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Microstructural design of aerated food systems by soft-solid materials

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ABSTRACT

The mechanism of adsorbing particles in creating super stable bubbles has been underlined and described but designing particles with these characteristics based of food grade materials is still a challenge. Moreover, food systems are rarely "pure" and the presence of more than one functional ingredients at a given formulation is usually the norm. This highlights the importance of mixed systems where particles and surface active ingredients are present. It has been demonstrated that particles made from food based materials although often not able to stabilised foams on their own, mostly due to limitations in size and hydrophobicity, they can aid significantly in the stability of foams without their ability to adsorb on the interface being a limiting factor. Evidence is presented where particles made from protein (whey) and hydrocolloid (κ-carageenan) sources can significantly extend the life of foams by affecting the rheological properties of these systems in both a macro and micro level. The technology of creating fluid gels poses an advantage in the production of these particles in a scalable manner that can provide solutions for industrial applications that demand liquid and powder formulations. The importance of surfactants (high or low molecular weight) that are either intrinsically present or added in the systems is also being underlined. Finally, a universal mechanism is proposed which allows the design of particulate systems from soft-solid materials that can produce edible liquid foams with enhanced stability.

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Contents

1. Introduction

Numerous food products contain bubbles within their structure which in most cases play an important role either by contributing to the texture of the product or its visual appearance or both. Such attributes play a major role in the way the end-user is experiencing the consumption of such products. Bubbles, therefore define the texture of commercial products that are sold aerated like bread, wafers, ice cream, chocolate mousse, meringues and aerated chocolate. Foam is also an important element of products which is formed at the point of consumption such as cappuccinos, whipped cream, milk shakes and more. Consumer needs being naturally adapted to the modern way of life and the prevailing sense of time scarcity among the consumers as individuals, are strongly driven by convenience (Jabs & Devine, 2006). Frequently, consumption of products takes place at the point of sale and in many cases the same experience is sought at home or *on-the-go*. This is not always easy

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since experienced personnel in combination with sophisticated equipment are often involved in the preparation of these products.

At the same time, an increasing interest in incorporating bubbles in foods as a way to reduce their energy density is emerging. Increasing the amount of air incorporated within edible matrixes has shown a growth in the feeling of fullness (satiation) amongst individuals which led them to reduce their caloric intake without affecting their feeling of hunger (Arboleya, García-Quiroga, Lasa, Oliva, & Luis-Aduriz, 2014). On a further note, if the bubbles present are small enough, they can potentially be undetectable since their oral perception can be reduced much alike particles which when smaller than 25 μm are generally not perceived (Engelen, Van, Schipper, & Bosman, 2005). The design of air filled emulsion via the inclusion of a gas within emulsion droplets, resembling an air in oil in water (a/o/w) double emulsion, is another example of how bubbles can be utilised in order to decrease the fat content of emulsion based foods (Tchuenbou-Magaia, Norton, & Cox, 2009).

Foams are therefore systems with intriguing aspects. They are associated with luxury, primary examples of which are *champagne* and *soufflé* (Campbell & Mougeot, 1999) and they can provide solutions to reduce calorie intake that can aid towards the prevention of obesity which is already advancing into an epidemic (WHO, 2000). Nevertheless, foams are very delicate structures and their thermodynamic instability makes them difficult to create and stabilise for sufficient time.

Their much shorter lifetime compared to other colloidal systems like emulsions (a few minutes compared to months) is a result of a series of elements of their structure (Walstra, 2003). Firstly, the interfacial tension of the air-water interface is a fivefold larger than that of the oil-water (Dickinson, 2010). Moreover, the solubility of gases in water is much higher than that of oil leading to faster transfer of gas from small bubbles to bigger ones led by the difference in Laplace pressure (Kinsella, 1981). The kinetics of disproportionation (or coarsening) in foams are therefore much faster compared to the ones of Oswald ripening in emulsions. Furthermore, foams are prone to drainage, which is the flow of water through the films of the bubbles due to gravity as a result of the large difference in density between air (or any gas) and water (Bergeron & Walstra, 2005). These mechanisms, summarised in Fig. 1, take place simultaneously causing bubbles to coalesce and create larger ones until the foam completely collapses.

A way to contain this is by solidifying the foam before it becomes unstable, as in the case of bread and aerated chocolate, but this is not always desirable. Liquid foams play an integral role in the experience associated with many foods and beverages. Furthermore, foams are structures that can potentially deliver new experiences to consumers from aroma release to visually enhancing traditional products. Consequently, finding ways to understand further how to construct aqueous systems with enhanced foaming properties is of great interest. Moreover, designing formulations that are in powder form and upon reconstitution can exhibit high foamability and high foam stability is of great interest for the *prepare-at-home* and vending industry. So far, formulations used in these applications are not performing to the desired standard making the products inferior to the ones prepared in an artisanal way.

Foams are usually stabilised by amphiphilic substances which have a tendency to reside on the air/water interface and as a result reduce the interfacial, or in this case, surface tension. When the surface tension is reduced, less energy is required for bubbles to exist and their life is significantly extended (Dickinson, 2010). Food foams are commonly stabilised by proteins which are classified as high molecular weight surfactants and are ingredients naturally occurring in foods that are cheap with low toxicity (Wilde, Mackie, Husband, Gunning, & Morris, 2004). Proteins, once adsorbed on an interface, unfold and rearrange their secondary and tertiary structure exposing the hydrophobic regions to the hydrophobic phase (Fang & Dalgleish, 1997). The inherent properties of proteins are dependent on the content and composition of amino acids, the molecular size, the shape, the conformation, net charge and charge distribution, the hydrophobic/hydrophilic character of their surface and inter-protein interactions (Kinsella, 1981). Moreover, their functional properties rely also on extrinsic factors like the pH, the ionic strength and the temperature of the system they are present at and also the interaction with other components present (Zhu & Damodaran, 1994a).

Another way of stabilising foams is by the use of colloidal particles when those have the ability to accumulate at the interface of two immiscible fluids, in a similar manner to surfactants (Binks, 2002). This phenomenon was first studied by Ramsden (1903) and Pickering (1907) who noticed that colloidal particles could adsorb on water interfaces with oil or air and provide similar results to surfactants like saponin, the mechanism, especially when it is applied on solid particles adsorbing on the oil-water interface of emulsion droplets is commonly known as Pickering stabilisation (Dickinson, 2010). Adsorbing particles can have an amphiphilic nature due to the presence of two distinct areas of hydrophobicity, the so-called "Janus" particles (Walther & Müller, 2013).

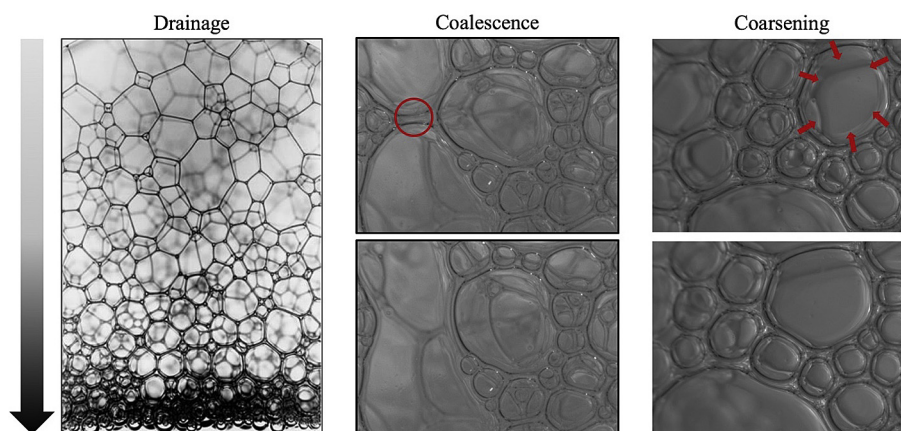**Fig. 1.** The three main mechanisms responsible for destabilisation of foams. The arrow shows the direction of flow of the liquid continues phase and the intensity depicts the concentration gradient of liquid within the foam. The circle shows the point where two bubbles come close to each other and coalesce. The arrows show the direction of gas diffusion from the smaller bubbles to the larger on which increases in size over time.

Nevertheless, amphiphilicity is not necessary for adsorption on interfaces. Homogeneous solid particles can strongly adsorb on the interface (Binks & Horozov, 2005). The key parameter that determines this ability of solid particles to attach to interfaces is their wettability as this is defined by the three-phase contact angle θ. This is the angle formed between the tangents of the solid surface and the liquid-gas (or liquid-liquid) interface as it is measured within one of the liquids in each point of the three-phase contact line at the point where the solid and the two phases meet (Hunter, Pugh, Franks, & Jameson, 2008). When the contact angle of the particles is around 90° then the particles have the tendency to reside on the interface and reduce the surface free energy. The energy of attachment of a particle to the fluid-fluid interface (either a/w or o/w) is related to both the surface tension and the contact angle (Binks & Horozov, 2005). Assuming the particle is small, less than a few μm in diameter (r), the energy (E_{des}) required to remove it from the interface is given by Equation (1).

$$E_{des} = \pi r^2 \gamma_{aw}(1 \pm cos\theta)^2 \qquad (1)$$

Where the ± sign is negative for removal towards the water phase or positive for removal towards the air (or oil) phase. This indicates the importance of the size of the particles, since very small ones (<0.5 nm) similar to the majority of surfactant molecules, can be easily detached and therefore not make very effective stabilisers (Binks, 2002).

Although adsorption of particles on interfaces in pure particle systems is much slower compared to surfactants Binks (2002), they have demonstrated to be able to form close-packed layers at the gas-liquid interface which generates a strong barrier that can retard or even eliminate the destabilisation of foams (Dickinson, 2010). It has also been previously shown that particle-stabilised foams can endure disproportionation (the main source of foam instability explained further on) for days or weeks compared to minutes or hours of the equivalent foams stabilised by LMW or polymers such as proteins (Kostakis, Ettelaie, & Murray, 2006). The condition that defines the stability of a bubble against disproportionation is the Gibbs stability criterion (Equation (2)) according to which, when the interfacial elasticity E is greater than half of the surface tension the pressure inside the bubble decreases during the decrease of the radius of the bubble.

$$E > \frac{\gamma}{2} \qquad (2)$$

This slows down the dissolution of the bubble which eventually stops when the Laplace pressure reaches zero. When this takes place, the bubble distorts and adopts faceted shapes (Rio, Drenckhan, Salonen, & Langevin, 2014). Particles adsorbed on the surface of the bubbles can be very effective in achieving this whilst proteins also increase the elasticity of the interface but usually cannot stop shrinkage completely (Dickinson, 2010). Particles present in foams can provide stability whether they are able to adsorb on the interface or simply remain on the continuous phase. When adsorption takes place, they form rigid films that are stable against drainage and disproportionation which is evident from an increase of the interfacial elasticity and viscosity. When there is adsorption is not taking place, or is limited, the particles either go through a percolation process and create a gel-like network or act as corks reducing the drainage of the continuous phase due to gravity (Rullier, Novales, & Axelos, 2008).

The behaviour of particles in mixed aerated systems in the presence of surfactants depends of parameters such as their hydrophobicity and size. If the particles are reasonably hydrophilic, the foams produced can be further stabilised from the particles present in the aqueous phase within the foam lamella that

accumulate in the Plateau borders significantly slowing down drainage (Binks, 2002). It is well described how the presence of suspended particles affects the viscosity of solutions. Factors such as the shape, size volume fraction and inter particle interactions influences the viscosity suspensions (Mueller, Llewellin, & Mader, 2010). Apart from the presence of particles impacting the rheological properties of the bulk it also affects the viscosity within the Plateau borders in more complicated ways. The mechanism which is proposed to be taking effect in systems like this involves the presence of concentration gradients caused by the fact that particles become trapped in the borders whilst the pure liquid drains causes increase in the localised viscosity within those channels. An illustration of this mechanism is found in Fig. 2. A prerequisite for this mechanism to work is that surface active species are present and their function is to overcome the energy barrier associated with the formation of a new interface and provide the short-term stability of this newly formed air/water interface. On a second step, the particles present will alter the flow properties of the plateau borders and contribute to the long-term stability of the foams. The ways that these particles affect the flow inside the Plateau borders is not yet completely understood. This can be further explored by either quantifying the viscosity inside a Plateau border via a suitable micro-rheology technique or by studying the mobility of the interface at the plateau border level (Clarke, Lazidis, Spyropoulos, & Norton, 2017; Pitois, Louvet, Lorenceau, & Rouyer, 2008).

In the case of hydrophobic particles, they can intrude the a/w interface causing instability and coalescence leading to foam instability via the bridging-dewetting mechanism. Finally, if particles have an intermediate hydrophobicity and they are partially wetted, they can accumulate on the bubble surface providing a strong barrier preventing shrinkage and coalescence (Hunter et al., 2008). In this case, the presence of surfactants is not necessary or can lead to competitive adsorption which can either create instability (Mackie, Gunning, Wilde, & Morris, 1999). The hydrophilicity of particles can be either intrinsic or extrinsic. Increasing the hydrophobicity of particles can be achieved by modifying their surface either chemically or by electrostatics (Gonzenbach et al., 2006). Silica particles for example that have been extensively studied in stabilising emulsions and foams usually have their hydrophobicity modified with a silylating agent which reacts the silanol groups on their surface (Binks & Horozov, 2005).

Although particles have demonstrated an increased potential in producing ultra-stable foams in most cases the material that they

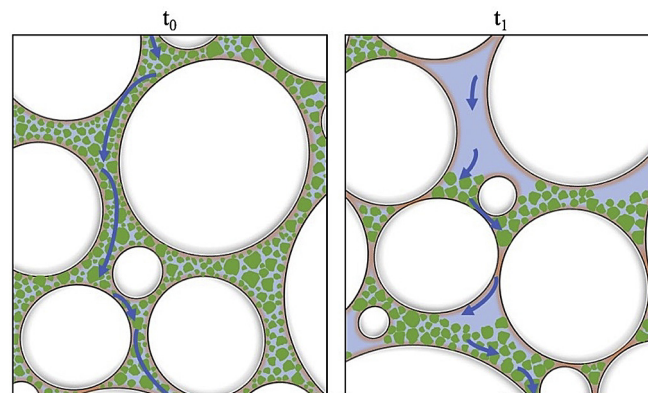**Fig. 2.** Schematic illustration of the universal mechanism proposed, showing how the stability of a foam containing amphiphiles on the bubble interface and particles that do not necessarily adsorb present in the Plateau borders is realised. After the initial fast draining of the continuous phase (t_0) the larger particles remain trapped in the spaces amongst the bubbles impeding the flow and reducing the rate of drainage (t_1).

are made of is not food grade (Dickinson, 2010). In some cases, where food grade materials were used to produce particles that can produce stable foams, the method of manufacturing the particles requires the use of solvents (like ethanol and acetone) via the solvent attrition method. This method was utilised in the case of shellac wax and ethyl cellulose particles (Campbell, Holt, Stoyanov, & Paunov, 2008) and hypromellose phthalate (Wege, Kim, Paunov, Zhong, & Velev, 2008). Moreover the availability of food grade materials that are genuinely hydrophobic is limited as in the case of cellulose which is abundant in nature but in order to be used to create hydrophobic particles needs to be modified as in the case of nanofibrils made from cellulose by electrostatically binding octylamine that have the ability to create very stable foams (Cervin, Johansson, Benjamins, & Wågberg, 2015). However, a few food grade materials have shown potential in producing particles that can effectively stabilise foams such as chitin (Tzoumaki, Karefyllakis, Moschakis, Biliaderis, & Scholten, 2015), modified and non-modified (Zhang et al., 2015) starches, coffee particles (Gould, Garcia-Garcia, & Wolf, 2016; Illy & Navarini, 2011) and cocoa particles (Gould et al., 2016). Nevertheless, since it has been demonstrated that particles can stabilise foams very efficiently and better that surfactants and proteins alone there is interest in exploring further the possibility of designing particles from food grade materials can effectively stabilise foams.

The aim of the current publication is to provide an overview of alternative methods of designing and producing particulate structures from soft food grade materials via suitable processing routes. Soft particles produced from different sources like whey proteins and κ-carrageenan via the fluid gel production method and their ability to control the drainage of foams providing enhanced stability is presented.

2. Types of soft particulates

2.1. Protein based structures

The foaming properties of proteins can be enhanced by altering their structure, this can be directly achieved by changing the environmental conditions such as the pH, the ionic strength and the temperature and has been underlined in several studies. Whilst pH and salt concentration affects the charge of the proteins there is no general model regarding foaming ability and stability that covers all proteins. Some studies indicate that proteins in the lack of charge at the isoelectric point (pI) are more mobile and adsorb faster to the interface (Davis, Foegeding, & Hansen, 2004), form more viscoelastic films due to high packing at the interface (Kinsella, 1981) and that the low solubility at these conditions allows the presence of steric mechanisms prolonging foam stability (Walstra & Roos, 1993). On the contrary, other studies show that whilst proteins at the pI aggregate, this has an adverse effect on foaming properties (Rodriguez Patino, Delgado, & Linares Fernandez, 1995; Rodríguez Niño, Sánchez, Ruíz-Henestrosa, & Patino, 2005). Moreover, Fujioka and Matsumoto (1995) observed an increase of the viscoelastic properties of albumen foam when the pH was higher than the pI. This behaviour was attributed to the competing effects of the interfacial properties of the adsorbed protein layers and the electrostatic repulsion affecting the drainage. Whilst the protein aggregates can either directly partially adsorb on the interface or anchor on other non-aggregated proteins that is already adsorbed there they have an affinity with the interface. Their large size provides the steric barrier which prevents the interfaces from coming too close and coalesce. This in combination with the presence of electrostatic repulsion amongst the charged species when far from the pI intensify the disjoining pressure and increase the stability of the system (Damodaran, 2005).

Heat treatment of proteins on the other hand has generally shown a positive effect on their foaming properties which is mainly attributed to the increase in their surface hydrophobicity due to the exposure of hydrophobic patches in their surface which are otherwise hidden in the internal structure (Damodaran, 2005). It has been shown that whilst controlled heating can improve the foaming properties of proteins, extensive heating has an adverse effect. Zhu and Damodaran (1994b) have indicated that in the case of whey proteins heating does not necessarily increase the surface hydrophobicity but has an impact on the overall hydrophobicity which becomes more important when proteins adsorb on the interface and unfold exposing additional hydrophobic groups. The structural changes in the proteins present in whey do not only affect their hydrophobicity but also promote polymerisation of the species to gel like structures known as aggregates. More specifically, they form in a two-step mechanism where the first step involves the partial unfold of proteins due to denaturation and disruption of their quaternary, tertiary and secondary structure. On a second step, the exposed moieties of the uncoiled polypeptide segments can interact through physical (electrostatic and hydrophobic) or chemical interactions at those specific points and form a three-dimensional network. When cysteine is amongst the protein structure, the exposed sulfhydryl groups can cross link via disulphide bonds (Monahan, German, & Kinsella, 1995; Zayas, 1997). In turn, these changes affect the foaming proteins of the whey solutions and the extent of heating (both in time and temperature) has been shown to be an important parameter (Patel, Kilara, Huffman, Hewitt, & Houlihan, 1990). Whilst moderate heat denaturation seems to improve the foamability and foam stability, extended heating in both temperature or time seems to have an adverse effect due to the complete depletion of the monomeric proteins. This observation has been connected to the ratio of monomeric to polymeric proteins present in the system after the heat treatment. Zhu and Damodaran (1994b) have demonstrated the importance of both monomeric and polymeric proteins on the foaming properties of protein systems. The specifically demonstrated that increasing the ratio of native to denatured WPI up to 40:60 increased the stability of the produced foams. Further increase of the amount of denatured protein had a negative effect on foam stability due to the reduction of the amount of monomeric proteins which due to their high surface activity and smaller relative size can diffuse fast to the interface and adsorb offering the sort term stability necessary for the formation of foams. Foaming ability therefore, has shown to be optimal at lower concentrations of denatured WPI (60:40 native to denatured ratio). The same behaviour was also documented by Bals and Kulozik (2003) who observed that SFT of whey protein solutions decreased with increasing the degree of denaturation up to 34% while further increase caused an increase of the SFT. This indicates that native proteins contribute significantly to the foam generation because they are smaller and more flexible and can diffuse fast and adsorb at the surface during the creation of the foam. However, the denatured polymeric protein species have a significant contribution to the stability of the foams by adsorbing on the surface at a later stage increasing the viscoelasticity of the films.

Foams made from heat treated whey proteins have shown an increase in stability but are still not able to provide long term stability. The main reason is the limited ability of proteins to create barriers around the bubbles that can stop completely the diffusion of gas between the droplets. This can be achieved when gelation can take place on the interface and create a rigid barrier that prevents bubbles from shrinking and therefore limits coarsening. A type of proteins that can provide such stability are hydrophobins which are met in filamentous fungi and have the ability of creating highly viscoelastic layers on the a/w interface and completely

stopping coarsening (Cox, Aldred, & Russell, 2009). A way that common proteins can be optimised to increase the stability of foams is by reducing the drainage of the liquid in foam lamella since drainage can further lead to coalescence and coarsening. This depends strongly on the physical properties of the bulk and in particular its viscosity (Ridout, Mackie, & Wilde, 2004). The need therefore to find ways to control more efficiently the rheological properties of liquids of both in bulk but also within the Plateau borders and finally the ability to create interfaces with high rigidity that will be resistant to bubble shrinkage and rupture is crucial. A way that this can be achieved is the use of whey protein structures obtained through controlled heat induced aggregation. These structures can provide the decrease in drainage necessary that will have a great impact on the overall stability of a foams by making use of the mechanism illustrated in Fig. 2.

The gelling properties of proteins have been utilised in order to create microstructures that can structure water and enhance the rheological properties of solutions. Several of these are based on whey proteins since they can gel easily through heating and are able to produce gels or aggregates that are stable towards further processing that entails heating or shearing. These types of microstructures come under several names like derivatised whey protein (Firebaugh & Daubert, 2005; Hudson & Daubert, 2002; Hudson, Daubert, & Foegeding, 2000; Lazidis et al., 2014), micromanipulated whey (Purwanti, Moerkens, van der Goot, & Boom, 2012), whey protein sheared gels (Walkenström, Windhab, & Hermansson, 1998), microgels (Donato, Schmitt, Bovetto, & Rouvet, 2009; Nicolai, 2016; Schmitt, Bovay, & Rouvet, 2014), fluid gels (Lazidis et al., 2016; Moakes, Sullo, & Norton, 2015a) or aerogels (Chen, Wang, & Schiraldi, 2013; Selmer, Kleemann, Kulozik, Heinrich, & Smirnova, 2015). The manufacturing route of these systems usually involves heat treatment that enables the aggregation or gelation of the whey proteins accompanied by size reduction which can take place either during the gelation or after.

A technology that is able to provide particulate structures that can enhance the stability of foams while allowing production in a continuous manner that has potential in industrial exploitation is fluid gels. These systems can be created by subjecting a gelling biopolymer solution into the turbulent field of a shearing device, such as a common pin stirrer, whilst subjecting the biopolymer to gelling conditions. The choice of conditions that can trigger the gelation depend on the type of biopolymer but also on the desired outcome. Some examples that can be utilised are the addition of salts (eg. addition of Ca salts in alginate solutions), the decrease or increase of temperature and the change in the pH (Bradbeer, Hancocks, Spyropoulos, & Norton, 2015; Fernández Farrés & Norton, 2014; Garrett, 1993; Norton, Jarvis, & Foster, 1999). These parameters can either be altered independently or in combination in order to achieve the desired outcome.

The process of creating fluid gels has been employed in the production of whey protein particles taking advantage of the ability of whey proteins to aggregate and gel when heated. Therefore, by combining the application of heat with a shear field on whey protein solutions, over a critical concentration (10% w/w), the formation of discrete protein particulates was realised. Whey protein fluid gel systems have been created within the turbulent field of a vane geometry of a rheometer which resulted in discrete whey protein particulates (Moakes et al., 2015a). The size of the particulates can be adjusted by increasing the shear rate applied accordingly. A range of shear rate from 200 to 800 s^{-1} achieved a range of particle sizes from 40 to 120 μm. Whey proteins fluid gels also have been utilised to encapsulate oil by creating whey protein gel capsules around the oil droplets (Moakes, Sullo, & Norton, 2015b). This was possible by adding oil (up to 20% vol. fraction) to whey protein solutions (15% wt.) and then subjecting them to

heating and shearing. This approach demonstrates a potential in the addition of liquid oil in formulations targeted for the production of foams while diminishing the antifoaming performance of oils.

The structure of whey proteins, like that of all charged species, is dependent on the pH. The same applies to their gels, so when whey proteins are heated while they are highly charged (far from their *pI*) they form the initial bonding process amongst the entities is restricted to an extent and takes place in linear forms forming clear gels (Clark, Kavanagh, & Ross-Murphy, 2001). When whey proteins are heated while they have the least charge (close to the *pI*) the electrostatic repulsions are weak and the proteins aggregate more easily forming typically opaque gels (Fitzsimons, Mulvihill, & Morris, 2007). The pH affects not only the structure of quiescent whey protein gels but also the structure and therefore the behaviour and functionality of the whey protein fluid gels. Whey protein fluid gels have been created by subjecting 12% wt. whey protein isolate (WPI) solutions at different pH values to a continuous heat and shear treatment within a jacketed pin stirrer (Lazidis et al., 2016). The whey protein fluid gels made at pH 5 consisted of smaller protein aggregates (around 10 μm) than when made at pH 8 which yielded significantly larger aggregates (around 150 μm). This was due to the fact that at pH 5 the lack of charge led to the formation of spherical aggregates already in the solution before heating, after heating under shear the aggregates gelled into compact spherical particles. At pH 8, since the whey proteins tend to form strands upon gelling, heating under shear led to a suspension of particles with larger sizes. Moreover, the fluid gels made at pH 8 were subject to further re-ordering which led to stiffening and transition to quiescent looking gels after one day. This was expected to be taking place due to the larger number of available −SH groups present in protein gel structures made at higher pH values which can further form S-S bridges over time changing the mechanical properties of the whole system (Klemaszewski & Kinsella, 1991). Nevertheless, diluting the fluid gels, post production, to lower protein concentrations prevented the further reaction of the available −SH groups preventing re-ordering. Both fluid gels made at pH 5 and pH 8 resembled concentrated particle suspensions. Heat treating the whey proteins under these conditions led to aggregation of the majority of the proteins to insoluble fractions allowing a fraction of the proteins to resist aggregation either completely or to an extent which in turn permitted the presence of a significant portion of soluble protein material as suggested by subjecting the systems to electrophoresis. This soluble fraction contributed significantly to the surface tension of these systems (Fig. 3). The adsorption kinetics show a gradual adsorption of the protein species to the surface which is typical for proteins. In the case of the protein particulates the rate of adsorption is slower than the native proteins and the surface tension at the equilibrium is higher. The size of the particulates present seems to affect both the rate of adsorption and the final surface tension as shown that the larger particulates made at pH 8 adsorb more slowly to the surface and obtain a higher surface tension compared to the smaller particulates made at pH 5 and the in turn the native WPI. The presence of both denatured insoluble protein and native proteins as mentioned already allows the enhancement of the foaming properties. The soluble proteins, being more mobile, diffuse faster to the interface providing the necessary reduction of the surface tension and allowing the short-term stability of bubbles. Isolation of the protein particles from the soluble proteins by centrifugation and resuspension former in water did not allow the production of bubbles during aeration (results not shown). This underlines the importance of the soluble fraction and their contribution in the formation of air bubbles. This is also demonstrated by the ability of the fluid gel systems to produce foams with similar overrun values
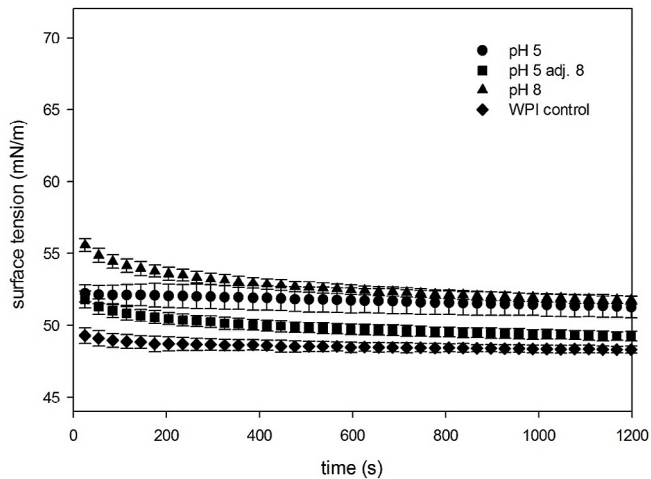
Fig. 3. Evolution of surface tension of whey protein fluid gels over time compared to a WPI control (adapted from Lazidis et al., 2016).

to native whey proteins as shown in Fig. 4. The larger protein particulates remain on the bulk phase amongst the bubbles whilst probably a limited amount anchors to the interface and the other protein species already there. Their presence on bubble films and the plateau borders reduces the drainage of the liquid and therefore increases the stability of the foam as exhibited in Fig. 5. The main factor that appears to play an important role in the stability of the foams is the charge of the protein species which increases the magnitude of the electrostatic repulsions amongst the particulates that in turn increases the viscosity and introduces a yield stress. The fact that at higher pH smaller particles cannot be created at the shear conditions available was a limiting factor. In order to overcome that, fluid gels prepared close to the *pI* (pH 5) were taken to pH 8 after production. This change in pH while had an effect on the charge of the particulates did not affect their size. The change in charge also affected the viscosity and mechanical properties of their suspensions. All this allowed the design of particulates that are relatively small in size and therefore can offer a high packing density and provide suspensions with enhanced mechanical properties both on a macro and micro level and therefore were able
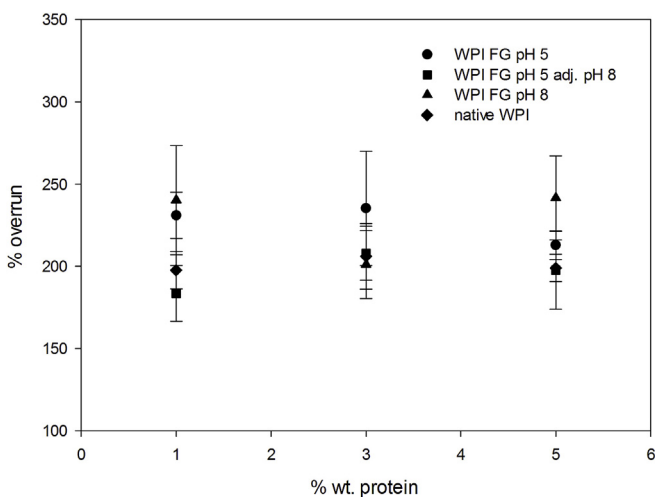

Fig. 4. Foaming ability of whey protein fluid gels made at pH 8 and pH 5 before and after the readjustment of the pH to 8 post production. Native whey protein isolate at the same protein concentrations was used as a control (from Lazidis et al., 2016).

to produce very stable foams.

The performance of the whey protein fluid gels in producing stable foams have verified the mechanism described in Fig. 2 and underlines the effectiveness that particulate structures can have on controlling the drainage in foams and how this in turn affects significantly their overall stability. This stresses the importance of particulate structures made of food materials such as proteins. Other proteins can be utilised in a similar way to create systems that will include polymeric peptides that will act as the particles and monomeric species which will act as the surfactant that will provide the short-term stability necessary. Globular proteins such as egg white, soy and pea proteins also heat denature in a similar manner with whey and by tuning the conditions (concentration, ph and ionic strength) similar systems can be achieved that would show a great potential in stabilising foams. Moreover, other proteins can aggregate via different mechanisms such as enzymatically or by pH reduction of pH such as caseins that can be explored further in creating particles that can have enhanced functional properties. The production of particles is not need to be limited to the method of creating fluid gels via a stirring devise. More disruptive technologies can be utilised to limit the polymerisation of substances within aqueous media into discrete particles that can facilitate the formation of particulate systems. Comparable technologies that can be adopted are sonication and high pressure processes (e.g. high pressure homogenisation and microfluidisation). Furthermore, as demonstrated with the freeze dried protein particles (Lazidis et al., 2014) can be gelled in static conditions and after drying have their size reduced. This can be achieved by using an appropriate technology for drying such as drum drying, vacuum belt drying, spray drying in combination with a milling method to produce small particles such as hammer, plate or ball milling.

2.2. Hydrocolloid based structures

Apart from using proteins to create fluid gels which have the advantage of offering the surface activity needed to produce foams, as described in the previous section, other colloidal species can be used. These in conjunction with surfactants can offer systems that can produce stable foams via the same mechanism described and illustrated earlier (Fig. 2). As it has been extensively demonstrated, fluid gels can be created by other gelling hydrocolloids such as natural polysaccharides. Polysaccharides that gel upon cooling are suitable to create fluid gels like low acid gellan (Bradbeer et al., 2015) and κ-carrageenan (Gabriele, Spyropoulos, & Norton, 2009; Garrec, Guthrie, & Norton, 2013). The particles present in these types of fluid gels are inherently hydrophilic and therefore are not likely to adsorb on the air/water interface or reduce the surface tension of water. This leads to either modifying the material and make it hydrophobic or add a surfactant that can provide the reduction in surface tension necessary for stabilising bubbles. Then while the surfactant aids in the formation of the bubbles and helps in establishing the short-term stability of the bubbles, the discrete polysaccharide particles present in the fluid gels can increase the mechanical properties of the films and most importantly the local viscosity at the Plateau borders and slow down.

Fluid gels prepared from κ-carrageenan where whey protein was added post production have shown potential in creating very stable foams. The concentration of the κ-carrageenan is the most significant factor affecting the viscosity of these fluid gels (Fig. 6) while the concentration of the protein had an effect only on the fluid gel with the highest concentration of polysaccharide. This shows that the influence of the charged proteins is more significant on the viscosity of the system with the harder particles indicating an effect of the charge and the particle density. The added protein
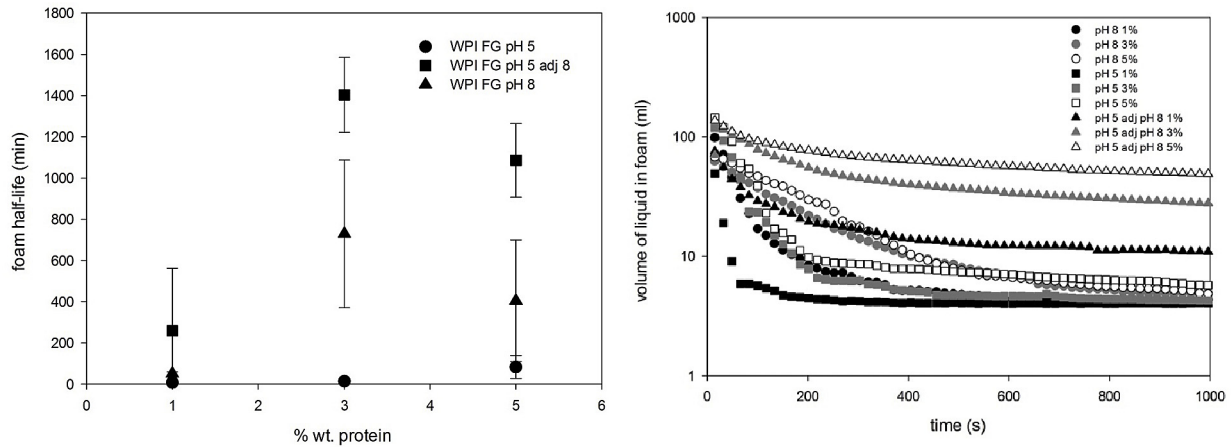
Fig. 5. (a) Foam stability expressed as foam half-life of the different whey fluid gels against the protein concentration. (b) evolution of the amount of liquid present in the foam of the different whey fluid gel systems over time (from Lazidis et al., 2016).
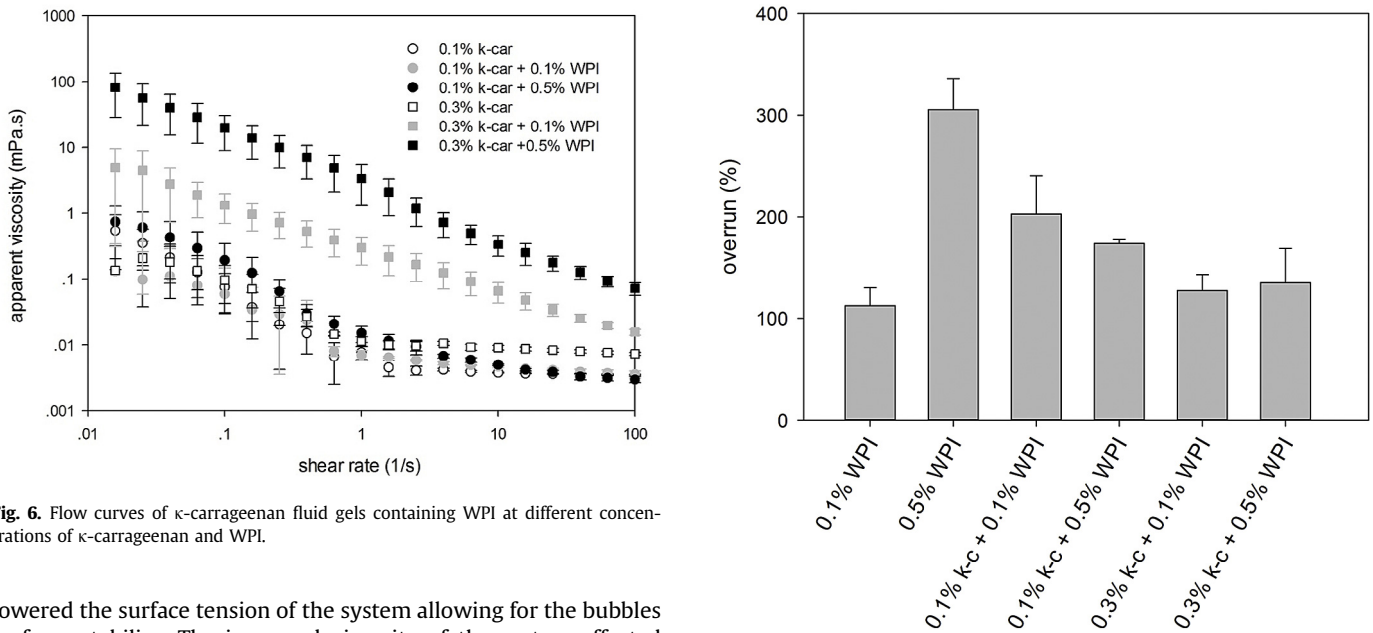

Fig. 6. Flow curves of κ-carrageenan fluid gels containing WPI at different concentrations of κ-carrageenan and WPI.

Fig. 7. Stability of foams stabilised by κ-carrageenan fluid gels containing WPI at different levels compared to foams made of WPI alone.

lowered the surface tension of the system allowing for the bubbles to form stabilise. The increased viscosity of the system affected negatively the foaming ability of the system, especially at the highest κ-carrageenan concentration, which indicates that the increasing viscosity can make foaming harder since by affecting the amount of air that can be incorporated in a system due to the higher energy barrier (Fig. 7). On the other hand, the stability of the foams correlates well with the viscosity of the systems (Fig. 8). This shows that the mechanism of stability relies on the viscosity of the fluid gel but also on the presence of the particles which in the narrow gaps of the bubble surfaces and plateau borders have a greater effect on the flowing properties of the bulk phase. The particles as in the case of the whey protein fluid gels provide this jamming effect illustrated in Fig. 2, which is known for reducing drainage and producing more stable foams (Jarpa-Parra, Tian, Temelli, Zeng, & Chen, 2016).

Other gelling hydrocolloids have the potential to create structures that can produce systems with enhanced foaming properties other alone or in conjunction with surfactants. Surface active hydrocolloids can be used either alone or in combination with non-surface active ones to create fluid gels that can produce very stable foams. Some surface active hydrocolloids that can be used are hydrophobically modified celluloses (hydroxypropyl cellulose and

methylcellulose), propylene glycol alginate, agar, gum arabic, pectin and certain galactomannans (e.g. guar gum, fenugreek gum) (Dickinson, 2003; Ellis, Norton, Mills, & Norton, 2017; Raffa, Wever, Picchioni, & Broekhuis, 2015). Some of them have thickening properties but are not able to form gel structures that is necessary for the formation of fluid gels. In that case, they can be used in combination with gelling ones in mixed systems that depending on presence and type of interactions amongst the species can have very interesting properties.

Fluid gels pose several advantages compared to other pathways of creating particulate structures. They can be produced easily in a continuous manner as it has been already demonstrated. Adjusting the parameters during production such as the type and concentration of the hydrocolloid, the presence and level of salts, the temperature and the rate that is being applied and finally the shear rate allows the tailoring of the system to the desired functionality. A variety of polysaccharide based colloids can be used to create these
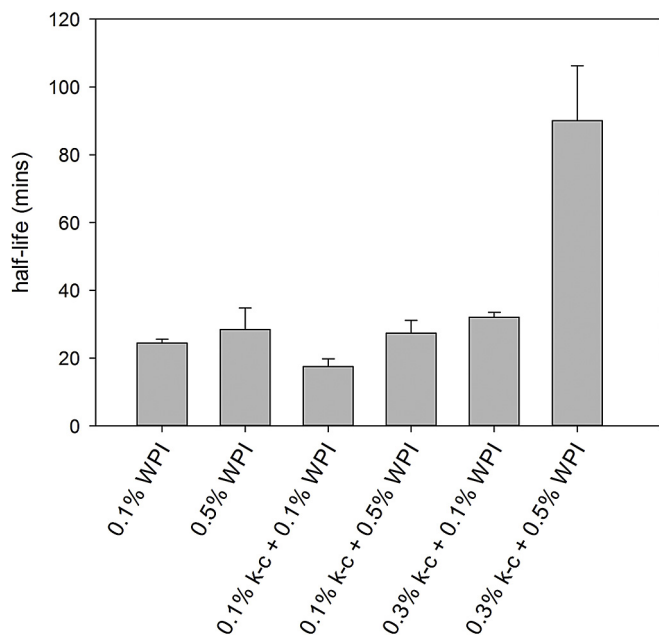
Fig. 8. Foaming ability of κ-carrageenan fluid gels containing WPI at different levels compared to WPI alone.

particle systems alone or in mixed systems. Examples of hydrocolloids that can be utilised are agar, gellan, alginate, xanthan, maltodextrin, gelatine, pectin and more. Moreover, the choice of hydrocolloid (such as whey protein) can allow the production of heat stable fluid gels that can be processed further with high temperature operations such as pasteurisation or even sterilisation. Fluid gel technology allows the production of more concentrated systems than other microgel production methods that work on very dilute systems. Fluid gels can also be further dried via different methods such as spray drying (Lazidis et al., 2016), oven dried, drum dried etc. to powder forms. It is therefore a technology that is versatile and has high potential for industrial exploitation.

3. Conclusions

The mechanism by which particles with the correct hydrophobicity and size have been designed in order to irreversibly adsorb on the a/w interface and produce ultra-stable foams is well described in the literature. Producing this type of particles from food based materials that are recognisable by the consumer is challenging. Ordinary food ingredients such as proteins and hydrocolloids can be used to create particulate structures which may partially adsorb on the a/w interface or not but contribute significantly in enhancing the stability of foams.

When designing particles made from soft-solid edible materials that have potential as foam stability enhancers one needs to take into account the mechanism described here. In these systems, the presence of surface active molecules, either being of protein nature or other low molecular weight surfactants, is necessary to provide the short-term stability of the bubbles during the aeration process. This is accomplished by the ability of these species to adsorb relatively fast to the interface and reduce the surface tension allowing therefore the creation of the bubbles and therefore the foam. On a second step, particles present in the system will affect the viscosity and elasticity, especially when soft materials are used to create them, both in the bulk but also in the Plateau border level. Whilst in the first instances after the creation of the foam the excess of the continuous phase drains fast through the foam a large

number of particles remains in the space between the bubbles and also accumulates in their junction zones (nodes) either due to the affinity of these particles with the interface itself or with what is on the interface already. This accumulation of particles increases their local concentration at the Plateau borders which in turn causes a significant increase in the local micro-rheology. When this is achieved, the drainage is significantly slowed which has a large impact on the overall foam stability as it has been demonstrated in systems stabilised by whey protein and κ-carrageenan particles. An illustration of this mechanism is presented in Fig. 2.

The use of proteins to create the particles allows the retention of surface active monomers to the final fluid gel. These monomers naturally act as surfactants providing the system with the necessary surface tension for bubbles to be produced and no other surfactants are necessary. Moreover, proteins and other charged species provide an additional feature of significance since they tend to offer higher values of elasticity and yield stress both in the bulk and consequently within the foam structure allowing the production of more viscoelastic foams with higher stability.

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