Bioaccessibility of Nutrients and Micronutrients from Dispersed Food Systems: Impact of the Multiscale Bulk and Interfacial Structures

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ABSTRACT

Many food systems are dispersed systems, i.e. possess at least two immiscible phases. This is generally due to the coexistence of domains with different physicochemical properties separated by many interfaces which control the apparent thermodynamic equilibrium. This feature was and is still largely studied to design pharmaceutical delivery systems. In food science, the recent intensification of in vitro digestion tests to complement the in vivo ones holds promises in the identification of the key parameters controlling the bioaccessibility of nutrients and micronutrients. In this review, we present the developments of in vitro digestion tests for dispersed food systems (mainly emulsions, dispersions and gels). We especially highlight the evidences detailing the roles of the constituting multiscale structures. In a perspective section, we show the potential of structured interfaces to allow controlled bioaccessibility.

KEYWORDS

Bioavailability, controlled release, protein, starch, lipid, polysaccharide, micelle, hydrolysis.

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INTRODUCTION

Because of the various physicochemical properties of their constituents, many food systems are dispersions. This means they are not homogeneous but present domains with molecules remaining insoluble in the matrix (the continuous or bi-continuous phase). These domains are in fact both bulk and interfacial *multiscale structures*, sizing from few *nanometers* to few *millimeters*. Aguilera (2006) gave some illustrations for these structures in food, either naturally occurring or generated by processing.

This dispersed state is a chance for functional food design as each domain can be seen as a potential micronutrient reservoir. In *micronutrient*, *micro* does not refer to the length scale but to the mass scale because micronutrients must be dosed for optimal benefits, just like drugs (Venkatesh Mannar 2003). To go on with this analogy, micronutrients must be released from the food matrix to the digestive environments in order to be available for given absorption sites (mostly small intestine but also stomach). The released fraction of a given nutrient from a food matrix is defined as the nutrient *bioaccessibility*. It is part of a more general quantity, the *bioavailability*, defined as the fraction of a (micro)nutrient from a food matrix that is utilized for normal body functions (Fairweather-Tait and Southon 2003). The bioavailability concept appeared in the 60s and started to grow in the 70s. Bioaccessibility is a recent concept which appeared in the 90s as scientists realized that the matrix itself influences

bioavailability. The reviews of Faulks and Southon (2004) and of Parada and Aguilera (2007) accounted for the early evidences showing the role of structures. Duchateau and Klaffke (2008) gave some illustrative examples based on product structure. One recent review focused on the role of structures for lipid bioavailability (including bioaccessibility) (McClements et al. 2009a), and two others on their role for lipid digestion in emulsions (Singh et al. 2009, Golding and Wooster 2010). McClements et al. (2009b, 2010) gave principles to design delivery systems for enhanced *bioactivity* (which is the metabolic part of bioavailability).

Our review specifically focuses on the bioaccessibility of nutrients and micronutrients from dispersed food systems. In the first section, we draw the link between bioaccessibility and controlled release and briefly summarize the systems that pharmaceutical science uses. In the second section, we present the in vitro studies from various dispersed food systems in the chronological order. In the third section, we discuss the results to determine the current knowledge, highlighting the multiscale structures and their possible roles in bioaccessibility. In the fourth section, we evaluate the potential of structured interfaces to control bioaccessibility.

1. LINK BETWEEN BIOACCESSIBILITY AND CONTROLLED RELEASE

The *controlled release* concept (for its many nuances, see Zanowiak 2005) emerged from the need to improve drug action. To do so, it was realized that the drug should be delivered at specific sites (*targeted* or *topical*) with specific rates. So, it is a matter of controlling the spatiotemporal behavior of a drug in physiological conditions. The means to achieve such a control were termed *delivery systems*, ranging from the infusion set to the molecular assembly of a drug vehicle. The corresponding food science concept is *(micro)encapsulation*, which deals with the construction of the *delivery systems* as well as their *controlled release* (Shahidi and Han 1993, Gibbs 1999, Gouin 2004, Desai and Park 2005, Champagne and Fustier 2007,

Luykx et al. 2008, Acosta 2009, Augustin and Hemar 2009, Huang et al. 2010). It can be specifically based on polysaccharides (Kosaraju 2005), on polar lipids (Taylor et al. 2005, Leser et al. 2006, Flanagan and Singh 2006) or on proteins (Chen et al. 2006, Livney 2010). The main difference between the above concepts and *bioaccessibility* is that the latter always refers to studies in biological environments (either real *in vivo* or artificial *in vitro*), only possibly for the others. This is why our review accounts for the controlled release, delivery systems and (micro)encapsulation literatures, but only presents the results obtained in the biological environments relevant to oral administration.

In this context, pharmaceutical science is advanced with the development of biologically relevant delivery systems. Among the first candidates were liposomes (reviews by Gregoriadis 1995, Ulrich 2002, Torchilin 2005). In parallel, synthetic and natural polymeric systems (including hydrogels) appeared in various forms:

- biodegradable polymers (Uhrich et al. 1999),
- nanoparticles (Janes et al. 2001, Couvreur and Vauthier 2006),
- block copolymer micelles (Kataoka et al. 2001, Torchilin 2001, Gaucher et al. 2005),
- polymers sensitive to stimuli of e.g. magnetic or electric fields, ultrasound, temperature, pH, ionic strength, molecules (Kost and Langer 2001, Jeong and Gutowska 2002, Kikuchi and Okano 2002, Peppas et al. 2000), specifically of temperature (Bromberg and Ron 1998, Chilkoti et al. 2002), specifically of pH (Gupta et al. 2002), specifically of molecules like glucose or protein (Miyata et al. 2002),
- cross-linked polymers (Hennink and van Nostrum 2002, Berger et al. 2004),
- dendrimers (Malik et al. 2000).

These systems, although transposable, are not directly applicable to food science. Some other ones are more readily applicable, as specifically developed for oral administration:

- lipid-based formulations (Porter et al. 2008, Muller et al. 2000, Lawrence and Rees 2000, Shah et al. 2001, Gursoy and Benita 2004),
- biopolymers like alginate (Gombotz and Wee 1998), chitosan (He et al. 1999, Ravi Kumar 2000, George and Abraham 2006), their mixture (Hari et al. 1996), gelatin (Tabata and Ikada 1998), cellulose derivatives (Siepmann and Peppas 2001), copolymers from lactic and glycolic acids (Desai et al. 1996, Freiberg and Zhu 2004), cyclodextrin (Hirayama and Uekama 1999),
- polyelectrolyte multilayers (Qiu et al. 2001, Peyratout and Dahne 2004).

We will show in the third section that the exploration of such systems for foods is still poor although it may bring very promising perspectives.

2. BIOACCESSIBILITY FROM DISPERSED FOOD SYSTEMS

There are actually only a few typical dispersed food systems: emulsions, dispersions, foams and gels. We now report the main results for these systems in vitro (unless stated otherwise).

2.a. Emulsions

An emulsion is a system of at least two immiscible phases. One phase is usually dispersed as droplets in the other, and stabilized by molecules able to *act* at their *surfaces* (which is why these molecules are called *surfactants*). In food, the most common emulsion is the oil-in-water emulsion but water-in-oil or multiple emulsions also exist.

Note that because of the complexity and variety of the artificial media used for emulsions, we only detail the most common ones in table 1.

2.a.1. Some early studies

Pioneers focused on digestion of emulsified TriAcylGlycerols (TAG), the main process being hydrolysis by lipases, cutting TAG to finally release Free Fatty Acids (FFA) and MonoAcylGlycerols (MAG). Loevenhart and Souder (1907) showed that bile salts or lecithin

(both are constituents of bile) or whole bile accelerate the hydrolysis of various TAG by pancreatic lipase. For emulsions of alkyl esters of fatty acids, Weinstein and Wynne (1936) observed that the hydrolysis by pancreatic lipase increased with the length of the fatty acid chain and decreased with the length of the alcohol chain. On the other hand, there was no clear trend for emulsions of different TAG. Schonheyder and Volqvartz (1945) found that the pancreatic lipase in the presence of a bile salt had a much higher affinity for insoluble than for molecularly solubilized TAG. Sarda and Desnuelle (1958) also reported that pancreatic lipase activity was low for solubilized esters but high when emulsions of either soluble esters or insoluble esters were formed. It increased with the droplets specific interfacial area. More results from the lipases point of view were reviewed by Desnuelle and Savary (1963). Carey and Small (1970) described the bile micelles and their roles on emulsion digestion at the lipid/water interface and in the bulk as carriers. Maylie et al. (1971) discovered that a small protein from pancreas they named co-lipase was necessary for the activation of pancreatic lipase. Brockerhoff (1971) studied the interactions between pancreatic lipase, albumin and bile salts and explained the activation by a mechanism of prevention of both hydrophobic bonding and unfolding of the lipase. Nevertheless, the activity was inhibited at high albumin concentrations, and the author postulated that it should not be so using co-lipase.

From 1971, many researchers studied the interactions between pancreatic lipase, co-lipase and bile constituents (mostly bile salts). Borgstrom (1975) and Borgstrom and Erlanson (1973) confirmed his previous result (Borgstrom 1967) that a high bile salts concentration (above the Critical Micelle Concentration CMC) was necessary to solubilize lipids from emulsions. But adding lipase and co-lipase to the system revealed that individual bile salts above the CMC could inhibit lipolysis, which could be restored by co-lipase. Vandermeers et al. (1975) confirmed this result and suggested a mechanism whereby a complex is formed in the bulk before it can adsorb at interfaces. Momsen and Brockman (1976) confirmed this hypothesis

using various techniques. Lairon et al. (1978, 1980) compared the use of whole bile and bile salts alone and found that whole bile enhanced lipolysis by pancreatic lipase and co-lipase. This was explained by the formation in the bulk of a complex of lipase, co-lipase and whole bile constituents (salts, phospholipids, cholesterol and proteins), followed by its adsorption. As bile lipids are highly hydrophobic, they were thought to enhance the adsorption compared to bile salts alone. Another explanation was taken from Linthorst et al. (1977) who found that triolein was emulsified better by fatty acid soaps or phosphatidylcholine than by bile salts alone. Mixtures were also efficient, but only below the CMC. This suggested that the presence of bile lipids or lipolysis products could enhance lipase activity by an effect of increased specific interfacial area. With human milk fat globules, Blackberg et al. (1981) found that phospholipase A2 had the same properties than co-lipase for the activation of pancreatic lipase in the presence of a bile salt.

Latter, Hermoso et al. (1997) and Pignol et al. (2000) confirmed the role of a complex by neutron studies of pancreatic lipase and co-lipase association with micelles of bile salts, oleic acid, lysolecithin or lecithin alone or in combinations. Only micelles or mixed micelles in a specific size range (13-26 Å) were found to complex with lipase/co-lipase in the bulk, resulting in an enhanced lipase activity.

This kind of studies on the intestinal medium itself became scarce nevertheless the following mainly refers to small intestine studies, with the use of at least pancreatic lipase, co-lipase and bile salts (unless stated otherwise). The focus indeed changed from the biological to the food science point of view, the parameters shifting from the medium to the emulsion composition.

2.a.2. Effect of the emulsified lipids

Gargouri et al. (1986) compared the activity of gastric lipase on Short or Long Chain TAG (SCT or LCT) emulsions. A lower activity was obtained with LCT, in contrast with the result of Weinstein and Wynne (1936) with pancreatic lipase. The result of Gargouri et al. (1986)

was confirmed in different cases (Deckelbaum et al. 1990, Armand et al. 1992, Borel et al. 1994). Tiss et al. (2001) found that gum arabic, often used to stabilize emulsions or to normalize viscosity during lipolysis, inhibited or enhanced human pancreatic lipase activity in the absence or in the presence of co-lipase, respectively. With increasing chain length of the TAG, the decrease of lipase activity was less pronounced with than without gum arabic. Marangoni et al. (2007) designed an emulsion with MAG in a liquid-crystalline form at the interfaces allowing a control of in vivo TAG and FFA release. Bonnaire et al. (2008) compared crystalline and liquid (supercooled) tripalmitin droplets lipolysis and found at least 50% more FFA release for the liquid state than for the crystalline state.

Borgstrom (1967) showed that the solubilization of emulsified lipids in individual bile salts solutions was only significant for MAG compared to TAG and DAG (DiAcylGlycerols). The shorter the fatty acid chain, the higher the solubility. For other lipids such as cholesterol or sitosterol, polarity was found to be an important parameter. Borel et al. (1996) introduced lipophilic carotenoids in emulsions stabilized by phosphatidylcholine and investigated their transfer to the intestinal medium. The polar zeaxanthin was mostly located at the interface and was able to transfer without lipolysis whereas the apolar β-carotene was not at the interface and was only able to transfer with lipolysis. Tyssandier et al. (2001) went on by investigating other parameters and found a reverse relationship between carotenoid hydrophobicity and transfer efficiency. A minimum concentration of bile salts (above the CMC) was required for the transfer to take place. The transfer depended on pH, higher for neutral than acidic. Gervais et al. (2009) prepared different milk emulsions enriched in conjugated linoleic acid through dairy cows diet or synthetic additions in the form of FFA or TAG. FFA bioaccessibility studied in a dynamic gastrointestinal set-up including a gastric step (the TIM) was not affected by the method of enrichment. Short chains FFA were more bioaccessible than long ones and unsaturated FFA were more bioaccessible than saturated ones, except stearic acid.

2.a.3. Effect of the free fatty acids

Gargouri et al. (1986) found a decrease of the rate of hydrolysis by gastric lipase as a function of time they explained by an inhibition due to the progressive release of FFA. This was confirmed by Borel et al. (1994), but only for isolated studies, not in the case of pancreatic lipolysis following gastric lipolysis. Pafumi et al. (2002) studied how FFA progressively inhibit TAG hydrolysis by gastric lipase. They detected a growth of the droplets and the formation of spherical protrusions at their surfaces, which were found to be mainly composed of FFA trapping gastric lipase.

2.a.4. Effect of the interfacial molecules

Borgstrom and Erlanson (1973, 1978) found that a high surfactant concentration (above the CMC) or protein concentration inhibited lipolysis even in the presence of co-lipase. The presence of a bile salt restored lipolysis. The authors postulated that the bile salt desorbed the surfactant or protein but allowed lipase adsorption in the presence of co-lipase. Gargouri et al. (1983, 1984) studied the effects of surfactants, food emulsifiers or proteins. They confirmed that all of them inhibited lipase and co-lipase activity, which could be restored in the presence of a bile salt. Gargouri et al. (1987) found that gastric lipase could also be inhibited by proteins, but only for those adsorbing quickly at the oil/water interface (bovine serum albumin, soybean protein and myoglobin) compared to those adsorbing slowly (ovalbumin, melittin, β-lactoglobulin). Wickham et al. (1998) found no effect of the interfacial charge (zeta potential) of emulsions stabilized by phosphatidylcholine on lipolysis in the presence of individual bile salts of different hydrophobicities. But the lag time before lipolysis was shorter when the bile salt adsorbed at the interface, in agreement with the mechanism of surfactant desorption. Shima et al. (2004) found that in W/O/W emulsions, a higher concentration of either the hydrophilic (polyglycerol esters of fatty acids) or the hydrophobic (polyglycerol polyrincinoleate) emulsifier delayed lipolysis. Tsuzuki et al. (2004) studied the role of

lysophosphatidylcholine, phosphatidylcholine and individual bile salts on hydrolysis of emulsified TAG or MAG. For TAG, lipolysis activity was decreased in the presence of lysophosphatidylcholine. Upon addition of phosphatidylcholine or a bile salt, activity was restored. For MAG, lipolysis activity was lower and the presence of lysophosphatidylcholine had a smaller effect. Mun et al. (2006) studied the FFA release from emulsions stabilized by a) anionic lecithin, b) anionic lecithin + cationic chitosan or c) anionic lecithin + cationic chitosan + anionic pectin. Only in case b) was the release inhibited, attributed to a protective layer of chitosan around the droplets and to bridging flocculation. In case c), the authors hypothesis was that the complex desorbed. Beysseriat et al. (2006) confirmed that bridging flocculation can occur with tween 80 + cationic chitosan at the interface whereas depletion flocculation can occur with tween 80 + anionic pectin, and pectin was not found at the interface. Mun et al. (2007) found that lipase alone was always able to release FFA from emulsions stabilized by different surfactants, except with tween 20. The addition of bile extract increased the release, especially with tween 20. Overall, the release fraction followed the order tween 20 < lecithin < whey protein isolate < sodium caseinate. Wright et al. (2008) found that pancreatin (i.e. pancreatic juice extract, containing proteases, amylases…) and bile extract concentrations, especially the latter, played a key role in the bioaccessibility of β-carotene from emulsions with no other surfactant than bile constituents. It was also enhanced by a more neutral pH compared to acidic, with an optimal at pH 8.0. Yin et al. (2008) reported that increasing degree of polymerization of polyglycerol esters of fatty acids stabilizing emulsions decreased β-carotene release in a gastric environment containing pepsin. Reis et al. (2008), using the TIM, correlated a reduced lipolysis of tricaprylin by pepsin and fungal lipase in the presence of different surfactants (Sn-2 monopalmitin or β-lactoglobulin or lysophosphatidylcholine). Lipolysis by pancreatin in the presence of fresh bile was only restricted in the case of Sn-2 monopalmitin, and at a similar high level for β-lactoglobulin or

lysophosphatidylcholine. Sandra et al. (2008) did not observe a significant difference in the FFA release from lecithin, β-lactoglobulin or cross-linked (by heat treatment) β-lactoglobulin emulsions. Fernandez-Garcia et al. (2008) reported a statistical analysis strategy to optimize emulsifiers composition for maximal carotenoids bioaccessibility using pepsin then pancreatic lipase and bile extract. Chu et al. (2009) investigated the effect of galactolipids (monogalactosylDAG or digalactosylDAG) stabilizing emulsions on lipolysis. An inhibitory effect was found for the di- but not the mono- galactolipid. In the presence of lecithin, there was less inhibitory effect so lipolysis was favored. It was suggested that digalactosylDAG resists displacement by bile salts at the oil/water interface. Klinkesorn et al. (2009, 2010) varied the concentration and molecular weight of chitosan added to emulsions stabilized by lecithin in the presence of pancreatic lipase alone. The higher the concentration of chitosan, the less FFA but the more glucosamine released. The molecular weight only had an effect on the glucosamine, increasing its release. Additional maltodextrin had no effect whereas an increasing pectin concentration increased the FFA release, attributed to the ability of the anionic pectin to bind with and remove the cationic chitosan from the interface. White et al. (2009) compared the bioaccessibility of the lipophilic α-tocopherol and FFA from sunflower oil body suspensions and sunflower oil emulsions stabilized by tween 20 or whey protein isolate, incubated with pepsin then with pancreatin, pancreatic lipase and a bile salt. Both release fractions in the micellar phase followed the order oil body < whey protein isolate < tween 20. When expressed as molar concentrations in the micellar phase, the effect of the surfactant disappeared. Bezelgues et al. (2009) prepared emulsions containing lipophilic α-tocopherol or lycopene, stabilized by either whey protein isolate, sodium caseinate or milk fat globule membrane. The bioaccessibility during incubation in first pepsin then in pancreatin and bile extract was about two times higher with milk fat globule membrane than with the isolated proteins. In any cases, lycopene was about 10 times less bioaccessible than α-

tocopherol. Macierzanka et al. (2009) investigated the role of physiological surfactants (phosphatidylcholine and bile salts) on the hydrolysis by pepsin then trypsin and α-chymotrypsin of emulsions stabilized by β-lactoglobulin or β-casein. Both proteins underwent more hydrolysis at the interfaces than in the aqueous phase, especially β-lactoglobulin. But both proteins were also desorbed by the physiological surfactants so the authors concluded that most of the protein hydrolysis took place in the aqueous phase. Sarkar et al. (2009, 2010a) studied the hydrolysis of β-lactoglobulin by pepsin (with or without mucin) in emulsions and found it is much more hydrolyzed at the interfaces than in the aqueous phase. The hydrolysis rate increased in the presence of mucin or sodium chloride. Bridging flocculation followed by coalescence occurred in the emulsions, again more pronounced in the presence of mucin or sodium chloride. Sarkar et al. (2010b, 2010c) went on studying this system in an intestinal medium with pancreatin and bile extract. Bile salts were thought to be responsible for the displacement of β-lactoglobulin from the oil/water interface. When β-lactoglobulin was replaced by lactoferrin to stabilize emulsions, there was substantially less displacement by bile salts but the coalescence rate and the FFA release increased. Liang et al. (2010) compared the release of α-tocopherol from β-lactoglobulin gelled emulsions in the presence of pepsin and/or pancreatin. The release was complete after 6.5 hours of either incubations but was only of 25% after 0.5 hour pepsin followed by 6 hours pancreatin. This was understood as an inhibition of release by β-lactoglobulin partial hydrolysis products at the oil/water interface. Nik et al. (2010) compared the hydrolysis by pepsin of β-lactoglobulin or α-lactalbumin in solution and at the oil/water emulsion interface. They confirmed that β-lactoglobulin was more resistant in solution and found in contrast that α-lactalbumin was more resistant at the oil/water interface. For emulsions stabilized by β-lactoglobulin, Hu et al. (2010) found that the most important parameter increasing the FFA release was the concentration of calcium chloride. When alginate was also added, the release was

dramatically reduced, whereas the addition of high-methoxy pectin had almost no effect. Using lysolecithin or caseinate instead of β-lactoglobulin had only a small effect on the hydrolysis rate. Lesmes et al. (2010), using caseinate and/or lactoferrin, and Li and McClements (2010), using β-lactoglobulin or tween 20 or lecithin or lysolecithin, also found no significant effect of the surfactant. In contrast, Gudipati et al. (2010) was able to decrease the hydrolysis rate by putting multilayer of citric acid esters of MAG-DAG (Citrem), chitosan and alginate at emulsion interface compared to Citrem alone. The lower rate was achieved with the intermediate multilayer emulsion made of Citrem and chitosan.

2.a.5. Effect of dietary fibers

Lairon et al. (1985) found that wheat bran inhibited lipolysis whereas cellulose, xylan and low-methylated pectin had almost no effect. Inhibition was always more pronounced with emulsified SCT. The water-soluble extract of wheat bran was thought to contain a protein in part responsible for the inhibition. Hendrick et al. (1992) confirmed these results and specified in their case that the water-soluble extract of oat bran was entirely responsible for the inhibition. Pasquier et al. (1996) found a reduced pancreatic and gastric lipases activity when dietary fibers viscosified emulsions stabilized by egg phosphatidylcholine and cholesterol, especially those inducing high viscosities (guar gum). This was not understood by the viscosity itself but either by the change in the mean droplet size or by an inhibitory effect of protein moieties from the fibers able to reach the interface (gum arabic). Minekus et al. (2005) studied emulsions stabilized by either egg yolk or skim milk in the TIM (they developed in the 90s). They explained a dramatically reduced FFA and cholesterol bioaccessibility in the presence of dietary fibers by a depletion flocculation mechanism by the biopolymer (partially hydrolyzed guar gum), counteracting bile activity in the bulk. Na Nakornpanom et al. (2010) followed the release of oil from emulsions digested in vitro by pepsin. The release was increased by the presence of dietary fibers from soy whereas there was no release when the

dietary fibers were pre-hydrolyzed by pectinase. In both cases, a further in vitro digestion by trypsin with or without bile extract lead to more oil release.

2.a.6. Effect of droplet size

Sarda and Desnuelle (1958) reported that the lipase activity increased with the droplets specific interfacial area. This was confirmed by Shima et al. (2004) who protected a hydrophilic salt in W/O/W emulsions and followed its release during lipolysis. They found that the larger the initial oil mean globule diameter (0.71, 2.2 and 32 μm), the lower the degree of lipolysis and the lower the salt release. After 1 hour incubation, the mean globule diameters were 27, 26 and 23 μm respectively. This agrees with the trends observed by Armand et al. (1992, 1999) and Borel et al. (1994) for the relation between the degree of lipolysis and the mean droplet diameter of emulsions stabilized by a mixture of surfactants. However, Armand et al. (1999) found in vivo that the mean droplet diameter increased during incubation with final values just below 10 μm whereas Armand et al. (1992) found in vitro that the mean droplet diameter remained stable or decreased during incubation with final values close to 1 μm. Hur et al. (2009) adopted complex in vitro compositions, based on Versantvoort et al. (2005), to mimic three digestion steps: mouth then stomach then small intestine. They studied the systems of Mun et al. (2007) with a large (around 5 μm) or a small (around 2 μm) initial mean droplet diameter. In all cases, coalescence was not observed, the mean droplet diameter decreased during digestion, especially during the intestinal step, and the final values were all close to 1 μm, not significantly influenced by the surfactant. Li and McClements (2010) found that the lipolysis rate of β-lactoglobulin emulsions decreased with increasing mean droplet diameter. When the lipolysis rate was normalized by the interfacial area, the trend reversed. This was explained by a higher concentration of lipase per unit interfacial area with increasing mean droplet diameter.

2.a.7. Other effects

Juhel et al. (2000) compared the effect of a green tea extract (containing 25% catechins) on the lipolysis of emulsions stabilized by phosphatidylcholine. They found that gastric lipase was totally inhibited and pancreatic lipase about 80% inhibited by the green tea extract with SCT emulsions. For LCT emulsions, inhibitions were less pronounced (about 97% and 66.5% respectively). These results were related to the altered emulsification of LCT in the presence of green tea extract.

Sanz and Luyten (2006, 2007) studied the release of both water- and fat-soluble soy germ extracts from thickened custards with or without fat in artificial mouth (human saliva) then stomach (pepsin) then small intestine (pancreatin, bile extract and trypsin). There were no, low and high releases in each medium respectively. Thickening lowered bioaccessibility much more using carboxymethylcellulose than starches. The bioaccessibility of the fat-soluble genistein was enhanced in the presence of fat at an optimal concentration of 3%. In any cases, genistein was only released in the presence of the bile extract.

Chung et al. (2008), Burgar et al. (2009) and Kosaraju et al. (2009) found that Maillard reaction between a protein (sodium caseinate or whey protein isolate) and a carbohydrate (high-amylose starch and/or glucose) increased the resistance of tuna oil to dissolution by pepsin then pancreatin solutions. Oil was released during pepsin then pancreatin dissolutions only with the whey protein isolate formulation, not with the sodium caseinate one.

Herrero-Barbudo et al. (2009) studied the bioaccessibility of vitamins A and E from commercial fortified skimmed or whole milks using in vitro compositions similar to those of Versantvoort et al. (2005). For vitamin A, the degree of hydrolysis was found to be higher in the skimmed than in the whole milk, whereas the amount transferred into taurocholate micelles was not affected. For vitamin E, the same trend was observed with no hydrolysis in the whole milk which resulted in no transfer into taurocholate micelles.

Day et al. (2010) designed an experiment based on Raman spectroscopy to image the bioaccessibility of FFA and lipophilic micronutrients (vitamin D3 or progesterone) during lipolysis of emulsions with no other surfactant than a bile salt. When no lipase was present, a significant amount of vitamin D3 was released into the micellar phase. When lipase was present, vitamin D3 or progesterone were found to remain in the droplets, explained by their low solubility in the lipolysis products. The rate of lipolysis was found to depend on the lipophilic micronutrient or the initial mean droplet diameter.

For specific results about the behavior of emulsions in artificial oral steps, the reader is referred to the work of van Ruth et al. (2002) and the review of van Aken et al. (2007).

2.b. Dispersions

Starch is the main food constituent of many semi-solid dispersions, such as pasta, breakfast cereal and biscuit. The main structure, starch granule, is actually made of several substructures, due to the organization of its two main constituents: amylose and amylopectin. A classification was made according to digestibility (hydrolysis degree): Rapidly Digestible Starch (RDS), Slowly Digestible Starch (SDS), Resistant Starch (RS, not digested at all). We now present the main results highlighting the link between the digestibility and structures in starch dispersions.

2.b.1. Some early studies

Like lipolysis in emulsions quantifying the release of FFA, hydrolysis of starch dispersions was the initial major in vitro development, as it quantifies the release of saccharides. Major advances came from Columbia University concerning the methodology, the roles of salts, amylases and starch origin (Sherman et al. 1910, Kendall and Sherman 1910, Sherman and Baker 1916, Sherman et al. 1919). Balls and Schwimmer (1944) reviewed some works attributing low hydrolysis of raw starch granules to a surface layer protection. In contrast, the

authors could hydrolyze different raw starches completely using extracts of hog pancreas and aspergillus oryzae (containing amylases). Salts such as calcium chloride were confirmed to catalyze hydrolysis. The source of starch was found to be a determining factor whereas the granules size was not. Schwimmer (1945) completed these results by the observation that the hydrolysis rate of cooked wheat starch increased compared to raw wheat starch.

Most of the studies reported below focuses on the small intestine, with the use of at least one amylase (pancreatic α-amylase or pancreatic α-amylase + amyloglucosidase unless stated otherwise). Authors usually investigated many parameters simultaneously, which makes it difficult to interpret their results. In the following, we only report the main conclusions of each article except when a statistical analysis is available.

2.b.2. Effect of granules structure

Leach and Schoch (1961) and Gallant et al. (1972, 1973) observed by microscopy that various starches were attacked differently by amylases, either only at the granules surface, resulting in slow hydrolysis (potato, high-amylose maize), or into the granules through pores or channels, resulting in fast hydrolysis (corn, sorghum, maize, waxy maize, wheat, tapioca). Hood and Arneson (1976) compared the hydrolysis (by amylases from hog pancreas or aspergillus oryzae) of raw and hydroxypropylated tapioca starch. Microscopy revealed that starch granules were destroyed by pancreatic α-amylase, resulting in a porous structure. Knutson et al. (1982) found a proportionality between the rate of hydrolysis and the specific interfacial area of granules for different maize starches. Benmoussa et al. (2006) investigated the impact of granules morphology on hydrolysis by pancreatic α-amylase (with or without a previous pepsin step). Three different morphologies were obtained using three different sorghum starches. With collapsed (toroidal shape) or porous (presenting channels) granules, the hydrolysis was faster than with regular spherical ones because α-amylase could access the granule core. Zhang et al. (2006a) apparently contradicted this finding with several native

cereal starches, for which the hydrolysis by pepsin, pancreatin, pancreatic α-amylase, amyloglucosidase and invertase was slow even in the presence of pores. However, they also observed a layered structure of the amorphous and crystalline regions (onion-like), which was more likely thought to be the cause of the slow hydrolysis. Mahasukhonthachat et al. (2010) and Dhital et al. (2010a, 2010b) studied the hydrolysis kinetics of various starches by α-amylase then pepsin then pancreatin and amyloglucosidase. By milling the granules using different techniques or by sorting them by sedimentation, they found that the specific interfacial area (related to granule size) and the porosity were the main factors governing the hydrolysis kinetics. Zhang et al. (2010) investigated the structures formed in a Canna edulis Ker starch during hydrolysis by pancreatic α-amylase, pancreatin and amyloglucosidase. The measurement of a single length scale suggested that channels into the granules were responsible for the initiation of the hydrolysis. Blazek and Copeland (2010b) compared the hydrolysis of waxy (usually 100% amylopectin) and high-amylose wheat starch granules and confirmed the waxy one was quickly hydrolyzed through channels whereas the high-amylose ones were slowly hydrolyzed only from their surface.

2.b.3. Effect of amylose

Knutson et al. (1982) found that a low amylose content was related to a higher rate of hydrolysis for different maize starches. Sievert and Pomeranz (1989) confirmed with six different starches that a higher amylose content increased the resistance to hydrolysis by bacterial α-amylase and amyloglucosidase. Increasing the number of heating/cooling cycles during preparation notably increased the RS, which was identified as recrystallized amylose. Cairns et al. (1995,1996) studied the in vitro and in vivo structures of hydrolyzed pea amylose. They also concluded that RS was composed of recrystallized amylose in the form of a semi-crystalline material. Planchot et al. (1995) compared the hydrolysis of various starches. Except for wrinkled pea starch, a high amylose content prevented hydrolysis much more than

a low amylose content. A major role was attributed to the porosity of the granules, very high for low-amylose and only superficial for high-amylose starches. Vesterinen et al. (2002) used starches with different amylose contents to form weak to strong gelatinized dispersions, hydrolyzed by human saliva α-amylase in vitro. The more the amylose content was, the higher the storage modulus and the lower the hydrolysis were. This was correlated to pH changes in the mouth in vivo except for very strong dispersions. Evans and Thompson (2004) studied the hydrolysis of various native starches. Low-amylose starches presented less RS than high-amylose ones. For the latter, this was related to the observation of a resistant layer near the surface. Hu et al. (2004) confirmed that the higher the amylose content in rice starches, the more the RS and the slower the hydrolysis by pepsin then pancreatic α-amylase and amyloglucosidase. Sandhu and Lim (2008a) compared the structures of corn and mango kernel starches and their hydrolysis. A lower resistance for corn was attributed to a lower amylose content and a lower crystallinity together with the observation of a porous granule structure. In the contrary, the granule surfaces were smooth in the case of mango kernel.

2.b.4. Effect of amylopectin

Biliaderis (1982) studied the hydrolysis of acetylated smooth pea or hydroxypropylated waxy maize starches. In all cases a reduced hydrolysis was obtained compared to the native starch, which was related to changes in the amylopectin structure. Zhang and Oates (1999) investigated the hydrolysis of different varieties of sweet potato starch. They found that a higher amylopectin content induced a higher gelatinization temperature and a lower degree of hydrolysis. Surface roughness was found to be a good indication that extensive hydrolysis occurred. Zhang et al. (2006b) hydrolyzed several native cereal starches by pepsin, pancreatin, pancreatic α-amylase, amyloglucosidase and invertase. The crystal morphology was found to be a determining factor, with a slower hydrolysis in the case of a semi-crystalline structure with short chains of amylopectin. Benmoussa et al. (2007) studied the

impact of amylopectin structures on the hydrolysis of twelve rice starches by α-amylase, amyloglucosidase and invertase. The prevalence of long and intermediate/short amylopectin linear chains resulted in slow hydrolysis whereas the prevalence of very short chains resulted in rapid hydrolysis. This effect could also be predicted by viscosity measurements.

2.b.5. Effect of gelatinization

Gelatinization is the process of heating (possibly heat cycling) starch in the presence of water, resulting in the swelling of granules and solubilization of amylose. Sagum and Arcot (2000) characterized starch digestibility of three rice varieties with different amylose contents. The resistance to hydrolysis was found to increase with the amylose content but was always significantly reduced after gelatinization. Slaughter et al. (2001, 2002) found that gelatinization increased the rate of hydrolysis of various starches, especially the ones containing amylose, which had a native low hydrolysis. The addition of guar galactomannan to gelatinized starches reduced the rate of hydrolysis, either by binding α-amylase or covering starch granules. Parada and Aguilera (2009) hydrolyzed gelatinized potato starch. Increasing the degree of gelatinization decreased the starch granules size (and influenced other shape parameters) and increased the in vitro hydrolysis degree or the in vivo glycemic response. Although many structural parameters were investigated, their contributions to the digestibility were not clearly distinguished. Miao et al. (2010) studied the effect of gelatinization of waxy maize starch on its hydrolysis. Heating to a temperature higher than 60 °C resulted in less RS due to changes in structural parameters, but the authors were not able to separate their effects. They nevertheless concluded that SDS mainly consisted in amorphous regions and a small portion of ordered double helix structure.

2.b.6. Effect of retrogradation

Retrogradation is the process of cooling (possibly heat cycling) starch after gelatinization, resulting in its recrystallization. Bornet et al. (1989) found a correlation between the in vivo

responses and the short times degree of hydrolysis of different starches. Legume starches with high contents of amylose available for retrogradation were found to give especially low in vitro hydrolysis and in vivo responses. Eerlingen et al. (1994) investigated the effect of the heating/cooling cycling protocol on the hydrolysis of a gelatinized waxy maize starch. They found that the higher the retrogradation extent, the lower the hydrolysis susceptibility. Fredriksson et al. (2000) controlled the retrogradation degree of waxy maize or high-amylopectin potato gelatinized starches by cooling/heating cycling and found that a higher amount of retrograded amylopectin resulted in a reduced hydrolysis. Sasaki et al. (2009) prepared starch dispersions from three varieties of rice having different amylopectin chain distributions. The lower the proportion of short chains was, the better the recrystallization by retrogradation was, leading to a higher resistance to hydrolysis. Park et al. (2009) studied the impact of constant (4 °C) or cycled (4-30 °C) temperature storage on the hydrolysis of gelatinized waxy maize starch. Both storages induced a retrogradation which reduced hydrolysis, with a more pronounced effect with cycling. This was related to a more perfect crystal structure and to a softer starch dispersion (reflecting the amorphous region state).

2.b.7. Interplay of amylose/amylopectin

Zhang et al. (2008a, 2008b, 2009) specifically attributed the SDS to amylopectin and the RS to amylose as the result of hydrolysis of eighteen maize starches by pepsin, pancreatin, pancreatic α-amylase, amyloglucosidase and invertase. Starches having a high content of amylopectin short chains or a high content of amylopectin long chains indifferently presented more SDS. This was explained by a higher amount of amylopectin branches in the first case whereas it was explained by the effect of retrogradation on the crystalline structure in the second case. A minimum was reached around a short/long chains weight ratio of 0.5. Hickman et al. (2009) subjected corn and wheat starches to a heat treatment followed by β-amylolysis. The heat treatment formed a network which was nearly destroyed by the

enzymatic treatment. Thus, the latter had the main impact on the starch hydrolysis by pancreatin and amyloglucosidase. The amount of RS indeed increased due to an increase of the amylopectin branch density and a general decrease of chain length, leading to a more efficient amylose/amylose association.

2.b.8. Effect of crystallinity

Gerard et al. (2001) studied the hydrolysis of all usual crystal morphologies of starch using maize mutants. No effects of the crystallinity level and of the amylose content were found whereas a high content of B-type morphology crystals was always associated with a high resistance to hydrolysis. Chung et al. (2006) evaluated the impact of the crystallinity on the hydrolysis of waxy rice starch. The starch crystal state was controlled by partial gelatinization or retrogradation of a fully gelatinized starch. In any cases, the hydrolysis rate decreased with increasing crystallinity. At a similar crystallinity, the partially gelatinized starch was less hydrolyzed than the retrograded one. This was related to a less ordered semi-crystalline arrangement for the latter. Fassler et al. (2006) compared full gastrointestinal dynamic (the TIM) and static in vitro protocols to quantify RS. Both methods were in good agreement with an in vivo study when retrograded maltodextrin was used. In contrast, the methods diverged when high-amylose maize was used. This was related to more severe conditions in the dynamic method, leading to structural rearrangements and a lower residual crystallinity. Ao et al. (2008) treated maize starch enzymatically to modify its structure. Hydrolysis by either pancreatic α-amylase or by pancreatin and amyloglucosidase was slowed by the enzymatic treatment, presumably because it shortened the amylopectin branch chains allowing the production of more resistant crystal morphologies, and because it increased the branch density, creating more resistant linkages.

2.b.9. Statistical analyses

Yang et al. (2006) then Shu et al. (2006, 2009) studied the hydrolysis by pepsin then pancreatic pancreatic α-amylase of mutant rice starches. Using a statistical analysis, they found that the hydrolysis degree was reduced with higher RS, amylose and lipid contents. Capriles et al. (2008) studied the hydrolysis of amaranth starch by pepsin then pancreatic α-amylase and amyloglucosidase in different products. Only small effects were seen but in any cases amaranth starch was found to be a RDS, attributed to small granules, high level of amylopectin, and low gelatinization temperature above which the crystalline and granular structures are lost. Sandhu and Lim (2008b) compared the hydrolysis of six legume starches. Digestibility was found to decrease with the granule diameter, with the amylopectin molecular weight (because it increased starch crystallinity) and with the amylose molecular weight. Blazek and Copeland (2010a) conducted a statistical analysis of the results of hydrolysis of 35 wheat starches characterized by 22 properties in 5 different states (native, gelatinized, retrograded, complexed with monopalmitin, treated enzymatically). The properties that statistically affected hydrolysis were the amylose content, the complexation with monopalmitin, the amylopectin chain length distribution, the enzymatic treatment and the granules size. Once gelatinized or retrograded, the hydrolysis of all starches was not statistically different.

Some more results about starch digestibility are described in the reviews of Colonna et al. (1992), Asp et al. (1996), Gallant et al. (1997), Oates (1997), Buleon et al. (1998), Haralampu (2000), Hoover and Zhou (2003), Sajilata et al. (2006), Lehmann and Robin (2007) and more recently Zhang and Hamaker (2009), Dona et al. (2010), Singh et al. (2010). Woolnough et al. (2008) made a more general review about carbohydrates digestion in vitro. They concluded that many methods are not quantitatively consistent so standardization is needed.

2.b.10. Effect of starch/lipid complexation

Holm et al. (1983) made amylose/lipid complexes using oleic acid or lysolecithin, which were submitted to a bacterial α-amylase and pancreatin. Compared to pure potato amylose, the complexes were slowly hydrolyzed, especially using lysolecithin. Czuchajowska et al. (1991) investigated the influence of complexing lipid and maize starch on the generation of RS by heating then cooling. Compared to pure starch, the amount of starch resisting hydrolysis was reduced by the lipid, with a reduction following the order lysophosphatidylcholine > sodium stearoyl lactylate > hydroxylated lecithin. This was understood by a competition for amylose chains between retrogradation and complex formation. Seneviratne and Biliaderis (1991) created potato amylose/monostearin helical inclusion complexes of various supermolecular structures. The higher the degree of organization of helices into larger domains of ordered chains, the lower the rate and extent of hydrolysis. Complexes with a greater crystallinity were more resistant, but were nevertheless fully degraded with enough time and enzyme concentration. Guraya et al. (1997) used different lipidic emulsifiers to form complexes with 100% amylopectin (waxy) or 79% amylopectin rice starches, submitted to α-amylase from human saliva. Emulsifiers with fatty acid chains of at least 18 carbons and of saturated type were found to reduce digestibility more than those with shorter chains of any types. The waxy starch did not form complexes with most of the emulsifiers, contrary to the other starches containing amylose. Cui and Oates (1999) studied the hydrolysis of complexes made of different lipids and sago starch. The degree of hydrolysis at different times decreased when complexation was done, with a reduction depending on the lipid used (lysophosphatidylcholine > monomyristin > monopalmitin > monostearin). Gelatinization increased the degree of hydrolysis in any cases. Retrogradation completely reversed the order of reduction by lipids, with pure starch being less hydrolyzed than complexes. Using pure amylose or amylose/lipid complexes resulted in almost no hydrolysis compared to starch (containing 27% amylose). These results confirmed the competition hypothesis between the

amylose/lipid complex formation and the retrogradation of amylose. Crowe et al. (2000) investigated the hydrolysis of potato amylose, amylopectin or starch and their complexes with individual FFA, lysolecithin or cholesterol. Retrogradation of amylose reduced its hydrolysis. All lipids except stearic acid and cholesterol reduced the hydrolysis of amylose. In the contrary, there was no effect of FFA on the hydrolysis of amylopectin and only a small effect for the starch, which was related to its amylose content. Tufvesson et al. (2001) used the emulsifier monopalmitin to form complexes with low-amylose potato or high-amylose maize starches under heat treatments. Hydrolysis was investigated using pancreatic α-amylase, whereas the RS content was investigated using human saliva then pepsin then pancreatin and amyloglucosidase. Complexation with monopalmitin reduced the rate of hydrolysis of potato starch, especially heat-treated ones. The rate of hydrolysis of the pure maize starch (about half that of pure potato starch) decreased by heat treatments but increased when complexes were also formed. Results for the RS content were similar, decreasing in the presence of complexes for both starches. This showed there was a competition between the amylose/lipid complex formation (favored by heat treatments) and the retrogradation of amylose. Gelders et al. (2005) studied the effect of the degree of polymerization of pure amylose from different sources on the hydrolysis of complexes made with docosanoic acid or monostearin. The resistance to hydrolysis increased with the degree of polymerization of amylose and the temperature at which the complexation was done. Docosanoic acid complexes induced more resistance than monostearin complexes. Lalush et al. (2005) investigated the complexation of potato amylose with conjugated linoleic acid. Release tests were performed using either pancreatin or α-amylase from aspergillus oryzae or amyloglucosidase or β-amylase from sweet potato. Release of conjugated linoleic acid was proportional to the starch hydrolysis degree, decreasing in the order cited previously for the enzymes (with a full hydrolysis using pancreatin). Lesmes et al. (2008, 2009) tried to complex starches differing in amylopectin

content with stearic acid to design a controlled release system tested using pancreatin. Only the starch containing 100% amylopectin was not able to bind FFA molecularly, but seemed to entrap it physically. By varying the saturation of long chain FFA, they made different complexes with potato amylose, and hydrolyzed them by pancreatin. The polymorphism was found to play a role, associated to a slower release in the case of molecular binding compared to physical entrapment. The role of the saturation was not elucidated as it also influenced the complexes size, decreasing with saturation. Cohen et al. (2008) made amylose/genistein complexes with pure potato amylose or high-amylose corn starch, and hydrolyzed them with pancreatin. The release was low at various pH, but high in the presence of pancreatin, indicating that the enzymes played a role. The apparent release was lower for pure amylose but this could again be due to a larger complexes size. Yang et al. (2009) investigated the complexation of potato amylose or β-cyclodextrin with conjugated linoleic acid. Release tests were performed using pepsin or pancreatic α-amylase and amyloglucosidase. Pepsin induced some release only from β-cyclodextrin. In the artificial intestinal medium, release was correlated with the starch hydrolysis degree, and after 15 hours, both tended towards 100% for amylose whereas they were around 20% for β-cyclodextrin.

2.b.11. A real food case: pasta

In the study of real food dispersions, most of the works focused on pasta. Fardet et al. (1998, 1999) investigated the role of several parameters modifying the protein network of pasta on the hydrolysis of wheat starch by human saliva or pancreatic α-amylase. The presence of pepsin degraded the protein network, resulting in more starch hydrolysis. The protein role was confirmed by increasing its content, resulting in a delayed starch hydrolysis, presumably because protein nodes protected starch. Different heat treatments or geometries of the protein network did not affect the hydrolysis. Duodu et al. (2002) studied the proteins digestibility by pepsin (with or without a previous bacterial α-amylase step) of sorghum as a flour or a protein

body dispersion. In the latter, where the proteins and starch were separated, the digestibility was increased. Upon cooking, the digestibility was decreased. With maize as a flour or a protein body dispersion, those effects were not observed, presumably because maize oligomeric proteins had higher molecular weights and formed less disulphide bonds than sorghum ones. In any cases, the α-amylase step only slightly increased proteins digestibility. Tudorica et al. (2002) investigated the wheat starch hydrolysis in pasta enriched in insoluble (pea, inulin) or soluble (guar) dietary fibers. A lower hydrolysis by pancreatic α-amylase with the latter was understood as the result of an entrapment of starch granules within a protein-fiber-starch network whereas insoluble fibers were thought to disrupt the protein matrix. Brennan et al. (2004) complemented the work on inulin pasta by adding a pepsin step before the pancreatic α-amylase step. They found a reduced hydrolysis with increasing inulin concentration, presumably because it reduced water absorption and gelatinization and formed a barrier around starch granules. Kim et al. (2008) varied the protein matrix structure of pasta through mechanical processing. This affected the hydrolysis of wheat starch by pepsin then pancreatin and amyloglucosidase. A higher hydrolysis degree was obtained when the proteins were dissociated from the starch granules by the processing, indicating that digestibility could be controlled by the starch/protein interactions. For a specific review about structures and digestibility in pasta, the reader is referred to Petitot et al. (2009).

2.c. Foams

The in vitro digestibility of only one aerated product was investigated: bread, a solid foam. For desserts like mousses or crème Chantilly (whipped creams), the starting matrix is usually an emulsion so they were studied as such.

Bread was studied extensively (white bread is even a reference for the glycemic index) and its matrix is a cereal starch dispersion so many data exist. The early investigations of Blake

(1916) allowed the identification of several molecules constituting bread and their products during hydrolysis by saliva. Gluten was found to slow down the hydrolysis. The impact of structure came from studies of botanical entities (bodies, cell walls, tissues) and their disruption upon thermal, chemical or mechanical processing. Although suspected before, one of the first proofs was obtained in vitro for leguminous starch hydrolysis by pancreatin and trypsin, which was facilitated when granules were released from broken fibrous cells (Wursch et al. 1986). Bread digestion in vitro was then studied through the prism of multiscale structures (Bjorck et al. 1994 and references therein). Holm and Bjorck (1992) investigated the hydrolysis by pancreatic α-amylase with or without pepsin of starches in various breads. The main difference appeared when whole-grain wheat (intact kernels) was used instead of wheat flour, slowing down the hydrolysis due to the presence of cell walls. The use of oat bran (rich in dietary fibers) had the same effect. If pepsin was not included, those effects were not seen and the hydrolysis was slowed down, suggesting a role of protein which was not observed in vivo (because pepsin and other proteases were present). Brennan et al. (1996) confirmed the role of dietary fibers using guar gum in wheat bread and found it reduced starch hydrolysis by pepsin then pancreatic α-amylase because guar galactomannan formed a physical barrier around the granules in addition to increasing digesta viscosity. Hoebler et al. (1999) substituted wheat for a high-amylose maize in bread and found that the hydrolysis of starch was reduced because some crystalline amylose was not gelatinized during processing, identified as RS. Englyst et al. (1999) designed an in vitro protocol with pepsin, pancreatin, amyloglucosidase and invertase to evaluate the glycemic response to carbohydrates in various food dispersions (corn flakes, white bread, cooked white spaghetti, and cooked pearled barley). The in vitro measurements of the rapidly available glucose were correlated to in vivo glycemic responses. The food structure was suspected to play a role but the conclusions were uncertain as the overall carbohydrate compositions were all different. Walsh et al. (2003) used

a three steps (oral, gastric and intestinal) protocol to measure the bioaccessibility of isoflavonoids from soy bread. The oral step was performed in vivo by chewing, then the following steps were done in vitro, using pepsin for the gastric step, and using bile extract, pancreatic lipase and pancreatin for the intestinal step. Increasing the concentration of the bile extract was found to have the main impact, enhancing the release of isoflavonoids, which were not released at all in the absence of bile extract. This effect was thus related to the micellarization of isoflavonoids in bile salts. Berti et al. (2004) compared the hydrolysis of starch by pepsin then pancreatic α-amylase for breads with or without gluten. They confirmed that the digestibility of starch was reduced by gluten, presumably because its network prevented α-amylase accessing the granules. Overall, their in vitro results did not correlate well with in vivo data, overestimating the starch digestibility. This was understood by the high protein content in breads, which stimulated insulin secretion in vivo, not taken into account in vitro. Kean et al. (2008) followed the approach of Walsh et al. (2003) for the bioaccessibility of carotenoids (especially lutein and zeaxanthin) from breads and other products made of yellow corn (whole-grain or not), but the oral step was done in vitro using α-amylase. The bioaccessibility of carotenoids was generally higher in dry products, except for the apolar carotenes bioaccessibility, higher in porridge, a wetter product. One interpretation was that it depended on the food composition and preparation method. Mateo Anson et al. (2009) studied the bioaccessibility of ferulic acid from wheat fractions and breads using the TIM. In any cases, it was very low except when free ferulic acid was added to the ingredients. It was concluded that in the grains, the ferulic acid was bound to different cell walls polysaccharides, restricting its release.

2.d. Gels

As dairy products represent a large part of food gels, they were investigated earlier than novel gels made of polysaccharides. For that matter, milk proteins are still the first choice ingredients for the design of gels as delivery systems (Livney 2010). Siu and Thompson (1982) modified a commercial cottage cheese whey by succinic anhydride and evaluated its protein hydrolysis by pepsin then pancreatin. The amino acids release was greatly reduced at high levels of succinylation, which was related to the percent of amino acids bound to succinic anhydride. Such reduction was not obtained in vivo in the rat, presumably because other proteases were present and because succinyl amino acids could be absorbed. Arkbage et al. (2003), using the TIM, studied the bioaccessibility of folate from yogurts fortified with folic acid or folate, with or without folate-binding proteins (in the form of Whey Protein Concentrate WPC). Both folic acid and folate gave a high folate bioaccessibility, which was reduced in the presence of WPC, especially with folic acid. This was correlated with the observation that WPC was less hydrolyzed with folic acid, suggesting more stable complexes than with folate. Remondetto et al. (2004) compared the bioavailability of iron from filamentous or particulate whey protein hydrogels. They found that both structures were hydrolyzed to similar extents by pepsin or pancreatin, but only the filamentous hydrogel released more iron than in the corresponding saline solutions without enzymes. Most of the iron release took place during the intestinal step, showing that filamentous hydrogel protected iron during the gastric step. Han et al. (2008) made a gel based on alginate and chitosan to encapsulate ascorbic acid, β-carotene, or ferrous fumarate. For all micronutrients, the release was low in the gastric step with pepsin then increased gradually during the intestinal step with pancreatin. Tedeschi et al. (2008) compared the release of a green tea extract (containing 20% catechins) from a filamentous β-lactoglobulin hydrogel in gastric or intestinal media similar to those used by Minekus et al. (2005) except there was no bile salt. The release was found to be significantly higher in the intestinal medium only after three hours of dissolution. Somchue et

al. (2009) encapsulated α-tocopherol in β-lactoglobulin or hen egg white gels coated by alginate. Release was measured in the presence of pepsin then pancreatin. Without the alginate coating, most of the α-tocopherol was released during the gastric incubation. With the alginate coating, almost no α-tocopherol was released during the gastric step but it was released during the intestinal step, faster for the β-lactoglobulin gel and depending on the alginate concentration.

2.e. Other dispersed systems

El Kossori et al. (2000) made complexes of sodium caseinate with different dietary fibers in order to reduce protein hydrolysis by pepsin then pancreatin. A reduction of the nitrogen release was always obtained at high fiber concentrations (20 or 25 %), following the order prickly pear extracts (pulp or skin) > locust bean gum > carrageenan > gum arabic > citrus pectin > alginate (almost no effect). There was no correlation with the increased viscosity due to the polysaccharide so specific casein/polysaccharide interactions were rather suspected. Mouecoucou et al. (2003, 2004a,) made complexes of β-lactoglobulin with different dietary fibers in order to reduce protein hydrolysis by pepsin alone or followed by trypsin and chymotrypsin. β-lactoglobulin alone or in complexes was found to resist hydrolysis by pepsin. Nevertheless some nitrogen release was measured and increased in the form of complexes, even though pepsin activity was reduced in the presence of dietary fibers. When trypsin and chymotrypsin followed, hydrolysis was found to increase. The nitrogen release was reduced in the form of complexes, especially with xylan compared to gum arabic or low-methylated pectin. Mouecoucou et al. (2004b) made similar experiments using peanut protein isolate complexed with the same polysaccharides. They all reduced the nitrogen release in the small intestine but this was attributed to the hydrolysis of proteins and high molecular weight peptides for gum arabic and xylan, whereas this was attributed to interactions with high

molecular weight peptides for low-methylated pectin, as the hydrolysis was not increased. Nacer et al. (2004) investigated the mechanism of β-lactoglobulin digestion by pepsin in the presence of different pectins. All of them reduced pepsin activity but nevertheless lead to a higher nitrogen release, presumably because it favored complexes at the expense of β-lactoglobulin aggregates, increasing the proportion of soluble β-lactoglobulin.

Nacka et al. (2001) studied the potential of squid lipid liposome to deliver polyunsaturated FFA from TAG or phospholipids. Dispersed liposomes were found to keep their structure and to aggregate at acidic pH, which was partially reversible when further neutralized. Incubation in bile salts lead to lipids solubilization, favored when an initial acidic step was done. Phospholipase A2 had a better activity in the absence of bile salts, because the liposomes were not destructured to form mixed micelles. Takahashi et al. (2008) encapsulated a ukon extract into soybean lecithin liposomes submitted to pepsin then pancreatin and analyzed the released curcumin. Encapsulated or pure ukon extract released only a small fraction of curcumin in the pepsin step. In the pancreatin step, the encapsulated ukon extract released no curcumin whereas the pure ukon extract released 45% curcumin. Overall, only 10% curcumin was released from the liposomes whereas 54% curcumin was released from the pure ukon extract.

Kim et al. (2006) encapsulated isoflavone in MCT and β-galactosidase in MCT or polyglycerol monostearate. A gastric test was done using pepsin and an intestinal test was done using pancreatin, lipase and bile salts. The releases of isoflavone or β-galactosidase were similar and low at the end of the gastric step at any pH between 2 and 5, but the release of β-galactosidase was faster. The releases of isoflavone or β-galactosidase were similar and high during the intestinal step at any pH between 7 and 9. They were low only at pH 6 with isoflavone being less released.

Gunasekaran et al. (2007) designed whey protein hydrogels and β-lactoglobulin particles for controlled release purpose but only studied the enzymatic hydrolysis by pepsin or trypsin of the β-lactoglobulin particles. They were degraded more in gastric conditions than in intestinal conditions, all the more in the presence of enzyme.

Vitaglione et al. (2008) discussed the potential of cereal dietary fiber to deliver phenolic compounds into the gut. They reported that a high ratio of soluble fibers to insoluble fibers is needed to enhance the phenolic compounds bioaccessibility. This effect of fibers solubility was also found for minerals bioavailability by Greger (1999). Thus, researchers tried to either increase this ratio or to functionalized insoluble fibers. Hsu et al. (2008, 2009) chose the second strategy by micronization of insoluble fibers from carambola or cellulose (with or without an esterification by lactic acid) to control the release of α-tocopherol. The micronization and the esterification increased the rate and amount of α-tocopherol released in a gastric medium with pepsin, but the esterification had a much more pronounced effect. This was explained by a higher loading of fibers for the esterification. In any cases, insoluble fibers from carambola had higher loadings and releases. This was attributed to the high level of anionic rhamnose-rich pectic polysaccharides on the surface of these fibers. In vivo studies in the rat confirmed that higher levels of vitamin E in plasma could be maintained using the treated carambola fibers.

3. BIOACCESSIBILITY AND MULTISCALE STRUCTURES

In order to determine the current knowledge, we now discuss the results presented above, highlighting the contribution of structures to bioaccessibility. To do so, we picture a model aerated food dispersion containing the main nutrients as well as dietary fibers, hydrophilic and lipophilic micronutrients (HMN and LMN). Such a dispersion can be described at three length scales at least: macroscopic, mesoscopic and supramolecular (fig. 1). One must keep in mind

that most of the in vitro results were obtained either on simplified dispersions of one or two nutrients or using a reduced number of biomolecules representing one or two parts of the digestive tract. So the interactions described here might change in a real food environment.

Focusing on emulsion digestion at the droplet scale (mesoscopic), it is established that in excess of lipase, the rate of lipolysis increases with increasing specific interfacial area (decreasing droplet size). The reverse trend can be found when normalized by the interfacial area, which shows that lipase concentration is not high enough to cover the whole interfacial area in small droplets emulsions (Li and McClements 2010). In addition, solubility also increases with decreasing droplet size (Acosta 2009). The interaction of droplets with some biopolymers may lead to flocculation, as was shown by Minekus et al. (2005) for depletion flocculation by partially hydrolyzed guar gum (fig. 2A) or by Sarkar et al. (2010a) for bridging flocculation by mucin (fig. 2B).

At the supramolecular scale, interactions between enzymes and surfactants occur in the bulk and at interfaces. Most of the work was done in the intestinal part with measurements at the emulsion scale (macroscopic) to indirectly deduce the roles of molecules. Many authors worked on the ternary system bile/pancreatic lipase/co-lipase. Most of the results shows that the three components are needed to give a maximal lipolysis (fig. 3). Bile salts play a major role by displacing surfactants (including proteins) from interfaces. At high concentrations (above the CMC), all of them inhibit pancreatic lipase in the absence of co-lipase, and only bile salts allow lipase activity in the presence of co-lipase. These interactions are illustrated by the results of Tsuzuki et al. (2004) for the presence of lysophosphatidylcholine inhibiting lipolysis, restored by individual bile salts (fig. 4). Another example, in the presence of bile salts, digalactosylDAG was found to inhibit lipolysis more than lecithin alone or in mixtures whereas monogalactosylDAG had almost no effect (fig. 5). The theory of Lairon et al. (1978, 1980) describing the formation in the bulk of a complex made of lipase, co-lipase and whole

bile constituents (salts, phospholipids, cholesterol and proteins) adsorbing as a superhydrophobic entity seems to explain quite well the different interactions.

Nevertheless, the role of the surfactants stabilizing the emulsions before digestion is still not known in the details. Mun et al. (2007) found very contrasted emulsion intestinal lipolysis degrees only by changing the stabilizing surfactant, with or without bile extract (fig. 6). From their results, it seems that low molecular weight (LMW) surfactants (notably tween 20) inhibit lipolysis more than high molecular weight (HMW) ones (milk proteins, notably whey protein isolate). This was confirmed by Reis et al. (2008) with the spectacular effect of Sn-2 monopalmitin compared to β-lactoglobulin. In contrast, White et al. (2009) or Li and McClements (2010) did not find significant differences between LMW and HMW. These results could also be interpreted from the surfactant charge point of view, as tween 20 and Sn-2 monopalmitin are nonionic whereas the others are anionic in intestinal conditions. This could also explain the calcium chloride effect seen by Hu et al. (2010), because it brings the emulsions towards neutral charge. A special case of inhibition is thought to be due to the water-soluble protein moiety of dietary fibers, counteracting bile activity in the bulk and maybe able to reach interfaces.

Concerning the lipids, all the studies presented here concluded that lipases activity increases with decreasing TAG chain length. Saturated TAG were found to release less FFA than unsaturated ones but this effect could only be due to the physical state of the lipid phase, as shown by Marangoni et al. (2007) or Bonnaire et al. (2008). Many authors reported that the generation of FFA during digestion inhibits further lipolysis by gastric lipase. The theory of Pafumi et al. (2002) stating that FFA trap gastric lipase at the interface is convincing, but seems to be incomplete as the (physiological) surfactants competition for the interface likely plays a role (Reis et al. 2009). Finally, there are evidences that hydrophobicity plays a role too as TAG, DAG and MAG partition from droplet core to surface respectively, and only the

most hydrophilic micronutrients transfer into mixed micelles without lipolysis (Borel et al. 1996, Tyssandier et al. 2001). For lipophilic micronutrients, lipolysis is needed as they concentrate in the core of the doplets (Day et al. 2010). In any cases, a high concentration of bile is needed for the transfer to occur (fig. 7). As already mentioned, there are experimental confirmations that mixed micelles play a role in the transfer (Hermoso et al. 1997 and Pignol et al. 2000) but only scarce indications about a possible role of phospholipid vesicles (Somjen and Gilat 1985).

Some results for protein-stabilized emulsions show that proteins are hydrolyzed differently in the bulk and at interfaces (Mackie and Macierzanka 2010). This seems to be dependent on the protein conformations as well as the presence of physiological surfactants. As the latter desorb proteins, there is no clear indication about trypsin or chymotrypsin activity at interfaces.

As for the droplet scale in emulsions, it was found at the granule scale for starch dispersions that the rate of hydrolysis increases with the specific interfacial area. At the same scale, the bulk and interfacial porosity of the granules was related to digestibility by many authors (fig. 8). It seems that only certain amylopectin/amylose structures allow amylase penetration. A higher amylose content resulted in less porous structures, as reported by Planchot et al. (1995), Sandhu and Lim (2008a) or Blazek and Copeland (2010b). There is actually a large amount of studies reporting a decreasing hydrolysis with an increasing amylose content (table 2), whatever the state of the starch is (native, gelatinized or retrograded). Besides, at a given hydrolysis time, gelatinization is always found to increase the hydrolysis degree compared to native starch (fig. 9), and retrogradation to decrease it compared to gelatinized starch (table 2). The gelatinization effect might be related to several factors, among which a decrease in crystallinity or a decrease in the granule size were emphasized. The retrogradation effect is mostly explained by the formation of a semi-crystalline structure, which is even more

resistant if organized as concentric layers of amorphous and crystalline regions within the granules (fig. 8F). For example, we plotted in fig. 10 the data of Hu et al. (2004) for gelatinized or retrograded rice starches. Despite large error bars, there is a decreasing trend for the hydrolysis degree with the amylose content, which is more pronounced between 13-27% than between 0-13% amylose content.

At the biopolymers scale, there is no evidence for the mechanism but some authors found that amylose should be partially crystalline to induce such an effect. Gerard et al. (2001) even found that the crystal morphology has more influence on hydrolysis than the amylose content, the B-type morphology being the most resistant. The amylopectin structure also plays a role in the limitation of hydrolysis, essentially through its degree of crystallinity. Contradictory results about its chain length were elucidated by Zhang et al. (2008a, 2008b, 2009) who found that both a high content of long chain or a high content of short chain lead to a high SDS amount (fig. 11). This is explained by two mechanisms: retrogradation of the crystalline structure or a high amount of amylopectin branches, respectively.

For starch dispersions containing other components, some results are also recurrent. One is the role of proteins (including gluten proteins) forming network or bodies around the starch granules, as a chemical (disulphide bonds) or as a physical (protective layer) barrier (fig. 12). A similar physical effect is attributed to intact cell walls or dietary fibers coming from the use of whole-grain cereals or botanical polysaccharides (figs. 12, 13 and 14). This was confirmed recently for maize starch hydrolysis in the presence of guar gum (Dartois et al. 2010). Unlike Vitaglione et al. (2008) stating that phenolic compounds or minerals bioaccessibility is favored by a high soluble to insoluble dietary fibers ratio, we do not have enough evidences in vitro to attribute the reduced starch hydrolysis to a specific type of dietary fibers.

The formation of starch/lipid complexes is also associated to a reduced starch hydrolysis degree, yet only for pure amylose or starches with a high amylose content. Pure amylopectin

does not complex with lipids, although it might be able to form a physical trap for some lipids, as suggested by Lesmes et al. (2008, 2009). In starches with a low amylose content, a competition for amylose chains between retrogradation and complexation is thought to be responsible for an increased starch hydrolysis degree. The nature of the lipid appears to be an important parameter but was not studied systematically enough, and contradictory results exist about the roles of e.g. chain length and saturation. By studying the release of lipids from complexes during starch hydrolysis, two independent studies (Lalush et al. 2005 and Yang et al. 2009) recently found that the release extent was correlated to the hydrolysis degree (fig. 15).

Statistical analyses of data appear to be necessary when a large number of parameters interact. The recent recovery of the most important factors influencing starch digestion proved it can be an efficient way to set the focus on certain mechanisms (Blazek and Copeland 2010a). Another promising way is the use of computer simulations to apprehend the roles of multiscale structures (Nielsen et al. 2004).

Although not as advanced as pharmaceutical delivery systems, some new dispersions modulating bioaccessibility were recently tested in vitro. Protein gels in the form of particles or filaments are able to protect micronutrients from the gastric medium and release them in the intestinal medium. Coating or complexation with certain polysaccharides or dietary fibers allowed the modulation of the release or protein hydrolysis, attributed to the presence of some protein moieties inhibiting or delaying the enzymatic processes. Phospholipid liposomes also present some interesting release properties.

To our knowledge, no systematic comparison of bioaccessibility of micronutrients is available between an aerated product and its matrix (commonly a starch dispersion or an emulsion or both). However, depending on the stability of the foam in the gastrointestinal tract, an effect might be expected.

A matter to consider is the design of the artificial media for in vitro hydrolysis. The most used compositions for emulsions are reported in table 1. We see that some salts are almost always used (NaCl, $CaCl_2$ and HCl or KCl). The main enzymes are also present, with notable changes, e.g. from isolated bile salts to bile extract (containing phospholipids and cholesterol…), or from pancreatic lipase and co-lipase to pancreatin (containing proteases and amylases…). For starch dispersions, the main focus is on the small intestine but the use of juice extracts is growing, especially for real products like pasta and bread, for which a gastric step using pepsin is usually added. From the fundamental point of view, these substitutions could be detrimental as it brings many components in the media, increasing the potential interactions between them, making the mechanisms difficult to interpret at the supramolecular scale. From the complex systems point of view, despite the use of real products and artificial media, the hydrolysis of the nutrients are usually not investigated simultaneously. There is consequently no insight about the role of different hydrolysates interactions on simultaneous hydrolyses kinetics. To develop in vitro test as a predictive tool for in vivo response, we believe there is a need to standardize the artificial media, making them as realistic as possible. So far, those of Versantvoort et al. (2005) appear to be the most suitable ones for this purpose, although they are based on a rather old in vivo data collection in the Geigy Scientific Tables (Lentner 1981).

4. BIOACCESSIBILITY AND INTERFACES

We saw there are many strategies to control the bioaccessibility (the prerequisite for bioavailability) of (micro)nutrients based on dispersed objects usually made using interactions in the bulk. Nevertheless, despite the obvious role interfaces play in the reactivity and transfer of (micro)nutrients in dispersions, efforts to design delivery systems at the interface level are scarce (McClements et al. 2009b, 2010).

Many model systems and theories were used to understand the role of interfaces in the transfer of solutes from an aqueous phase (micellar or not) to a lipid phase, using emulsions or droplets (Goldberg et al. 1967, 1969, Suzuki et al. 1970, Bikhazi and Higuchi 1971, Surpuriya and Higuchi 1972, McNulty 1975, Miller 1986, Olbrich et al. 2000, Khare et al. 2003, 2004, Ly and Longo 2004) or model membranes (Scholtens et al. 1979, Guy et al. 1981, 1982, Amidon et al. 1982, Leahy and Wait 1986, Knepp and Guy 1989, Marrink and Berendsen 1996, Paula et al. 1996). For technical reviews, see Hanna and Noble (1985) and Tsukahara (2006). This approach allows the study of a key step for bioavailability: intestinal cell absorption, that is from the biological point of view.

From the food point of view, the bioaccessibility from dispersed systems is the opposite problem, that is to understand the role of interfaces in the transfer of solutes from a dispersed phase (lipid, insoluble domains, liposomes…) to the aqueous phase (micellar or not). This problem was examined by Ghanem et al. (1969) who found that gelatin adsorbed at the hexadecane/water emulsion interfaces considerably decreased the release rate of diethylphthalate, attributed to a hexadecane/gelatin condensed film. Scholtens et al. (1979) also found a similar effect for KCl transfer from water to 1-butanol with polyvinyl alcohol at the interface, attributed to the hydrodynamic effect of partial interface rigidification. Gupta et al. (2008) performed simulations showing that interfacial transfer across a monolayer of surfactants is controlled by steric repulsion in a percolation network, denser for surfactants with longer chains.

In emulsion science, a similar problem is Ostwald ripening, which is the exchange of matter between droplets (Taylor 1998). In the details, there are several processes: molecular solubilization and diffusion, micellar solubilization and transport from the bulk or from the interface (Kabalnov 1994, 1996, Todorov et al. 2002, Dungan et al. 2003, Pena and Miller 2006). For the latter, two hypotheses remain: approach of the interface by bulk micelles or

nucleation of loaded micelles from the interface, depending on the surfactant charge. Although there is a dilatation or a shrinkage of the droplets interfacial area during Ostwald ripening, the interfacial viscoelastic properties were just recently taken into account in the theory by Meinders and van Vliet (2004). This confirmed that interfaces can be designed to control mass transfer.

A few strategies are already used to specifically structure interfaces in order to modify their viscoelastic properties. Interfacial polymerization (Fessi et al. 1989, Khare et al. 2003, 2004) or cross-linking (Groboillot et al. 1993, Dickinson 1997) are convenient methods. Nevertheless, they use reagents that are not food-grade to modify proteins or polysaccharides (usually transglutaminase or glutaraldehyde). Various alternatives exist, but not as efficient as the chemical way (Murray 2002). An appealing one is heat treatment, which is quite easy and universal, as it allows modifications of all kinds of nutrients. The adsorption of protein/polysaccharide complexes at interfaces also shows promises, especially when combined to heat treatment to initiate a Maillard reaction (Dickinson 2008, Augustin and Hemar 2009). A challenge is the focalization of treatments at interfaces, as these treatments usually affects both bulk and interface. Moreover, biopolymers are extremely responsive to the physicochemical environment, making it difficult to control their properties in environments in constant change like gastrointestinal media. On the other hand, this also gives many possibilities in the design of associations, what pharmaceutical science explores thoroughly (Peppas et al. 2000). A food science transposition is the development of interfacial multilayer (usually three layers) of proteins and/or polysaccharides based on electrostatic interactions (McClements 2009b, 2010). Another interesting system is exclusively based on solid (nano)particles at interfaces. They give the so-called Pickering emulsions or foams a high stability against Ostwald ripening, presumably because they impart the interfaces a high dilatational elasticity (Dickinson 2010). So far, the most studied and successful particles are

based on silica, which is not food-grade. The first adaptations to food dispersions explored the properties of proteins and/or polysaccharides (including starch granules modified by octenyl succinate anhydride) to form structured systems at interfaces depending on the physicochemical conditions (spheres, filaments, tubes…). Hydrophobin, a fungal protein, was identified to impart high dilatational and shear viscoelasticities to interfaces, correlated to a high emulsion and foam stability against Ostwald ripening (Linder 2009, Blijdenstein et al. 2010). Many lipids are able to form assemblies in the bulk, but do not seem able to rigidify interfaces enough to stabilize dispersions alone (Leser et al. 2006, Dickinson 2010). Finally, we note that the oil/water interface is widely studied as far as digestion is concerned, but the air/water interface not much. This is probably because the gas phase can not carry (micro)nutrients. Nevertheless, many of them are able to adsorb at the air/water interface, and so do enzymes. The design of structured interfaces in foams could then be another possible way to control bioaccessibility.

As many processes in the digestion of food dispersions occur at the interface level, a link is likely to exist between static/dynamic interfacial properties and bioaccessibility. Studies of mixtures of biomolecules at interfaces in the spirit of the works of Verger and de Haas (1976) were recently revived by Maldonado-Valderrama et al. (2008), with new insights on interfacial composition and viscoelasticity. This approach should help to understand the dynamics of (physiological) surfactants competition for the interface during lipolysis directly at the supramolecular scale. Moreover, it should also help to understand how structured interfaces are e.g. able to both increase storage stability and control (micro)nutrients delivery.

CONCLUSION

The behaviors of dispersed systems being largely controlled by their structures, in vitro digestion of food dispersions were analyzed from the multiscale point of view. We

highlighted the role of bulk structures in the bioaccessibility of (micro)nutrients, and showed that interfacial structures are also very important because many if not all enzymatic processes occur at interfaces. In fact, bulk interactions could even appear as strategies to enhance interfacial activities of enzymes and carriers.

However, to be able to control bioaccessibility from such complex systems as food dispersions, interactions between bulk and interfacial structures have to be understood in the presence of numerous components. As shown in fig. 1, we are still far from this complete understanding. Intestinal hydrolysis is representative of such complexity, as it implies many couplings between bulk and interfacial processes and is greatly influenced by food composition. If the general mechanism is known with simplified systems using bile salt/lipase/co-lipase, we are less advanced as far as whole bile is concerned, as the exact roles of some constituents (phospholipids, cholesterol, proteins) and their assemblies (complexes, mixed micelles, vesicles) are not studied enough. Moreover, it depends on the properties of molecules pre-adsorbed at interfaces. If a dietary fiber is added, bindings are known to occur in the bulk and presumably at interfaces. In a real food system, hydrolysates from all nutrients interact, what would likely modify each specific process. In starch dispersions, the impact of the molecular organization of amylopectin/amylose on hydrolysis is partially known but requires refinements, especially as far as amylose semi-crystalline structure is concerned. This would also be important for starch/lipid complexes, as lipid essentially interacts with amylose. Studies about the role of the lipid nature in these complexes are also needed.

Recently, new strategies were used to design delivery systems in food dispersions, mostly based on biopolymers (proteins, polysaccharides), marginally on (phospho)lipids. Particles, filaments, tubes were developed in the bulk for this purpose, and just start to appear at interfaces, as it is recognized that interfaces play a key role in the control of dispersions thermodynamics and kinetics. In the context of digestion, many processes occur at interfaces,

so controlling their properties would allow the control of (micro)nutrients bioaccessibility. Direct measurements at the supramolecular scale also give the in vitro study an added value else than just its low cost and high availability compared to the in vivo study, e.g. access to the local dynamical mechanisms.

Finally, in order to use in vitro test to predict in vivo bioaccessibility, we propose to standardize the artificial media to be as complete as possible, based on in vivo characterizations of juices. These media could be systematically used whatever the complexity of the food is. For fundamental studies, we recommend a progressive addition of the components starting with the presumed main one (for example α-amylase for starch). To our opinion, this approach is a prerequisite to make sure that mechanisms in real foods and environments do not differ significantly from simplified systems due to possible multiple interactions. In this context, the use of statistical analyses, physicochemical models or computer simulations is required as many parameters influence the data.

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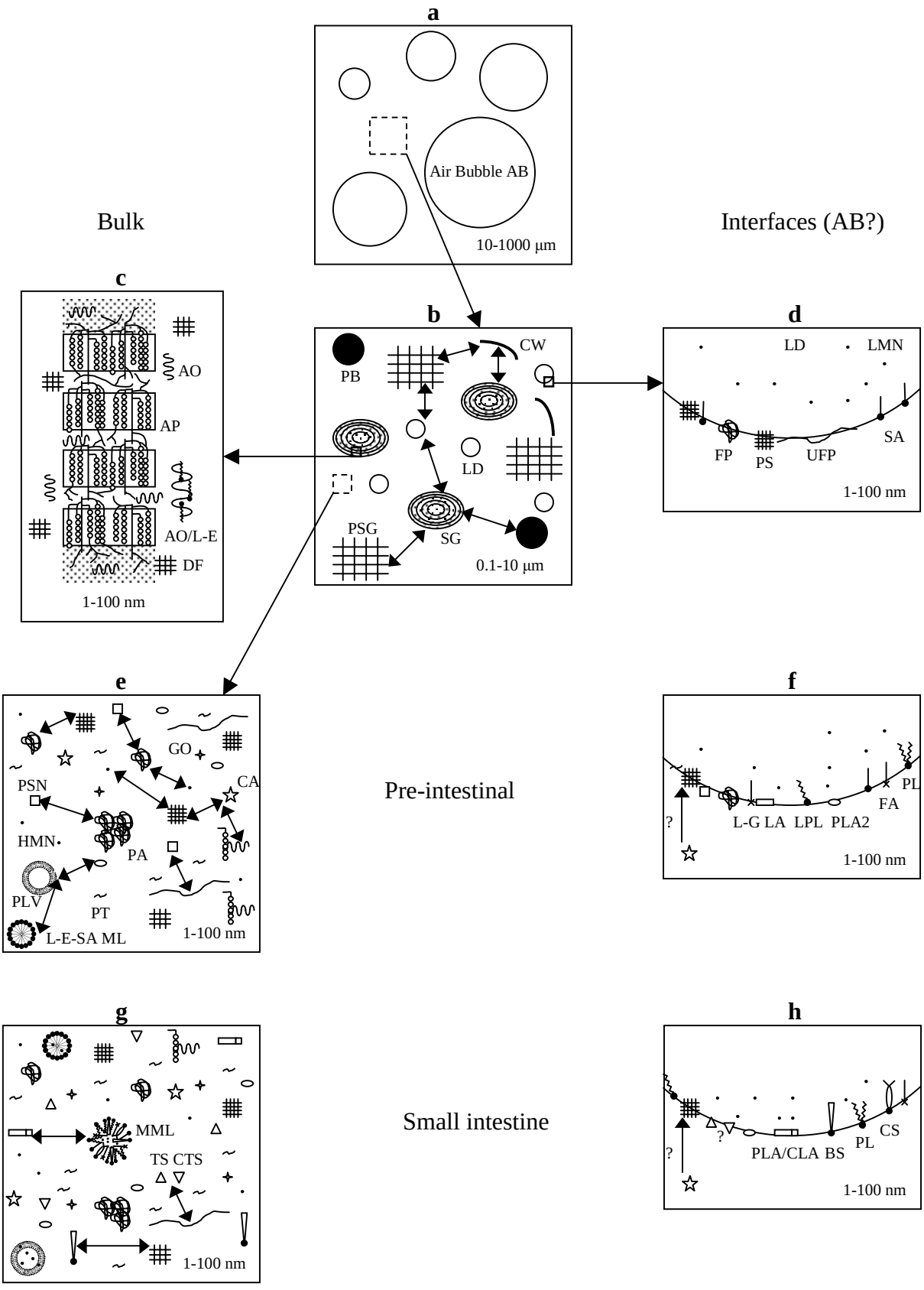
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PS
UFP
1-100 nm
e
GO
PSN
CA
HMN
PA
PLV
PT
L-E-SA ML
1-100 nm
Pre-intestinal
f
PL
FA
?
L-G LA LPL PLA2
1-100 nm
g
MML
TS CTS
1-100 nm
Small intestine
h
CS
PL
?
?
PLA/CLA BS
1-100 nm

Figure 1

Figure 1: Multiscale structures in a model aerated food dispersion (which could be ice cream or some cereal product) before and during digestion (arrows indicate bulk interactions). (**a**) At macroscopic length scales, only bubbles seem to interact. (**b**) At mesoscopic length scales, dispersed structures interact, namely starch granules (SG), lipid droplets (LD), polysaccharide gels (PSG), protein bodies (PB) and cell walls (CW). (**c**) At supramolecular length scales, the starch biopolymers amylopectin (AP) and amylose (AO) constitute crystalline and amorphous layers respectively. Amylose forms complexes with lipids or emulsifiers (AO/L-E). Dietary fibers (DF) may also interact with starch at these length scales. (**d**) At the lipid droplets and the air bubbles interfaces, molecules of polysaccharide (PS), folded or unfolded protein (FP or UFP), and surfactant (SA) compete for adsorption. Lipophilic micronutrients (LMN) may be present in the lipid droplets. In the bulk, lipid or emulsifier or surfactant micelles (L-E-SA, ML), protein aggregates (PA) or hydrophilic micronutrients (HMN) may be present. During the pre-intestinal steps of digestion, in the bulk (**e**), carbohydrases (CA, including amylases), pepsin (PSN) and phospholipase A2 (PLA-A2) generate glucose (GO), peptides (PT) and lysophospholipids (LPL) respectively. The latter may form vesicles, similar to phospholipid vesicles (PLV). Many other interactions are shown (**e**). At interfaces (**f**), lingual and gastric lipases (L-G LA) hydrolyze triacylglycerols into a diacylglycerol and a fatty acid (FA), FP or UFP may be hydrolyzed by PSN. During the intestinal step of digestion, in the bulk (**g**), the same structures still interact with each other and with bile constituents (bile salts BS, cholesterol CS, PL) and enzymes (trypsin TS, chymotrypsin CTS, pancreatic lipase and co-lipase PLA-CLA). In addition to PLV and ML, various mixed micelles (MML) may form between BS, CL, PL, LPL, L-E-SA and FA. These structures can solubilize LMN and/or HMN. At interfaces (**h**), PLA, CLA and bile constituents can adsorb individually or as complexes, producing a monoacylglycerol (MAG) and two FA. Throughout digestion, as LD becomes more and more hydrolyzed, lipids are solubilized in the form of FA and MAG, making the LMN available at interfaces. Question marks stand for uncertainty for some molecules activity at interfaces.

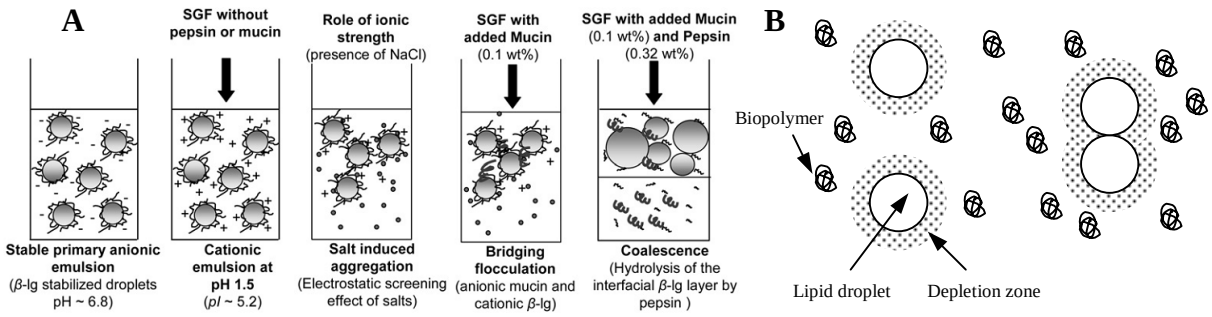

Figure 2

Figure 2: (A) Schematic diagram illustrating the behaviour of β-lactoglobulin-stabilized emulsions in a simulated gastric environment containing both pepsin and mucin. From Sarkar et al. (2010a) with permission of Elsevier. (B) Schema of the depletion flocculation mechanism adapted from Minekus et al. (2005).

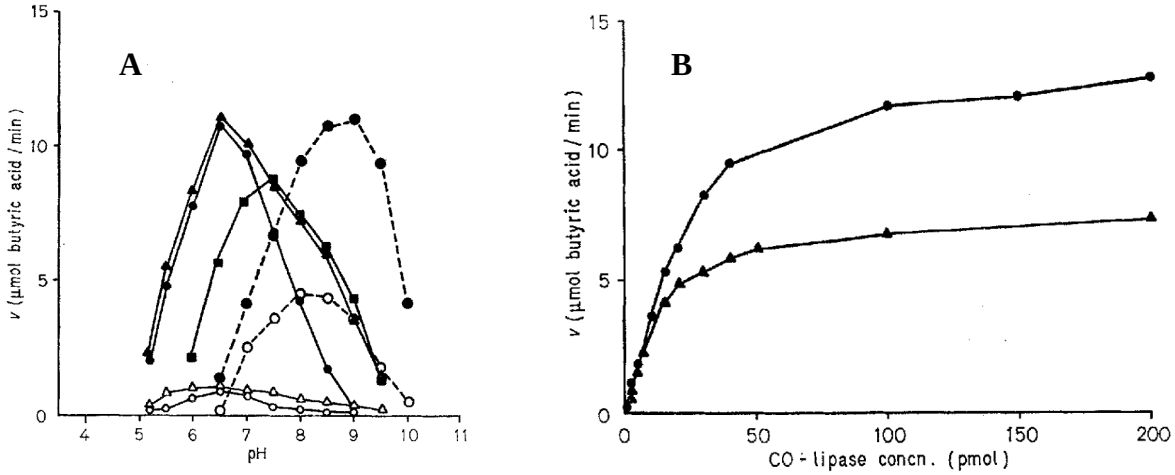

Figure 3

Figure 3: (A) *pH activity curves for porcine pancreatic lipase (25 pmol) using tributyrine as substrate, 1 mM Tris-maleate buffer, 150 mM NaCl and 1 mM $CaCl_2$ in the absence (open symbols) and the presence (closed symbols) of 50 pmol co-lipase.* (circle, full line) 4 mM sodium taurodeoxycholate; (triangle) 6 mM sodium taurocholate; (square) 4 mM sodium glycochenoxydeocholate and (circle, dashed line) 4 mM sodium deoxycholate. (B) *Effect of the amount of co-lipase on the activity of rat pancreatic lipase.* 4 mM sodium taurodeoxycholate, 150 mM NaCI, 1 mM $CaCl_2$, 2 mM Tris-HCl pH 6.7. (triangle) 25 pmol lipase and (circle) 50 pmol lipase. Lipase and co-lipase concentrations in pmol per 15 mL incubation volume. From Borgstrom and Erlanson (1973) with permission of John Wiley and Sons.

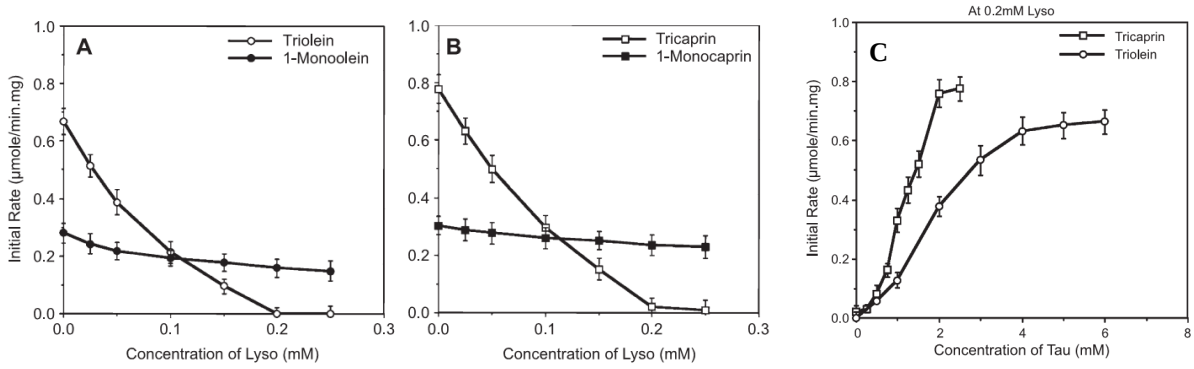

Figure 4

Figure 4: (A-B) Influence of lysophosphatidylcholine (Lyso) on the hydrolysis of tricaprin, 1-monocaprin, triolein and 1-monoolein by pancreatic lipase. (C) Influence of taurodeoxycholic acid sodium salt (Tau) on hydrolysis of the lipid emulsion composed of lysophosphatidylcholine and tricaprin or triolein. From Tsuzuki et al. (2004) with permission of Elsevier.

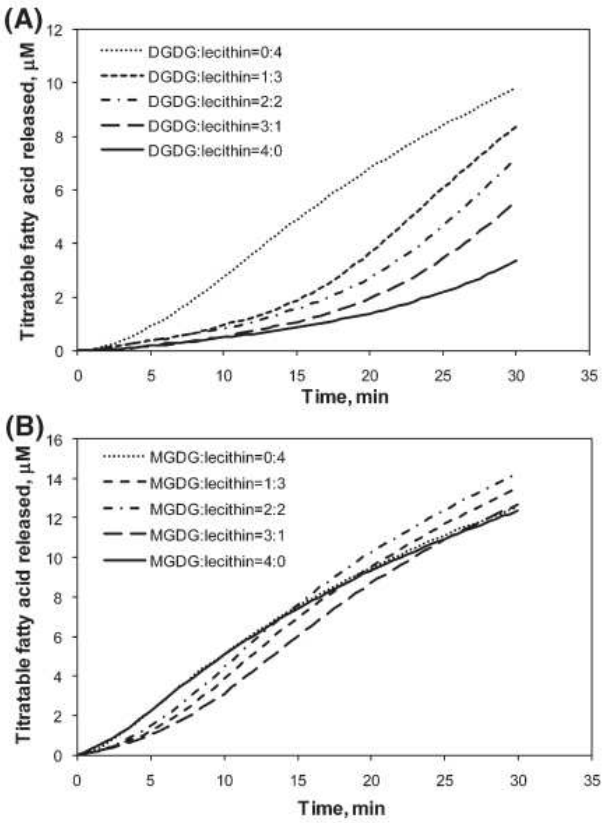

Figure 5

Figure 5: Titratable free fatty acid released from olive oil emulsions as a function of pancreatic lipase digestion time at various (A) DGDG/lecithin and (B) MGDG/lecithin molar ratios. The total lipid (DGDG or MGDG plus lecithin) concentration for all systems was 0.426 mM, and the oil concentration was 0.2% w/v. The lipolysis experiments were performed in the presence of 9.7 mM bile salt mixture, 10 nM colipase, and 2 nM lipase at 37 °C. From Chu et al. (2009) with permission of the American Chemical Society.

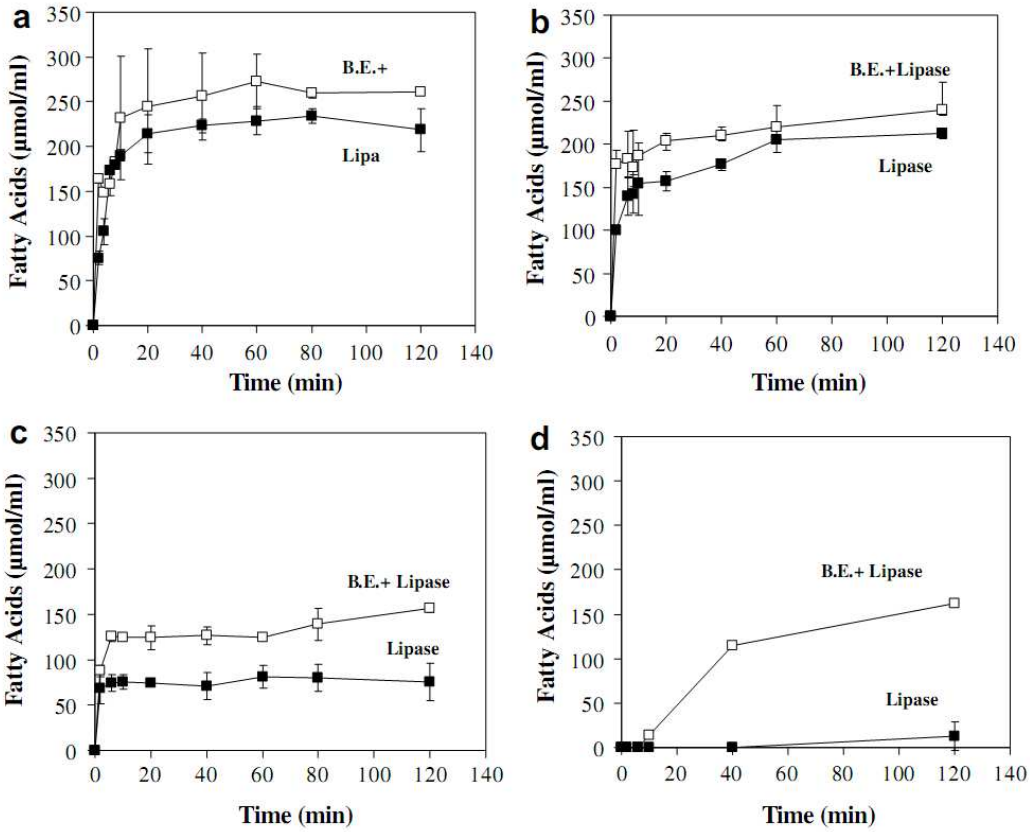

Figure 6

Figure 6: The time dependence of the amount of fatty acid (µmol) released from emulsions stabilized with (a) sodium caseinate, (b) WPI, (c) lecithin and (d) Tween 20 after hydrolysis with pancreatic lipase in the absence and presence of bile extract (5 mM phosphate buffer, pH 7.0). From Mun et al. (2007) with permission of Elsevier.

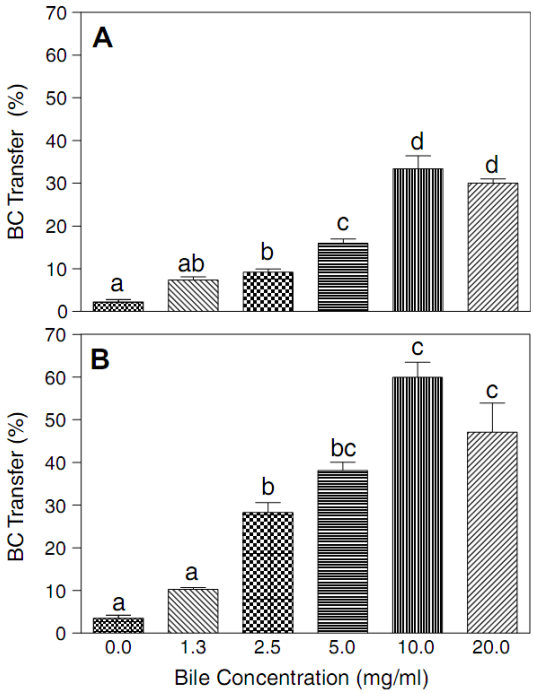

Figure 7

Figure 7: Influence of bile extract concentration on β-carotene transfer from the oily to the aqueous phase at (A) 0.4 and (B) 2.4 mg pancreatin/ml digestate. From Wright et al. (2008) with permission of Elsevier.

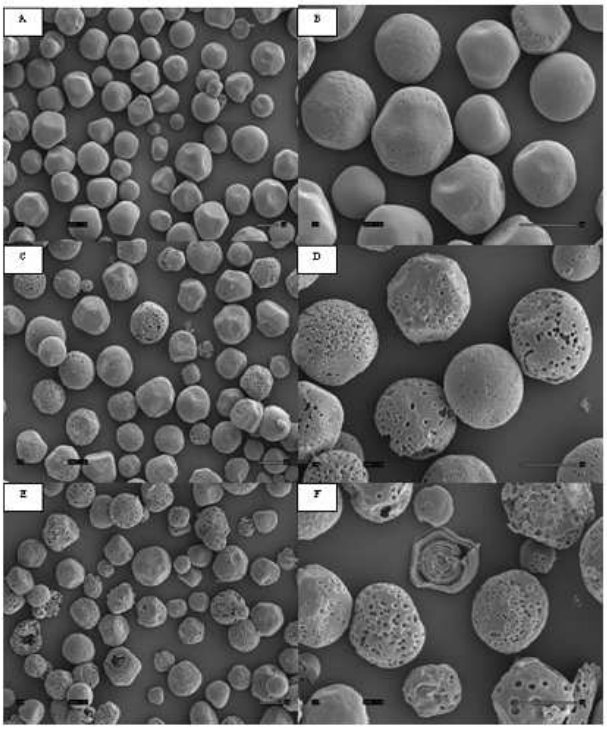

Figure 8

Figure 8: Scanning electron micrographs of high protein digestibility mutant sorghum line 111: (A) undigested (1000 x), (B) undigested (2500 x), (C) 30min digestion (1000 x), (D) 30min digestion (2500 x), (E) 1 h digestion (1000 x), and (F) 1 h digestion (2500 x) (bar equals 10 μm). From Benmoussa et al. (2006) with permission of Wiley-VCH Verlag GmbH & Co. KGaA.

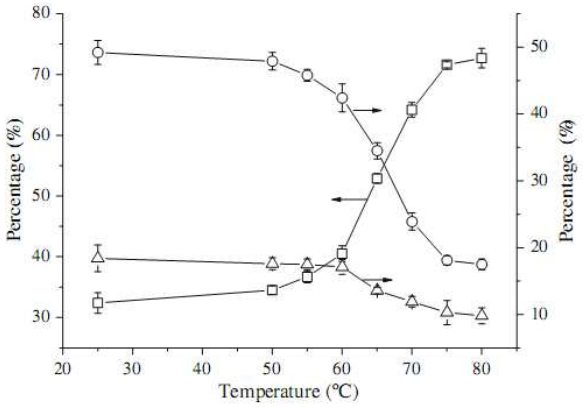

Figure 9

Figure 9: RDS (square), SDS (circle), and RS (triangle) content on the basis of Englyst assay of waxy maize starch granules in excess water heated to specific temperature. From Miao et al. (2010) with permission of Elsevier.

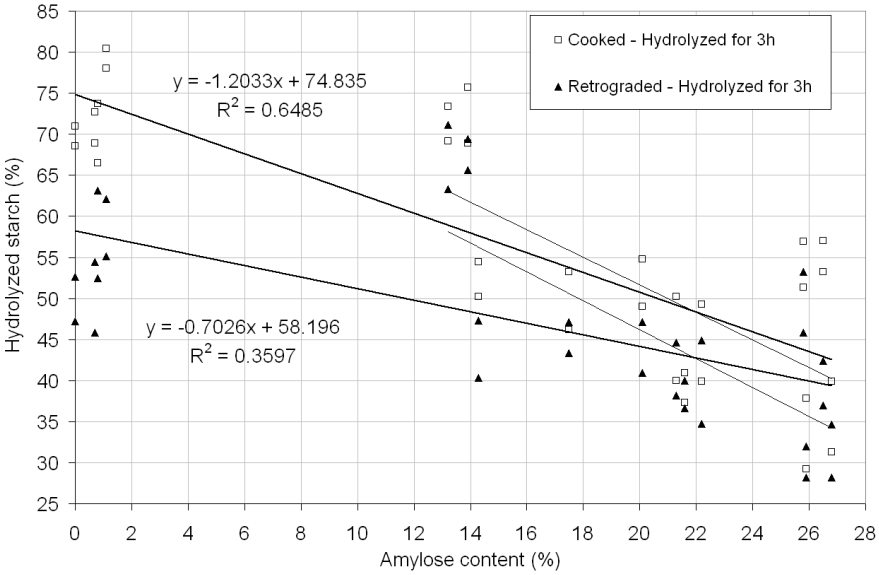

Figure 10

Figure 10: Percentage of hydrolyzed starch for varieties of cooked or retrograded rice starch varying in amylose content (for one amylose content, the maximal and minimal hydrolysis percentages are plotted). Starches were hydrolyzed for 3 hours. Linear regressions apply to the whole data sets (thick line) or to the data sets between 13-27% amylose content (thin line). Data are from Hu et al. (2004).

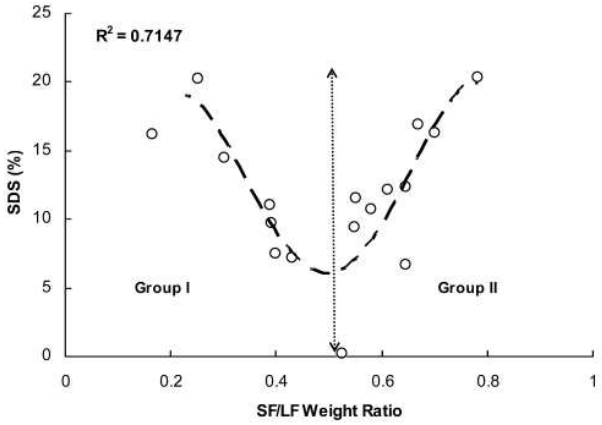

Figure 11

Figure 11: Parabolic relationship between proportion of Slow Digestible Starch and the weight ratio of the short-chain fraction (SF, DP < 13) to the long-chain fraction (LF, DP ≥ 13) of debranched amylopectin. The two groups of starch samples were divided at the dotted line with the lowest percent SDS. From Zhang et al. (2008a) with permission of the American Chemical Society.

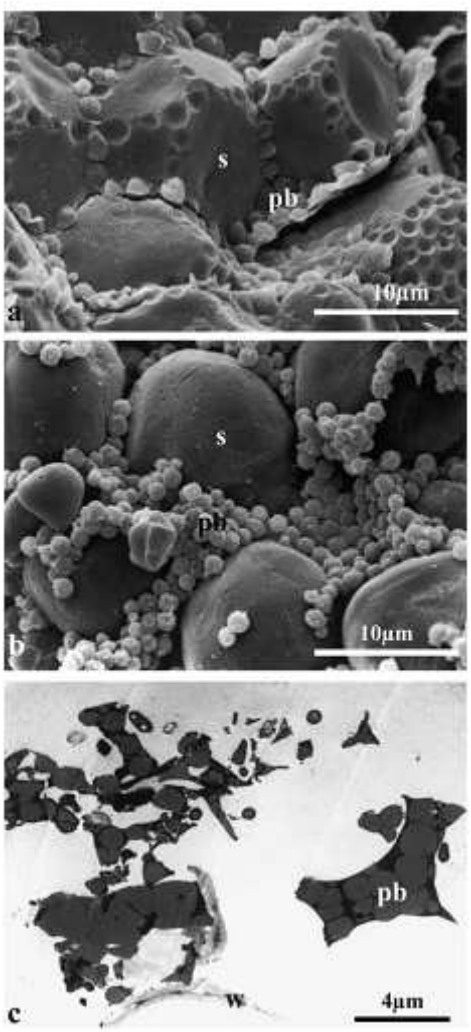

Figure 12

Figure 12: (a) Scanning electron micrograph of the vitreous endosperm of NK 283 sorghum showing tightly-packed starch (s) and protein bodies (pb) embedded in cytoplasmic matrix protein. (b) Scanning electron micrograph of floury endosperm of NK 283 sorghum showing loose packing of starch and protein bodies. (c) Transmission electron micrograph of pb-enriched sample of NK 283 sorghum showing wedges of protein bodies embedded in matrix protein and fragments of cell wall (w). From Duodu et al. (2002) with permission of Elsevier.

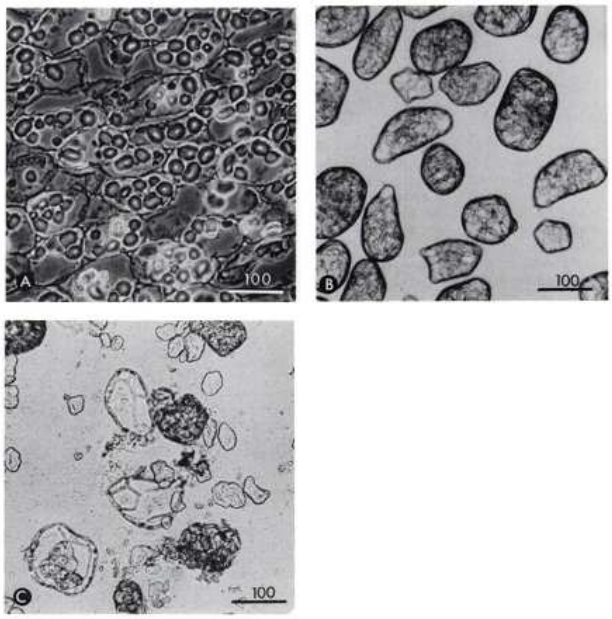

Figure 13

Figure 13: Optical micrographs of white kidney bean submitted to various treatments (scale in μm). (A) Bean soaked in cold water for several hours; starch granules fill the cell (phase contrast). (B) Bean soaked and cooked. The intact cells are filled with gelatinized starch. (C) Bean soaked, cooked, and blended. Gelatinized starch granules are released from broken cells. From Wursch et al. (1986) with permission of the American Society for Nutrition.

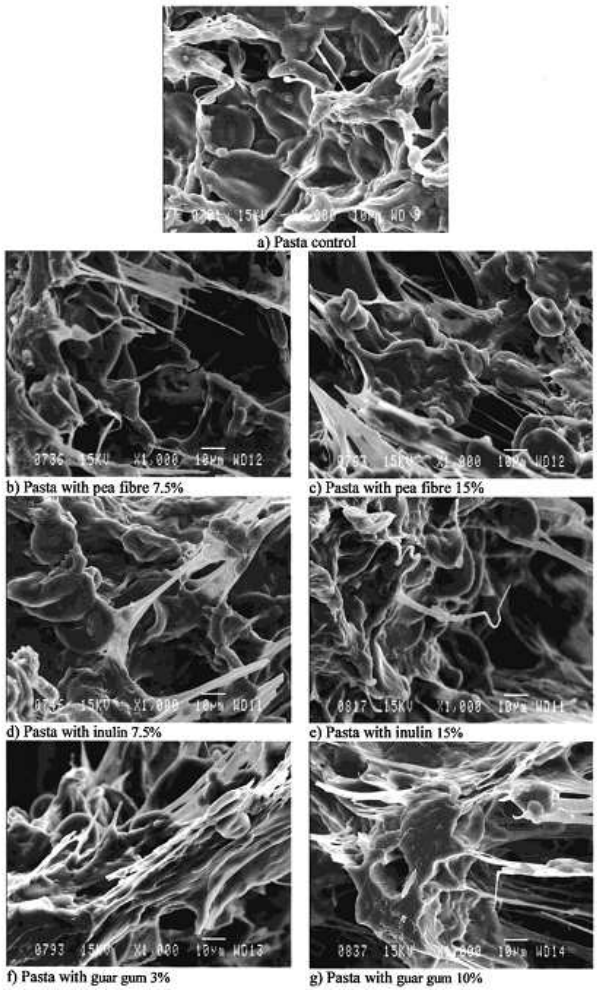

Figure 14

Figure 14: SEM micrographs of cooked pastas: (a) pasta control; (b) pasta with pea 7.5%; (c) pasta with pea fiber 15%; (d) pasta with inulin 7.5%; (e) pasta with inulin 15%; (f) pasta with guar gum 3%; (g) pasta with guar gum 10%. From Tudorica et al. (2002) with permission of the American Chemical Society.

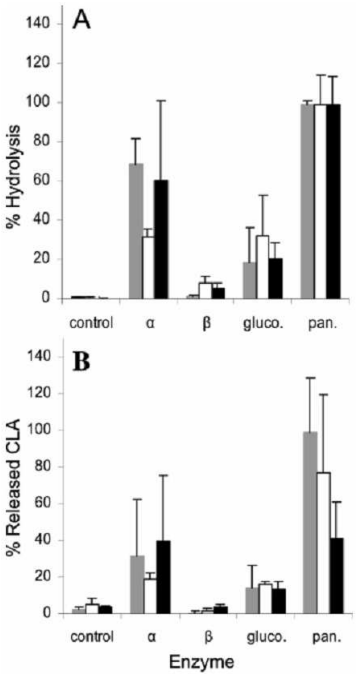

Figure 15

Figure 15: Extent of hydrolysis (%) (A), and Conjugated Linoleic Acid release (%) (B) of amylose-CLA complexes created in water/DMSO solution at 90 °C (gray bars), 60 °C (white bars), and 30 °C (black bars). Hydrolysis was performed by pancreatin (pan), amyloglucosidase (gluco), α-amylase (α), and β-amylase (β) at concentrations of 35 units/mL. The control contained no enzyme. From Lalush et al. (2005) with permission of the American Chemical Society.

Authors	Gastric enzymes	Gastric medium	Intestinal enzymes	Intestinal medium
Borgström and Erlanson 1973			1.67 nM rat pancreatic lipase (8 $mmol.min^{-1}.mg^{-1}$) **or** 1.67 nM porcine pancreatic lipase (11.5 $mmol.min^{-1}.mg^{-1}$) **and** 3.3-13.3 nM porcine co-lipase (40 $mmol.min^{-1}.mg^{-1}$)	0.1-10 mM pure bile salt 150 mM NaCl 1 mM $CaCl_2$ 2 mM Tris-HCl pH 5-10
Gargouri et al. 1983			1.65-5 nM equine pancreatic lipase	1-10 mM pure bile salt 1 mM NaCl 0.5 mM $CaCl_2$ 1 mM Tris-HCl pH 9
Borel et al. 1994 * (Armand et al. 1992)	13.16 or 26.32 g/L human gastic juice (lipase 25.2 U/mg) **or** 1.47 mg/L rabbit gastric lipase (450 U/mg)	150 mM NaCl 6 mM $CaCl_2$ 30 µM BSA pH 4 **or** 5.4	25 (10-160) nM porcine pancreatic lipase (1370 U/mg) 50 (50-800) nM porcine pancreatic co-lipase (1590 U/mg)	8 (6) mM mixed bile salts 150 mM NaCl 0.5 (0.5-20) mM $CaCl_2$ 2 mM Tris-HCl pH 7.5
Wickham et al. 1998			20 nM porcine pancreatic lipase (5600 U/mg) 100 nM porcine pancreatic co-lipase	1-10 mM pure bile salt 150 mM NaCl 5-30 mM $CaCl_2$ 2 mM Tris-HCl pH 7.5
Tsuzuki et al. 2004			0.1 g/L porcine pancreatic lipase 0.16 g/L porcine pancreatic co-lipase	0.1-10 mM pure bile salt 10 mM HEPES 0.025-0.25 mM lysophosphatidylcholine pH 7
Shima et al. 2004		0.4 g/L KCl 0.06 g/L KH_2PO_4 8 g/L NaCl 0.35 g/L $NaHCO_3$ 0.0475 g/L Na_2HPO_4 1 g/L glucose 10^5 units/L penicillinG 0.1 g titer/L streptomycin 5.9578 g/L HEPES pH 1.2	1 g/L porcine pancreatic lipase (46 U/mg)	1 g/L bile powder 0.4 g/L KCl 0.06 g/L KH_2PO_4 8 g/L NaCl 0.35 g/L $NaHCO_3$ 0.0475 g/L Na_2HPO_4 1 g/L glucose 10^5 units/L penicillinG 0.1 g titer/L streptomycin 5.9578 g/L HEPES pH 7.4
Beysseriat et al. 2006		pH 2	2 g/L porcine pancreatin	12 g/L bile extract 100 mM $NaHCO_3$ pH 5.3 then 7.5
Sanz and Luyten 2006, 2007 *	200 g/L human saliva **then** 0.07 g/L porcine pepsin	53 mM NaCl 1 mM $CaCl_2$ 14.8 mM KCl 5.7 mM Na_2CO_3 pH 2.5	64.1 g/L porcine pancreatin 2 mg/L bovine trypsin	18.3 g/L bile extract 6.85 mM NaCl 1 mM KCl 0.15 mM $CaCl_2$ 0.22 mM Na_2CO_3 pH 6.5
Mun et al. 2007 * (Bonnaire et al. 2008)			8 g/L (40 g/L) porcine pancreatic lipase	25 g/L bile extract 5 mM (10 mM) phosphate buffer pH 7
Wright et al. 2008 *			0.1-4.8 g/L porcine pancreatin	1.25-20 g/L bile extract 103 mM NaCl 33.3 mM $NaHCO_3$ pH 6.5
Yin et al. 2008	3.2 g/L pepsin	2 g/L NaCl 3.6 g/L HCl 36% pH 1.5		

Reis et al. 2008 * (Minekus et al. 2005) * TIM	600 U/mL pepsin (2500-3500 U/mg) 40 U/mL *rhizopus oryzae* lipase	4.8 g/L NaCl 2.2 g/L KCl 0.22 g/L $CaCl_2$ 1.5 g/L $NaHCO_3$ (pH from 4.6 to 1.8)	*Duodenal juice:* 17.5 g/L pancreatin 33.3 mg/L trypsin	500 g/L fresh bile (18.75 g/L fresh bile) 1.25 g/L NaCl 0.15 g/L KCl 0.06 g/L $CaCl_2$ pH 6.5 (5.8)
			Jejunal juice: 17.5 g/L pancreatin	500 g/L fresh bile 1.25 g/L NaCl 0.15 g/L KCl 0.06 g/L $CaCl_2$ pH 6.8
			Ileal juice	5 g/L NaCl 0.6 g/L KCl 0.25 g/L $CaCl_2$ pH 7.2
Chung et al. 2008 *			0.486 g/L porcine pancreatic lipase (329 U/mg)	2.8 mM mixed bile salts 208 mM MES 76.4 mM NaCl 10.4 mM $CaCl_2$ pH 6.5
Fernandez-Garcia et al. 2008 *	0.5 g/L pepsin	pH 2	0.929 g/L pancreatic lipase	5.58 g/L bile extract 92.9 mM phosphate buffer 139.4 mM NaCl 3.58 mM $CaCl_2$ pH 7
White et al. 2009 *	36 g/L pepsin (2800 U/mg)	100 mM HCl pH 2	10 g/L porcine pancreatic lipase (100-400 U/mg) 2 g/L porcine pancreatin	40 mM pure bile salt 490 mM $NaHCO_3$ pH 7
Burgar et al. 2009 *	3.2 g/L porcine pepsin (800-2500 U/mg)	8.4 g/L HCl 36% 2 g/L NaCl pH 1.2	100 g/L pancreatin (1x USP)	6.8 g/L K_2HPO_4 15.4 mM NaOH pH 6.8
Versantvoort et al. 2005 * Hur et al. 2009 *	*Saliva:* 0.290 g/L α-amylase (1.5 U/mg)	0.2 g/L urea 0.015 g/L uric acid 0.025 g/L mucin 0.896 g/L KCl 0.2 g/L KSCN 0.888 g/L NaH_2PO_4 0.570 g/L $NaSO_4$ 0.3 g/L NaCl 1.694 g/L $NaHCO_3$ pH 6.8	*Duodenal juice (60%):* 9 g/L pancreatin (1x USP) 1.5 g/L porcine pancreatic lipase (100-400 U/mg)	0.1 g/L urea 1 g/L BSA 7.012 g/L NaCl 3.388 g/L $NaHCO_3$ 0.564 g/L KCl 0.215 g/L HCl 37% 0.2 g/L $CaCl_2.2H_2O$ 0.080 g/L KH_2PO_4 0.050 g/L $MgCl_2$ pH 8.1
	Gastric juice: 2.5 g/L pepsin (800-2500 U/mg)	0.650 g/L glucose 0.020 g/L glucuronic acid 0.085 g/L urea 0.330 g/L glucosamine hydrochloride 1 g/L BSA 3 g/L mucin 2.752 g/L NaCl 0.266 g/L NaH_2PO_4 0.824 g/L KCl 0.4 g/L $CaCl_2.2H_2O$ 0.306 g/L NH_4Cl 7.75 g/L HCl 37% pH 1.3	*Bile juice (30%)*	30 g/L bile extract 0.250 g/L urea 1.8 g/L BSA 5.259 g/L NaCl 5.785 g/L $NaHCO_3$ 0.376 g/L KCl 0.180 g/L HCl 37% 0.222 g/L $CaCl_2.2H_2O$ pH 8.2
			Solution (10%)	Bicarbonate 1 M pH 6.5-7
Macierzanka et al. 2009	50 mg/L porcine pepsin (3300 U/mg)	150 mM NaCl (1 mg/L-2.32 g/L phosphatidylcholine) pH 2.5	2.5 mg/L porcine trypsin (13800 U/mg) 10 mg/L bovine α-chymotrypsin (40 U/mg)	7.4 mM mixed bile salts 150 mM NaCl (1 mg/L-2.32 g/L phosphatidylcholine) pH 6.5

Table 1

Table 1: Main artificial media compositions used for the in vitro digestion of emulsions. To be representative of digestive juices, concentrations are relative to the medium before incubation (not normalized by the lipid content or the specific interfacial area, for example). The enzymatic unit (U) is generally defined as 1 μ equivalent fatty acid titrated per min. The authors followed by * are cited with calculations from quantities (volumes or masses) given in their articles.

Starch	Amylose content	Period of hydrolysis	Native starch hydrolysis degree	Gelatinized starch hydrolysis degree	Retrograded starch hydrolysis degree	Authors
Waxy maize Dent corn Amylomaize 5 Amylomaize 7	0% 20% 50% 70%	4h	75-100% 50-75% 5-25% 10-35%	65-90% 50-70%		Knutson et al. 1982
Waxy maize Potato Wheat Maize Pea Amylomaize 5 Amylomaize 7	0% 20% 25% 26% 33% 53% 70%	1h	2.5% RS 4.4% RS 7.8% RS 7% RS 10.5% RS 17.8% RS 21.3% RS		25.2-43% RS	Sievert and Pomeranz 1989
Manihot Wheat Smooth pea	17% 27% 35%	3h	5% 20% 15%	70% 60% 35%		Bornet et al. 1989
Waxy maize	0%	2h	8% RS	0% RS	48h 20°C 5% RS 24h 6°C + 48h 40°C 18% RS 24h 6°C + 29d 40°C 42% RS	Eerlingen et al. 1994
Waxy maize Wheat Maize Smooth pea Wrinkled pea Potato Amylomaize	?	29h	88% 90% 79% 91% 72% 5% 2%			Planchot et al. 1995
Rice	11% 20% 31%	2h	8.6% RS 9.2% RS 12.9% RS	1% RS 1.6% RS 2.2% RS		Sagum and Arcot 2000
Waxy rice Rice Potato Wheat	1.4% 16.1% 23.2% 27.5%	2h	104.7 μM/min 73.6 7.48 11.03	136.9 μM/min 72.3 129.3 135.6 (61.6 with galactomannan)		Slaughter et al. 2001, 2002
Waxy maize Amylomaize 7 Potato	0% 70% 100%	5 min	16.9% 6.5% 10.9%			Vesterinen et al. 2002
Waxy maize Corn ae du Amylomaize 5 Amylomaize 7 ae su2 Potato Gelatinized potato	?	2h	5% RS 24.4% RS 40.6% RS 66% RS 69.5% RS 69.5% RS 74% RS 0.3% RS			Evans and Thompson 2004
Waxy rice	?	3h	89.9%	90.3% (60°C) 90.9% (65°C) 91.6% (70°C) 96.3% (100°C)	After 100°C gel 96.6% (2 days) 96% (5d) 94.9% (7d)	Chung et al. 2006
Potato	?	1h	50-55%	70-75% (46% gel) 70-80% (73% gel) 75-90% (88% gel) 95-100% (100% gelatinization)		Parada and Aguilera 2009

Wheat: Waxy Commercial High-amylose	 2% 25% 42.8%	2h	 34.1% 22% 16.1%	 60% 60% 62%	 45% 50% 46%	Blazek and Copeland 2010a

Table 2

Table 2: Hydrolysis degree of starches with different amylose contents, in the native, gelatinized (gel) or retrograded states. RS means resistant starch, when no information was available for the hydrolysis degree.