retrogradation is more likely in high amylose starches. It is noted in baked products that become “stale,” no longer “fresh” tasting or handling (a “fresh” baked good indicates that the starch is still in existence as a gel form). It also observed in leftover, long-grain rice. Due to its high amylose content, leftover rice gets hard.

Amylopectin retrogradation requires more time than amylose retrogradation, and as a result is the primary factor resulting in staling. During the staling period, the amylopectin molecules revert back to their original firm state as rigid crystalline granules (Vaclavik & Christian, 2007). Retrogradation of starch in food is a concern as it affects food product quality. The stability of starch-containing food products during cold storage in particular is greatly affected by the extent of retrogradation. Freeze-thaw cycles result in extensive retrogradation and syneresis (Niba, 2006).

2.1.4 Type of starch modification

Modified starches have been developed for long time and its applications in food industry are really significant nowadays (Abbas *et al.*, 2010). Starches can be modified by chemical, physical and enzymatic treatments are starch modifications, these treatments help to alter the structure and affecting the hydrogen bonding in a controllable manner to enhance and extend the structure application (Murphy, 2000). Chemically or physically or dual modified starches are meant to accentuate their positive characteristics, diminish their undesirable qualities, or add new attributes (Kerry & James, 2009). The alterations take place at the molecular level, with little or no change taking place in the superficial appearance of the granule (Murphy, 2000).

2.1.4.1 Chemically modified starches

The properties of starch structure can be changed under certain conditions, and the degree of change is highly associated with the original structure of the starch granule. Chemical modification is the mainstream of modified starch in the last century; as well many developments of chemical modification of starches have been introduced in food, pharmaceutical and textile industries (Abbas *et al.*, 2010). Therefore, chemical modification is the most common industrial means of enhancing starch properties, entails reaction or treatment of starch with chemical reagents to introduce new chemical substituent groups, effect molecular scission, or promote oxidation or molecular rearrangements (Wurzburg, 1986). Starch modification patterns can be chemically tracked and understood at the universal (general extent of substitution or modification), granular (outline of modification within the granule), and molecular (pattern of reaction on individual starch molecules) levels (Kerry & James, 2009). So, these levels provide useful fundamental insight and understanding into starch modification practices and also many commercial derivatives are produced by the addition of reactive, organic reagents to aqueous starch slurries while controlling alkalinity (Kerry & James, 2009; Chiu & Solarek, 2009). The most common chemical modification generally involves esterification, etherification or oxidation of the available hydroxyl groups on the α-D-glucopyranosyl units that make up the starch polymers (Chiu & Solarek, 2009; Steve *et al.*, 2005). Consequently, chemical modification of starch results in improved molecular stability against mechanical shearing, high temperature hydrolysis and acidic; obtaining desired viscosity; electronegative, increasing interaction with ion, or electropositive substances; and reducing the retrogradation rate of unmodified starch (Steve *et al.*, 2005).

2.1.4.2 Physically modified starches

Physical modification of starch can be carried singly or coupled with chemical reactions to change the granular structure and convert native starch into cold water soluble starch or into small crystallite starch (Steve *et al.*, 2005). Physical modification involves heat/moisture treatment as well as full disintegration of granules by precooking/pregelatinisation and treatments of controlled heat and water/ moisture applications like annealing, extrusion or spray-cooking (Miyazaki *et al.*, 2006; Bergthaller, 2004). However, the heat-treatment processes include heat–moisture and annealing treatments. Both modifications without any gelatinization cause damage to granular integrity, or loss of birefringence (Abbas *et al.*, 2010). The properties achieved through these types of modifications vary according to the treatment temperature, heating time, and botanical unmodified starch, but are especially impacted by the starch moisture content during treatment (Kerry & James, 2009).

2.1.4.3 Multiple modifications

In many cases, not only one type of modification is sufficient to impart all necessary properties to a starch intended for a specific application. So, starches are often subjected to a combination of chemical or physical modification schemes to tailor the collective starch properties for a particular end use (Kerry & James, 2009). Dual modification has been demonstrated to provide stability against acid, thermal and mechanical degradation of starch and to delay retrogradation during storage, traditionally refers to a starch that has been both stabilized and a combination of substitution and cross-linking, and is commonly employed to enhance stability to retrogradation (stabilization) and to impart tolerance to acid, high shear, and prolonged heating conditions (cross-linking) (Singh *et al.*, 2007; Kerry & James, 2009).

2.1.5 The use of Acid-Thinned Starch in Confectionery Industry

Starches used in gum candies are generally modified with hydrochloric acid, and termed “acid-thinned’’ starches (Singh Sandhu *et al.*, 2007). Acid-thinned starches are obtained by reducing the concentration of concentrated starch slurry with a mineral acid at 40–60°C, to get a necessary viscosity (Niba, 2006). A raw starch and dilute acid are heated to temperatures less than the gelatinization temperature. Once the starch is mixed into a food product, it appears less viscous in hot form, but forms a strong gel upon cooling (Vaclavik & Christian, 2008). Acid thinned starches can be prepared by chemical, physical, and enzymatic methods (Agboola *et al.*, 1991). Acid modified, is used extensively in food, textile and paper industries (Wurzburg, 1986). The most common use of thin-boiling starches is in jelly gum candies where a hot fluid material is deposited into moulds and allowed to gel to a specific texture and shape (Mason, 2009). Hydrolyzed starches are produced when a concentrated suspension of starch (30–40 g/100 g solids) is treated with acid, at temperatures lower than those of gelatinization (30–60 ºC), during one or many hours of reaction time (Singh Sandhu *et al.*, 2007).

2.2 Non Starch Polysaccharides (NSPs)

2.2.1 Type of non-starch polysaccharide

Non-starch polysaccharides are usually called hydrocolloids and in the older literature it is called gums or food gums (BeMIller, 2011). NSPs are major components of plant materials used in rations for monogastrics, complex carbohydrates formed by the condensation of large numbers of monosaccharide units (Williams *et al.*, 1997; Choct & Kocher, 2000; Stef *et al.*, 2009; Vaughan *et al.*, 2009). They are the major part of dietary fibre and can be measured more precisely than total dietary fibre including celluloses, hemicelluloses, pectins and oligosaccharides (a-galactosides, etc.) glucans, gums, mucilages, inulin, and chitin (and exclude lignin) (Williams *et al*,. 1997 and Stef *et al.*, 2009). They can also be divided into water-soluble and water-insoluble fractions; fractions which have greater relevance to their nutritional values (Williams et al,. 1997). NSP are classified into three main groups, i.e. normally cellulose, non-cellulosic polymer and pectic polysaccharides (Choct & Kocher, 2000).

2.2.2 Pectin

2.2.2.1 General description of pectin

Pectin is a group of polysaccharide substances present in the cell walls of all plant tissues. Plant tissues contain hemicelluloses (polymers of galacturonic acid) known as protopectins which cement the cell walls together (Vaughan *et al*,. 2009; Whistler, 1973). They are particularly prevalent in fruits and vegetables (Steve *et al.*, 2005). Pectin functions as an intercellular cementing material when combination with cellulosic material (Whistler, 1973). Commercial pectins used as food additives are hetero-polysaccharides which contain at least 65% by weight of galacturonic acid-based units (May & Consultant, 2000). The traditional use of pectin is as a gelling agent, and this has largely set the type of fruit from which commercial grades can be manufactured (Phillips & Williams, 2000). As a result of its properties, commercial pectin used in production of food often has sugar added to standardize viscosity and to prevent clumping when the pectin is added to water (Burey *et al.*, 2009). For example, the application of pectin is as a gelling agent in jams and jellies. (Brejnholt, 2009).

2.2.2.2 Monosaccharide composition of pectin

Pectins which are used in food are high molecular weight heteropolymers containing a majority (at least 65% by weight) of galacturonic acid units (May and Consultant, 2000). Pectins are a family of complex polysaccharides consisting of galacturonic acid that contains 1,4-linked α-D galactosyluronic residues with partial methyl esterification of the carboxyl groups, as shown in Figure 1 (Hans & Frank, 2009; Steve *et al*., 2005; Vaclavik, & Christian, 2008).

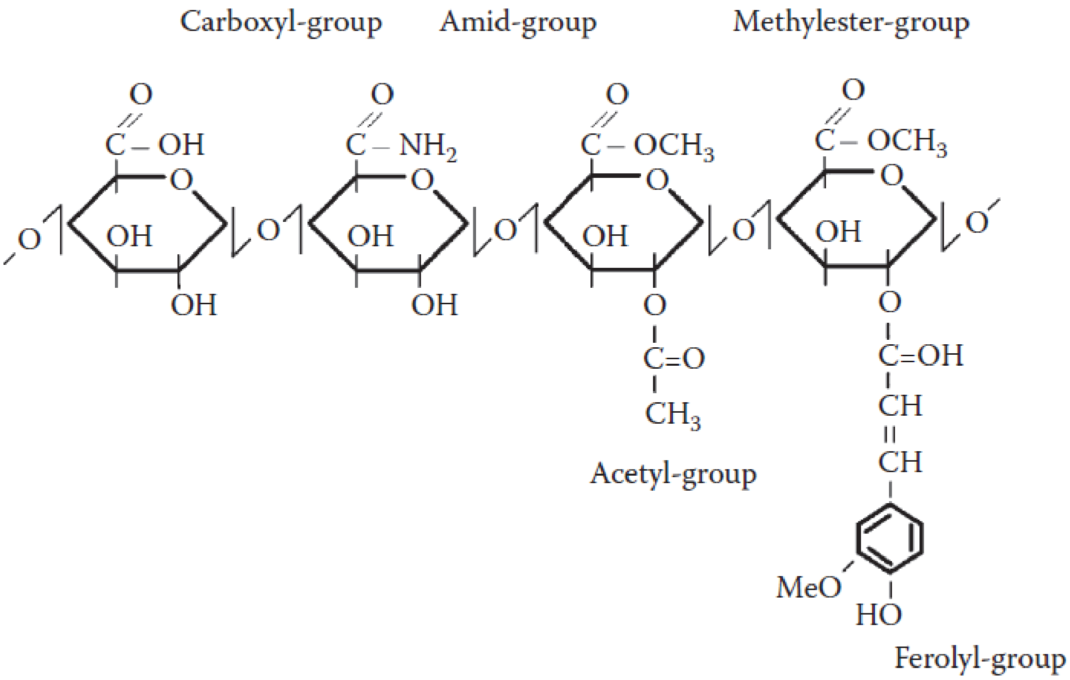

Figure 2.1 Chemical structure of pectin (Hans & Frank, 2009).

Depending on the pectin source and the extraction mode, the carboxyl groups of galacturonic acid units (the acid group may be free or naturally esterified are partly esterified by methanol) and, in certain pectins, are partially acetylated (May & Consultant, 2000 and Jordi *et al*., 2002).

Some of the carboxyl groups along with the galacturonic acid chain are esterified with methanol (Vaclavik & Christian, 2008). Each glycosidic linkage is a cross-planar bond, because it is formed by reaction of one hydroxyl group located above the plane of the first ring with another hydroxyl group located below the plane of the second ring (Steve *et al*., 2005; Sharma *et al.*, 2006; Vaclavik, & Christian, 2008). The chemical structure and composition of pectin is different from plant to plant, but as citrus, apple and, to a minor extent, sugar beet are the main commercial pectin sources (Sharma *et al.,* 2006). Though, pectins are derived from the breakdown of more complex protopectins which are present in the plant tissue, and also contain a range of neutral sugars, including rhamnose, galactose, arabinose and lesser amounts of other sugars such as glucuronic acid, L-fucose, D-glucose, D-mannose and D-xylose are sometimes found in side chains (Phillips & Williams, 2000 ; Jordi *et al*., 2002). Accordingly, these sugar units are present in a non-random structure, which consists of blocks of differing character retaining fragments of the original plant cell wall structure, pectin concentration in the middle lamella is estimated to be in the order of 10–30% and pectins form large numbers of both nonspecific entanglements and cross-links through Ca^2+, which lead to strong cohesiveness in the structure (Phillips & Williams, 2000; Jordi *et al*., 2002). It is known that pectins interact with other pectin molecules and cell components through covalent and non-covalent bonding including ionic bonding, hydrogen bonding, hydrophobic interactions and Van derWaals force forming various cross-linkages (Brejnholt, 2009). The use of purified enzymes has shown that pectin extracted under very mild conditions contains both linear blocks (smooth regions), consisting of homopolygalacturonic acid which are separated in the polymer by D-galactosyluronic-rich regions, and blocks of more highly substituted rhamnogalacturonan regions (hairy regions) which themselves contain several types of structures (Phillips & Williams, 2000; Sharma *et al.,* 2006). Commercial pectins are prepared mostly from some by-products of the food industry. Commercial pectins can also be amidated, as amidation improves the gelling ability of low methoxy pectins in that they need less calcium to gel and are less prone to precipitate at high calcium levels (Sharma *et al.,* 2006; Steve *et al*., 2005). In certain pectins, a proportion of the hydroxyl groups will also be acetylated (Phillips & Williams, 2000). It has been known from studies that the properties of pectin are dependent on pH, and on the percentage of acid group present in the form of ester (degree of esterification), indicating that among many factors that affect the yields and properties of pectin extracts, temperature and, in the case of low-DE pectin, the presence of chelating agents are the most important (Phillips & Williams, 2000; Sharma *et al.*, 2006).

2.2.2.3 Properties of pectin

The properties of the pectin substances are depending on the molecular weight and degree of substitution, for example water solubility, viscosity, coagulability, gelling tendency, and stability toward enzymes changes directly with increasing degree of esterification (Glicksman, 1969). Pectin is soluble in water, but not soluble in organic solvents because pectin has carboxylic acid groups, hence pectin is a polyelectrolyte (polyelectrolyte properties of pectins are briefly exposed) or a weak organic acid (Hans & Frank, 2009; Rinaudo, 1996). The viscosity of pectin solutions depends on several factors, including the degree of methylation of the pectin, concentration, temperature, pH, and presence of salts concentration and also its dependence on concentration, due to the polyelectrolytic nature of the biopolymer in displaying a peculiar behavior that differs considerably from neutral polysaccharides (Glicksman, 1969; Rao & Silva, 2006). Decreasing the concentration or the grade of pectin increases the viscosity and changing temperature decreases the viscosity in a similar manner (Glicksman, 1969). On the other hand, pectins are absence of external salt or at low ionic strength; pectin chains exist in an extended conformation because the strong intramolecular electrostatic repulsion and the solutions show the highest viscosity (Steve *et al.*, 2005).

The primary physicochemical property of pectin is its ability to gel and gel strength generally increases with increased molecular weight for High methoxyl (HM) and low methoxyl (LM) as pectins can form gel at concentration above 0.5 ~ 1% (Steve *et al.*, 2005; Brejnholt, 2009). HM and LM are high molecular weight and high polymer concentration favor gel formation and enhance gel strength (Steve *et al.*, 2005). Other intrinsic and extrinsic factor such as type and volume of co-solutes, pH, and the gelation mechanism of pectins is mainly governed by their degree of esterification (DE). There are also important factors affecting the gelation mechanisms of HM and LM pectin (Steve *et al.*, 2005; Sharma *et al.*, 2006). HM pectin gels in acidic conditions and in the presence of sugar and HM pectins form thermally irreversible gels at sufficiently low pH (pH <~ 3.6) and in the presence of sugars or other co-solutes at a concentration greater than ~50% by weight (Brejnholt, 2009; Steve *et al.*, 2005). However, Gelation of LM pectin is favoured by increased soluble solids, but decreased by increasing pH, or by increasing the level of sequestrant and lower concentration of sugar but requires the presence of cations which, when referring to food, is generally calcium (Brejnholt, 2009; May & Consultant, 2000).

Even when sufficient pectin and sugar are present in the system, gel will not form until the pH is reduced below the critical value of about pH 3.6. For most slow-setting pectins, optimum performance is at pH between 2.8 and 3.2, while rapid-setting pectins perform best in a range of 3.0-3.4 (Glicksman, 1969). Adding calcium to the product may give a firmer texture. Effects of calcium salts on pectin viscosity are very important (Glicksman, 1969; Brejnholt, 2009). By adding calcium ions, viscosity increases sharply as the degree of methylation decreases, thus freeing more carboxyls for cross-linking of the chains by calcium ions (Glicksman, 1969).

2.2.2.4 Applications and beneficial health effects of pectin

Pectin enjoys a unique position in its main market as it is generally used as gelling agents in various food applications including dairy, bakery, and fruit products, that of sale for use in jams, jellies, and preserves, and is almost free of competition from other gums (Rinaudo, 1996; Whistler, 1973). In place of confectionery products such as fruit-flavoured marshmallows, which have a soluble solids content of approximately 80%, HM pectin confers texture and stabilises the foam in the product. It has long been used in traditional jams and jellies, whereas low-calorie, low-sugar jams, and jellies cannot be made with HM pectins, and are usually best prepared with amidated LM pectins (Rinaudo, 1996; Brejnholt, 2009; May & Consultant, 2000). The type of pectin used should be matched to the product, and, in general, lower solids require the use of a ‘high reactivity’ or ‘fast setting’ LM pectin. (May & Consultant, 2000). Pectin gels can be used as an alternative to gelatin in fruit desserts and amidated LM pectins are used to prepare milk gels and desserts. Pectins are also used as a protein dispersion stabiliser in acidified dairy products such as yogurt and milk-based fruit drinks, and other protein drinks prepared from soya and whey (Rinaudo, 1996).

2.2.3 Carboxymethylcellulose (CMC)

2.2.3.1 General description of CMC

Generally carboxymethylcellulose (CMC) as its sodium salt is the most widely used cellulose ether (Melissa *et al.*, 2003). CMC is powder, light tan to white in colour, odorless, tasteless, free-flowing powder that is fairly hygroscopic (Cash & Caputo, 2009). Carboxymethylcellulose (CMC) or cellulose gum is a charged, water-soluble polysaccharide derived from alkali modified forms of cellulose found in plant, water-soluble CMC capable of forming very viscous solutions (Steve *et al.,* 2005; Vaclavik & Christian, 2008; Richey, 2006; Fennema, 1996). Since CMC is non-toxic and non-allergic, it has been used to increase the viscosity of foods, used as a binder, thickener or emulsifier in various products including ice creams and also used extensively in aqueous paper coatings for controlling coating viscosity (Richey, 2006; Vaclavik and Christian, 2008)

2.2.3.2 Composition of CMC

CMC is a cellulose derivative (long-chain polymers) with carboxymethyl groups (-CH2-COOH) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone (Fennema, 1996; Cash & Caputo, 2009). Chain length or degrees of polymerization (DP) of CMC are impact solubility and other solution characteristics (Cash & Caputo, 2009; Majewicz & Podlas, 2000). CMC solutions could be pseudoplastic or thixotropic, depending on its molecular weight DP and degree and pattern of substitution (Steve *et al.,* 2005). The average number of hydroxyl groups substituted per anhydroglucose unit is known as the degree of substitution (DS) (Majewicz & Podlas, 2000; Murray *et al.*, 2000). DS with the carboxyl groups is generally between 0.6 to 0.95 per monomeric unit for a maximum DS value of three, and occurs at O-2 and O-6, and occasionally at O-3 positions (Steve *et al.*, 2005; Majewicz and Podlas, 2000). Most commercial sodium carboxymethylcellulose (CMC) products have a DS in the range 0.4–0.8, in common applications. When used as a food ingredient, it has a DS of 0.7 (Fennema, 1996; Melissa *et al.*, 2003). The structure of CMC is depicted in Figure 2.2 CMC aids in redispersion, acts as a barrier to reassociation by giving the particles a stabilizing negative charge, consists of long, fairly rigid molecules that bear a negative charge due to numerous ionized carboxyl groups, electrostatic repulsion causes its molecules in solution to be extended (Fennema, 1996).

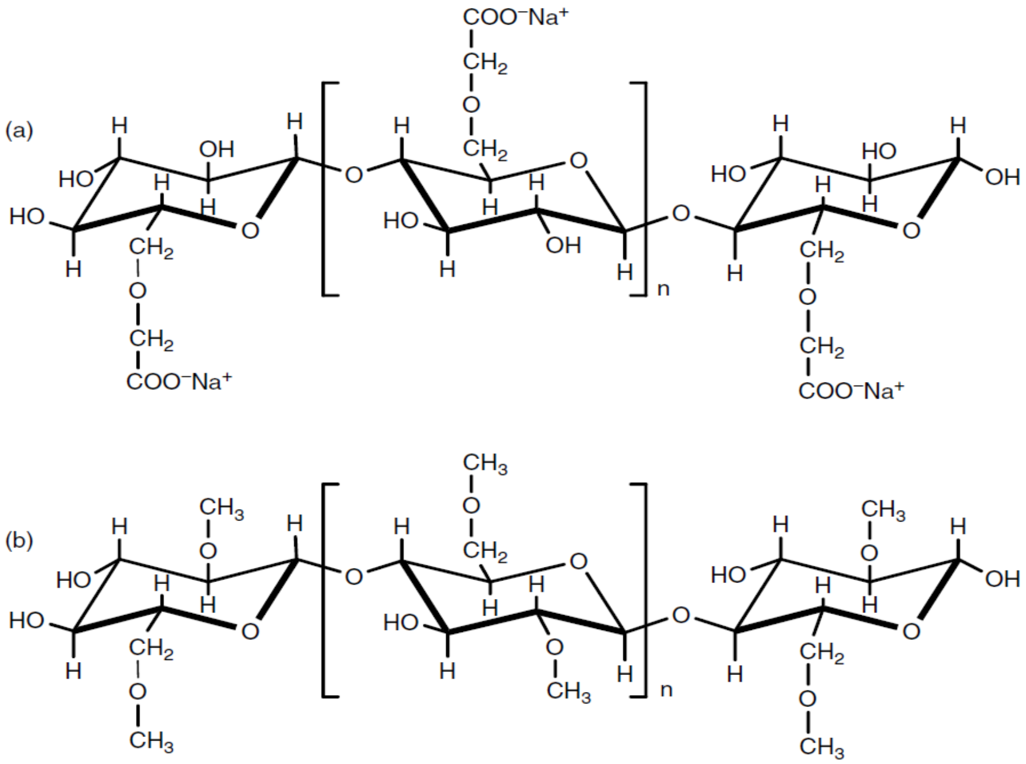

Figure 2.2 Structural features of chemically modified cellulose: (a) Carboxymethylcellulose (CMC); (b) Methylcellulose (MC) (Steve *et al.*, 2005).

2.2.3.3 Properties of CMC

CMC is highly water-soluble in water and gives a clear and colourless solution (Steve *et al.*, 2005). Cellulose gum with a longer chain length has a higher viscosity, solution viscosity depends on DP, but it is possible to produce 1% aqueous solutions with viscosity of 5,000 mPas at ambient temperatures (Cash & Caputo, 2009; Murray *et al.*, 2000). The rate of dissolution also increases with increasing substitution and decreasing molecular weight and viscosity but then small increases in molecular weight lead to large increases in viscosity (Majewicz & Podlas, 2000; Cash & Caputo, 2009). An extremely rapid viscosity development from as medium to high viscosity can exhibit pseudoplastic flow behaviour (Steve *et al.*, 2005; Murray, Limited, & Reigate, 2000). Solutions are viscosity stable at ambient temperature over a wide range of pH and gelling properties of CMC are influenced by polymer concentration, DP, pH type, and level of metal cations (Majewicz & Podlas, 2000; Steve *et al.*, 2005)

2.2.3.4 Applications and beneficial health effects of CMC

The viscosity production is the primary property of CMC, thus it is widely and extensively used as a food gum (Murray *et al.*, 2000; Fennema, 1996). CMC gives a more rapid viscosity than guar gum (Murray *et al.*, 2000). CMC is used in the food industry as a thickener, stabilizer, and suspending agent (Steve *et al.*, 2005). CMC is used in many food applications because it is completely nontoxic and its high hygroscopicity prevents foods from drying (Melissa *et al.*, 2003). CMC is most often used to provide the rapid build-up of viscosity (Murray *et al.*, 2000; Cash & Caputo, 2009). Hence, CMC has been used in many products and industries, instant products such as vending drinks and powdered drink mixes with fine grind (Murray