13

Thermoplastic Extrusion in Food Processing

Caroline Joy Steel, Maria Gabriela Vernaza Leoro, Marcio Schmiele, Reinaldo Eduardo Ferreira and Yoon Kil Chang
University of Campinas
Brazil

1. Introduction

Extrusion cooking was first introduced in food and feed processing in the late 1950s. Since then, the systems involved have grown in popularity, efficiency and flexibility. Extrusion cooking technology is most used for cereal and protein processing in the food industry and is closely related to the pet food and feed sectors. In the last decade, the development of extruders has evolved to yield sophisticated products, new flavour generation, encapsulation and sterilisation.

Thermoplastic extrusion is considered a HTST (High-Temperature, Short-Time) process in the food industry, and it permits, with little or no modification of the basic equipments and appropriate process control, the production of a great variety of food and feed products (Camire et al., 1990; Chang et al., 2001; El-Dash, 1981). This technique has been widely used with raw materials such as corn, wheat, rice and, especially in recent years, with soy (Chang et al., 2001; Kadan & Pepperman, 2002).

Depending on the raw materials and of the characteristics desired for the final product, extruders operate with low, medium or high shear; however, thermoplastic extruders are used for high shear. As examples, pasta and processed meat products are produced with low shear (cold extrusion); meat analogues and some pet foods are produced with medium shear; and expanded snack products, breakfast cereals and textured vegetable proteins are produced with high shear (thermoplastic extrusion).

For Fellows (2000), the two main factors that influence the characteristics of extruded products are: raw material characteristics and operational conditions of the extruder. As main characteristics of the raw material, the following can be highlighted: type of material, moisture content, physical state, chemical composition (quantity and type of starch, proteins, fats and sugars) and pH of the material. The operational parameters that can be pointed out as important are: temperature, pressure, die diameter and shear force, with the latter being influenced by the internal design of the extruder and by its length; as well as screw geometry and rotation speed.

Guy (2001) and Stanley (1986) relate the following advantages to the thermoplastic extrusion process: versatility, low costs, high production yields, good quality products and no effluents.

2. Equipments

The use of thermoplastic extrusion in food processing is facilitated by the dynamism of extruders, which can be divided into two types: single-screw and twin-screw extruders (Riaz, 2000).

Extruders are composed of five main parts: (i) the pre-conditioning system; (ii) the feeding system; (iii) the screw or worm; (iv) the barrel; (v) the die and the cutting mechanism (El-Dash, 1981), which can be seen in Figure 1. Also, they can vary with respect to screw, barrel and die configuration. The selection of each of these items will depend on the raw material used and the final product desired (Riaz, 2000).

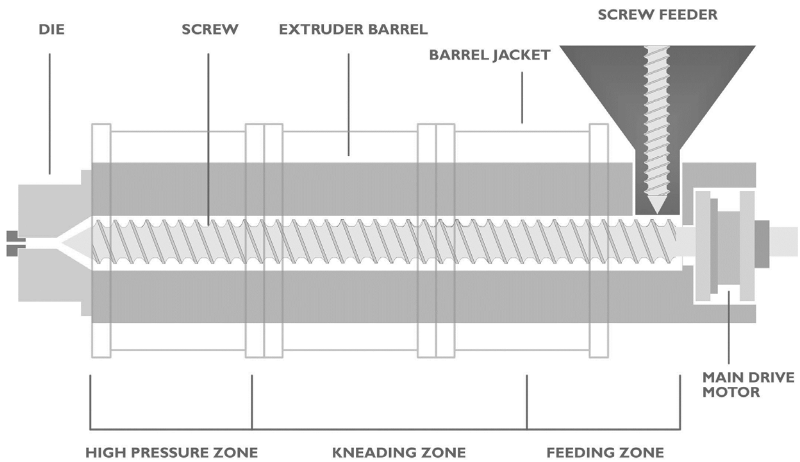


Fig. 1. Schematic representation of an extruder including its main parts and zones

In the extrusion process, the dry or pre-conditioned material (generally between 15 and 30% moisture content) is fed to the extruder through a screw feeder, reaching the feeding zone. The screw in this zone presents greater depth and pitch of the worm flight, and has as main function the transportation and homogenizing of the raw material. The material is conducted from the feeding zone to the compression zone. In the compression zone, there is a reduction in screw depth and pitch, with a consequent increase in shear rate, temperature (110 - 180ºC) and pressure (20 – 30 atm). In this zone, the conversion from a solid material to a fluid melt starts to occur. In the subsequent high pressure zone, the screw has its depth and pitch reduced even more, resulting in higher shear and maximum heat generation. Thus, the extruded mass reaches maximum temperature and pressure and a reduction in viscosity immediately before exiting the extruder (Fellows, 2000; Riaz, 2000). The material, under high pressure, is expelled through the die and, in contact with ambient pressure, expands to its final format and cools rapidly through water flash-off (Fellow, 2000). In material that is not previously conditioned, water is added, in liquid or vapour form, during the process (El-Dash, 1981). The product that leaves the extruder is generally submitted to a drying process, reaching values close to 3% moisture content, as is the case of extruded snacks (Riaz, 2000).

2.1 Pre-conditioning

Pre-conditioning with steam or water has always been an important part of the extrusion process. Recent research has shown that efficient throughput of the extruder is almost doubled if the starting material is pre-conditioned with steam or water (Guy, 2001). There are many applications of extruded cooked food products where pre-conditioning plays a key role in the overall extrusion process. These products include direct expanded and flaked breakfast cereals, pre-cooked pasta, textured vegetable proteins, meat analogues, extruded bread crumbs, and third-generation snacks.

Pre-conditioning is not applied to all extrusion processes. In general, this step is applied when moisture contents around 20 to 30% and long residence times of the material are used. Pre-conditioning favours uniform particle hydration, reduces retention times within the extruder and increases throughput, increasing the life of the equipment, due to a reduction in the wearing of barrel and screw components, also reducing the costs of energy involved in the process (Huber & Rokey, 1990). Depending on screw configuration, the residence time of the material inside the extruder can vary from 5 seconds to more than 2 minutes, with the average residence time of the material in the pre-conditioner being 3 minutes. Pre-conditioning occurs with the addition of hot water (80-90°C) or steam, through spray nozzles, with the use of steam reducing energy consumption of the equipment up to 60% during the process. The most commonly used pre-conditioners have 2 axis of different diameters and rotation speeds, guaranteeing a residence time between 2 to 4 minutes and a production capacity between 300 and 18,000 $kg.h^{-1}$. When it is necessary to add melted fats or oils during pre-conditioning, it is best to do it at the end of the equipment, because if addition is done at the beginning, a coating may be formed over the particles, making water penetration more difficult. The main aim of pre-conditioning is to uniformly hydrate the raw material in order to eliminate any dry core (Strahm, 2000).

2.2 Feeding system

Most raw materials used in food extrusion are solid. The feeding system is normally composed of a holding bin where the material is loaded and the discharge of the material can occur through a vertical feeding screw, a horizontal feeding screw, a horizontal vibrating trough system, a disk feeder or a volumetric belt feeder. It is necessary to guarantee a constant and non-interrupted feeding of the raw materials into the extruder for an efficient and uniform functioning of the extrusion process (El-Dash, 1981). When liquids are added, they can be dosed using a rotameter, orifice and Venturi meters, positive displacement meter, magnetic flow meter or metering pumps (Chessari & Sellahewa, 2000).

2.3 Screw

The screw of the extruder is certainly its most important component, not only to determine cooking degree, gelatinization and dextrinization of starch and protein denaturation, but also to ensure final product quality. Screws can be mono-piece (composed of a unique piece) or multi-piece (composed of various elements) (El-Dash, 1981). Screw elements can vary in number and shapes, each segment is designed for a specific purpose. Some elements only convey raw or pre-conditioned material into the extruder barrel, while other segments compress and degas the feedstock. Others must promote kneading, backflow and shear.

Some kneading screws have interrupted flights to improve dispersive mixing, increase backflow, or increase mechanical energy dissipation into the extruder (Huber, 2001). Main characteristics of screw design include: (i) screw length; (ii) screw diameter; (iii) screw channel depth; (iv) screw channel width; (v) axial flight land width; (vi) clearance between screw and barrel; (vii) screw helix angle; (viii) leading flank angle; (ix) trailing flank angle; (x) screw pitch; (xi) direction of drag flow; (xii) direction of pressure flow and (xiii) direction of leakage flow (Figure 2) (El-Dash, 1981). The screw pitch (t) is the distance between corresponding points on adjacent thread profiles, and the number of parallel screw channels or leads (n) is defined as the number of screw pitches in the axis distance that the helix advances in one turn.

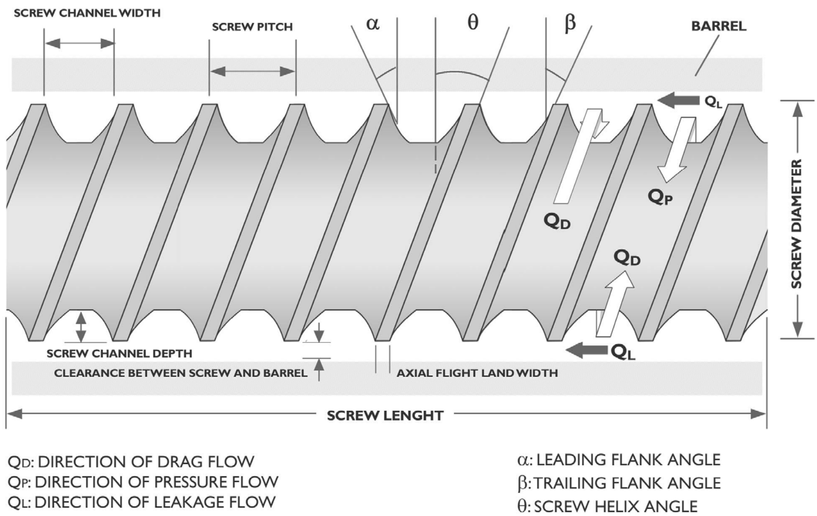


Fig. 2. Main characteristics of screw design

2.4 Barrel or sleeves

The barrel is divided into feeding, kneading and high pressure zones (Figure 1).

The sleeves surrounding the screw can be solid, but they are often jacketed to permit circulating of steam or superheated oil for heating or water or air for cooling, thus enabling the precise adjustment of the temperature in the various zones of the extruder. And most sleeves are equipped with pressure and temperature sensing and temperature control mechanisms as well (El-Dash, 1981).

In twin-screw extruders, the sleeves are usually smooth but can be constructed with longitudinal or helical grooves (Huber, 2000). In single-screw extruders, the sleeves are usually fluted on the inside, with either straight or spiral grooves. Parallel grooves are often cut or more often cast into the barrel. Spiral grooves provide high forward flow, while straight grooves hinder it. The latter thus result in a lower flow rate, but more mechanical shear. The clearance between the screw and its sleeve is usually kept to a minimum to reduce leakage flow (El-Dash, 1981).

2.5 Die

The die presents two main functions: give shape to the final product and promote resistance to material flow within the extruder permitting an increase in internal pressure. The die can present various designs and number of orifices (El-Dash, 1981). Dies may be designed to be highly restrictive, giving increased barrel fill, residence time and energy input. Die design and its effects on functional properties and quality of a final product are many times overlooked.

2.6 Cutting mechanism

The cutting mechanism must permit obtaining final products with uniform size. Product size is determined by the rotation speed of the cutting blades. This mechanism can be horizontal or vertical (El-Dash, 1981).

2.7 Types of extruders

Two types of extruders are used for food production: (i) single-screw extruders and (ii) twin-screw extruders. Single-screw extruders are the most common extruders used in the food industry. Twin-screw extruders are used for high-moisture extrusion, products that include higher quantities of components such as fibres, fats, etc. and more sophisticated products.

2.7.1 Single-screw extruders

Single-screw extruders are the most common extruders applied in the food industry. The classification of single-screw extruders can be defined based on process or equipment parameters such as: conditioning moisture content (dry or wet), solid or segmented screw, desired degree of shear and heat source. From a practical point of view, the main classification used considers the degree of shear and the heat source (Riaz, 2000).

Regarding screw configuration, there are screws made up of only one piece or screws of multiple pieces. Single element screws may present different configurations: (i) screw with constant depth and flight – straight –; (ii) screw with constant flight and variable depth – tapered – (conical from the feeding extremity to the die extremity); (iii) screw with a reduction in depth just after feeding, becoming constant at the end – tapered-straight – and (iv) screw with flight openings – interrupted flight – to increase shear force due to the increase in leakage flow and turbulence of the material (El-Dash, 1981).

Screws of multiple elements can be built up to desired configuration due to the great number of possible formats, varying screw flight and depth. Usually this type of screw is divided into five sections, where the first section presents wide flight and great depth with the objective of homogenizing and conveying the material. In the second section, also known as the intermediate section, there is a reduction in parallel screw flight (or adjacent screw flight) and depth, resulting in even greater mixing of the material and beginning of shear, while the material is transported to the next section. The third section is responsible for an increase in shear and pressure, promoting structural changes in the material, which passes to the viscoelastic state. The increase in shear force in the third section can be reached with interruptions in screw flight favouring material turbulence. In the fourth section, due to the small clearance available for the material, there is high shear and an increase in the temperature of the molten mass, resulting in cooking of the product. In the last section, due to an even greater reduction in screw flight and depth, shear and heat generation promote final cooking of the product (El-Dash, 1981).

Extrusion conditions when using extruders that have single screws of multiple elements can be controlled varying the number of sections, screw configuration in each section and through the inclusion of shearlocks (El-Dash, 1981).

Single-screw extruders can be classified in four different types based on the degree of shear, as follows:

Cold forming extruders – operate with moderate conditioning moisture contents (30 - 40%), low shear and smooth internal barrel surface, deep flight and low screw speed. These are not used for thermoplastic extrusion. They are used to form compact products such as pasta, cookies, pastry doughs, processed meats and certain candies (Riaz, 2000).

High-pressure forming extruders – operate with low shear, grooved barrel and compression screw. They are used to produce pre-gelatinized flours and pellets (for post expansion by hot air or frying) (Riaz, 2000). The latter are considered 3rd generation products.

Low-shear cooking extruders – operate with moderate degree of shear, high compression screw and grooved barrel (straight or helicoidal) to favour mixing. Usually involve external heating (steam jacket or electric resistance) to improve cooking with the objective of pasteurization, enzymatic inactivation, protein denaturation and/or starch gelatinization (Riaz, 2000).

Collet extruders – operate with high shear, grooved barrel and screw with an increase in compression (through multiple shallow flights). Commonly used to produce expanded snacks from corn grits. Conditioning moisture content must be low (12 - 14%) and temperature high (150 – 175°C), resulting in partial dextrinization and gelatinization of starch. Due to the high pressure formed within the extruder, when exiting the die there is immediate expansion of the material (Riaz, 2000).

2.7.2 Twin-screw extruders

Twin-screw extruders are composed of two axis that rotate inside a single barrel; usually the internal surface of the barrel of twin-screw extruders is smooth. Depending on the position of the screws and their direction of rotation, four different types of configurations are possible: (i) co-rotating intermeshing screws; (ii) co-rotating non-intermeshing screws; (iii) counter-rotating intermeshing screws; and (iv) counter-rotating non-intermeshing screws. Conical intermeshing extruders also exist. Although intermeshing screws result in greater residence time of the material in the extruder, non-intermeshing screws cause greater degrees of shear, especially if they rotate in opposite directions. However, this type of extruder is little used in the food industry, even though they present more efficient displacement properties (El-Dash, 1981). The intermeshing configuration is more effective, as the two screws function as a positive pump, increasing the drag flow and reducing the slipping of material in the extruder. Non-intermeshing screws provide higher shear than intermeshing screws because of the open channel between them.

When the material enters the barrel, the ingredients are thoroughly mixed before further processing in the other zones of the extruder. In this initial step, the screw is designed with a large screw channel depth to provide enough space between the root of the screw and the barrel for sufficient mixing to take place, and often, the screws are reverse-threaded to permit intensive mixing and longer residence times before delivery. In the next zone, the diameter of the root increases rapidly while the channel depth becomes shallower in order to provide material cooking, thus increasing the pressure applied to the product, and the starchy content of food is gelatinized and the proteinaceous material denatured (El-Dash, 1981).

When needed, after the cooking zone, the material is forced to the depressurizing zone were the screw root diameter is much smaller, while the channel depth is much deeper than in the previous zone. To promote pressure reduction, a depressurizing valve can be opened to atmospheric pressure or to a vacuum pump. In the forming zone, the diameter of the screw root increases, reducing channel depth and resulting in an increase in the pressure applied. This pressure must be high enough to permit the extrusion of the product in the appropriate form through the die (El-Dash, 1981).

3. Raw materials and changes in major components

3.1 Raw materials

The most used raw materials in the extrusion process are starch and protein based materials. The structure of the extruded products may be formed from starch or protein polymers. Most products, such as breakfast cereals, snacks and biscuits are formed from starch, while protein is used to produce products that have meat-like characteristics and that are used either as full or partial replacements for meat in ready meals, dried foods and many pet food products (Guy, 2001).

In general, the chemical or physicochemical changes in biopolymers that can occur during extrusion cooking include: binding, cleavage, loss of native conformation, fragment recombination and thermal degradation. The composition of raw materials can be altered by physical losses including leakage of oil and evaporation of water and volatile compounds at the die. Since most chemical reactions occur in the high-pressure zone of the barrel, thermally labile compounds such as flavours and vitamins may be injected immediately before the die to minimize exposure to heat and shear (Riaz, 2000).

The structure of an extruded product is created by forming a fluid melt from a polymer and blowing bubbles of water vapour into the fluid to form a foam. The bubbles rapidly expand as the superheated water is released very quickly at atmospheric pressure. In the extruded structure, the fluid melt of the polymers forms the cell walls of the gas bubbles. After gas expansion, the rapid drop of temperature caused by water evaporation and the rapid rise in viscosity due to moisture loss, solidifies the cell structure. The rapid increase in viscosity is followed by the formation of a glassy state. Starch polymers are very good at this function and also expand well. Structure forming polymers must have a minimum molecular weight sufficient to give enough fluid viscosity to prevent or control shrinkages of an extrudate after it reaches its maximum expansion (Guy, 2001).

3.2 Starch

The major difference between extrusion processing and conventional food processing is that in the former starch gelatinization occurs at much lower moisture contents (12-22%).

Starch is contained in a large variety of plant crops, such as cereals (50-80% db starch), legumes (25-50% db), and tubers (60-95% db) (Colonna et al., 1998). The three major cereals in order of world production are wheat, rice and maize; moreover, other important crops are barley, rye, oats and sorghum. All these cereals are available as grains, which are milled to form flours rich in starch once first separated the endosperm from the hull or pericarp (Guy, 2001). Starch is present in endosperm cells, is insoluble in cold water and its main nutritional property is to supply energy (4 kcal/g) (Caldwell et al., 2000; Cheftel, 1986). Each cereal has a different composition of its flour which basically depends on the level of the non-starch components such as protein and fibres. For example, maize and rice flours are generally richer in starch than wheat flour due to the lower protein and fibre contents. Oat flours are high in both oil and fibre presenting the lowest starch content (Guy, 2001). Native starch is found in the form of discrete particles or granules, with defined sizes and shapes depending on the botanical source. The starch granule consists of two different glucose polymers: amylose and amylopectin, responsible for its physicochemical and functional properties (Bornet, 1993; Caldwell et al., 2000). The highly branched structure of amylopectin is more prone to shear, but both amylose and amylopectin molecules may decrease in weight (Collona et al., 1998). Amylose is a basically linear polymer, with linear α-1-4 glucosidic bonds, polymerization degree of 600 to 6000 glucose units and molecular weight of 10^5-10^6 Da. Amylopectin is a branched polymer, with linear α-1-4 glucosidic bonds and, at branching points, α-1-6 glucosidic bonds, in a proportion of 5-6%; it consist of approximately 10^6 glucose units, with a molecular weight of 10^8 Da. Starch contains different proportions of amylose and amylopectin, depending on its botanical origin. Starch from cereals has an amylose content that varies from 15 to 28% (Bornet, 1993).

Thermoplastic extrusion, depending on process conditions and raw material composition, causes swelling and rupture of the starch granule, completely or partially destroying the organized granule structure, reducing viscosity and releasing amylose and amylopectin (Camire et al., 1990; El-Dash et al., 1983). During thermoplastic extrusion, amylose and amylopectin are partially hydrolysed to maltodextrins, due to the high temperatures and shear inside the extruder (Cheftel, 1986; El-Dash et al., 1983).

An important consequence of starch degradation is the reduction in expansion. Highly expanded products may crumble easily due to thin cell walls, while dense products are often hard (Riaz, 2000).

Larger amylopectin molecules in corn flour had the greatest molecular weight reduction. High molecular weight (>10^7) starches disappeared during extrusion, and there was a general increase in starch molecules of 10^5 – 10^7 (Guy, 2001).

The physical nature of the cereal flour may affect the final extruded product. Some cereals present soft and floury endosperm. In this material, the starch granules and protein layer are only loosely bound together and the endosperm is broken down easily on milling to provide a mixture of separated starch and protein bodies. In the extruder, soft flour will create less mechanical energy between its particles and require less mechanical energy to process through the same screw configuration, a longer time being necessary before melt formation and less time for the transformation of the melt in the shearing section (high-pressure zone). On the other hand, in certain cereals, such as hard wheat, durum wheat, vitreous flint maize and some varieties of barley there is a strong bonding between the starch granules and the protein layers forming a hard particle of flour that requires more energy to break down and will generate more heat in the extruder. Therefore, if high expansion is required in a low moisture product, finely milled forms of harder endosperm types will give excellent results. If the product requires low to medium expansion, some of the hard material may be replaced by soft flour; and for low expansion in a dense product such as breading crumb, soft flour may be used (Guy, 2001).

Inside the extruder, starch goes through several stages. First, the initial moisture content is very important to define the desired product type. Once inside the extruder, and at relatively high temperatures, the starch granules melt and become soft, besides changing their structure that is compressed to a flattened form (Guy, 2001). The application of heat, the action of shear on the starch granule and water content destroy the organized molecular structure, also resulting in molecular hydrolysis of the material (Mercier et al., 1998). The starch polymers are then dispersed and degraded to form a continuous fluid melt. The fluid polymer continuum retains water vapour bubbles and stretches during extrudate expansion until the rupture of cell structure. The starch polymer cell walls recoil and stiffen as they cool to stabilize the extrudate structure. Finally, the starch polymer becomes glassy as moisture is removed, forming a hard brittle texture (Guy, 2001). The final expanded product presents air cells that are formed due to superheated water vapour pressure. When the temperature of the extrudate is reduced below its glass transition temperature (Tg), it solidifies and maintains its expanded form (Riaz, 2000).

According to Colonna et al. (1998), maximum expansion degree is closely related to starch content. Maximum expansion is obtained with pure starches (an increase of 500% in product diameter), followed by whole grains (400%) and with lower expansions for seeds or germ (150-200%); the starch content of these products is 100, 65-78, 40-50 and 0-10, respectively. The minimum starch content for expansion is 60-70% (Riaz, 2000).

3.3 Proteins

Proteins are biopolymers with a great number of chemical groups when compared to polysaccharides and are therefore more reactive (Mitchel & Areas, 1992) and undergo many changes during the extrusion process, with the most important being denaturation (Camire, 2000). Proteins are formed from chains of amino acids and have a wide range of physical sizes and forms in native raw materials. Proteins in general are classified, with respect to their solubility, in albumins, globulins, prolamines and glutelins with solubility in water, saline solution, alcohol solution and acid or alkaline solutions, respectively (Pereda et al., 2005).

During extrusion, disulfide bonds are broken and may re-form. Electrostatic and hydrophobic interactions favour the formation of insoluble aggregates. The creation of new peptide bonds during extrusion is controversial. High molecular weight proteins can dissociate into smaller subunits (Guy, 2001).

Enzymes, also proteins, lose their activity after being submitted to the extrusion process due to high temperatures and shear. Also, proteins lose their solubility in water and saline solution due to the temperature and specific mechanical energy to which the product is submitted (Camire, 2000).

One of the main applications of extrusion in high protein content foods is protein texturization. Texturization processes by extrusion can be used to obtain products that imitate the texture, taste, and appearance of meat or seafood with high nutritional value (Cheftel et al., 1992).

The use of raw materials with high protein contents in extrusion began around the 1970s, with the use of soy for the production of texturized soy products and meat analogues (Ledward & Mitchell, 1988; Mitchell & Areas, 1992).

In extrusion, the proteins that have been found to form a continuous structure are globular proteins from oilseeds such as soybeans, sunflower seeds, common beans, peas and cottonseed and from cereals, especially wheat gluten proteins (Riaz, 2000; Strahm, 2006).

The extrusion process, physically, converts protein bodies into a homogeneous matrix, while chemically, the process recombines storage proteins in some way into structured fibres (Stanley, 1998). Low moisture (up to 35%) extrusion of vegetable protein can be used to elaborate products to partially or totally substitute meat. Usually, these products are expanded and need to be re-hydrated before consumption. On the other hand, high moisture (>50%) extrusion results in products that do not need to be re-hydrated and can be consumed directly. In general, dry extrusion is applied when the aim is to produce meat extenders and wet extrusion is used for meat analogues (Noguchi, 1998). In dry extrusion, when the conditioned material passes through the die at a high temperature, the water in the material is changed into superheated steam, which expands the extrudate immediately. Water also makes the extrudate very soft, by reducing its viscosity drastically, so the material just after the die is not self-supporting. Therefore, cooling at the die is essential to increase the viscosity of the hot melt and reduce its fluidity so that the necessary pressure and temperature before the die can be maintained. When cooling is done appropriately, the correct amount of extrudate elasticity and fluidity can be obtained to allow a continuous "rope" structure without explosive puffing and the destruction of product integrity (Noguchi, 1998). The mechanism for structure creation with proteins is similar to that with starch in the sense that proteins must be dispersed from their native bodies into a free flowing continuous mass. Texturization occurs between the molecules as they flow in the streamlines to form laminar cross-linked products. Evaporation of water in the mass creates gas bubbles that form alveolar structures held in place by cross-linking in the protein layers (Guy, 2001).

Denaturation during the extrusion process of proteins results in reduction of protein solubility, favours digestibility and inactivates antinutritional factors (such as antitrypsin factor, lectins, etc.). Also, the extrusion of soy protein reduces the bitter taste and the undesirable volatile compounds related to this protein (Areas, 1992; Kitabatake & Doi, 1992).

During extrusion, protein structures are disrupted and altered under high shear, pressure, and temperature (Harper, 1984). In the extrusion of proteins, disulfide bonds are cleaved and undergo reorganization and polymerization. Disulfide bonds, non-specific hydrophobic and electrostatic interactions are the main bonds and interactions responsible for protein texturization by extrusion (Areas, 1992). Protein solubility decreases and cross-linking reactions occur and possibly, some covalent bonds form at high temperatures (Areas, 1992). Thermal plasticization of the protein mix at high moisture contents (60%) is possible at relatively high extrusion temperatures (>150°C). At moisture levels lower than 60%, plasticization requires higher temperatures. Apart from this, hydrophobic and electrostatic interactions favour the formation of insoluble aggregates, like the fibrous structure of meat analogues, for example (Li & Lee, 1996; Tilley et al., 2000; Li-Chan, 2004; Sluimer, 2005).

Protein reactions, including both non-covalent and disulfide bonds, form upon cooling. Protein–protein interactions may be enhanced by decreased temperature and by macromolecular alignment. Crystalline aggregation leads to parallel fibre formation of varying length and thickness. A wide range of interaction energy is possible for protein cross-linking with protein and other molecules due to the diversity of amino acids. Therefore, hydrophobic, cation–mediated electrostatic interactions, and covalent bonds also contribute to the stabilization of the three dimensional network formed during extrusion (Areas, 1992).

Also, during the extrusion process high temperatures are normally used, and these favour the Maillard reaction. Reducing sugars can be produced during the process and they can react with the free amine groups of lysine or other amino acids (Camire, 2000).

3.4 Lipids

Fats and oils can be described as lipids. Lipids have a powerful influence in extrusion cooking processes by acting as lubricants, because they reduce the friction between particles in the mix and between the screw and barrel surfaces and the fluid melt (Guy, 2001). In the extruder, fats and oils become liquid at temperatures > 40°C, being mixed with the other materials, and are rapidly dispersed as fine oil droplets.

The presence of lipids in quantities lower than 3% does not affect expansion properties, however, in amounts above 5%, reduction in expansion rate is considerable (Harper, 1994). Collona et al. (1998) suggest that the increase in lipid content can be corrected through the reduction in conditioning moisture content, so as not to affect the expansion index of second generation products (directly expanded snacks).

The type of starch and lipid present in the raw material influences the formation of the amylose-lipid complex, with free fatty acids and monoglycerides being more favourable to the formation of this complex than triglycerides (Mitchel & Areas, 1992; Harper, 1994; Camire, 2000).

Moreover, in wet protein extrusion, the presence of lipids does not support protein fibre formation since the lubricating effect of lipids decreases the shear effects and particle alignment (Akdogan, 1999).

3.5 Fibres

The term "fibres" covers a great variety of substances with different physical, chemical and physiological properties. Dietary fibre consists of fractions of vegetable cells, polysaccharides, lignin, and associated substances, which are resistant to hydrolysis by enzymes present in the digestive system of humans; however, some types of fibres may be fermented by bacteria in the colon. As many physiological effects of fibres seem to be related to their solubility in water, they are frequently classified as "soluble" and "insoluble" (Roberfroid, 1993; Stark & Madar, 1994).

Soluble fibres form a gel network or a viscous network, in determined physicochemical conditions, and thus bond water increasing viscosity, retarding gastric transit, reducing glucose, lipid and sterol absorption rates (Gorinstein et al., 2001). Soluble fibres are also seen as fermentable substrates, as they can modify the pH and the microflora of the colon, leading to a reduction or modification of mutagenic agents (Thebaudin et al., 1997). Insoluble fibres increase faecal volume, thus diluting its contents, which reduces the interaction between the intestinal mucosa and any carcinogenic component present. Apart from this, insoluble fibres reduce intestinal transit time, avoiding that mutagenic agents in the faeces interact with the intestinal epithelium (Thebaudin et al., 1997).

Research has shown that cooking fibres by extrusion can produce changes in their structural characteristics and physicochemical properties, with the main effect being a redistribution of insoluble fibre to soluble fibre (Camire et al., 1990; Guillon et al., 1992; Larrea et al., 2005). This effect would be the result of the rupture of covalent and non-covalent bonds between carbohydrates and proteins associated to the fibre, resulting in smaller molecular fragments, that would be more soluble (Fornal et al., 1987; Wang et al., 1993).

Various researchers have reported a reduction in expansion index (EI) when dietary fibre is added to the formulation (Hsieh et al., 1989; Ilo et al., 1999; Vernaza et al., 2009). The reduction in the expansion index due to fibre addition can be explained through different mechanisms: (i) fibrous materials found in the formulation of extruded products include materials composed of hemicellulose, cellulose and lignin. In normal extrusion conditions, these materials tend to remain firm and stable during processing, without size reduction. The physical presence of fibres in air cell walls reduces the expansion potential of the starchy film (Guy, 2001); larger particles, such as bran, tend to rupture air cell walls of the extruded product, causing a reduction in expansion index (Riaz, 2000); (ii) according to Colonna et al. (1998), maximum degree of expansion is closely related to starch content, with maximum expansion being obtained for pure starches. As bran contains high fibre content, it reduces the starch content of the formulations; (iii) non-starch polysaccharides, such as fibres, may bind water more strongly than proteins and starch during extrusion. This water binding capacity inhibits water loss at the die, that is, at the exit of the extruder, reducing expansion (Camire & King, 1991); (iv) the starch present cannot be totally gelatinized in the presence of fibre and is thus not capable of supporting expansion (Camire & King, 1991); and (v) the porous structure of the extrudate depends of the plasticity of the mass before the die, for which starch is mainly responsible. Porosity, defined by the existence of fine pores and a tender structure, is influenced by alterations in the plasticity of the mass, affected by the composition of the mix. Formulations can be enriched by plasticizing substances or by non-plasticizing substances that retard expansion by diluting starch, as is the case of fibres (Colonna et al., 1998).

3.6 Moisture and temperature

In the extrusion process of expanded products with low moisture, the expansion of the final product is inversely related to the moisture of the raw material and directly related to the increase in extrusion temperature; however, the effect of moisture is more significant (Harper, 1994).

Water acts as a plasticizer for the starchy material that displaces itself within the extruder, reducing viscosity and mechanical energy, producing higher density products and inhibiting bubble growth. Studies carried out with corn grits demonstrated that expansion is inversely proportional to the moisture content of the material being extruded (Chinnaswamy, 1993; Colonna et al., 1998). With higher moisture, starch gelatinization is reduced and bubble growth is retarded, resulting in denser and less crunchy final products (Ding et al., 2005).

Inside the extruder, the product that contains molten starch in its composition, when leaving the extruder, has part of its water rapidly evaporated. This water loss is of 3 to 5% and contributes to cooling the product. Subsequent cooling occurs more slowly due to the low thermal conductivity of the extrudate. Also, when emerging from the die, the extrudate undergoes an abrupt pressure fall that also contributes to its expansion (Colonna et al., 1998). The expanded final product presents air cells that are formed due to superheated water vapour pressure. As the temperature of the extrudate is reduced below its glass transition temperature (Tg), it solidifies and maintains its expanded form (Riaz, 2000).

In high moisture extrudates, expansion occurs when the product exits the die, but the structure collapses before the necessary cooling, resulting in a dense and hard product (Harper, 1994).

Another important parameter for extrudate expansion is process temperature. Products do not expand if the temperature does not reach 100°C. Expansion increases with the increase in temperature when moisture content of the material is close to 20%, due to lower viscosity, permitting a more rapid expansion of the molten mass, or due to an increase in water vapour pressure. At low extrusion temperatures, expansion is reduced because starch is not completely molten. Radial expansion degree is proportional to temperature up to a certain value, decreasing at much higher temperatures. The reduction of expansion at very high temperatures is attributed to an increase in dextrinization, weakening starch structure (Colonna et al., 1998).

At high temperatures, the gel is more elastic, forming a matrix with small uniform cells, while at low moisture, the gel formed is not very elastic and the extruded material has large, not very uniform cells. It is expected that an increase in temperature should reduce viscosity of the molten material, favouring bubble growth and producing low density extrudates, with finer cells and greater crunchiness (Ding et al., 2005).

In high moisture extrusion, the properties of the protein extrudates are strongly influenced by extruder conditions (Thiebaud et al., 1996; Noguchi, 1998). Hayashi et al. (1991) reported that extruder barrel temperature was the most important parameter for the texturization of dehulled soybean. Melt temperature is a critical factor in protein cross-linking reactions. Increasing temperature from 140 to 180°C results in a proportional decrease in disulfide linkages formed in extruded soy protein isolates (Areas, 1992). Temperatures lower than 90°C hinder expansion and layer formation (Cheftel et al., 1992). At a given temperature, higher moisture contents result in softer and less texturized extrudates due to reduced protein–protein interactions and lower viscosity. At relatively lower moisture contents, higher barrel temperatures (140 to 180°C) result in better textures. At higher moisture levels, temperature needs to be decreased as moisture flash-off may cause considerable water loss if a cooling die is not used (Thiebaud et al., 1996).

High moisture levels combined with elevated temperatures yield extrudates that are very soft and not self-supporting after the die. However, a specially designed die which provides cooling at this section will increase the viscosity of the hot extrudate before exiting, contributing to the correct elasticity and fluidity required for texturization (Noguchi, 1998). The temperature at which solidification occurs is related to the plasticization temperature.

Low moisture (15 to 30%) extrusion tends to result in processes with greater generation of mechanical energy and products with lower density, while high moisture (50 to 70%) extrusion results in products with higher density, and is normally used in pellet production (Guy, 2001).

4. Influence on product quality

Extrusion-cooking is a process widely used in the food industry to manufacture snacks, crackers and expanded cereals. The degree of expansion in extruded products is an important characteristic which relates to the texture and sensory properties of extrudates (Lue et al., 1990). Extrusion-cooking has an important influence on product quality, emphasizing features like expansion, texture, shelf-life, colour and flavour.

For extrusion cooking, changes in ingredients such as sugar, salt and fibre, or processing parameters like screw design or speed and temperature, can affect extrusion system variables and product characteristics such as texture, structure, expansion and sensory attributes (Mendonça et al., 2000).

Products obtained with high temperatures and short extrusion process times normally present a porous, open structure, what confers to them a “crunchy” texture (Barrett, 2003).

Expansion occurs in both radial and axial directions, at different degrees, depending on the viscoelastic properties of the melt. Vaporization of moisture and cooling of the extrudate serve to bring the product from a molten to a rubbery state; and further drying is usually used to produce the brittle, fracturable texture typical of these products (Barrett, 2003).

Colour in extruded products is influenced by temperature, raw material composition, residence time, pressure and shear force (Guy, 2001; Mercier et al., 2001). During the extrusion process, several reactions happen and they in general affect the colour of the products. Among the most important, the most common are non-enzymatic browning (Maillard and caramelization) and pigment degradation. The process conditions normally used in thermoplastic extrusion (high temperature and low moisture content) are known to favour the reaction among reducing sugars and amino acids, that results in the formation of coloured compounds and the reduction of the amino acid lysine. If the browning is too intense, colours and flavours can be produced. Besides, changes in colour during the extrusion process can be an indicator to evaluate the intensity of the process in terms of chemical and nutritional changes (Ilo et al., 1999).

5. Influence on nutritional quality

The effects of extrusion cooking on nutritional quality are ambiguous. Benefits include destruction of antinutritional factors, gelatinization of starch, increased soluble dietary fibre and reduction of lipid oxidation. On the other hand, Maillard reactions between protein and sugars reduce the nutritional value of the protein, depending on the raw material types, their composition and process conditions. Besides, heat-labile vitamins may be lost to varying extents (Singh et al., 2007).

Starch digestibility is largely dependent on complete gelatinization. High starch digestibility is essential for specialized nutritional foods such as infant and weaning foods. Creation of resistant starch by extrusion may have value in reduced calorie products (Guy, 2001; Riaz, 2000).

The nutritional value of vegetable proteins is generally enhanced by mild extrusion cooking conditions due to the increase in digestibility (Asp and Björck 1989; Arêas, 1992), probably a result of protein denaturation and the inactivation of enzyme inhibitors present in raw materials, by the exposure of new active sites for enzyme attack (Colonna et al., 1989).

Processing nutritional food products at moisture levels below 20% has been proven to be uneconomical and nutritionally undesirable. Low-moisture extrusion results in production of certain undesirable dextrins as a result of increased shear energy inputs. Losses of vitamins and reduced amino acid availability are greatly accelerated as extrusion moistures are decreased. For this reason, vitamins and heat-sensitive nutrients are usually added post extrusion when processing at low moisture conditions (Huber, 2001).

Mild extrusion conditions (high moisture content, low residence time, low temperature) improve nutritional quality, while high extrusion temperatures (higher than 200°C), low moisture contents (lower than 15%) and/or improper formulation (e.g. presence of high-reactive sugars) can affect nutritional quality adversely. Also, to obtain a nutritionally balanced extruded product, careful control of process parameters is essential (Singh et al., 2007).

A benefit derived from extrusion-cooking is the partial or total destruction of potentially antinutritional factors, especially protease inhibitors, haemagglutinins, tannins and phytates, which limit utilization of nutrients in legume seeds. However, chemical alteration produced by thermal treatment could also result in decreased nutrient assimilation, including lower apparent absorption of certain minerals (Alonso et al., 2001).

Vitamin losses in extruded foods vary according to the type of food, moisture content, processing temperature and retention time. Generally, losses are minimal in cold extrusion. The HTST conditions in extrusion cooking, the short residence time of the extrudate and the rapid cooling as the product emerges from the die, cause relatively small losses of vitamins and essential amino acids (Fellows, 2000).

Extrusion cooking was reported by Saalia & Phillips (2011) as an efficient process to destroy or inactivate aflatoxins, if special conditions (high shear, high temperature, and adequate pH) are used.

Zhu et al. (1996) emphasized that by extrusion cooking, soybeans can be converted into high quality food ingredients. The short residence time and high temperature in an extruder reduce the damage to nutritional properties, but still adequately inactivate the enzymes responsible for the development of the undesirable off-flavour.

Minerals are heat stable and unlikely to become lost in the steam flash-off at the die. Extrusion can improve the absorption of minerals by reducing other factors that inhibit absorption, like phytates and condensed tannins. In addition, extrusion cooking usually increases the amount of iron available for absorption. For foods fortified with minerals prior to extrusion, some problems can be verified, like the formation of iron complexes with phenolic compounds that are dark in colour and detract from the appearance of foods; added calcium hydroxide can contribute to decrease expansion and increase lightness in colour of some products (Singh et al., 2007).

6. Influence on microbiological quality

One of the most important consumer requirements is the microbiological safety of food products. Most conventional extruded products such as snack foods and breakfast cereals are safe to eat because the raw materials are subjected to high temperatures (higher than 130°C) and the water activity of the product is low because the product is dried to a moisture content of less than five per cent. Although it is well known that most vegetative organisms, yeast and moulds are destroyed under typical extrusion conditions, the operating conditions under which spores are inactivated are not well understood (Guy, 2001).

The reduction of antinutritional factors, the increase of product microbiological safety and much better consumer acceptability are also related to extrusion cooking (Sumathy et al., 2007).

The extrusion process, as it is carried out at high temperatures, even with short residence times, eliminates a high amount of microorganisms (Baik et al., 2004). The extrusion process also allows obtaining lower water activity values in the final product, with values between 0.1 and 0.4. Therefore, it is possible to extend the shelf life of products (Fellows, 2000).

Fraiha et al. (2011) emphasize studies with heat-resistant microorganisms showing that shear stress may be involved in microbial load reduction during the extrusion process, predicting that mechanical forces might cause cell rupture. These authors studied a pre-treatment of *Bacillus stearothermophilus* spores in a 99% CO_2 modified atmosphere and checked that it did not affect cell viability during food extrusion. For them, heat was not the sole phenomena to explain cell death during extrusion, a mechanical damage of cells might be involved.

Okelo et al. (2006), studying the optimization of extrusion conditions for elimination of mesophilic bacteria during thermal processing of animal feed recipes, pointed out that, in general, thermal processing is designed to eliminate mesophilic organisms and not thermophilic organisms such as *Bacillus stearothermophilus*. It was predicted that most pathogenic organisms in feed would be inactivated by extrusion cooking through selecting extruder conditions within the experimental variable ranges that maximized spore destruction of thermophilic bacteria. This reduction would also likely include members of mesophilic *Bacillus cereus* group.

Mycotoxins are a risk to human health mainly via the intake of contaminated foods of plant origin, such as corn and wheat, which are consumed worldwide. The risk of exposure is therefore high for humans, and industrial processing methods that are effective in reducing mycotoxin contents in processed samples have received increased attention. Among them, extrusion cooking may be one of the most effective ways to reduce mycotoxin levels in processed products, especially if glucose or other additives such as ammonia or sodium bisulphite are included as ingredients. This is especially important since extruded products are highly popular in the food and feed market (Castells et al., 2005).

7. Products

7.1 Second and third generation snacks

The evolution of snacks occurred rapidly and can be divided into three generations. In the first, the raw material, such as whole grains, is processed through the combination of moisture, cooking temperature and drying. Only second and third generation snacks are produced by thermoplastic extrusion, and a flow diagram is shown in Figure 3.

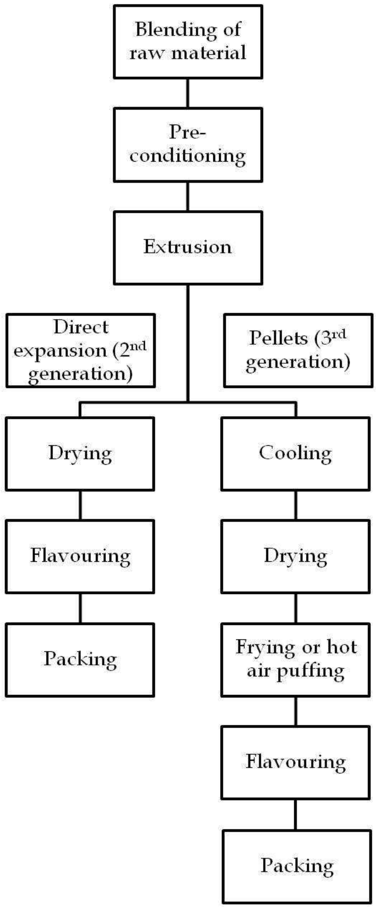


Fig. 3. Flow diagram for the production of second and third generation snacks

Second generation snacks or expanded snacks, where most extruded snacks are classified, are usually low in bulk density and are often marketed as high-fibre, low-calorie, high-protein and nutritional products (Lazou & Krokida, 2011). Different raw materials used to produce these kinds of snacks (i.e. flours and/or cereals and tubers starches and proteins) are processed in a extruder resulting in a continuous mass, that is cut into pieces of uniform size, being afterwards dried, flavoured and stored (Booth, 1990).

Third generation snacks or pellets are normally called "half products". These snacks are produced almost the same way as second generation snacks, however, when the product exits the extruder, it has the form of the die, that is, it is not expanded, being dried in this form. The expansion of the product occurs afterwards through frying, heating by hot air or in a microwave oven (Riaz, 2000; Carvalho et al., 2009). This kind of product presents a low moisture content (between 7 and 10%), high density and stability to be stored for a long time without microbial damage (Carvalho et al., 2009).

7.2 Breakfast cereals

Breakfast cereals (BCs) have been defined as "processed grains for human consumption". The breakfast cereal industry, in the United States, appeared at the beginning of the 20th century and has grown rapidly in the last few years, making BCs important economically viable products. Basic processes for the production of BCs include flaking, oven and gun puffing, baking, shredding and direct expansion (extrusion cooking). These processes convert raw and dense grains (7.7 kg/100 cm^3) into friable, crunchy or chewable products, adequate for human consumption, with apparent density in the range of 0.6 to 1.6 kg/100 cm^3 (Fast, 2000). Thermoplastic extrusion presents various advantages over the conventional processes used for BC production, such as shorter processing times and lower costs; less physical space necessary; greater flexibility for the production of a variety of products, simply changing the die, process conditions, initial formulation and final enrobing of the product, and particle size of the raw material (Huang, 1998; Bailey et al., 1991; Riaz, 2000).

The most commonly used cereals in extruded BC formulations are rice, wheat, oats and corn (Fast, 2000; Riaz, 2000). In the formulation of extruded BCs, a mixture of these cereals can be used, in the form of flours, grits or whole grain flours, and they can also be mixed with other ingredients such as starches, sugar, salt, malt extract or other liquid sweeteners, heat stable vitamins and minerals, flavourings, colorants and water, to vary appearance, texture, taste, aroma and other product characteristics (Riaz, 2000).

To produce BCs by extrusion cooking two different processes can be used: (i) pellet or shred production for manufacturing cereals such as cornflakes or shredded cereals with additional laminating and toasting processes after extrusion cooking, and (ii) directly expanded cereals production. Extruded flakes can be obtained by adding a blend of grains (flour, starches, etc.) and liquids (water, sweetener, colorants, etc.) directly to the extruder. The blend is forced through the barrel, where heat is applied to cook the dough, and then the product passes through a cooling section to prevent expansion, obtaining pellets after the die. Then the pellets pass through an equipment to be flaked and toasted. The process to obtain shredded cereals is similar to that of the flake process, with the exception that pellet sizes are not as critical, because they will be shredded without additional drying and tempering. Finally, the manufacturing process for extruded, puffed or expanded BCs follows the same steps, differing only at the end of the extruder, when the dough passes through a die that is designed to allow expansion after leaving the extruder because the moisture in the formula (whether natural or added) is released from a zone of elevated temperature and pressure to ambient conditions. The die holes control the shape of the finished cereal pieces, once they are cut with a rotating knife on the outer face of the die. The extruded products can be sugar-coated or coloured and flavoured to produce a variety of products for various tastes (Fast, 2000; Eastman et al., 2001). In expanded extruded products two important characteristics are expansion and texture. Extruded products are characterized for their expansion and usually maximum expansion is desired for expanded extruded snack products. For expanded extruded breakfast cereals a different structure is desired. It is necessary to obtain products with higher apparent density, lower porosity and thicker cell walls, as these products will be immersed in an aqueous medium, such as milk, and must maintain their texture during the longest time possible, absorbing the lowest quantity of moisture possible (Collona et al., 1998).

BCs can be considered protein sources (even though cereal proteins are incomplete due to limiting essential amino acids such as lysine), as they are often formulated with various different types of cereals and consumed with milk. When produced with whole grain flours, they can be considered sources of fatty acids and fibres. Breakfast cereals are sources of vitamins and minerals, as grains contain significant amounts of B-group vitamins, tocopherols, and minerals such as iron, zinc and copper, apart from being normally consumed with milk or yoghurt, considered important sources of calcium (Jones, 2001).

Nowadays, the development of new products in the BC segment aims at the production of breakfast cereals with a functional appeal. Recent research reports the use of antioxidants such as tocopherol and lycopene (Paradiso et al., 2008; Dehghan-Shoar et al., 2010) and fibres, such as β-glucans, gums and oat, wheat and passion fruit brans (Holguín-Acuña et al., 2008; Vernaza et al., 2010; Yao et al., 2011; Ryan et al., 2011).

7.3 Meat analogues

To human diets, especially those of vegetarians, the ingestion of high protein content products has been incorporated, including, for example, meat extenders and meat analogues, obtained through the extrusion process of vegetable proteins, resulting in a product with appearance and texture similar to the fibrilar structure of meat (Strahm, 2006; Macdonald et al., 2009). Meat extenders are obtained by thermoplastic extrusion at low moisture contents (20-35%) and meat analogues are obtained by thermoplastic extrusion at high moisture contents (50-70%). The raw materials commonly used to produce meat extenders are defatted soy flour and soy protein concentrate (SPC), whereas for the production of meat analogues, soy protein concentrate (SPC) and soy protein isolate (SPI) are used.

Amongst the main vegetable proteins used to produce meat analogues are proteins from legumes such as soybeans, common beans and peas, and from cereals, especially wheat proteins responsible for the formation of the gluten network (Riaz, 2000; Strahm, 2006).

The use of raw materials with high protein contents in extrusion began around the 1970s, with the use of soy for the production of texturized soy protein and meat analogues. Although researchers agree that, during extrusion of high protein content raw materials, denaturation, melting and alignment during mass flow occur, there is still a need to understand the physicochemical and rheological changes involved, once the phenomena that lead to the formation of the fibrilar structure from extruded vegetable proteins are not completely elucidated at a molecular level (Ledward & Mitchell, 1988; Mitchell & Areas, 1992).

Denaturation during the extrusion process of proteins results in a reduction of protein solubility, favours digestibility and inactivates antinutritional factors. Also, the extrusion of soy protein eliminates and/or reduces the bitter taste and the undesirable aroma and volatiles related to this protein (Areas, 1992; Kitabatake & Doi, 1992).

8. Future trends

In the last three decades, the development of extruders has advanced greatly. However, technical innovations will be continuously needed for the evolution of new generation extruders and complementary equipments targeting greater efficiency and higher productivity, increasing throughput, easing process control, enabling the production of numerous sophisticated snacks and improving final product quality. Also, it will always be vital to attend consumer requirements, which nowadays are closely related to nutrition and health foods that promote well-being and a positive life style.

Extruders permit the production of many foods of nutritional importance. The ability of extruders to blend diverse ingredients in novel foods can be exploited in the development of functional foods. Traditional snacks or breakfast cereals can be enhanced by the addition of extra fibres or whole grain flour as ingredients during extrusion, transformed into palatable cereal-based products that also promote beneficial physiological effects. Functional ingredients such as soy and botanicals (fruit, vegetables, cereals, etc.) that present high amounts of bioactive compounds can be used in the extrusion process to develop novel products with phytochemicals and other healthful food components. Improved chemical and immunoassay methods will undoubtedly facilitate research in this area. The extrusion process may have value in the formation of resistant starch and modified starch to promote reduced calories in food products. Extruders may also be interesting tools to obtain micro-encapsulated materials that have the objective of protecting sensitive additives (such as flavours, etc.), increasing their shelf-life and controlling the release of food ingredients at the right place and time. Carbohydrate matrices, such as hydrophobically-modified starches in the glassy state, have good barrier properties and extrusion is a convenient process enabling the encapsulation of flavours in such matrices.

In the future science and technology of the extrusion field, scientists and engineers should focus on the relationship between composition changes and product quality, evaluating and enhancing nutritional, sensory and functional properties of extruded foods.

9. References

Akdogan, H. (1999). High moisture food extrusion. *International Journal of Food Science and Technology*, Vol.34, No.3, (June 1999), pp.195-207, ISSN 1365-2621.

Alonso, R.; Rubio, L.; Muzquiz, M. & Marzo, F. (2001). The effect of extrusion cooking on mineral bioavailability in pea and kidney bean seed meals. *Animal Feed Science and Technology,* Vol.94, No.1-2, (November 2001), pp.1-13, ISSN 0377-8401.

Areas, J. A. (1992). Extrusion of food proteins. *Critical Reviews in Food Science and Nutrition*, Vol.32, No.4, pp.365-392, ISSN 1040-8398.

Asp, N. G. & Björck, I. (1989). Nutritional properties of extruded foods. In: *Extrusion cooking*, C. Mercier; P. Linko & J. M. Harper, (Eds.), pp.399-434, American Association of Cereal Chemists, ISBN 978-091-3250-67-8, Saint Paul, United States of America.

Baik, B.; Powers, J. & Nguyen, L. (2004). Extrusion of regular and waxy barley flours for production of expanded cereals. *Cereal Chemistry*, Vol.81, No.1, (January/February 2004), pp.94-99, ISSN 0009-0352.

Bailey, L. N.; Huack, B. W.; Sevatson, E. S.; Singer, R. E. (1991). Systems for manufacture of ready-to-eat breakfast cereals using twin-screw extrusion. *Cereal Foods World*, Vol.36, No.10, pp.863-869, ISSN 0146-6283.

Barrett, A. (2003). Characterization of macrostructures in extruded products. In: *Characterization of cereal and flours: properties, analysis and applications,* G. Kaletunç & K. Breslauer, (Eds.), pp.369-386, CRC Press, ISBN 978-0-8247-0734-7, Boca Raton, United States of America.

Booth, R. (1990). *Snack food,* Van Nostrand Reinhold, ISBN 978-812-3905-06-8, New York, United States of America.

Bornet, F. (1993). Technological treatments of cereals. Repercussions on the physiological properties of starch. *Carbohydrates Polymers*, Vol.21, No.2-3, pp.195-203, ISSN 0144-8617.

Caldwell, E. F.; Fast, R. B.; Ievolella, J.; Lauhoff, C.; Levine, H.; Miller, R. C.; Slade, L.; Strahm, B.S. Whalen, P. J. (2000). Unit operation and equipment. I. Blending and cooking. In: *Breakfast cereals and how they are made*, (2nd ed.) , R. B. Fast & E. F. Caldwell, (Eds.), pp.165-216, American Association of Cereal Chemists, ISBN 978-189-1127-15-1, Saint Paul, United States of America.

Camire, M. E.; Camire, A. & Krumhar, K. (1990). Chemical and nutritional changes in foods during extrusion. *Critical Reviews in Food Science and Nutrition*, Vol.19, No.1, pp.35-57, ISSN 1040-8398.

Camire, M. E. (2000). Chemical and nutritional changes in food during extrusion, In: *Extruders in food applications,* M. N. Riaz, (Ed.), pp.127-147, CRC Press, ISBN 978-156-6767-79-2, Boca Raton, United States of America.

Camire, M. E. & King, C. C. (1991). Protein and fiber supplementation: effects on extrudate cornmeal snack quality. *Journal of Food Science*, Vol.56, No.3, (May 1991), pp.760-763, ISSN 1750-3841.

Carvalho, A.; Vasconcelos, M.; Silva, P. & Aschieri, J. (2009). Produção de snacks de terceira geração por extrusão de misturas de farinhas de pupunha e mandioca. *Brazilian Journal of Food and Technology,* Vol.12, No.4, (October/December 2009), pp.277-284, ISSN 1516-7275.

Castells, M.; Marín, S.; Sanchis, V. & Ramos, A. (2005). Fate of mycotoxins in cereal during extrusion cooking: a review. *Food Additives and Contaminants,* Vol.22, No.2, (February 2005), pp.150-157, ISSN 1944-0049.

Chang, Y. K.; Hashimoto, J. M.; Moura-Alcioli, M. & Martínez-Bustos, F. (2001). Twin-screw extrusion of cassava starch and isolated soybean protein blends. *Molecular nutrition and food research*, Vol.45, No.4, (August 2001), pp.234-240, ISSN 1613-4133.

Cheftel, J. C.; Kitagawa, M. & Queguiner, C. (1992). New protein texturization processes by extrusion cooking at high moisture levels. *Food Reviews International*, Vol.8, No.2, pp.235-275, ISSN 1525-6103.

Cheftel, J. C. (1986). Nutritional effects of extrusion-cooking. *Food Chemistry*, Vol.20, No.4, pp.263-283, ISSN 0308-8146.

Chessari, C. J. & Sellahewa, J. N. (2001). Effective control processing. In: *Extrusion cooking: technologies and application,* R. Gay, (Ed.), pp.83-107, CRC Press, ISBN 978-084-9312-07-6, Boca Raton, United States of America.

Chinnaswamy, R. (1993). Basis of cereal starch expansion. *Carbohydrate Polymers*, Vol.21, No.2-3, pp.157-167, ISSN 0144-8617.

Colonna, P.; Tayeb, J. & Mercier, C. (1998). Extrusion cooking of starch and starchy products. In: *Extrusion cooking*, C. Mercier; P. Linko & J. M. Harper, (Eds.), pp.247-319, American Association of Cereal Chemists, ISBN 978-091-3250-67-8, Saint Paul, United States of America.

Dehghan-Shoar, Z.; Hardacre, A. K. & Brennan, C. S. (2010). The physico-chemical characteristics of extruded snacks enriched with tomato lycopene. *Food Chemistry*, Vol.123, No.4, (December 2010), pp.1117-1122, ISSN 0308-8146.

Ding, Q; Ainsworth, P.; Plunkett, A.; Tucker, G. & Marson, H. (2005). The effect of extrusion conditions on the physicochemical properties and sensory characteristics of rice-base expanded snacks. *Journal of Food Engineering*, Vol.66, No.3, (February 2005), pp.283-289, ISSN 0260-8774.

Eastman, J.; Orthofer, F. & Solorio, S. Using extrusion to create breakfast cereal products. *Cereal Foods World*, Vol.46, No.10, (October 2001), pp.468-471, ISSN 0146-6283.

El-Dash, A. A. (1981). Application and control of thermoplastic extrusion of cereals for food and industrial uses. In: *Cereals: a renewable resource, theory and practice*, Y. Pomeranz & L. Munich, (Eds.), pp.165-216, American Association of Cereal Chemists, ISBN 978-091-3250-22-8, Saint Paul, United States of America.

El-Dash, A. A.; Gonzales, R. & Ciol, M. (1983). Response surface methodology in the control of thermoplastic extrusion of starch. *Journal of Food Engineering*, Vol.2, No.2, pp.129-152, ISSN 0260-8774.

Fast, R. B. (2000). Manufacturing technology of ready-to-eat cereals. In: *Breakfast cereals and how they are made*, (2nd ed.), R. B. Fast & E. F. Caldwell, (Eds.), pp.15-86, American Association of Cereal Chemists, ISBN 978-091-3250-70-9, Saint Paul, United State of America.

Fellows, P. (2000). *Food processing technology: principles and practice*, (2nd ed.), CRC Press, ISBN 978-084-9308-87-1 Boca Raton, United States of America.

Fornal, L.; Soral-Smietana, M. & Szpenelowski, J. (1987). Chemical characteristics and physicochemical properties of the extruded mixtures of cereal starches. *Starch/Stärke*, Vol.39, No.2, pp.75-78, ISSN 0038-9056.

Fraiha, M.; Ferraz, A. & Biagi, J. (2011). Pre-treatment of thermoduric spores in CO_2 modified atmosphere and their survivability during food extrusion. *Ciência e Tecnologia de Alimentos,* Vol.31, No.1, (January/March 2011), pp.167-171, ISSN 0101-2061.

Gorinstein, S.; Zachwieja, Z.; Folta, M.; Barton, H.; Piotrowicz, J.; Zemser, M.; Weisz, M.; Trakhtenberg, S. & Martin-Belloso, O. (2001). Comparative contents of dietary fiber, total phenolics, and minerals in persimmons and apples. *Journal of Agriculture and Food Chemistry*, Vol.49, No.2, (February 2001), pp.952-957, ISSN 0021-8561.

Guillon, F.; Barry, J. L. & Thibault, J. F. (1992). Effect of autoclaving sugar-beet fibre on its physico-chemical properties and its *in vitro* degradation by human faecal bacteria.

Journal of the Science of Food and Agriculture, Vol.60, No.1, (September 1992), pp.69-79, ISSN 1097-0010.

Guy, R. (2001). *Extrusion cooking: technologies and applications*, Woodhead Publishing, ISBN 978-185-5735-59-0, Cambridge, United Kingdom.

Harper, J. M. (1994). Extrusion processing of starch. In: *Developments in carbohydrate chemistry*, (2nd ed.), R. J. Alexander & H. F. Zobel, (Eds.), pp.37-64, American Association of Cereal Chemists, Saint Paul, United States of America.

Hayashi, N.; Abe, H.; Hayakawa, I. & Fujio, Y. (1991). Texturization of dehulled whole soybean with a twin screw extruder and texture evaluation. In: *Food processing by ultra high pressure twin-screw extrusion*, A. Hayakawa, (Ed.), pp.133–146, CRC Press, ISBN 978-087-7628-21-7, Boca Raton, United States of America.

Holguín-Acuña, A. L.; Carvajal-Millán, E.; Santana-Rodríguez, V.; Rascón-Chu A.; Márquez-Escalante, J.; León-Renova, N. E. P. & Gastelum-Franco, G. (2008). Maize bran/oat flour extruded breakfast cereal: A novel source of complex polysaccharides and an antioxidant. *Food Chemistry*, Vol.111, No.3, (December 2008), pp.654-657, ISSN 0308-8146.

Hsieh, F.; Mulvaney, S. S; Huff, H. E.; Lue, S. & Brent, J. (1989). Effect of dietary fiber and screw speed on some extrusion processing and products variables. *Lebensmittel Wissenschaft und Technologie*, Vol.22, pp.204-207, ISSN 0023-6438.

Huang, W. N. (1998). Comparing cornflake manufacturing processes. *Cereal Foods World*, Vol.43, No.8. pp.641-643, ISSN 0146-6283.

Huber, G. R. (2000). Twin-screw extruders. In: *Extruders in food applications*, M. N. Riaz, (Ed.), pp.81-114, CRC Press, ISBN 978-156-6767-79-8, Boca Raton, United States of America.

Huber, G. R. & Rokey, G. J. (1990). Extruded snacks. In: *Snack food*, R. G. Booth, (Ed.), pp.107-138, Van Nostrand Reinhold, ISBN 978-044-2237-45-5, New York, United States of America.

Huber, G. R. (2001). Snack foods from cooking extruders. In: *Snack foods processing*, E. W. Lusas & R. W. Rooney, (Eds.), pp.315-368, CRC Press, ISBN 978-156-6769-32-9, Boca Raton, United States of America.

Ilo, S. & Berghofer, E. (1999). Kinetics of colour changes during extrusion cooking of maize grits. *Journal of Food Engineering*, Vol.39, No.1, (January 1999), pp.73-80, ISSN 0260-8774.

Ilo, S.; Liu, Y. & Berghofer, E. (1999). Extrusion cooking of rice flour and amaranth blends. *Lebensmittel Wissenschaft und Technologie*, Vol.32, No.2, (March 1999), pp.79-88, ISSN 0023-6438.

Jones, J. M. (2001). The benefits of eating breakfast cereals. *Cereal Foods World*, Vol.46, No.10, (October 2001), pp.461-467, ISSN 0146-6283.

Kadan , R. & Pepperman, A. (2002). Physicochemical properties of starch in extruded rice flours. *Cereal Chemistry*, Vol.79, No.4, (August 2002), pp.476-480, ISSN 0009-0352.

Kitabatake, N. & Doi, E. (1992). Denaturation and texturization of food protein by extrusion cooking. In: *Food extrusion: science and technology*, J. L. Kokini; C-T. Ho & M. V. Karwe, (Eds.), Marcel Dekker, pp.361-371, ISBN 978-082-4785-42-0, New York, United States of America.

Larrea, M. A; Chang, Y. K. & Bustos, F. M. (2005). Effect of some operational extrusion parameters on the constituents of orange pulp. *Food Chemistry*, Vol.89, No.2, (February 2005), pp.301-308, ISSN 0308-8146.

Lazou, A. & Krokida, M. (2011). Thermal characterization of corn-lentil extruded snacks. *Food Chemistry,* Vol.127, No.4, (August 2011), pp.1625-1633, ISSN 0308-8146.

Ledward, D. A. & Mitchell, J. R. (1988). Protein extrusion – More questions as answers? In: *Food structure: its creation and evaluation*, J. M. V. Blanshard & J. R. Mitchell, (Eds.), pp.219-229, Butterworth-Heinemann , ISBN 978-040-8029-50-6, London, United Kingdom.

Li-Chan, E. C. Y. (2004). Properties of proteins in food systems: an introduction. In: *Proteins in food processing*, R. Y. Yada, (Ed.), pp.2-26, Woodhead Publishing Limited, ISBN 978-084-9325-36-6, Cambridge, London.

Li, M. & Lee, T-C. (1996). Effect of extrusion temperature on solubility and molecular weight distribution of wheat flour protein. *Journal of Agricultural and Food Chemistry*, Vol.44, No.3, (March 1996), pp.763-768, ISSN 0021-8561.

Linko, P.; Hakulin, S. & Linko, Y-Y. (1983). Extrusion cooking of barley starch for the production of glucose syrup and ethanol. *Journal of Cereal Science*, Vol.1, No.4, (October 1983), pp.275-289, ISSN 0733-5210.

Lue, S.; Hsieh, F.; Peng, I. & Huff, H. (1990). Expansion of corn extrudates containing dietary fiber: a microstructure study. *Lebensmittel Wissenschaft und Technologie*, Vol.23, No.2, pp.165-173, ISSN 0023-6438.

MacDonald, R. S.; Pryzbyszewshi, J. & Hsieh, F. H. (2009). Soy protein isolate extruded with high moisture retains high nutritional quality. *Journal of Agricultural and Food Chemistry*, Vol.57, No.9, (May 2009), pp.3550-3555, ISSN 0021-8561.

Mendonça, S.; Grossmann, M. & Verhé, R. (2000). Corn bran as a fibre source in expanded snacks. *Lebensmittel Wissenschaft und Technologie*, Vol.33, No.1, (February 2000), pp.2-8, ISSN 0023-6438.

Mercier, C.; Linko, P. & Harper, J. M. (1998). *Extrusion cooking*, (2nd ed.), American Association of Cereal Chemists, ISBN 978-091-3250-67-8, Saint Paul, United States of America.

Mitchel, J. R. & Areas, J. A. G. (1992). Structural changes in biopolymers during extrusion. In: *Food extrusion: science and technology*, J. L. Kokini; C-T. Ho & M. V. Karwe, (Eds.), pp.345-360, Marcel Dekker, ISBN 978-082-4785-42-0, New York, United States of America.

Noguchi, A. (1998). Extrusion cooking of high-moisture protein foods. In: *Extrusion cooking,* C. Mercier; P. Linko & J. M. Harper, (Eds.), pp.343-370, American Association of Cereal Chemists, ISBN 978-091-3250-67-8, Saint Paul, United States of America.

Okelo, P.; Wagner, D.; Carr, L.; Wheaton, F.; Douglass, L & Joseph, S. (2006). Optimization of extrusion conditions for elimination of mesophilic bacteria during thermal processing of animal feed mash. *Animal Feed Science and Technology,* Vol.129, No.1-2, (August 2006), pp.116-137, ISSN 0377-8401.

Paradiso, V. M.; Summo, C.; Trani, A. & Caponio, F. (2008). An effort to improve the shelf life of breakfast cereals using natural mixed tocopherols. *Journal of Cereal Science*, Vol.47, No.2, (March 2008), pp.322-330, ISSN 0733-5210.

Pereda, J. A. O.; Rodríguez, A. I. C.; Álvarez, L. F; Sanz, M. L. G.; Minguillón, G. D. G. F.; Perales, L. H. & Cortecero, M. D. S. (2005). *Tecnologia de alimentos: componentes dos alimentos e processos,* Vol.1, Artmed, ISBN 9788536304366, Porto Alegre, Brazil.

Riaz, M. N. (2000). Introduction to extruders and their principles. In: *Extruders in food applications*, M. N. Riaz, (Ed.), pp.1-23, CRC Press, ISBN 978-156-6767-79-8, Boca Raton, United States of America.

Roberfroid, M. (1993). Dietary fiber, inulin and oligofructose: a review comparing their physiological effects. *Critical Reviews in Food Science and Nutrition*, Vol.33, No.2, pp.103-148, ISSN 1040-8398.

Ryan, L.; Thondre, P. S. & Henry, C. J. K. (2011). Oat-based breakfast cereals are a rich source of polyphenols and high in antioxidant potential. *Journal of Food Composition and Analysis*, Vol.24, No.7, (November 2011), pp.929-934, ISSN 0889-1575.

Saalia, F. & Phillips, R. (2011). Degradation of aflatoxins by extrusion cooking: effects on nutritional quality of extrudates. *LWT-Food Science and Technology,* Vol.44, No.6, (July 2011), pp.1496-1501, ISSN 0023-6438.

Singh, S.; Gamlath, S. & Wakeling, L. (2007). Nutritional aspects of food extrusion: a review. *International Journal of Food Science and Technology,* Vol.42, No.8, (August 2007), pp.916-929, ISSN 0950-5423.

Sluimer, P. (2005). *Principles of breadmaking: funtionality of raw material and process steps,* American Association of Cereal Chemists, ISBN 978-1891127458, Saint Paul, United States of America.

Stanley, D.W. (1998). Protein reactions during extrusion processing. In: *Extrusion cooking*, C. Mercier, P. Linko & L. M. Harper, (Eds.), pp.321–341, American Association of Cereal Chemists, ISBN 978-091-3250-67-8, Saint Paul, United States of America.

Stanley, D. W. (1886). Chemical and structural determinants of texture of fabricated foods. *Food Technology*, Vol.40, No.3, (March 1986), pp.65-68, ISSN 0015-6639.

Stark, A. & Madar, Z. (1994). Dietary fiber. In: *Functional foods: designer foods, pharmafoods, nutraceuticals*, I. Goldberg, (Ed.), pp.183-201, Springer, ISBN 978-083-4216-88-4, New York, United States of America.

Strahm, B. S. (2006). Meat alternatives. In: *Soy applications in food*, M. N. Riaz, (Ed.), pp.135-154, CRC Press, ISBN 978-084-9329-81-4, Boca Raton, United States of America.

Strahm, B. S. (2000). Preconditiong. In: *Extruders in food applications,* M. N. Riaz, (Ed.), pp.115-126, CRC Press, ISBN 978-156-6767-79-2, Boca Raton, United States of America.

Sumathy, A.; Ushakumari, S. & Malleshi, N. (2007). Physico-chemical characteristics, nutritional quality and shelf-life of pearl millet based extrusion cooked supplementary foods. *International Journal of Food Sciences and Nutrition*, Vol.58, No.5, pp.350-362, ISSN 0963-7486.

Tadmor, Z. & Gogos, C. G. (1979). *Principles of polymer processing*, Wiley, ISBN 978-047-1843-20-2, New York, United States of America.

Thebaudin, J. Y.; Lefebvre, A. C.; Harrington, M. & Bourgeois, C. M. (1997). Dietary fibres: nutritional and technological interest. *Trends in Food Science and Technology*, Vol.8, No.2, (February 1997), pp.41-48, ISSN 0924-2244.

Thiebaud, M., Dumay, E. & Cheftel, J. C. (1996). Influence of process variables on the characteristics of a high moisture fish soy protein mix textured by extrusion cooking. *Lebensmittel Wissenschaft und Technologie*, Vol.29, No.7, pp.526–535, ISSN 0023-6438.

Tilley, K. A.; Benjamin, R. E.; Bagorogoza, K. E.; Okot-Kotber, B. M.; Prakash, O. & Kwen, H. (2001). Tyrosine cross-links: molecular basis of gluten structure and function. *Journal of Agricultural Food Chemistry*, Vol.49, No.5, (May 2001), pp.2627-2632, ISSN 0021-8561.

Vernaza, M. G.; Chang, Y. K. & Steel, C. J. (2009). Efeito do teor de farelo de maracujá e da umidade e temperatura de extrusão no desenvolvimento de cereal matinal funcional orgânico. *Brazilian Journal of Food Technology*, Vol.12, No.2, (April/June 2009), pp.145-154, ISSN 1516-7275.

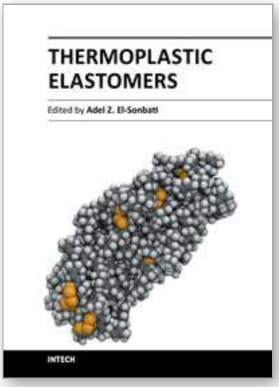
Vernaza, M. G.; Pedrosa, M. T.; Chang, Y. K. & Steel, C. J. (2010). Evaluation of the in vitro glycemic index of a fiber-rich extruded breakfast cereal produced with organic passion fruit fiber and corn flour. *Ciência e Tecnologia de Alimentos*, Vol.30, No.4, (October/December 2010), pp.964-968, ISSN 0101-2061.

Wang, W. M.; Klopfenstein, C. F. & Ponte, J. G. (1993). Effects of twin-screw extrusion on the physical properties of dietary fiber and other components of whole wheat and wheat bran and on the baking quality of wheat bran. *Cereal Chemistry*, Vol.70, No.6, pp.707-711, ISSN 0009-0352.

Wong, D. W. S. (1995). *Food enzymes: structure and mechanism*. Springer, ISBN 978-041-2056-91-8, New York, United States of America.

Yao, N.; White, P. & Alavi, S. (2011). Impact of beta-glucan and other oat flour components on physico-chemical and sensory properties of extruded oat cereals. *International Journal of Food Science and Technology*, Vol.46, No.3, (March 2011), pp.651-660, ISSN 0950-5423.

Zhu, S.; Riaz, M. & Lusas, E. (1996). Effect of different extrusion temperatures and moisture content on lipoxygenase inactivation and protein solubility in soybeans. *Journal of Agricultural and Food Chemistry,* Vol.44, No.10, (October 1996), pp.3315-3318, ISSN 0021-8561.



Thermoplastic Elastomers

Edited by Prof. Adel El-Sonbati

ISBN 978-953-51-0346-2
Hard cover, 416 pages
Publisher InTech
Published online 28, March, 2012
Published in print edition March, 2012

Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.