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Improving Nutrition Through the Design of Food Matrices

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1. Introduction

Increasing epidemiological evidence has linked the prevalence of diseases, such as obesity, cardiovascular disease, hypertension, type II diabetes mellitus, and even cancer, to dietary factors. Besides, overweight and obesity are major risk factors to the prevalence of the mentioned diet-related diseases. The obesity epidemic around the world has been attributed to energy imbalance, mainly because of increased food consumption and/or sedentary lifestyle. Changes in eating behavior and the massive amount of high-calorie foods readily available has allowed obesity to reach epidemic proportions around the world. The logical strategy to attack the obesity problem is lowering the total energy intake along with a reduction in fat and sugar/digestible carbohydrate intake, which can have a substantial impact on body weight (American Dietetic Association [ADA], 2005). In past years, the food industry developed "light" products by diminishing or replacing the amount of fat and/or sugar from high-calorie products. However, the replacement of fat and sugar decreases the palatability of foods and for consumers foods must be simultaneously safe, healthy, delicious and convenient (German & Watzke, 2004). Hence, the challenge for the food industry is much more complex than simply providing healthy foods; to provide healthy and delicious foods is the real challenge.

The control of digestion and the release of nutrients from the food matrix is an alternative approach to attack the obesity problem and other diet-related diseases. The concept of a food matrix points to the fact that nutrients are contained into a larger continuous medium that may be of cellular origin (*i.e.*, fruits and vegetables) or a structure produced by processing, where nutrients interact at different length scales with the components and structures of the medium (Aguilera & Stanley, 1999). Research on human digestion has often been undertaken with a view to changing the rates of digestion and delivery sites of macronutrients that might affect satiety and thus caloric intake. Several aspects of human eating behavior and food digestion may be relevant for identifying effective measures to treat or prevent diet-related diseases. Although most of people in developed and developing countries eat an unbalanced diet, an increasing part of the consumers are progressively more aware of the relationship between diet and health. Thus, the demand for functional food products that address specific health benefits is growing steadily (Palzer, 2009). The food industry is currently responding by reformulating its products, especially looking at

salt, sugar and fat content with a particular emphasis on healthier fat compositions (Lundin et al., 2008). New designed foods with lower amounts of fat, controlled release of bioactives, in-body self-assembly structures or slowly digestible starches are already being developed by the food industry. The structure of these products must be modified accordingly to equalize the physical (*e.g.*, rheology) and sensory (*e.g.*, taste and release of aromas) properties of the original food. Therefore, designed food structures are required to diminish the sensorial impacts of such product modifications.

The food industry has assembled considerable information about composition, biochemistry, structure, and physical properties of foods. The principles of process engineering of biomaterials and the fundamental role of food structure in understanding the behavior of foods during processing are well established (Aguilera, 2005; German & Watzke, 2004). This knowledge is the basis for the food industry to formulate, process, preserve and distribute foods. Although the total amount of a nutrient in natural and formulated foods may be obtained from composition tables, its bioavailability (*i.e.*, the rate and extent to which a nutrient contained in a food is absorbed and become available at the site of action) depend on many factors, for instance, food microstructure, processing conditions, presence of other components, among others. However, there is still a lack of information about the performance of foods inside our body, which has limited the capacity of the industry to create products with tailored nutritional properties. Therefore, this chapter is an attempt to relate how the changes induced in food matrices affect their physicochemical properties and macronutrient (protein, fat, and carbohydrate) bioavailability, improving the nutritional performance of tailored foods. This chapter initially reviews the current situation about consumer trends and health. Next, the structures of the main macronutrients are briefly revised and the steps of the digestion process are explained. Finally, examples of structured foods to improve nutrition are presented and discussed.

2. Why improving the nutritional performance of foods? Past and present situation

Health and wellbeing are the major drivers for the food industry today. Scientific evidence that the quantity, composition and microstructure of the food ingested affects health is growing steadily (Norton et al., 2007; Parada & Aguilera, 2007). Although food digestibility and nutrient bioavailability had not been taken into account in the food design until now; a better understanding of the relationship between food properties, digestion and absorption would help in the rational design of foods with enhanced nutritional properties. This section deals with modifications in consumer perception about foods and the increasing need for foods for health and wellbeing.

2.1 Changes in human eating behavior

As a consequence of changes in lifestyle, diet is increasingly affecting health. A fast-paced lifestyle has left less time to cook, thus the consumption of fast food meals (mostly cheap foods available in large quantities) is augmenting constantly. In developed and developing countries families are eating out of home more often, portion sizes of foods consumed are getting larger at the same time body weights of people continue to increase. Taking as example the United States, the incidence of obesity increased continuously over the past

decades (Fig. 1). Over-consumption of high–energy-dense (kcal/g) foods and beverages, and the increased portion sizes, may contribute to positive energy balance and lead to increasing incidence and prevalence of overweight and obesity. High-fat and sugar foods are problematic for the regulation of energy intake because they are high in energy density and very palatable. In addition, a decrease in physical activity due to the increasingly sedentary nature of many forms of work, changing modes of transportation, and increasing urbanization has contributed to the energy imbalance.

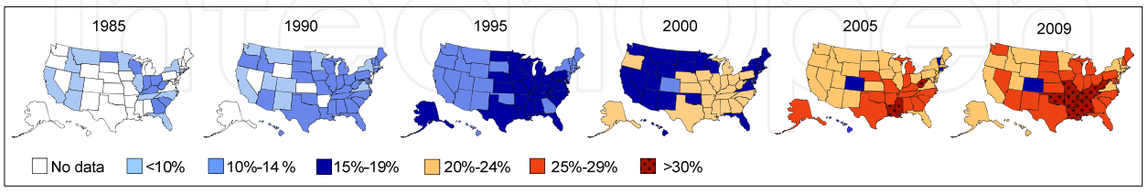


Fig. 1. Evolution of percentage of United States population by state, with a body mass index above 30, regarded as obese. Source: Centers for Disease Control and Prevention.

Nowadays, eating is driven by necessity and by pleasure. From the beginning of the humanity foods had been consumed to obtain energy and essential nutrients for living, but in modern societies foods are also consumed to have the pleasuring feeling of food flavors and textures into the mouth. Therefore, we eat because we have to and because we like to. As societies increase their purchase level, they begin to recognize the pleasurable aspects of eating, as comfort or reward and to satisfy, delight or stimulate the senses. The modern food industry has recognized this opportunity and much effort has been investing in the development of foods with enhanced sensory properties, transforming raw materials in palatable structures to gain acceptability from the consumer. Currently, we are surrounded by a huge variety of tempting high-calorie foods and cutting out or drastically restricting this kind of foods is simply not sustainable, probably because tastier foods are more rewarding and initiates some kind of seeking behavior.

The worldwide increase in the above mentioned diet-related problems are likely to change eating habits, processing technologies, and products. Hence, the food chain is facing a major challenge and now it is the consumer who indicate to producers what they want to eat. This global tendency is reshaping the industry into one that provides, in addition to safe and high-quality foods, products that contribute to the health and wellness of consumers. On this regard, the major food companies have understood that health and wellbeing are the major drivers for the current food industry, which is well represented in their logos, "*Good food, good* life" from Nestlé, "*Feel good, look good and get more out life*" from Unilever and "*The Beverage Institute for health and wellness*" from The Coca-Cola Company. The above are some examples of the messages that these companies want to give to the current health-conscious consumer.

2.2 Food-related diseases focused on obesity

Obesity, a preventable disease, with its co-morbidities such as the metabolic syndrome and cardiovascular diseases, are the major medical problems of the last decades. The health consequences and compromised quality of life associated with obesity provide major incentives to reduce the continuing obesity epidemic. The large numbers of children entering adulthood overweight together with weight gain in adulthood, produce an enormous burden in terms of human suffering, lost productivity and health care

expenditures. The solution to overweight and obesity problem is body weight maintenance after body weight loss. This seems simple, but the required conditions are difficult to achieve for many individuals. Fortunately, the evidence has shown that many of the health risks associated with obesity can be reversed with weight loss.

Once considered a problem only in developed countries, obesity is now dramatically increasing in developing countries. According to the World Health Organization (WHO, 2011), some important key facts about obesity are:

- Worldwide obesity has more than doubled since 1980.
- 1.5 billion adults were overweight in 2008.
- 43 million children under the age of five were overweight in 2010.
- 2.8 million adults die each year as a result of being overweight or obese.
- 44% of the diabetes burden, 23% of the ischemic heart disease burden and between 7% and 41% of certain cancer burdens are attributable to overweight and obesity.
- 2.3 billion adults will be overweight and more than 700 million obese by 2015.

According to Wansink (2007), over 85% of the population with weight problems has consumed an average excess of only 25 kcal/day over a prolonged period of time. A sustained reduction in daily calorie consumption could prevent or reduce this long term weight gain in a large proportion of the population, and thus to reduce the incidence of obesity and associated health problems. Fatty foods have high-energy density and palatability but exert a relatively weak effect on satiation (compared calorie per calorie with protein and carbohydrate foods), which may encourage calorie over-consumption (Marciani et al., 2007). Lowering energy density of foods can decrease energy intake independent of macronutrient content and palatability.

The human mechanism of appetite regulation is highly complex involving neurophysiological interactions between the gut and the brain. The stomach is able to signal by distension of its wall how full it is and, therefore, how much more should be eaten, and duodenal receptors sensitive to the nutrient content of the chyme (*i.e.*, semifluid mass of partly digested food expelled by the stomach into the duodenum) also signal satiety through the secretion of gut hormones. Besides, neurological pathways including the hypothalamus, where two major neuronal populations stimulate or inhibit food intake, and the brain steam are involved (Marciani et al., 2001a; Suzuki et al., 2010). Understanding the neurophysiological mechanism of appetite regulation could help to food technologists in developing more satiating foods.

The energy density of foods has been demonstrated to have a robust and substantial effect on both satiety and satiation. Satiety refers to the effects of a food or meal after eating has ended, whereas satiation (sensation of fullness) refers to the process involved in the termination of a meal (ADA, 2005). Satiation has been found to be independent of the administered macronutrient (fat, protein or carbohydrate) for isocaloric liquid foods, but it was linearly related to the meal volumes, suggesting that stomach distension is a key factor in the sensation of fullness (Goetze et al., 2007).

Enhancing the satiety level of foods while keeping a low energy density may restrict the daily food intake and the desire of overeating, which it can be a strategy for preventing over-consumption and energy imbalances. Reduced-energy foods should preserve the sensory properties of the original foods to play a potential role in helping against obesity. Designed foods with tailored mechanical properties of the material, low caloric density and designed flavor properties may help in developing new foods for a sustainable reduction in energy intake, thus helping us of fighting against obesity.

2.3 Evidence relating the impact of food structure on nutrition

Physicochemical and sensory properties of manufactured foods depend largely on the food matrix structure. Currently, there is an emerging interest in the impact of food structure on digestion behavior and its relationship to human nutrition (Lundin et al., 2008). New interest has arisen regarding the function that food structure may play once foods are inside the body and, consequently, in our nutrition, health and wellness. Attention is further supported by the increased belief that foods and not nutrients are the fundamental unit of nutrition (Jacobs & Tapsell, 2007). The last assumption is based on recent scientific data demonstrating that in the case of certain nutrients the state of the food matrix of natural or processed foods may favor or hinder their nutritional response *in vivo*.

In recent years, there has been an upsurge in efforts to understand how food structure influences the rates of macronutrients digestion. This research is being undertaken with a view to developing novel foods that regulate calorie intake, provide increased satiety responses, provide controlled lipid digestion and/or deliver bioactive molecules (Singh & Sarkar, 2011). Foods are consumed to maintain human biological processes and the food matrix influences these processes (Jacobs & Tapsell, 2007). It has been shown that disruption of the natural matrix may influence the release, transformation and subsequent absorption of certain nutrients in the digestive tract (Parada & Aguilera, 2007).

Food processing modifies physical and chemical properties of food and thus may influence the release and uptake of nutrients from the food matrix. In this complex scenario, food scientists have proposed to develop novel foods to control the impact of physical properties and food microstructure on the digestion behavior and its relationship to human nutrition, because in many cases the interactions between individual macronutrients control the rate of digestive processes, conditioning the absorption of nutrients. Thus, the release of nutrients from the food matrix as well as the interactions between food components and restructuring phenomena during transit in the digestive system becomes far more important than the original contents of nutrients (Troncoso & Aguilera, 2009).

2.4 Modifying the food matrix to minimize or maximize nutrients bioavailability

According to Aguilera (2005) "*the creation of new products to satisfy expanding consumer's demands during this century will be based largely on interventions at the microscopic level*". Thus, to make this next generation of designed foods, a combination of understanding of material chemistry and material science is needed, together with an understanding of how the processing affects food structure, chemistry and attractiveness (Norton et al., 2006).

The food industry is extremely innovative in terms of new products, but is highly traditional in term of processes. For a particular product type, a limited range of unit operations have been employed for some considerable time and the same process lines are used to make a range of different product structures. The current challenge is to develop novel functional structures through innovative processing or new units operations. It is conceivable that enhanced nutritional properties of foods may be achieved by proper assembly of hierarchical structures from the microscopic level up to the macroscale (*i.e.*, bottom up approach). These new fabrication techniques will require understanding and precise control of assembly processes at all scales.

Nutrient bioavailability is gaining considerable attention in food technology. While one of the ongoing concerns of the food industry has always been to produce and provide the consumer with safe foods, the nutritional and caloric composition is now becoming equally

important. For this reason, during the last years considerable research has been conducted to modify food matrices in basis on their physicochemical properties and effects on food digestion. For instance, the direct effect of physical properties (*e.g.*, microstructure, particle size and physical state) of foods has been evaluated by its influence on nutrient absorption. So, different intentional modifications could be induced by food technologists to design and fabricate foods with controlled bioavailability.

Foods can be viewed as delivery systems of macro and micronutrients to improve nutrition. Delivery systems to encapsulate, protect and deliver bioactive components are widely used by the pharmaceutical industry to carry these active agents to specific locations within the gastrointestinal tract (GIT) and release them at controlled rates. Using this knowledge the food industry, through the design of food matrices, is developing similar systems to encapsulate, protect and deliver food components. However, the effectiveness of the encapsulation process relies on the preservation of the bioavailability of the encapsulated component and the release of it in the correct portion within the GIT. As mentioned before, little it is known about the influence of food structure and breakdown on nutrient release in the GIT. This point is the primary importance because only what is released can be bioavailable for absorption (Parada & Aguilera, 2007).

Structuring matrices for nutrient delivery is a subject of enormous interest and several structuring food biopolymers are under study. To develop structured foods and develop a strategy for controlled release of food nutrients at desired sites in the GIT, it is essential to understand the kinetics of food disintegration and predict its digestion and subsequent metabolism. Biochemical, physiological, and physicochemical parameters that influence these processes need to be understood. This knowledge will benefit the food-processing industry in developing proper food structures for health purposes. The possibility of predicting the release of nutrients from food matrices under simulated GIT conditions is the upmost relevance in order to be able to define relationships between food matrix-nutrient, as well as for looking at the interactions of ingredients with the enzymes involved in the digestive process. Although *in vivo* methods provide direct data of bioavailability, ethical restrictions and complex protocols limit this type of studies when humans are used in biological research (Parada & Aguilera, 2007). Therefore, the need for validated *in vitro* methods is urgent in order to evaluate and compare the effect of the microstructure over the amount and the rate of nutrients release in the GIT.

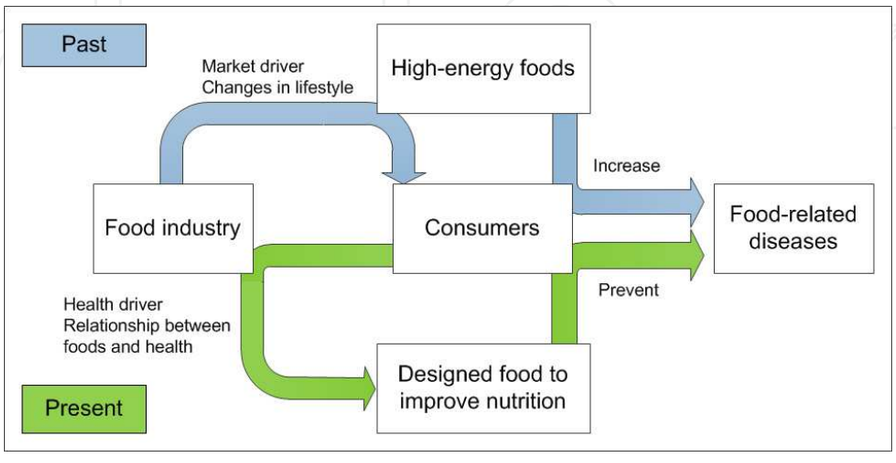


Fig. 2. Past and present scenarios of the relationship between consumers and food industry.

Summarizing, the terms "quality" and "health" are two main drivers of the modern food industry and the food microstructure influences both. Figure 2 gathers the principal subjects discussed in this section. To accomplish the ultimate goal of designing healthy foods with enhanced quality, knowledge of the overall food structure including the main building blocks of foods (proteins, carbohydrates and lipids) and a vast comprehension of the human digestion process are urgently needed to properly address the design of the future foods, which it will be discussed in the next sections.

3. Understanding the main food components and their structures

Foods consist of a complex group of components that differ in chemical composition and physical structure. Foods are largely composed by polymers (*i.e.*, proteins, carbohydrates, and lipids), micronutrients and water. Altogether, these components are arranged in different food matrices as the result of the multiple interactions that polymers can display under different conditions in an aqueous medium, as well as of the abundance of each respective substance. Proteins, carbohydrates and lipids are simple macromolecules made up of even simpler repeating units that play an important role in human nutrition. Each of these polymers has well-defined structures in the foods that contain them. This section discusses about the structure of proteins, carbohydrates, and lipids in foods and its impact on nutrient bioavailability.

3.1 Proteins

Protein is the most effective macronutrient found in foods providing satiety, on an energy equivalent basis, and protein hydrolysates comprising short chain peptides have been shown to induce release of satiety hormones, such as cholecystokinin (CCK), as part of this process (Lundin et al., 2008; Mackie & Macierzanka, 2010).

Proteins are certainly the most complex macromolecule encountered in foods. This complexity is evident in their secondary structure, which is intrinsically related to the sequence of amino acids (AAs) along the backbone. It is commonly recognized that 20 AAs form the building blocks of most proteins, being linked by peptide (amide) bonds. As a consequence, various proteins with different AA sequences will also differ in structure, modifying their physical properties.

Four levels of hierarchical organization are used to describe protein structure. The primary structure of a protein refers to the order of AA sequence in the polypeptide chain. The secondary structure describes the regular local conformations of the polypeptide backbone. The description of the overall three-dimensional folding of the protein is referred to as its tertiary structure. It involves the folding pattern of the polypeptide backbone including the secondary structures, arrangements of motifs into domains, and conformations of the side chains. Ultimately, the quaternary structure refers to the fourth-dimensional level of structure of protein complexes that may arise from the association of identical or heterogeneous polypeptide chains (Li-Chan, 2004). Changes in the secondary, tertiary, and quaternary structures without cleavage of backbone peptide bonds constitute "denaturation". In practical terms, denaturation means the unfolding of the native structure (Aguilera & Stanley, 1999). Protein denaturation usually has a negative connotation, since it is associated with loss of functionality in foods. However, it is often a prerequisite for improved digestibility, biological availability, and improved performance (*e.g.*, foam formation, emulsification or gelation). Denaturation not only affects the physical state of

proteins but also their susceptibility to pepsin and trypsin/chymotrypsin mixture during digestion (Troncoso & Aguilera, 2009).

The most important factor in proteolysis is the accessibility of the enzyme to substrate and this involves both exposure of the cleavage site and local flexibility of the molecule and its side chains (Mackie & Macierzanka, 2010). In addition, hydrolysis of food proteins by digestive enzymes generates bioactive peptides that may exert a number of physiological effects *in vivo*, for example on the gastrointestinal, cardiovascular, endocrine, immune and nervous systems. On the other hand, some proteolysis-resistant proteins may produce allergenic reactions. Different factors regulate the allergenic potential (*i.e.*, defined as immunoglobulin E-mediated hypersensitivity reactions) of protein foods, such as type and composition of AAs, physicochemical characteristics of proteins, and relative abundance of the allergen in the food.

It is known that β-lactoglobulin (β-lg), a recognized allergenic protein, is hardly hydrolyzed by enzymes such as pepsin and chymotrypsin, but not by trypsin. The relative resistance to proteolysis is generally explained by the compact globular tertiary structure of the protein at low pH (<pH 3), which protects most of the peptide bonds susceptible to enzyme action. Physical and/or chemical denaturation of β-lg generally leads to a higher rate of hydrolysis by gastrointestinal enzymes. Stănciuc et al. (2008) showed that thermal treatment caused partial unfolding of β-lg and consequently an increased rate of hydrolysis by both trypsin and chymotrypsin at 37 °C. This phenomenon was attributed to the accessibility of the specific peptide bonds to the enzymes being enhanced. After heating at 78°C, a decrease in hydrolysis after prolonged heating time was thought to be due to aggregation phenomena, which could have hidden some susceptible bonds. High pressure treatment (HP) of β-lg between 400 and 800 MPa promoted digestion by pepsin, because HP treatment caused significant unfolding of the protein molecule (Chicón et al., 2008; Zeece et al., 2008).

Aggregation (cross-linking) of proteins results in the formation of high-molecular-weight polymers. These modifications are expected to affect the kinetics of protein digestion due to the reduced availability of reactive sites to proteolysis. Depending on the pH, temperature and presence of ions, proteins can be transformed into fibrils, spherical micro-gels, micro-particles, fractal aggregates and gels (Schmitt et al., 2007). Such controlled aggregation allows the management of molecular interactions to achieve the desired protein structures. Enzymatically cross-linked β-casein decreased their digestibility in comparison with native β-casein (Monogioudi et al., 2011). Heat treatment of milk (sterilization) increases protein resistance to the *in vitro* digestion in comparison with unheated milk, probably because of the structural changes caused by denaturation and aggregation of whey proteins and/or casein with whey proteins through disulfide bounds (Almaas et al., 2006; Dupont et al., 2010). In addition, structuring β-lg into fibrils (formed by heating solutions at 80°C and pH 2.0 for 20 h) induces a more complete digestion by pepsin (Bateman et al., 2010).

Hence, by using carefully controlled processing parameters (mainly temperature, pH, ionic strength, and pressure), protein structures can be designed to release selected bioactive peptides, decrease allergenicity of protein and also induce a higher sensation of satiety during protein digestion.

3.2 Lipids

It is usually considered that, in the normal diet, some 25 to 30% of the total calories are conveniently supplied as lipid. Certain lipids are needed for good health (*e.g.*, essential fatty acids and fat-soluble vitamins). Nevertheless, the over-consumption of some dietary lipids (*e.g.*, cholesterol, saturated fats, and *trans*-fatty acids) increases the prevalence of some

public health problems, including cardiovascular disease and obesity (Simopoulus, 1999). In this scenario, an improved knowledge of lipid structure could address the rational design of dietary lipids to enhance or retard lipid digestion, aspect having strong nutritional and health impact.

Lipids are a chemically heterogeneous group of compounds characterized by their insolubility in water, but soluble in organic solvents. In general, lipids are conformed by fats and oils. The basic unit of natural fats and oils is the triglyceride (TG) molecule; however, others molecules, such as monoglycerides (MGs), diglycerides (DGs), and phospholipids (PLs), can be structuring dietary lipids too. The TG molecule consists of a glycerol backbone to which are acylated three fatty acids (FAs). Two FAs are at the ends of the glycerol molecule (sn-1 and sn-3 positions) pointing in one direction, while the third FA molecule in the middle (sn-2 position) is pointing in the opposite direction. The dietary FAs molecules that compose the TG structure may vary in the number of carbon atoms and the presence of double bounds from saturated FA to unsaturated FA. The type and position of the FA chains on the glycerol backbone affect the structure of the TG molecule and, consequently, its bioavailability. TGs containing short- and medium-chain FAs have higher rate of FA release during lipolysis than for long-chain FAs, and is faster for FAs at the sn-1 and sn-3 positions than in sn-2 position (Fave et al., 2004). On the other hand, a typical TG molecule can exhibit three physical states: crystal, bulk, and interface. These physical states will determine the properties and characteristics of the physical state of the lipid phases in foods, which vary from liquid to crystalline phases. The lipid phases in most foods are usually liquid at body temperature (~37^{o}C), but in some foods they may be either fully or partially crystalline. The crystallinity of the lipid phase may alter the ability of enzymes to digest the emulsified lipids. For example, the release rate of a lipophilic drug can be decreased with increasing crystallinity degree of lipid droplets (Olbrich et al., 2002). Hence, according to the above mentioned aspects, composition, structural organization and physical state of lipid phases will control lipid digestion. In addition, lipids have the property of forming, in the presence of water, different self-assembled structures. These mesophase structures include monolayers, micelles, reverse micelles, bilayers, and hexagonal phases. The aqueous medium behavior of lipids is determined by intrinsic parameters such as lipid polarity, length and branching of acylated fatty acids, presence of double bounds, among others (Ulrich, 2002). Mesophase structures of lipids have different sizes and configurations and, for this reason, they are finding many applications in food, pharmaceutical, and cosmetics industries. Nowadays, bilayer vesicles (*i.e.*, often called liposomes) have received widespread attention because of their ability to entrap functional components. This characteristic allows use of these structures as drug-delivery vehicles for controlling the release of incorporated agents.

The lipid molecules in foods may be organized into a number of different forms, including as bulk, structural, emulsified, colloidal, or interfacial structures (McClements, 2005). However, invariably, all ingested lipids ends up as an emulsion either by gastric emulsification or prior to ingestion during manufacturing process. The structure of these emulsions is determined by the nature of the lipid phase, the aqueous phase and the interface (Lundin et al., 2008). Particularly the properties of the interface modulate lipid digestion. The interface of emulsified lipids is determined by the physicochemical properties of lipid, such as lipid droplet size (which determines the interfacial area of lipid droplets), structure of lipid droplet, and the molecular structure of the TGs that constitute the lipid droplet (Armand et al., 1999). Several works have investigated the impact of emulsion structure on lipid digestion. For example, it has been demonstrated that a lower initial fat

droplet size facilitates fat digestion by lipase (Armand et al., 1999). Additionally, the composition of the emulsion interface can limit the lipase activity. Interfaces composed by phospholipid limit fat digestion in the absence of bile salts because there are few possible points where lipase can access the emulsified substrate (Wickham et al., 1998).
In principle, rational design of lipid structures may be a useful tool for food processors to control lipid digestibility and bioavailability. Nevertheless, there is clearly a need for further research to establish the key physicochemical factors that impact the performance of food lipids within the GIT.

3.3 Starch

Carbohydrates constitute the most heterogeneous group among the major food elements, ranging widely in size, shape, and function. Polysaccharides such as starch, cellulose, hemicellulose, pectic substances and plant gums provide textural attributes such as crispness, hardness, and mouthfeel to many foods. Many of them can form gels that will constitute their structure and also enhance viscosity of solutions owing to their high molecular weight (Aguilera & Stanley, 1999).
Although carbohydrates are not essential in the diet, they generally make up ~40–45% of the total daily caloric intake of humans, with plant starches generally comprising 50–60% of the carbohydrate calories consumed (Goodman, 2010). Hence, starch becomes the most important source of energy in the human diet. Due to its functionality, starch is used in a wide range of foods for a variety of purposes including thickening, gelling, adding stability and replacing expensive ingredients. There are a number of different structural scales to be considered in starch, ranging through the distribution of individual starch branches, through the overall branching structure of the starch molecules in a granule, to the macroscopic structure of the grain (Dona et al., 2010).
Starch is formed by two polymers of glucose, amylose and amylopectin. Starch is a plant storage polysaccharide synthetized in the form of granules (normally 1-100 μm in diameter) in which molecules are organized into a radially anisotropic, semi-crystalline unit. Starch molecule is composed of the straight-chain glucose polymer amylose (with α-1,4 glycosidic linkages) and the branched glucose polymer amylopectin (with α-1,6 glycosidic bonds) (Pérez et al., 2009). Normal starches, such as maize, rice, wheat and potato, contain 70–80% amylopectin and 20–30% amylose (Jane, 2009). Amylopectin, the major component in starch, strongly influences its physicochemical and functional properties.
There are several levels of structural complexity in starch granules. The first level is the "cluster arrangement", in which most starch granules are made up of alternating amorphous and crystalline shells. This structural periodicity is due to regions of ordered, tightly packed parallel glucan chains (crystalline zones) alternate with less ordered regions corresponding to branch points (amorphous zones). Thus, the starch granule appears to be formed by alternating concentric rings (growth rings).
Starch granules are insoluble in cold water and are densely packed in its native form. In the raw form, the native granule is generally indigestible for humans due to this semi-crystalline structure. The addition of water and the application of heat to native granules is essential to transform them into foods with pleasing textural attributes. Gelatinization and retrogradation are the main microstructural changes related to starch digestion. Gelatinization is the collapse (disruption) of the molecular order within the starch granule manifested in irreversible changes in properties such as granular swelling, native crystallite melting and starch solubilization (Mason, 2009). When granules of starch are heated in the

presence of water, the amorphous regions that pervade the whole granule swell (up to 50 times), forming a continuous gel phase. As the temperature exceeds a value between 50 and 80°C (depending on the crystallinity degree), the crystalline structure of the matrix is broken down. As gelatinization proceeds, the granule network is destroyed and amylose diffuses into the aqueous medium, increasing its viscosity. Further heating and/or shear disrupts the granule and a starch paste consisting of a continuous phase of amylose and amylopectin is formed (Aguilera & Stanley, 1999; Jane, 2009). The total amount of bioaccessible starch is the principal factor affected by the gelatinization process, thus a gelatinized granule is more digestible than a raw granule because the digestive enzymes can attack more easily the active sites. In fully isolated amylose or amylopectin molecules the digestion rate would be basically the same and occur relatively fast (less than 10 min). Then, the change in the total amount of digestible starch in a food can be explained because in most foods starch is present as a combination of raw or partly gelatinized granules (more resistant to digestion) and gelatinized granules (more digestible).

Retrogradation is the phenomenon occurring when the molecules comprising gelatinized starch begin to re-associate in an ordered structure (Mason, 2009). During aging, starch molecules can re-associate into crystalline segments (retrograde), losing water from the structure and undergoing an incomplete re-crystallization. Amylose and amylopectin have different behaviors, for example, amylose has a high tendency to retrograde and produce tough gels, whereas amylopectin, in an aqueous dispersion, is more stable and produces soft gels (Jane, 2009). Re-crystallization can lower the digestibility of starch because the resulting structure is less accessible to enzymes (Parada & Aguilera, 2011a).

Starch retrogradation and water-limited gelatinization should present an opportunity to redesign starchy foods aiming at reducing the glycemic response (GR), defined as the concentration of glucose in the blood after ingestion. An understanding of the internal organization of starch granules is crucial for food scientists and engineers to comprehend the functionalities and improve the nutritional properties of designed starch products.

4. Digestion: A step-by-step process controlled by different food structures

The manner in which a food is structured impacts its breakdown during digestion and consequently certain nutrional functions such as nutrient release and bioaccessibility (Parada & Aguilera, 2007). This requires understanding what happens inside the gut when a food is ingested and how the GIT behaves as the interface between the body and the food supply (Norton et al., 2007). The GIT is a highly specialized system that allows humans to consume diverse food matrices in discrete meals to meet nutrient needs. The main organs of the GIT include the mouth, the stomach and the small intestine. Figure 3 summarizes some components and phenomena occurring in the GIT during food digestion.

The digestive system is connected to the vascular, lymphatic and nervous systems to facilitate regulation of the digestive response, delivery of absorbed compounds to organs in the body and the regulation of food intake (Schneeman, 2002). In the mouth the food is broken down by the chewing action, mixed with saliva, and undergoes a temperature change as heat flow occurs (heating or cooling to body temperature). The foods are processed to the stage at which a bolus can be formed and swallowed, passing through the esophagus to the stomach (Lucas et al., 2002). The motility of the stomach (*i.e.*, with a maximum contraction force ranging from 0.1 to 1 N) continues the process of mixing food with the digestive secretions (Marciani et al., 2001b), now including gastric juice which contains acid and some digestive enzymes (*e.g.*, gastric lipase and pepsin), inducing further reduction of particle size, remixing and phase

separation (*e.g.*, oil and aqueous phases). Typically, there is an appreciable increase in the pH of the stomach contents after ingestion of a food, followed by a gradual decrease to around pH 2 over the next hour or so. After being ingested a food component may remain in the stomach for a period ranging from a few minutes to a few hours depending on its quantity, physical state, structure and location (Weisbrodt, 2001). In the stomach occurs a complex dynamic step affecting the kinetics and pattern of subsequent digestion in the small intestine. The action of the stomach continues to break down the food into smaller particles prior to passage to the small intestine (Hoebler et al., 2002). Once the chyme is in the small intestine, peristaltic motor activity propels it along the length of the intestine and segmentation allows mixing with digestive juices, which include pancreatic enzymes, bile salts (BSs) and sloughed intestinal cells. Digestion of macronutrients, which began in the mouth, continues in the small intestine primarily through the action of enzymes. Each of the macronutrients has a unique set of enzymes that break the macromolecules into sub-units that can be taken up by the absorptive systems in the intestinal cells, allowing the subsequent transport of nutrients to the systemic circulation (Salminem et al., 1998). In this section we give a brief overview of the basic physiological events that occur during the digestion of the main macronutrients (proteins, lipids and carbohydrates) found in natural and processed foods.

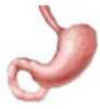
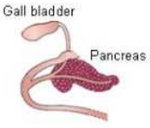
ORGANS	COMPONENTS	CONDITIONS	PROCESSES
Mouth 	Amylase (salivary α-amylase) Lipase (lingual lipase) Mucin, Salts	pH 5-7 Mechanical forces 5-60s	Mixing/Dilution Matrix disruption Structural changes Phase transitions Digestion
Stomach 	Proteases (pepsin/pepsinogen) Lipases (gastric lipase) HCl, Salts	pH 1-3 Gastric grinding (0.1-1 N) 30 min-4 hours	Mixing/Dilution Emulsification Droplet breakup/Coalescence Molecular interactions Competitive absorption Precipitation Gelification Digestion
Small intestine 	Proteases (trypsin, chymotripsin, elastase, carboxypeptidase) Lipases (pancreatic lipase, pancreatic lipase-related proteins, carboxyl ester lipase, phospholipase A2) Amylase (pancreatic α-amylase) Salts, Bile, Phospholipids	pH 6-7.5 Mixing 1-2 hours	Mixing/Dilution Emulsification Droplet breakup/Coalescence Molecular interactions Competitive absorption Surface denaturation Micellization Digestion Transport Absorption

Fig. 3. Summary of the major components and processes involved in the digestion of foods.

4.1 Protein digestion

Proteins typically make up about 10% of caloric intake in a normal diet, being a dietary component essential for nutritional homeostasis in humans. In general, ingested protein undergoes a complex series of degradative processes promoted by hydrolytic enzymes (*i.e.*, proteases) originating in the stomach, pancreas, and small intestine. The product of this proteolytic activity is a mixture of AAs and small peptides that are absorbed by the small intestinal enterocytes (Erickson & Sim, 1990). Consequently the nutritional value of protein, also known as protein quality, is related to its AA content, to its digestibility (which can be regulated by the food processing) and to the subsequent physiological utilization of specific AAs after digestion and absorption (Friedman, 1996).

Protein digestion begins in the stomach by the action of gastric proteases. When the bolus enters the gastric lumen is not only exposed to hydrochloric acid and salts but also to different pepsins, the major gastric proteases. An acidic milieu is required for the proteolytic activity of pepsins, with an optimum activity between pH 1.8 and 3.2 (Untersmayr & Jensen-Jarolim, 2008). The action of the gastric proteases results in a mixture of large polypeptides, smaller oligopeptides, and some free AAs. These hydrolytic products regulate diverse gastric functions that are under hormonal control, such as secretion of acid and pepsinogen and rate of gastric emptying (Erickson & Sim, 1990). Subsequently, the remaining proteins and polypeptides present in the chyme are released into the small intestine, where they are exposed to a variety of proteases and peptidases (see Figure 3) synthesized and released by the pancreas (*i.e.*, the major source of proteases in the digestive system), and by the specific peptidases of the brush border of the intestinal mucosa (Whitcomb & Lowe, 2007). The single AAs, di-, and tri-peptides resulting from the intestinal digestion are taken up by enterocytes (where small peptides of up to 3 AAs are split into AAs by cytosolic peptidases) and then are used as nutrients for the human body (Untersmayr & Jensen-Jarolim, 2008).

Nowadays, the fate of dietary proteins during gastrointestinal digestion has become of particular interest because of the potential role that digestion may play in determining the allergenic potential of foods. In this context, the fundamental role of the stomach as the primary organ of protein digestion is very well recognized, leading to the classification of proteins as digestion-resistant or digestion-labile proteins (Moreno, 2007). Resistance of proteins to pepsin digestion has been proposed as a marker for potential allergenicity because it does appear to be a characteristic shared by many food allergens (*e.g.*, β-lg, α-lactalbumin and casein in cow's milk, parvalbumin in fish, ovomucoid and ovalbumin in egg, tropomyosin in shellfish and seafood, and Ara h 1 and Ara h 3 in peanut) (Mills & Breiteneder, 2005). Hence, there are groups of proteins, such as storage proteins or structural proteins, more stable to proteolysis in the GIT. Consequently, it has been postulated that for a food protein sensitizing an individual, it must have properties which preserve its structure from degradation in the GIT (such as resistance to low pH, bile salts, and proteolysis), thus allowing enough allergen to survive in a sufficiently intact or immunologically active form to be taken up by the gut and sensitize the mucosal immune system (Moreno, 2007). In this scenario, further investigation is needed to reveal the mechanisms controlling the allergenic potential of foods, as well as the influence of the food matrix on the gastrointestinal digestion and absorption of protein allergens.

4.2 Lipid digestion

Lipids are a major source of calories (9 kcal/g) in our daily diets and food emulsions (*e.g.*, mayonnaise, sauces, dressings) a major carrier of fat calories. The composition, structure and properties of fatty foods change appreciably during digestion. The structural organization and properties of the lipids within the bolus depend on their initial structural organization within the food, as well as the duration and intensity of the mastication process. In most cases, the lipids in the bolus are present as oil droplets stabilized at their interfaces by particles, proteins or surfactants, which may vary in size from around a micrometer (for some food emulsions) to more than a millimeter (for some bulk fats). These emulsified oil droplets may have been present in the original food or they may have been formed within the mouth due to breakdown of a bulk fat phase and the interaction with proteins (Hernell et al., 1990). In general, there is still a relatively poor understanding of the physicochemical and structural changes that occur within the mouth when fatty foods are consumed,

although considerable progress has been made for some lipid foods such as emulsions and gels (Malone et al., 2003; Vingerhoeds et al., 2005).

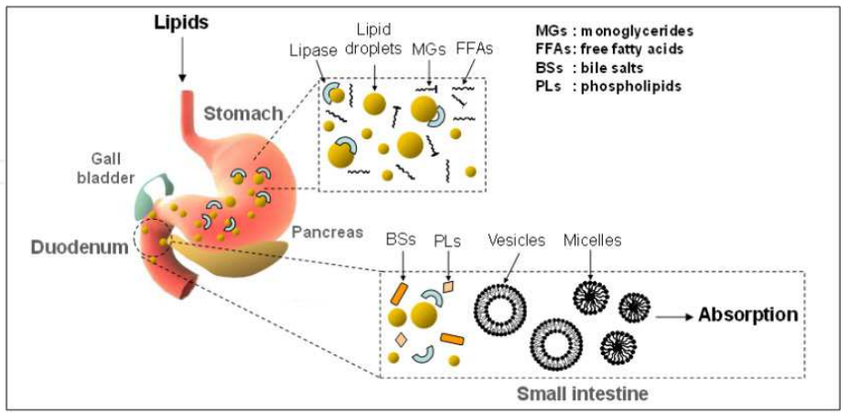


Fig. 4. Scheme of the digestive process of lipid foods.

After the food is swallowed it rapidly passes down the esophagus and enters the stomach, where it is mixed with acidic digestive juices containing gastric enzymes, minerals and various surface active compounds, and is also subjected to mechanical agitation due to movements of the stomach. During gastric digestion occurs breakdown of the food matrix structure, lipid droplet coalescence/disruption processes, and changes in the interfacial composition of the lipid phase due to adsorption/desorption of surface active substances (*e.g.*, proteins) to the surfaces of lipid droplets. Emulsion stability in the acidic gastric environment can readily be manipulated by altering the nature and state of the emulsifier agents, as revealed by non-invasive MRI studies in humans (Marciani et al., 2004). To be effective, the gastric lipase has to reach the surface of the lipid droplets in order to hydrolyze the emulsified TGs to DGs, MGs, and free fatty acids (FFAs). Typically, lipid hydrolysis stops when 10-30% of the FFAs have been released from the TGs (Armand, 2007). The emulsified lipids within the chyme are transferred from the stomach to the duodenum where they are mixed with sodium bicarbonate, BSs, phospholipids (PLs) and enzymes. The sodium bicarbonate secreted into the small intestine causes the pH to increase from highly acidic in the stomach to neutrality (pH 6.0-7.5) in the duodenum, where the pancreatic enzymes work most efficiently (Bauer et al., 2005). BSs and PLs are surface-active agents that can facilitate emulsification of the lipids by adsorbing to the droplet surfaces (Porter et al., 2007). The combined action of BSs and pancreatic juice brings about a marked change in the physicochemical form of the luminal lipid emulsion. In addition, the chyme is subjected to shear flow patterns in the small intestine that promote mixing and further emulsification. The lipid hydrolysis continues within the duodenum through the actions of lipases originating from the pancreas (Armand, 2007). A pancreatic lipase/colipase complex has to bind to the surface of the lipid droplet to hydrolyze the TGs to DGs, MGs, and FFAs, hence any compound covering the surface must be previously liberated (Jurado et al., 2006). Finally, lipid digestion continues in the small intestine with desorption and dispersion of insoluble lipid into an absorbable form. The digested lipids are solubilized in the lumen of the small intestine into at least two types of nanostructures: bile salt micelles and unilamellar vesicles. These assemblies are subsequently absorbed into the enterocyte´s brush border membrane lining the surface of the small intestine. Thus, the absorption of digested fat and fat-soluble molecules that occurs in the small intestine is usually >90% (relatively high efficiency)

(German & Dillard, 2006). Figure 4 shows a highly schematic diagram of lipid digestion in the GIT where it is possible to observe that the dynamics of lipid digestion leads to the breakdown of complex structures, which disassemble during transit in the GIT.

4.3 Carbohydrate digestion

Starch, sucrose and lactose are the most important digestible carbohydrates in the human diet. However, from a nutritional point of view, the starch is the main carbohydrate derived from foods contributing significantly to the exogenous supply of glucose and total food energy intake (Slaughter et al., 2001). Starch is stored in plants as partially crystalline granules that contain two distinct polysaccharide fractions - amylose and amylopectin (*i.e.*, both polysaccharides composed of glucose molecules linked by digestible glycoside bonds). Upon cooking in the presence of water starch granules swell and partly disintegrate, facilitating the action of degrading enzymes that progressively transform them into maltose and glucose. The main characteristic of starch, compared with simple carbohydrates, is its slow digestion in the small intestine, which it produces a moderate GR. Additionally, food microstructure also affects the kinetics of starch hydrolysis and, consequently, the GR of starchy products, which it can be considered a reflection of the final nutritive effect of the food (Parada & Aguilera, 2007). In this way, the effect of the microstructure on digestibility of starchy foods may be manifested in two ways: the degree of starch gelatinization and the effect of the food matrix (non-starchy). These microstructural factors change from one food to another, modifying the digestibility of starch and its glycemic response (Fernandes et al., 2005).
In humans there are several enzymes that hydrolyze starch. In the mouth, saliva contains α-amylase, enzyme that hydrolyses accessible starch, but since this starch remains in the mouth for a short period, the level of digestion is small. Once the food is partly digested in the mouth it is transported to the stomach, where there is no starch digestion but breakdown of food matrix will facilitate the access of hydrolytic enzymes to active sites for starch degradation in the small intestine. In the small intestine, the food receives pancreatic juice that contains pancreatic α-amylase, which hydrolyzes glycoside bonds producing glucose (absorbed in the intestinal epithelium), oligosaccharides and dextrins (Tester et al., 2004). However, it is known that the extent of starch digestion within the small intestine is variable and that a substantial amount of starch escapes digestion in the small intestine and enters the colon. The reasons for the incomplete digestion of starch may be separated into intrinsic factors (*i.e.*, physical form, presence of amylose-lipid complexes, and α-amylase inhibitors) and extrinsic factors (*e.g.*, chewing and transit through the bowel) (Cummings & Englyst, 1995).
Commonly, the GR is a way to know the bioavailability of starch and the nutritive effect of starchy foods. This metabolic response after food ingestion is not the same for different foods with the same amount of starch (Englyst & Englyst, 2005) and, principally, food processing affects this response. As an example, for many years it has been suggested that starch gelatinization affects the glycemic response (Björck et al., 1994).
In summary, food microstructure affects the nutritive value or quality of food products. However, the health benefit of different nutrients after absorption is not only conditioned by the food matrix, but also by the regular and harmonic functioning of the GIT. As mentioned before, designed food matrices can help in the prevention of diet-related diseases through through the controlled released of macronutrients or bioactive compounds. The next section deals with the latest research aiming to improve the nutritional performance of foods.

5. Structuring food matrices to improve bioavailability

The bioavailability of macro and micronutrients may be either increased or decreased by manipulating the microstructure of the foods that contain them. The food manufacturing processes affect the resulting structures and properties such as appearance, texture, taste, etc. However, food is ultimately going to be eaten. The ingestion of food leads to its breakdown and deconstruction through the different processes involved in the digestive stage (Lundin et al, 2008). Hence, food structures can be designed to control not only material properties before ingestion but also to control digestive breakdown rate and extent in the GIT. This section deals with the main aspects of designing protein, lipid and starch matrices in order to facilitate the rational design and fabrication of functional foods for improved health and wellness.

5.1 Protein systems

The food industry has widely used proteins in food formulations because possess unique functional properties. In addition to their contribution to the nutritional properties of foods through provision of AAs (that are essential for human growth and maintenance), proteins impart the structural basis for various functional properties of foods, such as water binding, gelling, foaming, and emulsifying. In particular, their ability to form gels and emulsions allow them to be an ideal material for controlling the rate of digestion and releasing of bioactive compounds at specific sites in the GIT.

Protein gels are undoubtedly the most convenient and widely used matrix in food applications. Food gels can be defined as three-dimensional continuous polymeric network holding large quantities of aqueous solution that shows mechanical rigidity during the observation time (Aguilera & Stanley, 1999). Gelation of food proteins and particularly of globular proteins (*e.g.*, egg white, soybean, and whey proteins) has received much attention lately among food scientists because they are a useful way to modulate texture and sensory perception of foods. Various processing routes, such as control of ionic strength, change in pH, heating, high pressure and enzymes are used to produce gels with different microstructural properties, which are strongly related to their aggregate molecular structure.

Two types of globular protein gels can be described depending on their microstructure: (i) fine-stranded gels, composed of more or less flexible linear strands making up a regular network characterized by its elastic behavior and high resistance to rupture, and (ii) particulate gels, composed of large and almost spherical aggregates, characterized by their lower elastic behavior and lower rupture resistance. Fine-stranded gels are created by linear aggregation of structural units maintained by hydrophobic interactions, whereas the particulate gels are produced by random aggregation of structural units essentially controlled by van der Waals interactions.

Protein gels can behave as pH-sensitive matrices through the presence of acidic (*e.g.*, carboxylic) or basic (*e.g.*, ammonium) groups in proteins chains, which either accept or release protons in response to changes in pH of the medium. This behavior could strongly influence the rate of molecule release by gels exposed to either gastric (low pH) or intestinal medium (neutral pH) by decreasing polypeptide chain interaction and thereby uptaking water inside the network and allowing the diffusion of molecules outward by osmotic pressure.

Gels of diverse mechanical and microstructural properties can be formed by controlling the assembly of protein molecular chains. Among the factors that modulate the release of protein molecules from gels, factors that promote gel breakdown play a major role.

Remondetto et al. (2004) showed that the release of nitrogen from cold-induced β-lg gels, as an index of matrix degradation, was slightly higher for particulate than for filamentous gels. In addition, the release of iron from these matrices was not correlated with the food matrix degradation at GIT conditions, suggesting that gel microstructure and not proteolysis influences the release of iron. In the case of particulate gels, the release of iron was lower due to its location inside aggregates that associate to form networks; in contrast iron is located at the outer surface of the linear aggregates of filamentous gels which it facilitates its release. Both types of gels may protect iron from gastric environment, but filamentous gels would release a larger amount of iron in the small intestine favoring the increase in iron absorption. In agreement with previous results, Maltais et al., (2009) found that fine-stranded cold-induced soy protein isolate (SPI) gels degraded more slowly than particulate gels, probably because their lower porosity slows down the digestion. Besides, the release of riboflavin was delayed from fine-stranded gels, because of the lower rate of protein digestion. From this study it was demonstrated that fine-stranded and particulate SPI protein gels were able to protect riboflavin from gastric conditions and release it under intestinal conditions. SPI films (*i.e.*, thin dehydrated gels) degraded more slowly as cross-linking density increases. Protein matrix undergoes a so-called first-order degradation during gastric and intestinal enzyme digestion. The behavior of the films was attributed to a more rigid structure and greater entanglement of the polypeptide chains in the SPI films due to increased cross-linking, leading to decreased penetration of digestive enzymes into the network (Chen et al., 2008).

Protein gel micro-beads have been recently used to encapsulate microorganisms with probiotic activity. The main challenge of this technique is to improve the survival of probiotics in the human digestive environment. Hébrard et al., (2006) produced whey protein isolate (WPI) beads containing yeasts from cold-induced gelation. Beads were resistant to acidification and pepsin attack during simulated human gastric digestion. Only about of 2% of initially entrapped yeasts were recovered in the gastric medium. In addition, WPI micro-beads were stable after incubation in simulated gastric juice in the presence of pepsin, allowing a targeted disintegration of protein matrices under physiological intestinal conditions (Doherty et al., 2011). Both results suggest that WPI beads might cross the gastric barrier and can deliver probiotics in the small intestine.

In conclusion, microstructure of protein gels largely affects the digestion of proteins and the release of bioactive compounds. If a digestive enzyme needs to degrade the gel matrix, then a large porosity and a and a high-pore interconnectivity would increase the rate of digestion. In addition, to design efficient systems for specific intestinal absorption of bioactive compounds or probiotics, gels should be gastroresistant. Hence, controlling microstructure and tailoring the porous structure of protein gels, it would give more opportunities for protection or release of a nutrient or a physiologically bioactive component in the GIT.

5.2 Lipid matrices

Many food scientists are currently focusing their efforts on developing novel lipid structures to decrease or increase the bioavailability of food lipids. In this context, much attention has been paid to the formulation of emulsion-based food systems to encapsulate, protect and release lipophilic constituents. A variety of emulsion-based delivery systems are already available (Figure 5), including conventional emulsions, nanoemulsions, solid lipid particles, multiple emulsions, and multilayer emulsions. Nevertheless, the structural design of these systems is still very far from an exact science due to their compositional and structural

complexity. Further research is still needed to achieve a detailed understanding of the molecular characteristics, structural organization, physicochemical properties, and functional performance of these delivery systems (McClements et al., 2009).

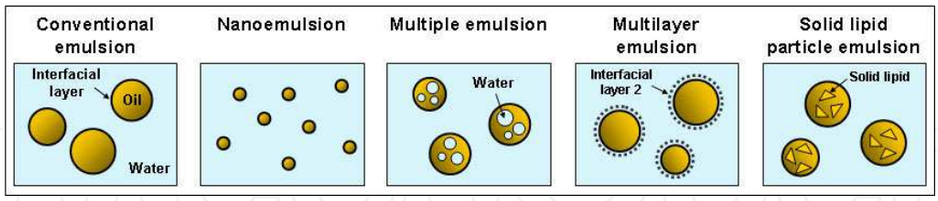


Fig. 5. Examples of different emulsions-based delivery systems

Conventional emulsions consist of oil droplets (~μm) dispersed in an aqueous medium, with the oil droplets being surrounded by emulsifier molecules. Oil-in-water (O/W) emulsions contain a non-polar region (the oil phase), a polar region (the aqueous phase), and an amphiphilic region (the interfacial layer). Then, within O/W emulsions it is possible to incorporate functional agents that are polar, non-polar, and amphiphilic (McClements, 2005). Nevertheless, conventional emulsions have some limitations (*e.g.*, physical instability) that promote the development of more sophisticated structured systems. Like conventional emulsions, nanoemulsions consist of small oil droplets (radius < 100 nm) dispersed within a continuous phase, with each droplet being surrounded by a protective coating of emulsifier molecules. However, nanoemulsions do have a number of advantages over conventional emulsions for certain applications due to their relatively small particle size: (i) they scatter light weakly and so tend to be transparent; (ii) they have high physical stability; (iii) they have unique rheological characteristics; and, (iv) they can greatly increase the bioavailability of encapsulated lipophilic components (Mason, et al., 2006). Additionally, the very small oil droplet size in nanoemulsions increases the digestion rate and the total amount of FFAs released during digestion in comparison with conventional emulsions (Li & McClements, 2010). This last characteristic may be of interest for the realization of lipid food for humans with disorders that prevent efficient digestion or absorption of lipids (*e.g.*, cystic fibrosis or pancreatitis) (Fave et al., 2004).

Multiple emulsions are systems in which dispersed droplets contain smaller droplets inside (Figure 5). Particularly, water-oil-water (W/O/W) emulsions consist of small water droplets contained within larger oil droplets that are dispersed in an aqueous continuous phase. Within these systems, functional components can potentially be located in a number of different ways. Water soluble components can be incorporated into the inner or outer water phase, while oil soluble components can be incorporated into the oil phase. Potential advantages of the multiple emulsions as delivery systems over conventional emulsions are: (i) functional ingredients could be trapped inside the inner water droplets and released at a controlled rate in the GIT; (ii) functional ingredients could be protected from chemical degradation; and (iii) reduction of the overall fat content of food products by loading the oil phase with water droplets (McClements et al., 2009).

The quality and functional performance of conventional O/W emulsions can be improved by the formation of multilayered interfaces using the layer-by-layer electrostatic deposition technique (Guzey & McClements, 2006). Multilayered emulsion delivery systems (Figure 5) may have a number of advantages over conventional single-layered emulsions: (i) improved physical stability to environmental stresses; (ii) greater control over the release rate of functional agents due to the ability to manipulate the thickness and permeability of the

laminated interfacial coating; and (iii) ability to trigger release of functional agents in response to specific changes of environmental conditions in the GIT, such as dilution and/or pH (McClements et al., 2009).

Finally, it is possible to control the physical location of a lipophilic component and to slow down molecular diffusion processes using conventional emulsions by crystallizing the lipid phase. These systems are known as solid lipid particle emulsions, which consist of emulsifier coated (partially) solid lipid particles dispersed in an aqueous continuous phase (Figure 5) (Videira et al., 2002). By controlling the morphology of the crystalline lipid matrix it is possible to obtain more precise control over the release kinetics of functional compounds. Additionally, both lipophilic and hydrophilic bioactives can be incorporated within the same system using solid lipid particle emulsions (McClements et al., 2009). Hence, there are a large number of different ways that can be used by food manufacturers to embed lipophilic compounds within food matrices with different degradation rates. However, the selection of a particular matrix is a matter of functional preference.

5.3 Starch

Elevated glucose levels and high postprandial blood glucose cause a metabolic stress concentrations associated with increased risk of diseases, such as type II diabetes, cardiovascular disease and obesity (Kim et al., 2008; Parada & Aguilera, 2011a). The slow digestion of starch, in comparison with simple carbohydrates (*e.g.*, glucose, fructose), involves a gradual release of glucose to the bloodstream, thus producing a low GR.

Different starchy foods (pasta, baked foods, among others) elicit different GRs. The extent of starch digestion within the small intestine is variable, depending on food physical form, and a substantial amount of undigested starch enters the colon, where may be fermented by bacteria or simply appear in faeces (Troncoso & Aguilera, 2009).

The starch in its native state is resistant to enzymatic digestion and the availability of starch chains to the digestive enzymes is increased as gelatinization progresses. Gelatinization breaks the weak hydrogen bonds between polymer chains, so the exposed polar groups can further interact with water molecules. Due to this biophysical phenomenon, the granule structure changes from a crystalline to a disordered structure that is more easily accessible for the digestive enzymes (Parada & Aguilera, 2011a). Digestibility is strongly influenced by shearing and heating of starch samples. Both heat and shear during the preparation of starch suspensions alter the progression towards gelatinization, which increases the availability of polysaccharide starch chains to digestive enzymes, thus affecting the rates of hydrolysis (Dona et al., 2010).

The degree of gelatinization of starch granules and the recrystallization of the released polymers is of vital importance in the breakdown of starch molecules into sugars during digestion, because both phenomena influence the susceptibility to enzymatic degradation. Hence, a nomenclature has emerged describing the susceptibility of starch to digestion by enzymes in the small intestine: rapidly digestible starch (RDS), slowly digestible starch (SDS) that has slow but complete digestion, while resistant starch (RS) is resistant to digestion (Parada & Aguilera, 2011a).

RS obtained through appropriate physical or chemical modification can withstand the environmental changes in the upper GIT and can be rapidly degraded by the enzymes produced by the colonic microbiota. The incomplete digestion of starch is related to the matrix surrounding starch, the nature and physicochemical properties of the starch *per se* at

the granule and molecular levels (*e.g.* granule size and amylose/amylopectin ratio), and the presence of other dietary components (*e.g.* sugar, dietary fiber and lipid) (Troncoso & Aguilera, 2009).

Starch granules in a real food are not isolated but exist within a three-dimensional matrix structure formed by proteins or other biopolymeric materials (such as fiber), which affects both the degree of gelatinization during processing and the digestion of starch (Giacco et al., 2001). If a food matrix is relatively impervious to enzymes and the granules are not properly exposed to their action, the digestion could be limited. The "encapsulation" of starch granules by a protein network is an important factor in explaining the slow degradation of starch by α-amylase in cooked pasta, the microstructure of the protein matrix as well as the physical state of starch (degree of gelatinization and retrogradation, amylose-to-amylopectin ratio, etc.) may explain the differences in the *in vivo* and *in vitro* enzymatic susceptibility of starch (Petitot et al., 2009).

The presence of a structured and continuous protein network is an important factor in explaining the slow degradation of starch in pasta. It had been shown that the degree of gelatinization and the interaction starch-gluten are a key factor during digestion of starch. Over-mixing could disrupt the gluten matrix producing an augmented rate of digestion; whereas higher heating temperatures produced a more compact structure (higher denaturation of gluten matrix) delaying digestion (Parada & Aguilera, 2011b). In agreement with these results, Kim et al. (2008) found that the disruption of the starch-coating protein matrix could be responsible for the increase in starch digestibility in pasta.

The degree of gelatinization and the gluten matrix conformation affect the digestibility of starch; the degree of gelatinization probably predominates in the extent of starch digestion, while the state of the gluten matrix is more related to the rate of digestion of starch.

Starch retrogradation and water-limited gelatinization should present an opportunity to redesign starchy products aiming at reducing the GR. Moreover, understanding the mechanisms by which the protein matrix slows down starch digestion could help to a rational design of new products with controlled starch digestion.

6. Conclusion

Recent knowledge supports the hypothesis that, beyond considering nutritional composition, food matrix microstructure may modulate various physiological functions in the human body and play detrimental or beneficial roles in some diet-related diseases. Advanced concepts in physical chemistry and material science provide a convenient and powerful framework for developing an understanding of the interactions and assemblies of food components into microstructure, which influence food macrostructure and functional properties. In turn, medical research coupled with food engineering approaches allow to obtain a deep comprehension of how foods behave during the digestive process. Advances in technologies for producing food matrices with tailored properties make possible the production of foods that have potential impact on the human health. This presents a challenge for the scientific community and the food industry due to the necessity of considering relationships between targets for functional food science and gastrointestinal behavior.

7. Acknowledgment

Author Zúñiga acknowledge to CIEN Austral for the financial support of this chapter.

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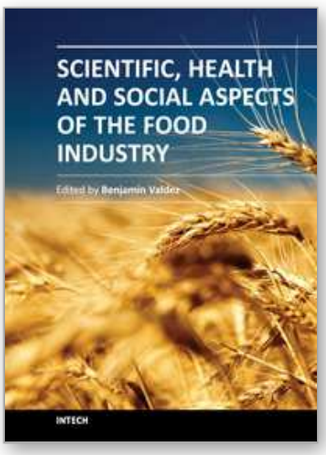

Scientific, Health and Social Aspects of the Food Industry

Edited by Dr. Benjamin Valdez

ISBN 978-953-307-916-5
Hard cover, 488 pages
Publisher InTech
Published online 01, February, 2012
Published in print edition February, 2012

This book presents the wisdom, knowledge and expertise of the food industry that ensures the supply of food to maintain the health, comfort, and wellbeing of humankind. The global food industry has the largest market: the world population of seven billion people. The book pioneers life-saving innovations and assists in the fight against world hunger and food shortages that threaten human essentials such as water and energy supply. Floods, droughts, fires, storms, climate change, global warming and greenhouse gas emissions can be devastating, altering the environment and, ultimately, the production of foods. Experts from industry and academia, as well as food producers, designers of food processing equipment, and corrosion practitioners have written special chapters for this rich compendium based on their encyclopedic knowledge and practical experience. This is a multi-authored book. The writers, who come from diverse areas of food science and technology, enrich this volume by presenting different approaches and orientations.

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