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Production and characterisation of resistant starch and its utilisation as food ingredient: a review

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REVIEW ARTICLE

Abstract

Starch is the storage carbohydrate in plants and also the largest source of carbohydrates in human food. Starch and starchy food products can be classified according to their digestibility as rapidly digestible starch, slowly digestible starch, and resistant starch (RS). Starch source, processing treatments, and chemical modification of starch are the main factors that influence the extent of starch digestion. RS has been defined as the sum of starch and starch degradation products not absorbed in the small intestine of healthy individuals by EURESTA (European Food-Linked Agro-Industrial Research-Concerted Action on Resistant Starch). There are four types of RS: physically inaccessible starch locked within cell walls (RS_1), native granular starch (RS_2), retrograded or crystalline starch (RS_3) and chemically modified starch (RS_4). The manufacture of RS involves acid/enzyme hydrolysis and hydrothermal treatments, retrogradation, extrusion and cross-linking. Extensive studies have shown that RS has physiological functions similar to those of dietary fibres such as protecting against colonic carcinogenesis and reducing the risk of diabetes, obesity, high cholesterol and other chronic diseases. RS offers an exciting new potential as a food ingredient since it is generally stable to heat treatments and survives in most food processes. The main use of RS has been as a functional ingredient in low-moisture food products particularly in bakery products such as bread and muffins, and in breakfast cereals.

Keywords: digestibility, functionality, physiological effects, resistant starch

1. Introduction

Starch is the principal carbohydrate found in nature and is the major source of carbohydrate in the human diet. Native starch occurs in the plastids of seeds, roots, tubers, and green plant leaves as partially crystalline granules. The major constituent of the starch granule is α-D-linked glucose, which occurs in two different polymeric forms; amylose and amylopectin. There are also limited amounts of phosphorus, lipids and proteins present in the granule. Starch granules differ with regard to size, shape, morphology and constituent composition, depending on their botanical origin, degree of maturity, weather and soil (BeMiller and Whistler, 2009; Eliasson and Gudmundsson, 1996).

Common starches normally consist of 20-25% amylose and 75-80% amylopectin, although there are natural mutants of maize, rice, sorghum and barley, which contain almost exclusively amylopectin (waxy starches) or high (55-70%) amylose (amylotype starches) (Buléon *et al.*, 1998; Chung *et al.*, 2003; Garcia-Alonso *et al.*, 1999; Shi *et al.*, 1998; Yoshimoto *et al.*, 2000).

Native starch granules are insoluble in cold water, due to their semi-crystalline structure. Heating of aqueous suspension of starch results in swelling of the granules, disruption of the crystalline parts and loss of birefringence. As the temperature increases, the granular order is destroyed and the viscosity increases with increasing swelling of the granules. This process is known as gelatinisation and is an important property of starch. After gelatinisation the polymer chains re-associate and return to a more ordered state which is called as retrogradation. Retrogradation results in gels or precipitates and is related to storage stability properties. The retrogradation of amylopectin is partially responsible for staling of bread (Eliasson and Gudmundsson, 1996).

There is general agreement among nutritionists and public health authorities that the insertion of fibres in the human diet provides health benefits. Many studies have found that people on diets high in fibre have reduced risks of certain diseases such as cancer, coronary heart disease, obesity and possibly diabetes (Telrandhe *et al.*, 2012). The commission of the European Communities defines 'fibre' as carbohydrate polymers with three or more monomeric units, which are neither digested nor absorbed in the small intestine (Fuentes-Zaragoza *et al.*, 2010). A fraction of starch was identified that could not be hydrolysed without prior chemical dispersion. This starch fraction, identified subsequently as retrograded starch, was termed resistant starch (RS; Englyst and Englyst, 2005). Thus, there are many components, such as resistant starches and the oligosaccharides, which, by their indigestible nature, could be considered to contribute to the total amount of dietary fibre in diet (Fuentes-Zaragoza *et al.*, 2010). Some recommendations have been made for general carbohydrate consumption by FAO and WHO. The acceptable macronutrient distribution range for carbohydrates is 55-75% of energy intake, and the adequate intake for total fibre is 25-38 g (WHO, 2003). These recommendations do not consider low digestible carbohydrates (LDC) consumption not recommend an upper limit for LDC intake based on potential gastrointestinal effects (Grabitske and Slavin, 2009).

Starch source, processing treatments, and chemical modification of starch are the main factors that influence the extent of starch digestion (Chung *et al.*, 2009). There are many studies in the literature on the digestibility of modified cereal and root starches. The effects of different treatments and modification techniques, such as pyrodextrinisation, heat-moisture treatments, cross-linking and acetylation, partial gelatinisation and retrogradation on slowly digestible starch (SDS) and RS formation in different starch sources have also been studied (Chung *et al.*, 2006; Han and BeMiller, 2007; Laurentín *et al.*, 2003; Wongsagonsup *et al.*, 2008). Guraya *et al.* (2001) reported a process for making SDS products by enzymatic modification of rice starch. The cooked normal and waxy rice starches were debranched with pullulanase, followed by heating and cooling. It was determined that, less debranching time and subsequent storage at 1 °C resulted in maximum SDS formation, while longer debranching time increased RS content. Güzel and Sayar (2010) investigated the effects of pyrodextrinisation, cross-linking with sodium trimetaphosphate (STMP), heat-moisture treatment, and gelatinisation-retrogradation processes on digestibility of borlotti bean, chickpea and white kidney bean starches. It was observed that, all modifications decreased the digestibility of cooked starches as compared with native starches. The highest decrease in digestibility was determined after gelatinisation-retrogradation treatment.

2. Definition and classification of resistant starch

In general, digestible starches are hydrolysed by the enzymes α-amylases, glucoamylase and sucrose-isomaltase in the small intestine to yield free glucose that is then absorbed (Nugent, 2005). However, not all starch in the diet is digested and absorbed in the small intestine (Ratnayake and Jackson, 2008).

Englyst *et al.* (1992), classified starch into rapidly digestible starch (RDS), SDS, and RS based on the rate of glucose released during starch hydrolysis by digestive enzymes. RDS consists mainly of amorphous and dispersed starch and is found in high amounts in starchy foods cooked by moist heat, such as bread and potatoes. SDS consists of physically inaccessible amorphous starch and raw starch with a type A and type C crystalline structure, such as cereals and type B starch, either in granule form or retrograded form in cooked foods (Sajilata *et al.*, 2006).

RDS is the starch fraction that causes a sudden increase in blood glucose level after ingestion. SDS is a starch fraction that is digested completely in the human small intestine, although more slowly than RDS. This behaviour is important for people with type II diabetes, who suffer from an inconsistent insulin response after consuming RDS (Englyst *et al.*, 1992).

EURESTA (European Food-Linked Agro-Industrial Research-Concerted Action on Resistant Starch) defined RS as the 'total amount of starch and the products of starch degradation that resists digestion in the small intestine of healthy individuals' (Jiang and Liu, 2002). The EURESTA definition describes RS in terms of its physiological functionality, rather than its physical or chemical characteristics. The resistance of starch to digestion is influenced by the nature of the association between starch polymers, with higher amylose levels in the starch being associated with slower digestibility rates (Brown, 2004). Retrograded starches refer to certain structural forms of RS. Retrogradation occurs when starch is cooked in water beyond its gelatinisation temperature and then cooled. In general, starches rich in amylose are naturally more resistant to digestion and also more susceptible to retrogradation (Nugent, 2005).

RS has been classified into four types (Englyst *et al.*, 1992; Sajilata *et al.*, 2006):

1. RS_1: starches which are physically inaccessible to digestion due to the presence of intact cell walls in grains, seeds or tubers.
2. RS_2: native starch granules that are protected from digestion by the conformation or structure of the starch granule as in raw potatoes, green bananas and high-amylose corn starch.
3. RS_3: starches mainly represented as retrograded amylose. This type is mainly present in cooked and subsequently cooled potato, in bread and in corn flakes.
4. RS_4: starches that have been chemically modified to decrease their digestibility, which include etherised, esterified or cross-linked starches.

RS_1 is heat stable in most normal cooking operations and enables its use as an ingredient in a wide variety of conventional foods. In raw starch granules, starch is tightly packed in a radial pattern and is relatively dehydrated. This compact structure limits the accessibility of digestive enzymes, various amylases, and accounts for the resistant nature of RS_2 such as, ungelatinised starch. RS_1 and RS_2 represent residues of starch forms, which are digested very slowly and incompletely in the small intestine.

RS_3 is mainly retrograded amylose formed during cooling of gelatinised starch, therefore most moist-heated foods contain some RS_3. Starch granules are disrupted by heating in an excess of water in a process known as gelatinisation, which renders the molecules fully accessible to digestive enzymes. Some sort of hydrated cooking operation is typical in the preparation of starchy foods for consumption, rendering the starch rapidly digestible (Haralampu, 2000). However, if these starch gels are then cooled, they form starch crystals that are resistant to digestion enzymes. This form of 'retrograded' starch is found in small quantities (approximately 5%) in foods such as cooked and cooled potatoes, as used in a potato salad (Fuentes-Zaragoza *et al.*, 2010). RS_3 represents the most resistant starch fraction and is entirely resistant to digestion by pancreatic amylases. RS_3 is of particular interest, because of its thermal stability. This allows it to be stable in most normal cooking operations, and enables its use as an ingredient in a wide variety of conventional foods (Haralampu, 2000).

Recently, Mermelstein (2009) reported that there is a fifth type of soluble polysaccharide called 'resistant maltodextrins'. They are derived from starch that is processed to purposefully rearrange starch molecules to render them soluble and resistant to digestion.

3. Physiological effects of resistant starch

Extensive studies have shown that resistant starches have physiological functions similar to those of dietary fibre (Bjorck *et al.*, 1986; Brown, 1996; Muir *et al.*, 1995; Raben *et al.*, 1994). RS is analysed as an insoluble dietary fibre but acts as soluble dietary fibre. It has been shown that the presence of RS in the colon might help to protect against colonic carcinogenesis. Some studies indicate that RS can reduce the risk of diabetes, obesity, high cholesterol and other chronic diseases associated with insulin resistance (Haralampu, 2000).

Fermentation of RS in the colon results in production of high concentration of short chain fatty acids, which has been related to lowering cancer risk. The short chain fatty acids, mainly acetate, propionate, and butyrate, stimulate colonic blood flow and fluid and electrolyte absorption. Butyrate is a preferred nutrient for colonocytes and, moreover, it inhibits the development of colonic cancer cells (Huth *et al.*, 2000; Wollowski *et al.*, 2001). Since RS almost entirely passes through the small intestine intact, it can act as a substrate for growth of the probiotic microorganisms (Wang *et al.*, 1999). Furthermore, RS containing food products have been shown to lower plasma cholesterol and blood lipids, and improve glucose tolerance (Charalampopoulos *et al.*, 2002; Niba and Hoffman, 2003; Voragen, 1998). Also RS was reported to enhance the absorption of a number of minerals in ileum in rats and humans (Lopez *et al.*, 2001; Younes *et al.*, 1995). The physiological properties of RS can vary widely depending on the study design and differences in the source, type and dose of RS consumed (Nugent, 2005).

Bird *et al.* (2006) determined that the incorporation (550 g/kg of starch) of Hi-maize (high amylose corn starch with high level RS) to the diet of rats for 7 days caused decreases in body weight and caecal pH, and increases in caecal weight and total short-chain fatty acids (SCFA) which are associated with the decreased incidence of colon cancer. Champ *et al.* (2003) also demonstrated a role for RS in the stimulation of bacteria able to produce butyric acid. There is evidence that butyrate may reduce the risk of malignant changes in cells.

Beards *et al.* (2010) examined the prebiotic potential of two different resistant starches, Nutriose FB 06 (indigestible dextrin produced by the hydrolysis of starch) and Actistar (modified food starch from tapioca). Significant increases in bifidobacteria have been observed in fermentation with Nutriose FB 06, but not those supplemented with the control and Actistar. According to SCFA analysis, acetate, propionate and butyrate contents were seen to be increased in fermentation with Nutriose FB 06. It was concluded that the differences between the behaviours of the resistant starches may be due to their different structures. Studies have shown that even thermally produced polymorphs of the same type of RS can have differing effects on the gut microbiota (Birkett *et al.*, 1996; Lesmes *et al.*, 2008).

Drzikova *et al.* (2005) produced an extrudate from oat meal and 20% of Novelose 330 (45.5% of RS_3, retrograded starch) addition. RS content of extrudate was found to be increased from 0.43 to 8.3% with the addition of Novelose 330. After simulated digestion, the digested extrudates were used to evaluate their physiological effects *in vitro*. A strong interaction was determined between the digested extrudates and bile acids. Also it was observed that during fermentation of digested extrudates, concentrations of SCFA and the molar proportion of butyrate increased.

Le Leu *et al.* (2009) investigated in rats the effects of feeding different forms of digestible corn starch as control and high amylose corn starches (Hylon VII, Hi-maize 1043, Hi-maize 240, Hi-maize 260 and Novelose 330) rich in RS. It was determined that the RS diets significantly increased SCFA and reduced pH in caecal content and faeces. Hi-maize 260 resulted in the highest butyrate concentrations. All RS diets prevented the mucosal atrophy as seen in the rats fed the control diet. It was concluded that the consumption of RS elicits a range of beneficial physiological and protective effects associated with the fermentation of RS.

4. Production of resistant starch

RS is found naturally in all starch-containing foods. However, there are many factors affect the amount of RS in food, such as the initial quantity and type of starch, how the food is processed, cooked and stored. Heat-processed foods can contain appreciable amounts of RS that can survive in incubation with amylolytic enzymes. RS formed during processing is mainly associated with amylose retrogradation (Brown, 1996).

The manufacture of RS involves acid or enzyme hydrolysis and hydrothermal treatments (annealing or heat-moisture treatments), extrusion and chemical modification (Brumovsky and Thompson, 2001; Gebhardt *et al.*, 2001; Köksel *et al.*, 2007, 2008a; Öztürk *et al.* 2009a,b,c, 2011; Wolf *et al.*, 1999; Woo and Seib, 2002). Heat treatments at high-moisture levels (>40% wet basis) have been termed annealing, and treatments performed at low-moisture levels (<35% wet basis) have been termed heat-moisture treatments (Jacobs and Delcour, 1998).

Starch has to be gelatinised to disrupt the granular structure and then retrograded for re-crystallisation of the starch molecules to form RS_3. Many factors, such as amylose content and chain length, autoclaving temperature, storing temperature and time may influence the crystallisation process and thus the formation of RS (Guraya *et al.*, 2001; Haralampu, 2000; Sajilata *et al.*, 2006). Retrogradation takes place very fast in linear amylose chain by means of hydrogen bonds. The branched structure of amylopectin inhibits its recrystallisation to some extent and it takes place over several days (Sajilata *et al.*, 2006). A higher content of amylose lowers the digestibility of starch due to positive correlation between amylose content and formation of RS (Berry, 1986; Sievert and Pomeranz, 1989; Tharanathan and Mahadevamma, 2003). However, high amylose starches require higher temperatures than normal starches to adequately gelatinise and require pressurised heating for complete cooking (Jeong and Lim, 2003).

High-crystalline starch can be obtained by acid hydrolysis of native starch in a heterogeneous system. Acid modified starches are produced by treating starch with an acid below gelatinisation temperature (Wang *et al.*, 2003). Acid hydrolysis changes the physicochemical properties of starch without destroying its granular structure. The acid preferentially attacks the amorphous regions, thus relative crystallinity increase in the starch granules (Hoseney, 1994; Atichokudomchai *et al.*, 2001). The retrogradation rate of acid-thinned starch gels was reported to increase with increasing hydrolysis. Acid-pretreated starch produced higher RS values than the native starch which might be attributed to increased rate of retrogradation in acid-hydrolysed starch (Wang *et al.*, 2003). Partial acid hydrolysis produces short linear chains enhancing the mobility of the molecules. The shorter linear chains appear to participate in the formation of resistant portions through rearrangement and recrystallisation of starch during autoclaving and cooling (Shin *et al.*, 2004).

Köksel *et al.* (2007) examined the effects of acid modification and heat treatments on RS formation of corn starch. Regular corn starch was acid hydrolysed with HCl at 40 °C for various periods of time (0.5-4.0 h). For RS formation, suspensions of native and acid hydrolysed starches were autoclaved at 121 °C for 30 min and stored at 95 °C for 2, 3, 4 days. The samples were dried at 50 °C in oven. It was found that the RS contents of the samples dried without storage increased from 8.1 to 13.9% as the hydrolisation degree increased. RS contents increased to 16.7% as a result of storage at 95 °C. For each storage period, the RS content increased as the hydrolisation degree increased up to 2.5 h. RS contents of the samples dried without storage were lower than those of the stored samples up to 3.5 h hydrolysis. In the samples prepared without storage, RS formation occurs only during drying. It was concluded that, there were two major factors affecting RS formation: the molecular size (hydrolysis time) and storage period after autoclaving. Molecular size influences RS formation by affecting the mobility of starch chains. For the stored samples, because of the availability of adequate time for RS formation, the molecular size of the samples plays the major role in RS formation. Optimum RS content was achieved at 2.5 h hydrolysis time and above this level the RS contents decreased due to excessive hydrolisation.

Effect of autoclaving cycles on RS content of acid modified corn starch was studied by Köksel *et al.* (2008b). Acid-modified corn starch samples were prepared at various hydrolysis levels (0.5-4.0 h) with HCl. For RS formation native and acid-modified starch samples were gelatinised and autoclaved for 1 or 2 cycles. While native and acid-modified starches did not contain any RS, the levels were found to increase to 13.5% as a result of storage at 95 °C after first autoclaving cycle. Second autoclaving cycle together with storage at 95 °C brought final RS contents of the samples incubated at 4 °C and 95 °C after the first cycle to comparable level.

Brumovsky and Thompson (2001) studied the production of RS by a hydrothermal treatment after partial acid hydrolysis of high amylose corn starch. Acid hydrolysis was done by incubating 35% (w/v) starch suspensions with 1% (w/w) HCl at 25 °C for 6, 30, and 78 h. Native and acid hydrolysed starches were then treated by annealing (ANN) or heat-moisture treatment (HMT). ANN was done at 70% moisture at 50, 60, or 70 °C for 24 h, and HMT was done at 30% moisture at 100, 120, or 140 °C for 80 min. After acid hydrolysis, either ANN or HMT tended to increase the yield of RS, with the greatest yield observed for HMT.

Öztürk *et al.* (2011) investigated the effects of acid hydrolysis, autoclaving-storing cycles and drying processes on RS contents of amylotype corn starches (Hylon V and Hylon VII). Starch samples were acid hydrolysed with HCl at 40 °C for 1, 2 and 3 h. Aqueous slurries (10%, w/w) of native and acid-modified starches were autoclaved at 135°C for 30 min and then they were stored at 4°C or 95°C for 24 h. The autoclaving-storing cycle was repeated for 3 times. The samples were oven-dried at 50 °C or freeze-dried. RS contents of the native forms of Hylon V and Hylon VII starch samples has been found as 43.0 and 53.0%, respectively. Hylon V and Hylon VII starch samples without heat treatment are in granular form and expected to include only RS2. It was determined that the RS contents of acid-hydrolysed samples did not differ from those of native starches, which might be due to low temperature applied during hydrolysis. Autoclaving-storing and drying processes induced RS3 formation. RS contents of oven-dried samples were higher than those of freeze-dried samples. The higher RS contents of oven-dried samples are probably due to retrogradation of starch during drying at 50 °C. Throughout the drying period in an oven, starch molecules may re-associate and form tightly packed structures which limit the accessibility by digestive enzymes. During freeze drying, in which the samples are dried in the frozen state, starch chains do not have mobility and cannot freely interact with each other to retrograde (Köksel *et al.*, 2008a). RS contents of the samples produced from Hylon VII were higher than those from counterpart Hylon V samples, as expected, due to the naturally higher amylose content of Hylon VII (Haralampu, 2000; Dimantov *et al.*, 2004).

Also the increased degree of debranching would give chains more opportunity to align and aggregate to form perfectly crystalline structures, thereby leading to the formation of more RS (Guraya *et al.*, 2001; Haralampu, 2000). Pullulanase (pullulan-6-glucanohydrolase, EC 3.2.1.41) and isoamylase (glycogen 6-glucanohydrolase, EC 3.2.1.68) are debranching enzymes that catalyse the hydrolysis of (1→6)-α-D-glucosidic linkages in the branching points in amylopectin (Richardson and Gorton, 2003). Berry (1986) reported that debranching of potato amylopectin with pullulanase before subjecting it to heating and cooling cycles substantially increased RS_3 content; this was attributed to an increase in linear starch chains resulting from debranching.

Öztürk *et al.* (2009a,b) investigated the effects of debranching, autoclaving-storing and drying processes on RS content in amylotype corn starches. High amylose corn starches (Hylon V and Hylon VII) were debranched with pullulanase (3-48 h) followed by autoclaving-storing cycles and drying in an oven (at 50 °C) or freeze-dryer. The samples were autoclaved at 123 or 133 °C and stored at 4 or 95 °C. The autoclaving-storing cycle was repeated up to 9 times. It was observed that the molecular weights of the samples decreased and RS contents increased with increased debranching time. Also, RS contents increased (up to 57.8%) with increasing autoclaving-storing cycles. RS contents of Hylon VII samples were found as higher than those of Hylon V samples. RS contents of oven-dried samples were higher than those of freeze-dried samples due to ongoing retrogradation of starch during oven drying at 50 °C.

In a research, the production of RS from non-conventional sources (unripe banana and mango) using an extruder was studied (González-Soto *et al.*, 2006). Commercial corn starch was also used for comparison. Amylose content was higher in banana and mango starches than in corn starch. The moisture content was adjusted to 35% and different screw rates (30, 40 and 65 rpm) were evaluated in extruder. Extruded products from mango presented a RS content that decreased when the screw speed increased. The RS content of the extruded product from banana starch at 40 rpm was found as the highest value (4.98%).

Shi *et al.* (2013) studied to produce RS from waxy corn starch was by pullulanase debranching and retrogradation at room temperature. The effects of debranching on structure and in-vitro digestibility of RS were also investigated. The resistance to digestibility of waxy corn starch with pullulanase treatment increased. The RS content raised up to 28% from 1.3% in native starch. It was also observed that the granular structure of native starch was destroyed by pullulanase debranching and retrogradation treatment and RS samples showed irregular shaped fragments. Crystal structure of samples changed from A type to a mixture of B and V type. Samples with higher RS showed higher relative crystallinity.

Chemical modification has also known to inhibit *in vitro* digestibility of starch (Wepner *et al.*, 1999). Cross-linking is applied to stabilise starch granule structure and to limit swelling properties. Increasing degree of cross-linking of starch inhibit the entrance of α-amylase into granules (Colonna *et al.*, 1992). Chemical modification of starch is performed by reaction with polyfunctional reagents such as STMP, phosphoryl chloride ($POCl_3$), and the mixed anhydride of acetic and adipic acid. Woo and Seib (2002) prepared RS samples by phosphorylation of wheat, waxy wheat, corn, waxy corn, high-amylose corn, oat, rice, tapioca, mung bean, banana, and potato starches with a 99:1 (w/w) mixture of STMP and sodium tripolyphosphate (STPP) at pH 10.5-12.3 and 25-70 °C for 0.5-24 h. They observed that, cross-linked RS_4 starch samples had 13-22% SDS and 36-66% RS. However after gelatinisation, RS levels decreased by 7-25% of ungelatinised levels, while SDS levels remained nearly the same.

5. Functional properties of resistant starch

Besides their nutritional value starches have been used for their functional properties. There are some studies investigating the swelling, solubility and water binding capacity values and emulsion properties (Herceg *et al.*, 2007; Taherian *et al.*, 2006) of various starches. Singh *et al.* (2005) found that pea starch had water binding capacity of 0.13-4.15 g/g and solubility of 12.5%. Aparicio-Saguilán *et al.* (2005) reported that solubility of native banana starch increased with increasing temperature. Autoclaved samples presented lower solubility than corresponding raw materials (native and lintnerised samples). Sandhu and Sing (2005) reported that solubility and water binding capacity values of starches from different maize lines were in the range of 15.3-22.4% and 77.6-88.5%, respectively. It was also reported that the acid modification increased solubility and gel strength and decreased viscosity of starches (Guraya *et al.*, 2001; Haralampu, 2000; Wang and Wang, 2001).

Proteins are commonly used as emulsion forming and stabilizing agents. On the other hand, starch cannot produce emulsion by itself, but might affect emulsion properties. Therefore, in the literature, the effects of starch preparations on the emulsifying properties of soy protein or albumin solutions were investigated (Köksel *et al.*, 2007, 2008a; Öztürk *et al.*, 2009a,b,c, 2011). It has been shown that specific interactions between proteins and polysaccharides may result in improved (Diftis and Kiosseoglou, 2003; Einhorn-Stoll *et al.*, 2005; Shepherd *et al.*, 2000) or may have negative influence (Schmitt *et al.*, 1998; Shim and Mulvaney, 2001) on emulsifying characteristics and rheological properties depending on type and amount of polysaccharides present.

The studies on functional properties of RS containing starches are limited. Köksel *et al.* (2007) investigated the acid modification, autoclaving and storage (95 °C for 2, 3, 4 days) on functional properties of corn starch. They observed that the rapid visco analyser (RVA) peak and final viscosity values of the samples decreased gradually with increasing hydrolisation level. In general, RVA viscosity values of the samples dried without storage were found as higher than those of the samples stored after autoclaving. Solubility and water binding values of autoclaved-stored samples were found as higher than those of the native and hydrolysed samples. The increase in water binding value was thought mainly due to the gelatinisation caused by autoclaving. As the hydrolysis time increased, water binding values of samples generally decreased. The native and acid hydrolysed samples affected the emulsion properties of soy protein inversely while the heat treated starches did not have a deteriorating effect on the emulsion capacity of the soy protein.

Köksel *et al.* (2008a) examined the effect of freeze drying on functional properties of acid hydrolysed and autoclaved (at 121 °C for 30 min) corn starch preparations with or without storage at 95 °C. Acid hydrolisation was performed with HCl at 40°C for 2, 3 and 4 h. It was observed that there were significant increases in solubility as the hydrolysis level of the lyophilised samples increased. All of the acid-hydrolysed and autoclaved-lyophilised samples were found had higher water binding values than those of native and heat treated oven-dried starch. Also, it was observed that the freeze drying improved emulsion properties of soy protein. Acid modification seemed to be a prerequisite to achieve improving effect of freeze drying. Pasting properties of the produced samples had been also examined. Cold viscosity was observed in the RVA curves of freeze dried samples produced by autoclaving of native and 2 h acid hydrolysed starch. A possible mechanism had been suggested to explain the lack or existence of a cold viscosity. Higher number of H-bonds in the oven-dried sample prevented water uptake and cold viscosity was not observed in this sample. The cold thickening ability of the freeze-dried samples could be due to the lower number of hydrogen bonds formed during lyophilisation. The cold-paste viscosity/cold thickening capacity is an important property in various food and industrial applications. It might influence the functional properties such as emulsion capacity and stability as well as foaming properties.

Basman *et al.* (2008) studied the effects of gum addition to pasting and emulsifying properties of RS preparation. The acid-hydrolysed corn starch sample was autoclaved and stored at 95 °C to obtain RS preparation. It was determined that the RS preparations had significantly lower peak and breakdown viscosities than hydrolysed starch. Gum addition (locust bean gum, 2.5 g gum/100 g starch) caused increases in all viscosity values. RS preparations with gum resulted in a cold thickening capacity. While native and hydrolysed starches had deteriorative effect on emulsion capacity and stability of soy protein, RS preparations (with or without gum) did not have a deteriorative effect.

Öztürk *et al.* (2009a,b) investigated the effects of debranching with pullulanase, autoclaving (123 or 133 °C), storing (4 or 95 °C) and drying (50 °C or freeze-dryer) processes on pasting (RVA) and functional properties (solubility, water binding, emulsion capacity and stability) of amylotype corn starches (Hylon V and Hylon VII). It was observed that the solubility and water binding values of the samples treated with autoclaving-storing cycles after debranching were higher than those of their respective native starches. Addition of native and autoclaved samples had improving effect on emulsion properties of albumin. However, debranching affected the emulsion capacity of albumin adversely, but improved the emulsion stability. Debranching and autoclaving-storing cycles caused decreases in peak, breakdown and final viscosity values in RVA analysis. Cold viscosity values of freeze-dried samples were found as higher than those of oven-dried samples might be due to higher number of H-bonds expected to be formed during oven drying. Öztürk *et al.* (2011) reported that the autoclaving-storing cycles after acid treatment enhanced the functional properties of high amylase corn starch samples (Hylon V and Hylon VII). Water binding and solubility values of hydrolysates were found as higher than those of respective native starches. Autoclaved-stored samples had higher water binding, solubility, emulsion capacity and emulsion stability values than those of respective acid-hydrolysed samples. The RVA viscosity values of the autoclaved-stored samples were found as higher than those of the hydrolysates.

Chung *et al.* (2010) examined the effect of γ-irradiation on pasting properties of cross-linked waxy corn resistant starches (RS_4). The cross-linked starches were found to be contained 56.1 and 63.5% of RS, respectively for 5 and 10% STMP/STPP cross-linking, and the RS contents decreased as their radiation dose increased. It was observed that, the RDS increased and the SDS decreased by the irradiation, for both native and cross-linked starches. The solubility of the native and cross-linked starches increased with increasing irradiation dose. It was determined the cross-linked starches did not swell in boiling water without showing pasting viscosity. However, the starches became swellable, forming pastes by irradiation. Woo and Seib (2002) determined the cross-linked RS_4 starch samples produced with a mixture of STMP and STPP had low swelling powers and solubility as compared to native forms. Also, the pasting curves of produced RS4 starches were observed not to rise above the baseline at 8% starch solids in a slurry.

Kahraman and Köksel (2013) examined the RS contents and functional properties of acid-modified high amylose corn starch subjected to two different heat treatments, HT1 (autuclaving-storing-drying) and HT2 (autoclaving-drying). It was found that the RS content increased by HT1 treatment as compared to HT2. Water absorption and solubility of the samples produced by both treatments were determined as higher than those of native and acid modified samples. Acid modified and heat treated samples were also found to improve emulsifying properties of soy protein.

6. Using of resistant starch as food ingredient

RS offers an exciting new potential as a food ingredient since it is generally stable to heat treatments and survives in most food processes. The main use of RS has been as a functional ingredient in low-moisture food products particularly in bakery products such as bread and muffins, and in breakfast cereals. RS offers a number of advantages over cellulosic sources of fibre such as bran. They are white in colour, have mild flavour and fine particle size and, in comparison to traditional fibres, have low water-holding capacity and minimal swelling due to their high melting temperatures (Sajilata *et al.*, 2006). Therefore, RS can be used as an ingredient with good sensorial and textural properties in final product. RS_3 has high thermal stability which allows it to be stable in normal cooking operations and enables its use as an ingredient in a wide variety of foods (Haralampu, 2000). A higher amount of RS in the daily diet is recommended due to its preventative and therapeutical health effects (Lehman *et al.*, 2003).

Aparicio-Saguilán *et al.* (2007) formulated cookies with a RS-rich powder (RSRP) prepared from autoclave-treated (at 121 °C for 1 h, 3 cycles) lintnerised banana starch. The RSRP was added to formula with ratio of 10, 15, 25 and 35% (in wheat flour basis). It was determined that, chemical composition of the cookies showed no difference in ash and lipid contents between control (100% wheat flour) and RSRP-cookies. The moisture content of the RSRP-cookie was higher and the protein content was lower compared with the control cookie. RSRP-cookies were found to have higher RS levels than control cookies. The hydrolysis index-based predicted glycemic index for the RSRP-cookies was found as 60.53, significantly lower than for control samples (77.62), suggesting a 'slowly digestible carbohydrate' feature for the RSRP-based goods. The effects of replacing wheat flour with RS on rheological properties of batters and baked muffins were studied in a research by Baixauli *et al.* (2008). RS (Hi-maize) was added to formula at the levels of 5, 10, 15 and 20% (by weight of total formulation). It was determined that the muffin volume and height and the number and area of gas cells decreased when the RS level reached about 15% or higher. The flow and linear viscoelastic properties of the batters indicated a decrease in the structure complexity with the increase in RS. The researchers suggested developing strategies, such as incorporating extra ingredients into formula, to increase baking performance in the presence of high levels of RS.

Basman *et al.* (2008) formulated low fat cookies using the acid modified corn starch and RS preparation with and without locust bean gum addition (2.5 g gum/100 g starch).

The acid-hydrolysed corn starch sample was autoclaved at 121 °C and stored at 95 °C for formation of RS preparation. It was determined that, 40% reduction of shortening caused significant decrease in spread ratios of control cookies with or without gum. However, utilisation of RS preparation with gum in low fat cookies caused increases in spread ratios. The hardness results indicated that the reduction in shortening increased the breaking strength of the cookies. Replacement of the reduced shortening by RS preparations caused a reduction in the hardness values of the cookies with or without gum addition. Using of starches with or without gum was determined not to change colour values of the cookies.

Basinci *et al.* (2008) investigated the utilisation of RS containing starch preparation as fat replacer in low fat cakes. Corn starch was acid modified with HCl for 2.5 h and acid-modified starch was autoclaved and stored at 95°C for 2 days to formation of RS preparation. The amount of shortening in cake formulation (AACC method no. 10-90; AACC, 2000) was reduced by 25, 37.5 and 50% and this was compensated by RS sample. It was determined that, the cakes had lighter crust colour, lower cake volume, volume index and symmetry index values, and harder crumb texture by reducing shortening. With the replacement of shortening by RS preparation, generally cakes had higher volume and symmetry index values, but harder texture and lighter colour values than the cakes prepared with lower shortening. This was thought to be due to high water holding capacity of the RS samples. The researchers also studied to produce low fat cakes with high RS content (Basinci *et al.*, 2009). For the production of low fat cakes, the shortening level was reduced by 50% and replaced by acid hydrolysed corn starch. Also, wheat flour in formula was replaced with commercial resistant starches (Hylon VII, CrystaLean, Novelose 330) at 15, 30 and 45% levels. To avoid unfavourable texture caused by high water holding capacity of the starches, 10 ml of extra water was added to the formula for each replacement level. It was observed that, the low fat cakes produced using acid hydrolysed starch had comparable volume, hardness, crumb colour and volume index values with the full fat cakes. Size distribution of cells of the cakes produced by using acid hydrolysed corn starch was found as more uniform than those of low fat cakes. Volume and hardness values of Hylon VII and CrystaLean supplemented cakes were not different from those of control cakes at 15% supplementation level. As the supplementation level increased, the cakes had significantly higher RS content and lighter crust colour for all starch samples. Uniformity of size distribution of gas cells was observed to disturbed at 45% RS addition level.

Öztürk *et al.* (2009c) investigated the effects of incorporation (1, 20 and 30%, flour basis) of commercial starches (Hylon VII, Novelose 330 and CrystaLean) on rheological and baking properties and also RS contents of breads. It was observed that the starch-supplemented doughs were weaker and absorbed more water than those of the base flour. Loaf volumes of the breads decreased above 10% level for Novelose and above 20% level for Hylon VII and CrystaLean supplementation. It was determined that the commercial starches did not have substantial deteriorative effect on crumb colour, external appearance and symmetry of breads. Crust colour values decreased at 30% addition level in Novelose- and CrystaLean-supplemented breads and above 10% addition level in Hylon VII-supplemented breads. Firmness of breads increased above 10% level for Novelose and above 20% level for Hylon VII and CrystaLean supplementation. RS contents of the breads increased significantly as the addition level of commercial starches increased.

Utilisation of Novelose 240 (N240, native RS) or Novelose 330 (N330, retrograded RS) in cheese to replace fat was studied by Montesinos-Herreroa *et al.* (2006). They have determined that, the hardness increased linearly with increasing starch content and was greater for N330 than for N240. Cohesiveness increased linearly with N240 content but was not influenced by N330. Over 50% of the fat content of cheese was replaced with resistant starches without impacting on melting ability. Korus *et al.* (2009) focused on partial replacement (10, 15 and 20%) of corn starch with tapioca (ActiStar, over 50% RS) and corn (Hi-Maize260, over 60% RS) RS preparations in gluten-free breads. It was found that the RS added breads had less hard crumb than bread without RS (control). The crumb hardness diminished with the increasing amount of RS preparation. Also it was observed that, RS influenced gelatinisation characteristics of gluten-free mixes. Their rising addition positively influenced gelatinisation temperature and decreased viscosity. It could be the reasons for lower hardness of bread, as compared to control. RS added breads contained more dietary fibre (the highest was 6.30 g/100 g) than control one. Sozer *et al.* (2007) investigated the using of RS in spaghetti production. RS type 3 (RS_3) was used to enrich spaghetti at 10% level. Also the bran added spaghetti was analysed and compared with control and RS added samples. The hardness and adhesiveness values of bran spaghetti were found as higher than the control and RS spaghetti. On the other hand hardness values of control and RS spaghetti were not different. They found the optimum cooking times as 12.5, 13, and 12 min for control, RS and bran containing samples, respectively. The water absorption of RS spaghetti was found as higher than control and bran spaghetti samples. Also while cooking, RS spaghetti found to gelatinise at a faster rate than bran and control spaghetti.

7. Conclusions

The goal of this review was to present a summary of the production and characterisation of RS and its utilisation as food ingredient. Intake of rapidly digestible carbohydrates undesirably enhances postprandial hyperglycaemia and may induce hypoglycaemic events. The rate of starch digestion determines the extent of glycaemic responses to dietary starches. Therefore, there has been much interest in carbohydrate ingredients such as slowly digestible and RS. Certain food processing methods, such as retorting, baking or drying at high temperatures, are known to slightly increase RS levels. RS contents of foods generally range between 0-4%. A higher amount of RS in the daily diet is recommended due to its preventative and therapeutical health effects. The potential physiological benefits of RS which is only degraded in the large bowel include the production of SCFA, a decrease in colonic pH, enhancement of faecal weight and output, alteration of intestinal bacterial activity, and reduction of secondary bile acid excretion. Due to its similar physiological properties, RS is generally considered as a constituent of dietary fibre. However, they are different from dietary fibres in that they are white in colour and exhibit no undesirable flavour. Increasing dietary fibre content in food products generally deteriorates the sensory and textural properties of foods. In contrast, it has been reported that RS provides better appearance, texture, and mouthfeel to food products than conventional fibres, demonstrating its potential as a food ingredient. Recently, RS has attracted interest as a 'low-carbohydrate' ingredient in food formulations mainly bakery products.

References

American Association of Cereal Chemists (AACC), 2000. Approved methods of the American Association of Cereal Chemists (10th Ed.). AACC, St. Paul, MN, USA.

Aparicio-Saguilán, A., Flores-Huicocheaa, E., Tovarb, J., García-Suáreza, F., Gutiérrez-Meraza, F. and Bello-Péreza, L.A., 2005. Resistant starch-rich powders prepared by autoclaving of native and lintnerized banana starch: partial characterization. Starch/Stärke 57: 405-412.

Aparicio-Saguilán, A., Sayago-Ayerdi, S.G., Vargas-Torres,A., Tovar, J., Ascencio-Otero, T.E. and Bello-Perez, L.A., 2007. Slowly digestible cookies prepared from resistant starch-rich lintnerized banana starch. Journal of Food Composition and Analysis 20: 175-181.

Atichokudomchai, N., Shobsngob, S., Chinachoti, P. and Varavinit, S., 2001. A study of some physicochemical properties of high-crystalline tapioca starch. Starch/Stärke 53: 577-581.

Baixauli, R., Sanz, T., Salvador, A. and Fiszman, S.M., 2008. Muffins with resistant starch: baking performance in relation to the rheological properties of the batter. Journal of Cereal Science 47: 502-509.

Basinci, F., Öztürk, S. and Köksel, H., 2009. Production of low fat cakes supplemented with enzyme resistant starch. 4th International Dietary Fiber Conference 2009. July 1-3, 2009. Vienna, Austria, pp. 133.

Basinci, F., Öztürk, S., Zencir, Y. and Köksel, H., 2008. Utilization of resistant starch preparations in reduced fat cakes. ICC International Conference Bosphorus 2008. April 24-26, 2008. Istanbul, Turkey, pp. 210.

Basman, A., Öztürk, S., Kahraman, K. and Köksel, H., 2008. Emulsion and pasting properties of resistant starch with locust bean gum and their utilization in low fat cookie formulations. International Journal of Food Properties 11: 762-772.

Beards, E., Tuohy, K. and Gibson, G., 2010. Bacterial, SCFA and gas profiles of a range of food ingredients following *in vitro* fermentation by human colonic microbiota. Anaerobe 16: 420-425.

BeMiller, J.N. and Whistler, J.N., 2009. Starch (3rd Ed.). Chemistry and technology. Academic Press, London, UK.

Berry, C.S., 1986. Resistant starch: formation and measurement of starch that survives exhaustive digestion with amylolytic enzymes during the determination of dietary fibre. Journal of Cereal Science 4: 301-304.

Bird, A.R., Brown, I.L. and Topping, D.L., 2006. Low and high amylose maize starches acetylated by a commercial or a laboratory process both deliver acetate to the large bowel of rats. Food Hydrocolloids 20: 1135-1140.

Birkett, A., Muir, J., Phillips, J., Jones, G. and O'Dea, K., 1996. Resistant starch lowers faecal concentrations of ammonia and phenols in humans. American Journal of Clinical Nutrition 63: 766-772.

Bjorck, I., Nyman, M., Pedersen, B., Siljestrom, M., Asp, N.G. and Eggum, B.O., 1986. On the digestibility of starch in wheat bread–studies *in vitro* and *in vivo*. Journal of Cereal Science 4: 1-11.

Brown, I., 1996. Complex carbohydrates and resistant starch. Nutritional Reviews 54: 115-119.

Brown, I.L., 2004. Applications and uses of resistant starch. Journal of the Association of Official Analytical Chemists International 87: 727-732.

Brumovsky, J.O. and Thompson, D.B., 2001. Production of boiling-stable type II resistant starch by partial acid hydrolysis and hydrothermal treatments of high-amylose maize starch. Cereal Chemistry 78: 680-689.

Buléon, A., Colonna, P., Planchot, V. and Ball, S., 1998. Starch granules: structure and biosynthesis. International Journal of Biological Macromolecules 23: 85-112.

Champ, M., Langkilde, A.M. and Brovns, F., 2003. Advances in dietary fiber characterization. 1. Definition of dietary fiber, physiological relevance, health benefits and analytical benefits. Nutrition Research Reviews 16: 71-82.

Charalampopoulos, D., Wang, R., Pandiella, S.S. and Webb, C., 2002. Application of cereals and cereal components in functional foods: a review. International Journal of Food Microbiology 79: 131-141.

Chung, H.J., Jeong, H.Y. and Lim, S.T., 2003. Effects of acid hydrolysis and defatting on crystallinity and pasting properties of freeze-thawed high amylose corn starch. Carbohydrate Polymers 54: 449-455.

Chung, H.J., Lee, S.Y., Kim, J.H., Lee, J.W., Byun, M.W. and Lim, S.T., 2010. Pasting characteristics and *in vitro* digestibility of γ-irradiated RS4 waxy maize starches. Journal of Cereal Science 52: 53-58.

Chung, H.J., Lim, H.S. and Lim, S.T., 2006. Effect of partial gelatinization and retrogradation on the enzymatic digestion of waxy rice starch. Journal of Cereal Science 43: 353-359.

Chung, H.J., Liu, Q. and Hoover, R., 2009. The impact of annealing and heat-moisture treatments on rapidly digestible, slowly digestible and resistant starch levels in native and gelatinized corn, pea and lentil starches. Carbohydrate Polymers 75: 436-447.

Colonna, P., Leloup, V. and Buleon, A., 1992. Limiting factors in starch hydrolysis. American Journal of Clinical Nutrition 46: 517-532.

Diftis, N. and Kiosseoglou, V., 2003. Improvement of emulsifying properties of soybean protein isolate by conjugation with carboxymethyl cellulose. Food Chemistry 81: 1-6.

Dimantov, A., Greenberg, M., Kesselman, E. and Shimoni, E., 2004. Study of high amylose corn starch as food grade enteric coating in a microcapsule model system. Innovative Food Science and Emerging Technologies 5: 93-100.

Drzikova, B., Dongowski, G., Gebhardt, E. and Habel, A., 2005. The composition of dietary fibre-rich extrudates from oat affects bile acid binding and fermentation *in vitro*. Food Chemistry 90: 181-192.

Einhorn-Stoll, U., Ulbrich, M., Sever, S. and Kunzek, H., 2005. Formation of milk protein-pectin conjugates with improved emulsifying properties by controlled dry heating. Food Hydrocolloids 19: 329-340.

Eliasson, A.C and Gudmundsson, M., 1996. Starch: physiochemical and functional aspects. In: Eliasson, A.C. (ed.) Carbohydrates in food. Marcel Dekker, New York, NY, USA, pp. 431-504.

Englyst, H.N., Kingman, S.M. and Cummings, J.H., 1992. Classification and measurement of nutritionally important starch fractions. European Journal of Clinical Nutrition 46: 33-50.

Englyst, K.N. and Englyst, H.N., 2005. Carbohydrate bioavailability. British Journal of Nutrition 94: 1-11.

Fuentes-Zaragoza, E., Riquelme-Navarrete, M.J., Sánchez-Zapata, E. and Pérez-Álvarez, J.A., 2010. Resistant starch as functional ingredient: a review. Food Research International 43: 931-942.

Garcia-Alonso, A., Jimenez-Escrig, A., Martin-Carron, N., Bravoa, L. and Saura-Calixto, F., 1999. Assessment of some parameters involved in the gelatinization and retrogration of starch. Food Chemistry 66: 181-187.

Gebhardt, E., Dongowski, G. and Huth, M., 2001. Resistant starch – a component in bifunctional high fibre extrudates. Ernaehrung 25: 202-208.

González-Soto, R.A., Sánchez-Hernández, L., Solorza-Feria, J., Núñez-Santiago, C., Flores-Huicochea, E. and Bello-Pérez, L.A., 2006. Resistant starch production from non-conventional starch sources by extrusion. Food Science and Technology International 12: 5-11.

Grabitske, H.A. and Slavin, J.L., 2009. Gastrointestinal effects of low-digestible carbohydrates. Critical Reviews in Food Science and Nutrition 49: 327-360.

Guraya, H.S., James, C. and Champagne, E.T., 2001. Effect of enzyme concentration and storage temperature on the formation of slowly digestible starch from cooked debranched rice starch. Starch/Stärke 53: 131-139.

Güzel, D. and Sayar, S., 2010. Digestion profiles and some physicochemical properties of native and modified borlotti bean, chickpea and white kidney bean starches. Food Research International 43: 2132-2137.

Han, J. and BeMiller, J.N., 2007. Preparation and physical characteristics of slowly digesting modified food starches. Carbohydrate Polymers 67: 366-374.

Haralampu, S.G., 2000. Resistant starch – a review of the physical properties and biological impact of RS_3. Carbohydrate Polymers 41: 285-292.

Herceg, Z., Režek, A., Lelas, V., Krešić, G. and Franetović, M. 2007. Effect of carbohydrates on the emulsifying, foaming and freezing properties of whey protein suspensions. Journal of Food Engineering 79: 279-286.

Hoseney, R.C., 1994. Principles of cereal science and technology. AACC Inc., St. Paul, MN, USA.

Huth, M., Dongowski, G., Gebhardt, E. and Flamme, W., 2000. Functional properties of dietary fibre enriched extrudates from barley. Journal of Cereal Science 32: 115-128.

Jacobs, H. and Delcour, J., 1998. Hydrothermal modifications of granular starch, with retention of granular structure: a review. Journal of Agricultural and Food Chemistry 46: 2895-2905.

Jeong, H.Y. and Lim, S.T., 2003. Crystallinity and pasting properties of freeze-thawed high amylose maize starch. Starch/Stärke 55: 511-517.

Jiang, G. and Liu, Q., 2002. Characterization of residues from partially hydrolyzed potato and high amylose corn starches by pancreatic α-amylase. Starch/Stärke 54: 527-533.

Kahraman, K. and Köksel, H., 2013. Formation of resistant starch from amylotype corn starch and determination of the functional properties. Quality Assurance and Safety of Crops & Foods 5: 295-302.

Köksel, H., Basman, A., Kahraman, K. and Öztürk, S., 2007. Effect of acid modification and heat treatments on resistant starch formation and functional properties of corn starch. International Journal of Food Properties 10: 691-702.

Köksel, H., Masatcıoglu, T., Kahraman, K., Öztürk, S. and Basman, A., 2008a. Improving effect of lyophilization on functional properties of resistant starch preparations formed by acid hydrolysis and heat treatment. Journal of Cereal Science 47: 275-282.

Köksel, H., Öztürk, S., Kahraman, K., Basman, A., Ozboy Ozbas, O. and Ryu, G.H., 2008b. Evaluation of molecular weight distribution, pasting and functional properties and enzyme resistant starch content of acid modified corn starches. Food Science and Biotechnology 17: 755-760.

Korus, J., Witczak, M., Ziobro, R. and Juszczak, L., 2009. The impact of resistant starch on characteristics of gluten-free dough and bread. Food Hydrocolloids 23: 988-995.

Laurentín, A., Cárdenas, M., Ruales, J., Pérez, E. and Tovar, J., 2003. Preparation of indigestible pyrodextrins from different starch sources. Journal of Agricultural and Food Chemistry 51: 5510-5515.

Le Leu, R.K., Hu, Y., Brown, I.L. and Young, G.P., 2009. Effect of high amylose maize starches on colonic fermentation and apoptotic response to DNA-damage in the colon of rats. Nutrition & Metabolism 6: 11-19.

Lehmann, U., Rössler, C., Schmiedl, D. and Jacobasch, G., 2003. Production and physicochemical characterization of resistant starch type III derived from pea starch. Nahrung/Food 47: 60-63.

Lesmes, U., Beards, E., Gibson, G.R., Tuohy, K.M. and Shimoni, E., 2008. Effects of resistant starch type III polymorphs on human colon microbiota and short chain fatty acids in human gut models. Journal of Agricultural and Food Chemistry 56: 5415-5421.

Lopez, H.W., Levrat-Verny, M.A., Coudray, C., Besson, C., Krespine, V., Messager, A., Demigné, C. and Rémésy, C., 2001. Class 2 resistant starches lower plasma and liver lipids and improve mineral retention in rats. Journal of Nutrition 131: 1283-1289.

Mermelstein, N.H., 2009. Analyzing for resistant starch. Food Technology 4: 80-84.

Montesinos-Herrero, C., Cottell, D.C., O'Riordan, E.D. and O'Sullivan, M., 2006. Partial replacement of fat by functional fibre in imitation cheese: effects on rheology and microstructure. International Dairy Journal 16: 910-919.

Muir, J.G., Lu, Z.X., Young, G.P., Cameron-Smith, D., Collier, G.R. and O'Dea, K., 1995. Resistant starch in the diet increases breath hydrogen and serum acetate in human subjects. American Journal of Clinical Nutrition 61: 792-799.

Niba, L.L. and Hoffman, J., 2003. Resistant starch and β-glucan levels in grain sorghum (*Sorghum bicolor* M.) are influenced by soaking and autoclaving. Food Chemistry 81: 113-118.

Nugent, A.P., 2005. Health properties of resistant starch. Nutrition Bulletin 30: 27-54.

Öztürk, S., Köksel, H., Kahraman, K. and Ng, P.K.W., 2009a. Effect of debranching and heat treatments on formation and functional properties of resistant starch from high amylose corn starches. European Food Research and Technology 229: 115-125.

Öztürk, S., Köksel, H. and Ng, P.K.W., 2009b. Characterization of resistant starch samples prepared from two high-amylose maize starches through debranching and heat treatments. Cereal Chemistry 86: 503-510.

Öztürk, S., Köksel, H. and Ng, P.K.W., 2009c. Farinograph properties and bread quality of flours supplemented with resistant starch. International Journal of Food Science and Nutrition 60: 449-457.

Öztürk, S., Köksel, H. and Ng, P.K.W., 2011. Production of resistant starch from acid-modified amylotype starches with enhanced functional properties. Journal of Food Engineering 103: 156-164.

Raben, A., Tagliabue, A., Christensen, N.J., Madsen, J., Holst, J.J. and Astrup, A., 1994. Resistant starch: The effect of post-prandial glycemia, hormonal response and satiety. American Journal of Clinical Nutrition 60: 544-551.

Ratnayake, W.S. and Jackson, D.S., 2008. Thermal behavior of resistant starches RS2, RS3, and RS4. Journal of Food Science 73: 356-366.

Richardson, S. and Gorton, L., 2003. Characterisation of the substituent distribution in starch and cellulose derivatives. Analytica Chimica Acta 497: 27-65.

Sajilata, M.G., Singhal, R.S. and Kulkarni, P.R., 2006. Resistant starch – a review. Comprehensive Reviews in Food Science and Food Safety 5: 1-17.

Sandhu, K.S. and Singh, N., 2005. Relationships between selected properties of starches from different corn lines. International Journal of Food Properties 8: 481-491.

Schmitt, C., Janchez, C., Desobry Banon, J. and Hardy, J., 1998. Structure and technofunctional properties of protein-polysaccharide complexes: a review. Critical Reviews in Food Science and Nutrition 38: 689-753.

Shepherd, R., Robertson, A. and Ofman, D., 2000. Dairy glycoconjugate emulsifiers: casein-maltodextrines. Food Hydrocolloids 14: 281-286.

Shi, M., Chen, Y., Yu, S. and Gao, Q., 2013. Preparation and properties of RS III from waxy maize starch with pullulanase. Food Hydrocolloids 33: 19-25.

Shi, Y.C., Capitani, T., Trzasko, P. and Jeffcoat, R., 1998. Molecular structure of a low-amylopectin starch and other high-amylose maize starches. Journal of Cereal Science 27: 289-299.

Shim, J. and Mulvaney, S.J., 2001. Effect of heating temperature, pH, concentration and starch/whey protein ratio on the viscoelastic properties of corn starch/whey protein mixed gels. Journal of the Science of Food and Agriculture 81: 706-717.

Shin, S., Byun, J., Park, K.H. and Moon, T.W., 2004. Effect of partial acid hydrolysis and heat-moisture treatment on formation of resistant tuber starch. Cereal Chemistry 81: 194-198.

Sievert, D. and Pomeranz, Y., 1989. Enzyme-resistant starch. I. Characterization and evaluation by enzymatic, thermoanalytical and microscopic methods. Cereal Chemistry 66: 342-347.

Singh, B., Nagi, H.P.S., Sekhon, K.S. and Singh, N., 2005. Studies on the functional characteristics of flour/starch from wrinkled peas (*Pisum sativum*). International Journal of Food Properties 8: 35-48.

Sozer, N., Dalgıc, A.C. and Kaya, A., 2007. Thermal, textural and cooking properties of spaghetti enriched with resistant starch. Journal of Food Engineering 81: 476-484.

Taherian, A.R., Fustier, P. and Ramaswamy, H.S., 2006. Effect of added oil and modified starch on rheological properties, droplet size distribution, opacity and stability of beverage cloud emulsions. Journal of Food Engineering 77: 687-696.

Telrandhe, U.B., Kurmi, R., Uplanchiwar, V., Mansoori, M.H., Raj, V.J. and Jain, K., 2012. Nutraceuticals-A phenomenal resource in modern medicine. International Journal of Universal Pharmacy and Life Sciences 2: 179-195.

Tharanathan, R.N. and Mahadevamma, S., 2003. Grain legumes-a boon to human nutrition. Trends in Food Science and Technology 14: 507-518.

Voragen, A.G.J., 1998. Technological aspects of functional food-related carbohydrates. Trends in Food Science and Technology 9: 328-335.

Wang, X., Conway, P.L., Brown, I.L. and Evans, A.J., 1999. The protective effects of high amylose maize (amylomaize) starch granules on the survival of *Bifidobacterium* spp. in the mouse intestinal tract. Journal of Applied Microbiology 87: 631-639.

Wang, Y.J., Truong, V.D. and Wang, L., 2003. Structures and rheological properties of corn starch as affected by acid hydrolysis. Carbohydrate Polymers 52: 327-333.

Wang, Y.J. and Wang, L., 2001. Structures and physicochemical properties of acid-thinned corn, potato and rice starches. Starch/Stärke 53: 570-576.

Wepner, B., Berghoper, E., Miesenberger, E., Tiefenbacher, K. and Ng, P.N.K., 1999. Citrate starch– Application as resistant starch in different food systems. Starch/Stärke 51: 354-361.

Wolf, B.W., Bauer, L.L. and Fahey, Jr., G.C., 1999. Effects of chemical modification on *in vitro* rate and extent of food starch digestion: an attempt to discover slowly digested starch. Journal of Agricultural and Food Chemistry 47: 4178-4183.

Wollowski, I., Rechkemmer, G. and Pool-Zobel, B.L., 2001. Protective role of probiotics and prebiotics in colon cancer. American Journal of Clinical Nutrition 73: 451-455.

Wongsagonsup, R., Varavinit, S. and BeMiller, J.N., 2008. Increasing slowly digestible starch content of normal and waxy maize starches and properties of starch products. Cereal Chemistry 85: 738-745.

Woo, K.S. and Seib, P.A., 2002. Cross-linked resistant starch: preparation and properties. Cereal Chemistry 79: 819-825.

World Health Organization (WHO), 2003. Diet, nutrition and the prevention of chronic diseases. WHO Technical Report Series 916.

Yoshimoto, Y., Tashiro, J., Takenouchi, T. and Tekeda, Y., 2000, Molecular structure and some physicochemical properties of high-amylose barley starches. Cereal Chemistry 77: 279-285.

Younes, H., Levrat, M.A., Demigne, C. and Remesy, C., 1995. Resistant starch is more effective than cholestyramine as a lipid-lowering agent in the rat. Lipids 30: 847-853.