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Murray, BS orcid.org/0000-0002-6493-1547 (2020) Recent developments in food foams. Current Opinion in Colloid & Interface Science, 50. 101394. ISSN 1359-0294

https://doi.org/10.1016/j.cocis.2020.101394

Current Opinion in Colloid & Interface Science

Recent Developments in Food Foams

--Manuscript Draft--

Manuscript Number:	COCIS-D-20-00038R1
Full Title:	Recent Developments in Food Foams
Article Type:	50: Thin Liquid Films and Foams
Short Title:	Food Foams
Keywords:	food; foams; Pickering; particles, biopolymers
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Abstract:	The scientific literature between from 2015 onwards (inclusive) with respect to foams and thin films in the context of foods has been reviewed. Proteins are the dominant foaming agents in foods and investigations of the classic, meringue-forming egg white protein still dominate the literature, since the unique properties of this system are still not properly understood. The current drive of many studies is to find suitable replacers of egg proteins, driven by consumer trends for more plant-based alternatives. This has led to investigations of the stabilizing properties of various protein aggregates, 'nanoparticles' and microgel particles as Pickering-type stabilizers of foams (Pickering foams). At the same time, other work has sought to manipulate the surface properties of biopolymer- and non-biopolymer -based particles by chemical means, in order to make the particles adsorb strongly enough. Few, truly novel foam stabilizers have emerged, but two include saponin aggregates and bacteria as particle-type stabilizers.
Author Comments:	Dear Editor, Thank you for the positive response to our review. I note your minor editorial comment and have inserted any missing page numbers or article numbers in the references where these are available. I also thank the Reviewer for their suggestions, which I have addressed as follows, allowing the opportunity to improve the MS further. Below I repeat Reviewer 1's comments/suggestions, followed by my response, in italics for clarity. It is not really clear where the Introduction ends and the material specific discussion starts. In the Introduction I have focused almost exclusively on the generic problems of stabilizing foams, though I have introduced Pickering foams as a special case. At the end of the Introduction I introduced Table 1, a sort of classification summary of the different types of stabilizer as a lead into the following sections, which discuss most of these in turn. However, to make this more clear, I have changed the last sentence of the Introduction to "The main classes and sub-class of foam stabilizer covered in this review are summarized in Table 1 and these will be discussed in the following sections." The Abstract features abbreviations and parentheses, which impairs the optical and reading pleasure. Later on also some sentences are placed parentheses: In my opinion, the parentheses are not needed. There is only one abbreviation in the Abstract, for egg white protein (EWP), which I subsequently used only once. I think this was introduced this mainly to keep the word count down. Nevertheless, I have removed this. There is one set of parentheses, around "Pickering foams". I think this is justified because the term is not entirely widespread yet, unlike Pickering emulsions. On page 7 there is a valid comment on the often-claimed link between foam stability

and interfacial properties. I think the comment is important and should be extended to interfacial shear rheology as well (right now only interfacial dilatational rheo is mentioned).

We agree entirely and so have extended the 4th sentence already there in paragraph 2 of page 7, so that this now reads “Once adsorbed, most proteins are also able to form a thin, viscoelastic, crossed-linked network that can resist further bubble deformation, up to a point, often more reflected in measurements of the interfacial shear rheological properties.”

For cellulose (page 13) one could also mention some of the recent published reviews on cellulose at interfaces (https://doi.org/10.1021/acs.chemmater.7b00531, https://doi.org/10.1016/j.cocis.2017.04.001, https://doi.org/10.1016/j.cis.2019.102089). These reviews not entirely focus on foams but might help the reader to understand cellulose interfaces better.

There have been a huge number of recent publications relating to cellulose and various colloidal systems so that it is impossible to know which to select unless they specifically relate to foams, the subject of this review. In addition, there is a lot of confusion between interfacial and network stabilization, which we have discussed. In the light of this, the best of Reviewer 1’s recommendations seem to be the 2nd and 3rd (Capron et al., 2017 and Bertsch & Fischer, 2020), which discuss the nature of cellulose surface activity and foams: we have therefore included these two in the revised MS, in the 3rd sentence of the section of cellulose and chitin, which now ends …” or the reason for any apparent natural surface activity of cellulose nanocrystals” with these references inserted.

The first recommendation (De France et al, 2017), relates to aerogels and NOT foams, so we have not included it since the above two cover the required topic adequately.

Page 14: Heading "Combinations of particles and other foaming agents". What do you mean by foaming agents? The foam stabilizing surface-active materials or the gas? In engineering nomenclature the foaming agent would be the gas. Just to avoid confusion.

I was not aware of this engineering nomenclature, so thanks to the Reviewer for bringing this to my attention. I have clarified this by changing the title heading to “"Combinations of particles and other foam stabilizing agents"

Page 16: Section on oleogel. It might be worth to check with two super-recent publications by Mishra et al. on fat foam generation (https://pubs.acs.org/doi/abs/10.1021/acs.cgd.9b01558) and the interfacial aggregation of differently treated triglycerides (https://pubs.acs.org/doi/10.1021/acs.langmuir.0c01195).

Again this is an area that is expanding rapidly, so that it is hard to keep up, so the recommendations of Reviewer 1 are very welcome. The second (Langmuir paper) actually refers to the work in the first (Crystal Growth and Design) paper, so we have included just the second, adding the sentence: “ Some these issues have been nicely discussed in a recent contributions from Mishra et al. [inserted] at the end of the “Oleogels and oleofoams” section.

[Inclusion of these additional reference has obviously activated some reference re-numbering].

Recent Developments in Food Foams

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For submission to Current Opinion in Colloid & Interface Science issue Thin Films & Foams

Abstract

The scientific literature between from 2015 onwards (inclusive) with respect to foams and thin films in the context of foods has been reviewed. Proteins are the dominant foaming agents in foods and investigations of the classic, meringue-forming egg white protein (EWP) still dominate the literature, since the unique properties of this system are still not properly understood. The current drive of many studies is to find suitable replacers of EWP, driven by consumer trends for more plant-based alternatives. This has led to investigations of the stabilizing properties of various protein aggregates, 'nanoparticles' and microgel particles as Pickering-type stabilizers of foams (Pickering foams). At the same time, other work has sought to manipulate the surface properties of biopolymer- and non-biopolymer -based particles by chemical means, in order to make the particles adsorb strongly enough. Few, truly novel foam stabilizers have emerged, but two include saponin aggregates and bacteria as particle-type stabilizers.

Keywords: food; foams; Pickering; particles, biopolymers

Introduction

Foam is an important component of many commonly consumed food and drinks (e.g., whipped creams, mousses, soufflés, ice creams, bread, cakes, carbonated beverages) and research into new types of foam and new foam-forming and foam-stabilizing agents continues to grow. Bubbles in consumer products can impart texture, colour, novelty and excitement for the consumer. Additional advantages are that, for air bubbles the bulk material is notoriously cheap, light to transport and is unlikely to result in allergic reactions (for clean air at least) ! If only things were so simple, however, because gas bubbles are one of the most difficult colloidal substances to produce, stabilize and control in large quantities, due to their tendency for relatively rapid creaming, dissolution and coalescence (relative to oil-water emulsions, for example). Consequently, great efforts have been made to design systems with improved foam properties, not least because bubbles represent a zero-calorie filler that might be used to replace other food components and have a beneficial effect on the long-term health and well-being of consumers. Thus, apart from the general case of filling the aqueous matrix of foods with more air, systems have been developed for trapping air bubbles in sugar crystals [1], fats and oils [2]●. In addition, there seems to be increasing awareness of the significance and potential of using foam as a 'processing aid'. Thus bubbles can be deliberately used to fractionate a wide range of more valuable surface active materials, whilst conversely foam may concentrate undesirable chemical species. In addition, foam structure may aid the drying and functional properties of dry powders. On the other hand, foaming is an undesirable phenomenon in other processes and understanding how to enhance the action on particles and surfactants in breaking the thin films between bubbles is also an important area of work. It is worth elaborating at the outset some of the colloidal difficulties referred to above, in order to understand the general direction of recent alternative strategies and formulations in the publications referred to later.

Firstly, in the majority of food foams the gas phase is air, nitrogen or carbon dioxide and the continuous phase is an aqueous solution, so that the discontinuous phase (gas) has reasonable (at least mM) solubility in the continuous phase. This is unlike most emulsions or solid dispersions and means that disproportionation, the equivalent of Ostwald ripening in emulsions and dispersions, is rapid when bubbles approach colloidal dimensions, i.e., *ca*. 1 μm. Adsorbed layers of even tightly packed low molecular weight surfactants (LMWS), or gel-like films of adsorbed macromolecules, offer little physical barrier to transport of gas molecules across interfaces, so that the only way to halt disproportionation completely is to use solid particles, i.e., Pickering stabilization (Pickering foams) as the stabilizing mechanism [3]. Adsorbed layers of such particles can provide a perfectly elastic barrier with high resistance to compression and desorption of the particles, 'hijacking' shrinkage of bubbles due to the higher internal gas pressure across curved interfaces. (The effect of the Laplace pressure difference across the air-water (A-W) interface is exacerbated by the higher A-W interfacial tension compared to that of the oil-water interface in emulsions). This has lead to the search for suitable solid particles that can fulfil this role. So far, the range of *food-grade* solids seem to be limited, so compromises may need to be made in terms of softer particles and/or loose particle aggregates to achieve adequate stability. At the same time, some degree of chemical modification, to impart the desired wetting characteristics to the particles, might need to be employed, although it should be recognized that there is consumer pressure to resist all such modifications. Physical modification, e.g., heating/cooling, shearing, sonication and complex formation between different ingredients via physical forces, are much more desirable and acceptable.

Secondly, higher gas-water tensions make bubble disruption under shear much more difficult, i.e., high capillary number (= dynamic viscosity x characteristic velocity/ interfacial tension), so that it is generally hard anyway to achieve the same sort of bubble sizes as in homogenization of oil-water systems, particularly if the viscosity of the continuous phase is increased by inclusion of high dissolved solids or thickening agents. Higher bulk viscosity may slow down bubble creaming, drainage and bubble collisions that normally accelerate coalescence, but high viscosity also slows adsorption of the surface active agent to the bubble surfaces. This is particularly relevant for Pickering foams, where the diffusion coefficient of particles and aggregates is already much lower than that of detergent-like molecules or even small globular proteins. Indeed, modelling work [4,5] has shown that it maybe almost impossible to *form* directly high volume fractions of micron-sized Pickering-stabilized air bubbles in any practical system, since such small bubbles will dissolve away before they achieve adequate particle surface coverage. The alternative route is to form larger bubbles initially then allow them to shrink to smaller size, wherein their particle coverage simultaneously increases if the particles already at the interface are irreversibly adsorbed due to their high desorption energy.

The above issues should be born in mind when considering the various new approaches discussed in the following review, some of which have already been discussed in other summaries elsewhere [6]. It is probably also worth stating at the start that two phenomena should be distinguished, since confusion frequently arises in the literature: foamability versus foam stability. Foamability is the capacity for foam formation: systems that have high foamability form large volumes of foam relative to the starting non-foamed liquid, i.e., high overrun. This does not necessarily mean that these foams will be stable for very long. Foam stability is the capacity of a foam, once formed, to persist. Throughout the following, unless explicitly stated, for brevity we will using the word ‘foaming’ to imply both foamability and foam stability. Bureiko et al. [7] have considered these issues in comparing the foaming of low molecular *versus* polymeric surfactants, like proteins, plus the competition between them in mixtures. The main classes and sub-class of foam stabilizer covered in this review are summarized in Table 1.

Table 1. ‘Index’ of the main classes and sub-classes of foam stabilizer discussed in this review.

Main class of stabilizer	**Sub-class and corresponding reference numbers**
egg white protein (EWP)	reviews 6, 75● general 10, 12, 13, 45, 46, 57, 63● + sugars & polysaccharides 14, 15, 16, 19 + wheat gluten hydrolysates 20, 21
other proteins	sodium caseinate 64● whey protein isolate 17, 102● pea, soy & lentil 18, 47, 48, 49, 59, 62

	wheat gluten & gliadins 20, 21, 22, 36 algal 58; mung bean 60; coconut 53; Quorn® mycoprotein 61 hydrophobin 34●
protein aggregates	β-lactoglobulin 24, 25, 38 lentil 59, 62 soy 49, 94
particles (Pickering)	reviews 28, 29, 30, 33 gluten hydrolysates 20, 21, 22; gliadins 36, 40● zein 39, 40●; hydrophobin 34● chitin 68●; cellulose 69, 70; starch granules 65 saponins 71-75 microgels 31, 32●, 82, $CaCO_3$ 83, 84● 'bacteria' 78-79, 81
protein hydrolysates	β-lactoglobulin 51, 56 oat 54● coconut 53, 60 pea 103 EWP 57
covalently cross-linked	α-lactalbumin 52 ovalbumin 13 Na caseinate, OSA-starch & tannic acid 64●
ultrasound-treated proteins	EWP 45, 46 faba bean 47
homogenized proteins	milk 42 pea protein 44
physical complexes & coacervates	whey protein + κ-carageenan 66 whey protein+ alginate 67 lentil protein + guar gum 62 pea protein + OSA-starch 63●
OSA-starch	63●, 64●, 79
fatty alcohols (oleogels/foams)	2●, 97, 98●, 99

Protein-stabilized systems

Egg white protein

Proteins, on their own or combined with other ingredients (see later), still comprise the most widespread foaming agents. It is remarkable that, the proteinaceous culinary foaming agent *par excellence* – egg white, is still the subject of intense investigation. This is connected with our incomplete understanding of the unique stabilizing properties of egg white protein (EWP) and its widespread traditional use in many foamed products, e.g., meringues, mousses, baked goods. At the same time there is strong drive to find plant-based alternatives to this 'animal-based' proteinaceous foaming agent, for reasons of environmental sustainability and the relative high proportion of individuals who are allergic to EWP.

The special characteristics of egg albumen stem from the fact that it consists of a mixture of proteins each of which themselves has some less common characteristics: (i) lysozyme, that has a relatively high positive charge at neutral pH, so that it can form electrostatic complexes (aggregates) with the majority of the other (negatively charged) EWP; (ii) ovomucin, a fibrous gelling agent that cannot be denatured up to at least 100 °C that imparts viscoelasticity to the albumen itself; (iii) ovalbumin, the major EWP, a glycoprotein that seems to have a tendency to spontaneous aggregate on adsorption the A-W interface [8],[9]. Daugelaite et al. [10]● have used new, high resolution electrical resistivity measurements as a function of height to investigate free drainage of EWP foams and concluded that the presence of protein aggregates in the Plateau borders has a significant beneficial effect in reducing foam drainage and increasing foam life-times. On the other hand, this tendency for aggregation in the bulk can reduce foamability.

These special features of EWP have lead to a number of treatments to further improve EWP foaming properties, reviewed recently by Gharbi and Labbafi [11]●. A novel treatment is wet ball milling [12], although this seemed to reduce foamability and foam stability due to increased disulfide- and surface hydrophobic-induced aggregation. Similar deliberately induced cross-linking prior to foaming was investigated by Li et al. [13], using hydroxyl radical-induced oxidation of ovalbumin. Moderate oxidation improved the foaming but excessive oxidation reduced it.

In many real products, thickening agents are often added to EWP to try and control the rate of film drainage, particularly when the viscosity of the aqueous phase is already high due the presence of high concentrations of dissolved solids – typically sugars in confectionery products. The higher initial viscosity slows down the incorporation of air to high overrun and inhibits the formation of small enough bubbles. Thickeners, typically polysaccharides, help reduce bubble creaming and drainage whilst the bubble size distribution is reduced to lower sizes by mechanical whipping. They also reduce drainage of the foam product on longer storage times after whipping has ceased, via high values of the low shear rate limiting viscosity or weak gel formation. Understandably, finding the optimum balance of the formulation and processing parameters to give the final desired bubble size distribution, texture, appearance, etc., is not simple and many workers have tried to explain the interaction of all these factors via multi-dimensional response surface studies [14-18]. Ptaszek et al. [19] have shown that a log-normal distribution provides the best description of the bubble size distribution in EWP foamed with pectin and xanthan, confirming the same turbulent eddy-induced Komolgorov mechanism of colloid breakup.

As mentioned above, there is increased interest in substituting EWP with plant-based alternatives. Wouters et al. [20] have shown some improvement in EWP foaming properties by partial substitution with enzymatically hydrolyzed wheat gluten. Gluten hydrolysates had much higher foamability than EWP, whilst EWP showed much higher foam stability than the hydrolysates, but mixtures gave both good foamability and foam stability, suggesting both materials were compatible at the interface. Further measurements of the surface pressure, surface dilatational elasticity (ε) and dilatational viscosity (κ) suggested that the lower molecular weight hydrolysates might dominate the interface with the EWP forming a secondary adsorbed protein layer. Wouters et al. [21] also showed that enzymatically hydrolyzed wheat gluten gives meringues with higher overrun than EWP in a standard recipe (i.e., including sugar) with no notable disadvantages in texture or appearance. More limited gluten hydrolysis seemed to be an advantage due to the formation of more hydrophobic peptides that exhibit higher ε [22].

In many of the studies referred to above and in those that follow, researchers seek to find a link between the interfacial properties of the adsorbed film and bubble stability. The link is not always easy to make. Certainly a high value of ε will help prevent bubble coalescence in the early stages of bubble formation, via the Gibbs- Marangoni mechanism, and many proteins are superior to LMWS in this respect, though the effect is lessened as the kinetics of adsorption increase. Once adsorbed, most proteins are also able to form a thin, viscoelastic, crossed-linked network that can resist further bubble deformation, up to a point. This can aid resistance to spontaneous coalesce but can lead to film fracture under the large deformations imposed by subsequent processing. Discussion of these aspects is not new [9] and beyond the scope of this review, but the recent study of Mezdour et al. [23]● is worthy of mention in this respect. Here the foaming of protein and LMWS solutions were compared under conditions where the equilibrium surface tensions and bulk viscosity were kept constant. Thus the main variables were thought to be the interfacial viscoelasticity and dynamics of surfactant adsorption/desorption. The main conclusion was that higher dynamic dilatational viscoelasticity and more rapid diffusion kinetics resulted in foams with smaller, more stable bubbles. These effects, plus the effect of shear rate in an industrial type mechanical aerators were used to develop a model to predict bubble size.

Protein aggregates

The tendency for EWP to form aggregates, referred to above, may be one explanation of it's excellent foam stabilizing properties, the aggregates providing a thicker and more mechanically resistant film that better resists thin film disruption and provides enhanced steric stabilization. This is providing the aggregates are still surface active and their larger size does not slow down too much their coverage of the A-W interface. In this respect, one might consider EWP as naturally providing something closer to Pickering-type stabilization, although the stabilizing particles are much more complex than traditional Pickering stabilizers. Dombrowski et al. [24,25] have studied the foaming properties of soluble heat-induced aggregates of pure β-lactoglobulin up to sizes of 1 μm. In general, foam stability increased with aggregate size, due to increased protein surface hydrophobicity, and correlated with maxima in the ε and κ. Hu et al. [26] reported similar findings with β-lactoglobulin aggregates of different size and shape - more fibrillar aggregates gave the highest values of

ε and foam stability. The effects of steam pressure and nozzle design on barista-style milk foams as noted by Jimenez-Junca et al. [27] are undoubtedly related to the different extents of milk protein aggregation induced.

Protein-based nanoparticles and microgels

Another way of improving the foaming properties of EWP is to convert the protein into protein microgels [28-30] For example, Li et al. [31] created submicron (360 nm) EWP microgel (EWPM) particles by homogenization of a thermally cross-linked EWP bulk gel and showed that the EWPM-stabilized aqueous foams via a Pickering-type mechanism. Foamability was less good than EWP-stabilized foams but the EWPM stabilized foams exhibited higher stability to disproportionation and coalescence, in agreement with higher interfacial shear viscosity (η_i) of adsorbed films of EWPM, that were less brittle and liable to fracture. Further work [32]● showed that combinations of EWP and EWPM could achieve the same foamability as EWP alone, whilst still improving stability to bubble shrinkage and coalescence. At the same time, the higher the ratio of EWPM to EWP in the mixtures, the more stable were the foams to freeze-thaw, oven-heating and even microwave heating. The improvement with the mixtures is similar to that obtained with mixtures of gluten hydrolysate and EWP referred to above [20], although here the EWP was not present as microgels but natural aggregates. One might ask what is the difference between a large fractal-type aggregate formed by bottom-up self-assembly of protein molecules and a microgel particle? However, a particle formed by top-down fragmentation of a bulk gel might be expected to retain *internally* the percolating network structure of its parent gel, whilst fractal aggregates do not necessarily have a percolating structure or hold large quantities of solvent. In this review we have reserved the term microgel for those particles that are specifically referred to as such by the authors. The deliberate formation of biopolymer-based particles and aggregates, including microgels, as stabilizing agents of foams (and emulsions) has been reviewed by Dickinson [30]. Microgels in particular have also been reviewed by Murray [29].

The use of protein microgel particles as foam stabilizers exploits the natural superiority of Pickering stabilization, whilst microgels may have other advantages (and disadvantages) compared to traditional solid Pickering stabilizers [28-30,33]. At the same time, other workers have sought to create or exploit other novel protein-based particles as stabilizers that may be considered insoluble in water, or have re-appraised existing proteins as particulate stabilizers. The latter include casein micelles, that may form structures in thin films that significantly curtail drainage [33] and hydrophobin, which is able to form extremely stable small bubbles that can also block drainage of water through the Plateau borders [34]●. The only barrier to use of hydrophobins in foods might be whether or not it represents as significant allergenic potential [35]. Peng et al. [36] created gliadin nanoparticles (diameter ≈ 100 – 200 nm) and showed that foaming decreased as the particles became more charged, due to slower adsorption and weaker dynamic dilatational moduli at the A-W interface, whilst effects of varying particle size were negligible. This highlights again the importance of obtaining adequate bubble coverage fast enough with particles

In terms of the minimum bubble surface coverage required for Pickering stabilization, it is well known that particles with a higher aspect ratio than spheres are far more effective. Self-assembly of protein fibrils produced by heating dilute solutions of proteins at low pH have been investigated by various workers and reviewed recently by Mohammadian and

Madadlou [37]●. Thus Peng et al. [38] have investigated β-lactoglobulin fibrils and found that film strength and bubble stability is a maximum close the pI, where the absorbed films have highest dilatational moduli but at the expense of foamability. Raising the pH slightly above the pI and re-introducing some charge to the fibrils improved foamability whist maintaining good foam stability.

One protein that naturally forms very water-insoluble particles (diameter ≈ 100 nm) is the maize storage protein zein and various workers have investigated zein as a natural Pickering stabilizer. Zou et al. [39] found that foams stabilized by zein alone broke down completely in less than 24 h, but if the anionic surfactant sodium dodecyl sulfate (SDS) was added the zein formed fractal clusters of much larger size that give much improved foam stability. Excess SDS reduced stability as adsorption became totally dominated by the LMWS, illustrating another generic difficulty with particle stabilizers. Wouters et al. [40]● also studied zein nanoparticles (size *ca.* 100 to 150 nm) and also when mixed with wheat gliadin nanoparticles (size *ca.* 130 to 140 nm), both produced via antisolvent precipitation. In agreement with Zou et al. [39], zein on its own showed very poor foaming, whilst the gliadin on its own was excellent and exhibited much higher surface dilatational moduli. Mixtures were generally worse than the equivalent gliadin concentration alone. This points to the fact that highly hydrophobic and insoluble particles, like the zein, may adsorb strongly, but if there are no cohesive forces between the particles, then the film has little resistance to expansion, as noted earlier for hydrophobins [41].

Modified proteins (physical and chemical)

Physical modification

In this section we will discuss work that has been done to deliberately modify the foaming properties of proteins by physical and chemical means. We have tried to separate out studies of mixtures of proteins with other non-proteinaceous materials, discussed in the following section, although non-covalent complex formation between proteins and other ingredients can still be thought of as a physical modification. We note again that only physical modification is likely to be accepted by regulatory bodies and consumers and also that, much of the work on modified proteins involves plant proteins, in the search for replacements for animal-derived proteins.

Tran et al. [42] have summarized the effects of high-pressure-jet processing on milk proteins in relation to their foaming properties. Apparently this can dissociate casein micelles and denature whey proteins, affecting the bulk viscosity and increasing, in particular, the foamability of whole milk. There is debate about how far the hydrodynamic forces exerted on proteins during their passage through high pressure homogenization can irreversibly affect their conformation [43]●● and therefore how this might affect their ensuing emulsification or foaming properties. It seems obvious that the larger the starting protein aggregates, the more likely it is that such aggregates will be disrupted. Djemaoune et al. [44] have shown that microfluidization only seems to affect the surface activity of pea albumin aggregates when the pH is such that the proteins are in a more compact form. It should always be remembered that the effect of high shear forces on emulsions can sometimes be related to minute contamination with the free-radical inducing transition metal elements in stainless steel.

Ultrasound treatment can also be used to effect physical modifications to proteins, although this can also induce chemical changes due free radical initiation at high power (i.e., sonochemistry). In this respect, there is a similarity with the effects of very high shear (see above), in that both physical and chemical changes might be induced. Sheng et al. [45] and Chen et al. [46] showed significant improvement in EWP foaming properties on sonication, ascribed to formation of aggregates via increased free sulfhydryl content and surface hydrophobicity. Martinez-Velasco et al. [47] used high-intensity ultrasound to increase the solubility and surface activity of faba bean protein isolate which led to improved foam stability but decreased protein digestibility.

Shao, Y. Y., et al. [48] and Wang et al. [49] showed that high quality foaming properties can be obtained by the action of much more simple physical processing, namely heating, of soy protein isolate solutions, again due to opening up of the proteins and exposing more hydrophobic groups. Ossa et al. [50] have shown that pH and temperature treatment are critical in determining the foaming properties of tofu-whey concentrates, an important 'waste' stream of tofu processing. Acidic pH values gave the best foamability and stability, ascribed to the adsorption of more aggregated protein as well as higher concentrations of soluble bean polysaccharides in the aqueous phase.

Chemical modification

Corzo-Martinez et al. [51] studied the effect of limited hydrolysis followed by glycation with galactose (via dry Maillard conjugation), and vice versa, on interfacial and foaming (foamability and foam stability) properties of β-lactoglobulin at pH 7 and pH 5. In particular, the system obtained after glycation followed by limited hydrolysis gave foams with exceptional stability, which might be related to the increase in elastic character and cohesion of the interfacial film, indicated by the increase of the surface dilatational modulus ε. Hardly any effect on foaming capacity was observed with the two treatments: hydrolysis followed by glycation, or *vice versa*.

Enzymes, although natural agents themselves, can be used to introduce new covalent cross-links between proteins and create new types of 'unnatural' aggregates. So, although these new aggregates may have improved foaming properties there are doubts about how easily their acceptance might be obtained for use in foods. Thus Dhayal et al. [52] have used transglutaminase or horseradish peroxidase (HRP) to cross-link α-lactalbumin to produce particles with hydrodynamic radii = 20 to 100 nm that gave improved foam stability cf. monomeric α-lactalbumin. However, the stability depended upon which enzyme was used, indicating that the location of the cross-links, i.e., the internal structure of the particles was also important (as might be expected) in terms of surface hydrophobicity, surface area. Kunarayakul et al. [53] have used a glutaminase enzyme to deamidate and improve the foaming properties of coconut protein.

The opposite approach, i.e., cleaving proteins into smaller fragment via enzymes, also continues to be extensively investigated. This has proved particularly useful for plant proteins, which tend to be relatively aggregated and water-insoluble, as demonstrated by Martinez and Pilosof [47] for sunflower protein. As a general rule any enzyme treatment of plant proteins that results in an improvement in aqueous solubility improves foaming properties, but as Bruckner-

Guhmann et al. [54]● showed with oat protein enzymatic hydrolysates, the efficacy depends on the type of enzyme via the different the cleavage patterns and subsequent effects on the (mixed) peptide solubility versus pH. One might also expect that with more extensive hydrolysis the smaller peptides become less effective as steric stabilizers, but this may be mitigated by low molecular weight peptide self-assembly. Li, T., et al. [55] have shown synthetically modified dipeptides to be very effective foam stabilizers, either via the peptides self-assembling (via metal ions) into fibre-like networks at the A-W interface or in the continuous phase to form a gel.

Commercial food grade proteins may contain a range of species with different susceptibilities to the same enzyme conditions compared to native proteins. For example, Pein et al. [56] showed that limited hydrolysis of β-lactoglobulin (fractionated from a whey protein isolate) with pepsin or alcalase, increased both foamability and/or foam stability. It was suggested this was due a combination of non-hydrolysed, native β-lactoglobulin plus more surface active peptides derived from denatured β-lactoglobulin. The denatured β-lactoglobulin was presumably a result of the drying of the whey protein isolate, which made it more accessible to the protease enzymes.

The use of food enzymes to modify food proteins still presents regulatory challenges but recently Jiang et al. [57] have applied natural lactic acid fermentation to EWP and showed a modest but significant foamability, presumably due to the opening up of the proteins and exposing more hydrophobic groups. Such ‘traditional’ enzymatic treatments may be more acceptable.

Other Novel Plant Proteins

Plant-based, non-modified proteins that have received relatively little attention to date include algal proteins [58]. Suitably extracted protein was reportedly superior to a whey protein isolate. In addition to the large amount of work done on soy protein [48,49], other legumes and pulses have been investigated, e.g., lentil protein aggregates [59] and mung bean proteins [60]. Lonchamp et al. [61] have investigated the properties of a currently unexploited bi-product from the Quorn® fermentation process. One fraction, isolated via ultrafiltration, displayed good foamability and foam stability, although the fraction contained a wide range of metabolites and cell fragments, so that is difficult to be sure which were the key components. It is noted that, like most plant proteins, considerable physical processing is required to improve the solubility and functionality of such proteins, whilst further enzymatic and/or chemical modification might improve this further, if permissible.

Complexes

Another way to improve the foaming properties of proteins is to combine them with other ingredients that may improve the protein solubility or moderate it’s surface hydrophobicity – although the two things are obviously connected. If surface hydrophobicity is too high, proteins will self-aggregate in the aqueous phase rather than adsorb; if surface hydrophobicity is too low then there is little driving force for adsorption. Of course the concept of surface hydrophobicity is of little use if the proteins change their conformation significantly during adsorption, as most do. Complexes between different proteins or proteins or polysaccharides can arise from electrostatic attraction and hydrogen bonding, whereas hydrophobic bonding may also operate between different proteins or proteins and lipids and surfactants. One can distinguish soluble complexes of dimensions similar to the constituent molecules and much larger coacervates, the latter appearing as colloidal particles in their own right. Here we also ignore any effects of proteins and polysaccharides where the polysaccharide merely acts as an independent thickening agent or induces depletion flocculation of the protein.

Jarpa-Parra et al. [62] demonstrated coacervate formation at mildly acidic pH between lentil proteins and guar gum, xanthan gum and pectin that gave much enhanced foam stability, due to an electrostatically cross-linked gel-like interfacial network. The aggregates also plugged the junctions of the Plateau borders in the same way as noted above with EWP aggregates [10] and with casein micelles [34]. Significantly, the proteins and polysaccharides phase separated segregatively at neutral pH and this led to a loss of foam stability.

Even more complicated foaming mixtures involve proteins and synthetically modified polysaccharides, such as starches modified with octenyl succinic anhydride (OSA-starches) [63,64], the latter also being surface active. Asghari et al. [63]● suggest waxy maize OSA-starch adsorption can exclude pea protein from the interface when the latter is still sufficiently aggregated to prevent enough hydrophobic protein residues accessing the interface. Zhan et al. [64]● studied an even more complex system of an OSA-starch, tannic acid and sodium caseinate, the latter being more surface active than pea protein or EWP. Tannic acid cross-links the caseinate films and makes them more rigid. Measurements of ε over a range of strains suggested that the OSA-starch increased the degree of strain softening on interfacial extension via more isolated adsorbed OSA-starch domains in between protein/tannic acid domains. With EWP, Asghari et al. [63]● suggested OSA co-adsorbs but de-mixing in the interface forces the EWP to form more closely packed regions that increases stability. These workers also compared the effect of the OSA-starches with dry heated (non-OSA treated) rice starch granules. Such dry-heating seems to make the granule surface more hydrophobic in some way [65], though it is not clear if this makes them sufficiently surface active to compete with protein adsorption. The dry-heated granules slowed down the drainage of EWP foams via some mechanism but they were not as effective as the OSA starches.

Wang et al. [66] showed that heating WPI with λ-carageenan in solution under neutral or near neutral pH can induce the formation of soluble complexes with improved functional properties compared to heating WPI then adding the carageenan afterwards. The explanation proposed was that heating the two components together resulted in enhanced electrostatic interactions between them, due to their more open molecular configurations. Xu et al. [67] have investigated similar complexes between WPI and sodium alginate. Foam stability was particularly improved (at low overall protein concentrations) at pH values where surface active soluble electrostatic complexes were formed between the oppositely net charged components at a relatively narrow (2:1 to 1:1) range of weight ratios of WPI to alginate.

All the above studies highlight the complexity of the different effects on foaming properties when there are different adsorbing and non-adsorbing macromolecules and/or particles present, although this is always likely to be the case in real food systems.

Novel, non-protein based systems

Two types of novel non-protein based foaming agents have been mainly investigated: polysaccharides that are modified to make them surface active and non-protein based particle (Pickering) stabilizers. Of the former, OSA-starch has already been mentioned above, though this has largely been used in admixture with other foaming agents, whilst with regard to the latter, polysaccharides are also relevant, in terms of water-insoluble cellulose and chitin particles.

Cellulose & chitin

Tzoumaki et al. [68]● have investigated the foaming of chitin nanocrystals. As with many Pickering foams, the importance of structuring of particles both at the interface and within the thin films between bubbles (affectively forming thin layers of a 'bulk' particle gel) was also considered. Even more work has been done on cellulose as a Pickering foam stabilizer, though debate continues how the cellulose can be made hydrophobic enough to adsorb efficiently enough at the A-W interface. Beatrice et al. [69] required free radical-oxidized nanocellulose in combination with various water-soluble (polysaccharide) thickening agents to produce adequate foaming properties. Another important observation was that, the effect of shear in these systems caused the cellulose nanofibres to flocculate and accumulate at bubble surfaces, though this depended on the attractive interaction between the cellulose and the polysaccharide thickening agents. Such aggregates can potentially act as *defoaming* agents, plus the more aggregated the particles become, the lower the surface area they can cover and so the coarser will be the foam produced. Ahmadzadeh et al. [70] combined chemically modified clay particles to improve the foaming properties of cellulose-based Pickering foams, for foam packing with enhanced physical properties.

Saponins

A relatively new set of Pickering particles that has emerged is based on the natural class of surface active molecules named saponins. Saponins have long been known to be highly surface active and excellent foaming agents in their own right, but Wan et al. [71] have shown that nanofibrils of glycyrrhizic acid can form networks at the A-W and O-W interfaces of oil droplets and bubbles as the system is emulsified and aerated simultaneously, i.e., an emulsion foam, much like whipped dairy cream. The jamming of the emulsion droplets in thin liquid films also enhances foam stability. On cooling the nanofibrils form a three-dimensional net (gel) that prevents coalescence of the droplets and bubbles within. The foam system could be destroyed rapidly on heating because of the melting of the bulk gel. In later work Ma et al. [72] showed that nanofibrils of glycyrrhizic acid alone can form multilayer networks at the A-W interface and also in the bulk aqueous phase, leading to extremely stable foams. Similarly, the foams could be rapidly destabilized by heating, via break-up of the fibrillar networks. This emulsion foam work is related to the findings of Chen et al. [73], who reported that aqueous foams stabilized by Quillaja saponin-coated 'nanodroplets' were far more stable than foams stabilized by the saponin alone, presumably because the droplets created thicker films between adjacent bubbles. The nanodroplets were of sunflower oil, prepared by sonication and with a mean size ca. 150 nm. Santini et al. [74] also investigated Quillaja saponin and mixed saponin-chitosan solutions. The results substantiated the high surface activity of the saponin and showed that it produced the high values of dilatational viscoelasticity. Another effect emphasized was that the highly charged chitosan molecules + saponin-induced aggregates may prevent thinning of the thin liquid films between bubbles. This therefore prevents coalescence during foam formation, aiding the subsequent saponin adsorption and stabilization of the bubbles. In addition, there is the possibility of electrostatic complex formation of chitosan with adsorbed saponin, increasing electrosteric stabilization of the bubbles. Gonzalez and Sorensen [75]● have recently reviewed work on saponins and investigated the foaming behaviour of those extracted from Soapwort (*Saponaria officinalis*) in the presence other common food ingredients (salt, sugar, ethanol) and conditions (pH and temperature). In general the foams were resistant to such formulation variations, apart from ethanol.

Whether such systems can overcome the potential toxicity (albeit in large quantities) of saponins remains to be seen, although saponins may have some health benefits in sequestering bile salts and so lowering blood cholesterol [76].

Bacteria-stabilized

It may seem odd to think of bacteria as particulate stabilizers, but it is well known that the high bacterial cell load in fermented products like yoghurt, along with the mucilages they produce, make a significant contribution to the texture and physical stability of such products. Only recently, however, have workers turned to the idea of bacterial cells themselves acting as Pickering-style particles [77,78]. Jiang et al. [79] have taken this a step further in chemically modifying the ‘surface’ of lactic acid bacteria (using the same octenyl succinic anhydride commonly used for starch modification) to improve their foaming properties. Although a low level of modification maintained cell viability, it is doubtful if such ingredients would be encouraged in real food stuffs. Foaming is a serious problem during anaerobic digestion of food waste and sewage streams He et al. [80], where it is believed that fatty acids generated are the main foaming agent [81]. It remains to be seen if certain bacterial cells themselves contribute to the foam stability by acting as Pickering stabilizers.

Combinations of particles and other foaming agents

The problem of particles adsorbing fast enough to the surface of gas bubbles in order to reach a high enough coverage to stabilize them [4,5] was touched upon in the Introduction. At the same time, there is the difficulty of finding native particles that have the correct wetting characteristics without resorting to chemical modification of their surfaces. Both these difficulties may be overcome via physical means by combining particles with other materials that also adsorb to the bubble surfaces and/or that adsorb to the particle surface and advantageously alter the particle contact angle at the bubble surface. In this way, particles may be made to be more strongly adsorbing or less strongly aggregating in solution and therefore more available for adsorption. Alternatively, combinations of particles with other surface active agents may impart the optimum characteristics to the absorbed film that give rise to high foamability and foam stability. In this way, Ellis et al. [82] used the unusual cationic surfactant lauric arginate to partially neutralize the charge on k-carageenan microgel particles so that this adsorbed more strongly but did not aggregate in solution, to improve their foaming characteristics. Similarly Binks et al. [83] used combinations of hydrophilic calcium carbonate particles and the LMWS sodium stearoyl-2-lactylate to improve the stability of foams to coalescence and disproportionation. The same technique was applied [84]● to other, more acceptable food surfactants, including β-lactoglobulin, sodium caseinate, sodium dodecanoate and the Quillaja saponins mentioned earlier. However, it was found that the higher molecular weight, structurally more complex proteins and Quillaja did not increase foam stability, only the LMWS. This is presumably because the latter adsorb 'head-down' on the inorganic particles and give 'clean' hydrophobic patches and the correct hydrophobic-hydrophilic balance for strong adsorption and a high barrier to particle desorption.

Novel applications of foams in foods

Foam mat drying

There has been increasing research into foam mat drying, where material is foamed and moisture removed by application of heat in some way. The higher surface area of the foam can have the advantage of accelerating the drying process, but mitigating against this are the low thermal conductivity of foam and also the increasing viscosity of the aqueous phase if thickening agents are employed or naturally present. Sangamithra et al. [85] have reviewed this technique, which may be particularly useful for drying fruit juices and pulps that are naturally very sticky due to the sugars they contain' but which also contain valuable colours and antioxidants [86-88] that may be easily damaged and lost in spray drying or prolonged heating. Heat may be applied in a number of ways: freezing stable foams then freeze-drying [86,87] or by application of microwave energy [89] to the wet foam, for example. The bubble size distribution, bubble packing and viscoelasticity of the thin liquid films all play a role in determining the efficiency of drying, all of which also depend on the original foam formulation.

Foam fractionation

Foam fractionation exploits the natural tendency of surface active material to accumulate at bubble surfaces and to become trapped in thin film lamellae as the foam drains. The mining industry has exploited this technique for many years in froth flotation, where foaming is used to accumulate and separate out valuable inorganic particulates via their natural tendency to adsorb at the gas-water interface or via introduction of froth floatation agents that deliberately make them do so. However, the technique potentially also has a number of food-related uses.

An interesting case is the work of Ayetigbo et al. [90] who added glycerol monostearate and sodium carboxymethyl cellulose to aid foaming of cassava pulp. In this case the foamed pulp had a significantly lower concentration of toxic cyanogens. In the opposite sense, Larson et al. [91] have shown that foaming concentrates perfluorinated surfactants that may be harmful to the environment. This alters the site-specific impact of such surfactants but potentially might be exploited to remove them from waste streams. Turing this round again, Le Toquin et al. [92]● have shown that foamed disinfectant agents are at least as effective as liquid solutions at the same concertation but generate far less toxic effluent due to lower run off. This has the potential for cleaning in place of food equipment as well as many other scenarios for disinfecting surfaces.

Foam fractionation of surface active material from a high viscosity bulk liquid is clearly more difficult and slow, but Li et al. [93] have developed a novel foam fractionation column with vertical sieve trays. This was applied to recovering yam mucilage from yam starch processing wastewater and resulted in significant enrichment. Li et al. [94] have pointed out that recovery of functionally useful protein from soy processing waste water, via foam fractionation, relies on preventing irreversible aggregation of the protein. Interestingly, their results suggested that most insoluble aggregates were formed in the *desorption* of protein from the A-W interface, i.e., aggregation was effectively induced via protein adsorption in the first place, similar to EWP. Addition of a defoaming agent based on LMWS therefore reduced the formation of aggregates. Liu et al. [95] used foam fractionation to recover lycopene from the tomato-based processing wastewater via tomato proteins as the collectors. Moreover natural rhamnolipids could be used to enhance foam stabilization via formation of a protein-lycopene complex.

Oleogels and oleofoams

Another way of reducing the overall calorie content of a fatty product is to incorporate gas bubbles directly into the lipid phase, i.e., an oleofoam. This can be achieved by stabilizing the bubbles with oil-dispersible particles, i.e., Pickering stabilization, or via gelation of the oil-phase, i.e., physically trapping the bubbles in a network with sufficient strength to resist movement of the bubbles via gravity or Brownian motion. In the latter case, termed an oleogel [2]●, the network may be provided by fat crystals inherent to the lipid itself, or other oil-insoluble particles introduced into the system. With oleogels there may also be some adsorption of the gelling particles the bubble surfaces, so that it may not always be clear which mechanism is dominant, analogous to water droplet stabilization in margarines via fat crystals. Binks et al. [96] have provided a clear example of pure Pickering stabilization of air-in-oil (A/O) foams via fluorinated inorganic particles (clays and zinc oxide). Stability depended upon both particle wettability and the amount of shear applied, so that some systems broke down or even inverted to O/A systems. If fluorinated particles could be avoided the latter might provide some interesting opportunities for flavour oil release from the dry powders.

Solely Pickering stabilization of A/O dispersions seems to rare - highlighting the difficulty of finding food-grade particles that easily disperse in oils but that are also sufficiently surface active at the A-O interface – much more work has been done on oleogels. Fameau et al. [97] have produced A/O foams (mean bubble diameter < 200 μm) based on an oleogel of fatty alcohols in sunflower oil. The foams are also most indefinitely stable as long as the fatty alcohol crystals do not melt. An interesting idea therefore, was to make the foams light responsive by also incorporating carbon black particles. On application of UV radiation the gel rapidly warmed, the crystals melted and the foam collapsed. Fameau et al. [98]● have reviewed these and other such responsive foams, where the switch from stability to instability can be induced by changes in the bulk or interfacial material on exposure to light, temperature, and magnetic fields. Heymans et al. [99] have produced a similar A/O system but based on monoglyceride crystals.

In all the above oleogel-stabilized foams, successful stabilization depends upon the size, shape and form of the crystals, which in turn depends on the time-temperature history any other physical processing of the system, the chemical composition of the crystals and their solubility in the continuous oil phase. In other words, the fat crystallization kinetics, which is difficult to control and an area that is still not fully understood. In addition, by analogy with aqueous foams, the bulk viscosity of the continuous phase and the effect of the crystallization on this viscosity determines the ease of incorporation of gas. Higher viscosity makes incorporation more difficult (lower foamability), but once incorporated the bubbles will be more stable.

New methods of studying foam formation and stability

As outlined at the outset, foams are relatively unstable compared to many other dispersions in food and this, combined with the relatively large size of bubbles, the tendency for bubbles to cream and pack closely together separated via very thin films, makes them particularly tricky beasts to study. It is therefore of interest to highlight some new methods and techniques that have been developed to improve our understanding of foam formation and destruction.

Many of these new methods centre around the development of microfluidic devices for production of dispersions under controlled and observable conditions, as reviewed recently by Deng et al. [100]●. Labarre and Vigolo [101]●● have developed a method for evaluation of foam stability after a deformation in a microfluidic device. Whether one or more row of bubbles forms in the channels and the size of these bubbles depends on: the gas and liquid pressure drop as bubbles are formed from the flow focussing nozzle; the viscosity of the liquid phase; the surface tension; the ease of bubble deformation at the channel walls. Laporte, M., et al. [102]● applied microfluidics to produce foams stabilized by combinations of whey protein isolate and xanthan gum, showing how on a minute scale this could be used to test and predict the effects of bubble size, bubble volume faction, continuous phase viscoelasticity and other solution conditions on bulk foam stability. Clarke et al. [103] have studied isolated foam channels created by withdrawing a specific frame geometry from surfactant solutions and using image analysis to monitor film thickness and drainage across the model Plateau borders created. Drainage for aqueous solutions of food grade LMWS, hydroxypropyl methylcellulose and hydrolyzed pea protein were studied. Novel distortions in the border thickness profiles were exhibited with the polymeric surfactants, ascribed to the much higher η_i produced with such stabilizers. In similar ways, the flow of bulk foam down microchannels can be tested, where wall slip or 'partial coalescence' with the wall are key factors controlling the flow, particularly for bubbles stabilized by particles [104]. Increasing particle coverage creates a more rigid and rough bubble surface that increases the frictional resistance to slip at the microchannel wall. Such effects can also be used to inhibit liquid ingress into narrow channels and capillaries [105].

Zhang et al. [106]●● reported a 'new' type of particle-stabilized foam material, capillary foam, which is stabilized by the synergistic action of particles and a small amount of an immiscible liquid - typically an oil for aqueous-based foams. The stabilization mechanism relies on the wetting of particles by the oil to some extent, which results in them sticking together via capillary bridges. The capillary foam is then formed by aeration of the flocculated dispersion. Alternatively, a particle stabilized foam can be formed first, then the oil added and the system re-agitated to distribute the oil to the particles. In this way, one indirectly tunes the capacity of the particles to stabilize the air-water interface via the particle affinity for the air-oil and oil-water interfaces and the spreading of a thin oil film around the bubbles. This results in foams that are then extremely stable. Oil soluble dyes can be added to make the foam appear highly coloured, or the oil film cured (solidified) to produce highly stiff, load-bearing dry foams. Whilst such systems have been deliberately designed, the effects are also important because of the inadvertent interaction of Pickering foams with oils in their potential usage as enhanced (crude) oil recovery agents and their sealing of capillaries and cracks as discussed above [104,105]. Simulating and visualizing the flow behaviour of such complex systems in order to understand them better also remains a great challenge, as discussed by Lipsa et al. [107].

Conclusions

Research into novel stabilizers of food foams continues apace, particularly with regard to particulate stabilizers (Pickering foams). Most of these systems still employ proteins as the key stabilizing ingredient, either in the form of particles of some type, or as modifiers of the surface properties of other particulate material. Many of these studies seek to include stable air bubbles as bulking agents and calorie-lowering agents, at the same time seeking to find replacements for traditional stabilizers based on animal proteins (e.g., dairy and egg proteins). Whilst in most food foams the bulk liquid phase is aqueous, interesting work on air-in-oil foams (oleofoams and oleogels) represent additional novel ways of influencing food texture and stability for the benefit of consumers.

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Recent Developments in Food Foams

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For submission to Current Opinion in Colloid & Interface Science issue Thin Films & Foams

Abstract

The scientific literature between from 2015 onwards (inclusive) with respect to foams and thin films in the context of foods has been reviewed. Proteins are the dominant foaming agents in foods and investigations of the classic, meringue-forming egg white protein still dominate the literature, since the unique properties of this system are still not properly understood. The current drive of many studies is to find suitable replacers of egg proteins, driven by consumer trends for more plant-based alternatives. This has led to investigations of the stabilizing properties of various protein aggregates, ‘nanoparticles’ and microgel particles as Pickering-type stabilizers of foams (Pickering foams). At the same time, other work has sought to manipulate the surface properties of biopolymer- and non-biopolymer -based particles by chemical means, in order to make the particles adsorb strongly enough. Few, truly novel foam stabilizers have emerged, but two include saponin aggregates and bacteria as particle-type stabilizers.

Keywords: food; foams; Pickering; particles, biopolymers

Introduction

Foam is an important component of many commonly consumed food and drinks (e.g., whipped creams, mousses, soufflés, ice creams, bread, cakes, carbonated beverages) and research into new types of foam and new foam-forming and foam-stabilizing agents continues to grow. Bubbles in consumer products can impart texture, colour, novelty and excitement for the consumer. Additional advantages are that, for air bubbles the bulk material is notoriously cheap, light to transport and is unlikely to result in allergic reactions (for clean air at least) ! If only things were so simple, however, because gas bubbles are one of the most difficult colloidal substances to produce, stabilize and control in large quantities, due to their tendency for relatively rapid creaming, dissolution and coalescence (relative to oil-water emulsions, for example). Consequently, great efforts have been made to design systems with improved foam properties, not least because bubbles represent a zero-calorie filler that might be used to replace other food components and have a beneficial effect on the long-term health and well-being of consumers. Thus, apart from the general case of filling the aqueous matrix of foods with more air, systems have been developed for trapping air bubbles in sugar crystals [1], fats and oils [2]●. In addition, there seems to be increasing awareness of the significance and potential of using foam as a 'processing aid'. Thus bubbles can be deliberately used to fractionate a wide range of more valuable surface active materials, whilst conversely foam may concentrate undesirable chemical species. In addition, foam structure may aid the drying and functional properties of dry powders. On the other hand, foaming is an undesirable phenomenon in other processes and understanding how to enhance the action on particles and surfactants in breaking the thin films between bubbles is also an important area of work. It is worth elaborating at the outset some of the colloidal difficulties referred to above, in order to understand the general direction of recent alternative strategies and formulations in the publications referred to later.

Firstly, in the majority of food foams the gas phase is air, nitrogen or carbon dioxide and the continuous phase is an aqueous solution, so that the discontinuous phase (gas) has reasonable (at least mM) solubility in the continuous phase. This is unlike most emulsions or solid dispersions and means that disproportionation, the equivalent of Ostwald ripening in emulsions and dispersions, is rapid when bubbles approach colloidal dimensions, i.e., *ca*. 1 μm. Adsorbed layers of even tightly packed low molecular weight surfactants (LMWS), or gel-like films of adsorbed macromolecules, offer little physical barrier to transport of gas molecules across interfaces, so that the only way to halt disproportionation completely is to use solid particles, i.e., Pickering stabilization (Pickering foams) as the stabilizing mechanism [3]. Adsorbed layers of such particles can provide a perfectly elastic barrier with high resistance to compression and desorption of the particles, 'hijacking' shrinkage of bubbles due to the higher internal gas pressure across curved interfaces. (The effect of the Laplace pressure difference across the air-water (A-W) interface is exacerbated by the higher A-W interfacial tension compared to that of the oil-water interface in emulsions). This has lead to the search for suitable solid particles that can fulfil this role. So far, the range of *food-grade* solids seem to be limited, so compromises may need to be made in terms of softer particles and/or loose particle aggregates to achieve adequate stability. At the same time, some degree of chemical modification, to impart the desired wetting characteristics to the particles, might need to be employed, although it should be recognized that there is consumer pressure to resist all such modifications. Physical modification, e.g., heating/cooling, shearing, sonication and complex formation between different ingredients via physical forces, are much more desirable and acceptable.

Secondly, higher gas-water tensions make bubble disruption under shear much more difficult, i.e., high capillary number (= dynamic viscosity x characteristic velocity/ interfacial tension), so that it is generally hard anyway to achieve the same sort of bubble sizes as in homogenization of oil-water systems, particularly if the viscosity of the continuous phase is increased by inclusion of high dissolved solids or thickening agents. Higher bulk viscosity may slow down bubble creaming, drainage and bubble collisions that normally accelerate coalescence, but high viscosity also slows adsorption of the surface active agent to the bubble surfaces. This is particularly relevant for Pickering foams, where the diffusion coefficient of particles and aggregates is already much lower than that of detergent-like molecules or even small globular proteins. Indeed, modelling work [4,5] has shown that it maybe almost impossible to *form* directly high volume fractions of micron-sized Pickering-stabilized air bubbles in any practical system, since such small bubbles will dissolve away before they achieve adequate particle surface coverage. The alternative route is to form larger bubbles initially then allow them to shrink to smaller size, wherein their particle coverage simultaneously increases if the particles already at the interface are irreversibly adsorbed due to their high desorption energy.

The above issues should be born in mind when considering the various new approaches discussed in the following review, some of which have already been discussed in other summaries elsewhere [6]. It is probably also worth stating at the start that two phenomena should be distinguished, since confusion frequently arises in the literature: foamability versus foam stability. Foamability is the capacity for foam formation: systems that have high foamability form large volumes of foam relative to the starting non-foamed liquid, i.e., high overrun. This does not necessarily mean that these foams will be stable for very long. Foam stability is the capacity of a foam, once formed, to persist. Throughout the following, unless explicitly stated, for brevity we will using the word ‘foaming’ to imply both foamability and foam stability. Bureiko et al. [7] have considered these issues in comparing the foaming of low molecular *versus* polymeric surfactants, like proteins, plus the competition between them in mixtures. The main classes and sub-class of foam stabilizer covered in this review are summarized in Table 1 and these will be discussed in the following sections.

Table 1. ‘Index’ of the main classes and sub-classes of foam stabilizer discussed in this review.

Main class of stabilizer	**Sub-class and corresponding reference numbers**
egg white protein (EWP)	reviews 6, 77● general 10, 12, 13, 45, 46, 57, 63● + sugars & polysaccharides 14, 15, 16, 19 + wheat gluten hydrolysates 20, 21
other proteins	sodium caseinate 64● whey protein isolate 17, 105● pea, soy & lentil 18, 47, 48, 49, 59, 62

	wheat gluten & gliadins 20, 21, 22, 36 algal 58; mung bean 60; coconut 53; Quorn® mycoprotein 61 hydrophobin 34●
protein aggregates	β-lactoglobulin 24, 25, 38 lentil 59, 62 soy 49, 96
particles (Pickering)	reviews 28, 29, 30, 33 gluten hydrolysates 20, 21, 22; gliadins 36, 40● zein 39, 40●; hydrophobin 34● chitin 68●; cellulose 71, 72; starch granules 65 saponins 73-77 microgels 31, 32●, 84, $CaCO_3$ 85, 86● 'bacteria' 80-81, 83
protein hydrolysates	β-lactoglobulin 51, 56 oat 54● coconut 53, 60 pea 106 EWP 57
covalently cross-linked	α-lactalbumin 52 ovalbumin 13 Na caseinate, OSA-starch & tannic acid 64●
ultrasound-treated proteins	EWP 45, 46 faba bean 47
homogenized proteins	milk 42 pea protein 44
physical complexes & coacervates	whey protein + κ-carageenan 66 whey protein+ alginate 67 lentil protein + guar gum 62 pea protein + OSA-starch 63●
OSA-starch	63●, 64●, 81
fatty alcohols (oleogels/foams)	2●, 99, 100●, 101

Protein-stabilized systems

Egg white protein

Proteins, on their own or combined with other ingredients (see later), still comprise the most widespread foaming agents. It is remarkable that, the proteinaceous culinary foaming agent *par excellence* – egg white, is still the subject of intense investigation. This is connected with our incomplete understanding of the unique stabilizing properties of egg white protein (EWP) and its widespread traditional use in many foamed products, e.g., meringues, mousses, baked goods. At the same time there is strong drive to find plant-based alternatives to this 'animal-based' proteinaceous foaming agent, for reasons of environmental sustainability and the relative high proportion of individuals who are allergic to EWP.

The special characteristics of egg albumen stem from the fact that it consists of a mixture of proteins each of which themselves has some less common characteristics: (i) lysozyme, that has a relatively high positive charge at neutral pH, so that it can form electrostatic complexes (aggregates) with the majority of the other (negatively charged) EWP; (ii) ovomucin, a fibrous gelling agent that cannot be denatured up to at least 100 °C that imparts viscoelasticity to the albumen itself; (iii) ovalbumin, the major EWP, a glycoprotein that seems to have a tendency to spontaneous aggregate on adsorption the A-W interface [8],[9]. Daugelaite et al. [10]● have used new, high resolution electrical resistivity measurements as a function of height to investigate free drainage of EWP foams and concluded that the presence of protein aggregates in the Plateau borders has a significant beneficial effect in reducing foam drainage and increasing foam life-times. On the other hand, this tendency for aggregation in the bulk can reduce foamability.

These special features of EWP have lead to a number of treatments to further improve EWP foaming properties, reviewed recently by Gharbi and Labbafi [11]●. A novel treatment is wet ball milling [12], although this seemed to reduce foamability and foam stability due to increased disulfide- and surface hydrophobic-induced aggregation. Similar deliberately induced cross-linking prior to foaming was investigated by Li et al. [13], using hydroxyl radical-induced oxidation of ovalbumin. Moderate oxidation improved the foaming but excessive oxidation reduced it.

In many real products, thickening agents are often added to EWP to try and control the rate of film drainage, particularly when the viscosity of the aqueous phase is already high due the presence of high concentrations of dissolved solids – typically sugars in confectionery products. The higher initial viscosity slows down the incorporation of air to high overrun and inhibits the formation of small enough bubbles. Thickeners, typically polysaccharides, help reduce bubble creaming and drainage whilst the bubble size distribution is reduced to lower sizes by mechanical whipping. They also reduce drainage of the foam product on longer storage times after whipping has ceased, via high values of the low shear rate limiting viscosity or weak gel formation. Understandably, finding the optimum balance of the formulation and processing parameters to give the final desired bubble size distribution, texture, appearance, etc., is not simple and many workers have tried to explain the interaction of all these factors via multi-dimensional response surface studies [14-18]. Ptaszek et al. [19] have shown that a log-normal distribution provides the best description of the bubble size distribution in EWP foamed with pectin and xanthan, confirming the same turbulent eddy-induced Komolgorov mechanism of colloid breakup.

As mentioned above, there is increased interest in substituting EWP with plant-based alternatives. Wouters et al. [20] have shown some improvement in EWP foaming properties by partial substitution with enzymatically hydrolyzed wheat gluten. Gluten hydrolysates had much higher foamability than EWP, whilst EWP showed much higher foam stability than the hydrolysates, but mixtures gave both good foamability and foam stability, suggesting both materials were compatible at the interface. Further measurements of the surface pressure, surface dilatational elasticity (ε) and dilatational viscosity (κ) suggested that the lower molecular weight hydrolysates might dominate the interface with the EWP forming a secondary adsorbed protein layer. Wouters et al. [21] also showed that enzymatically hydrolyzed wheat gluten gives meringues with higher overrun than EWP in a standard recipe (i.e., including sugar) with no notable disadvantages in texture or appearance. More limited gluten hydrolysis seemed to be an advantage due to the formation of more hydrophobic peptides that exhibit higher ε [22].

In many of the studies referred to above and in those that follow, researchers seek to find a link between the interfacial properties of the adsorbed film and bubble stability. The link is not always easy to make. Certainly a high value of ε will help prevent bubble coalescence in the early stages of bubble formation, via the Gibbs-Marangoni mechanism, and many proteins are superior to LMWS in this respect, though the effect is lessened as the kinetics of adsorption increase. Once adsorbed, most proteins are also able to form a thin, viscoelastic, crossed-linked network that can resist further bubble deformation, up to a point, often more reflected in measurements of the interfacial *shear* rheological properties. This can aid resistance to spontaneous coalesce but can lead to film fracture under the large deformations imposed by subsequent processing. Discussion of these aspects is not new [9] and beyond the scope of this review, but the recent study of Mezdour et al. [23]● is worthy of mention in this respect. Here the foaming of protein and LMWS solutions were compared under conditions where the equilibrium surface tensions and bulk viscosity were kept constant. Thus the main variables were thought to be the interfacial viscoelasticity and dynamics of surfactant adsorption/desorption. The main conclusion was that higher dynamic dilatational viscoelasticity and more rapid diffusion kinetics resulted in foams with smaller, more stable bubbles. These effects, plus the effect of shear rate in an industrial type mechanical aerators were used to develop a model to predict bubble size.

Protein aggregates

The tendency for EWP to form aggregates, referred to above, may be one explanation of it's excellent foam stabilizing properties, the aggregates providing a thicker and more mechanically resistant film that better resists thin film disruption and provides enhanced steric stabilization. This is providing the aggregates are still surface active and their larger size does not slow down too much their coverage of the A-W interface. In this respect, one might consider EWP as naturally providing something closer to Pickering-type stabilization, although the stabilizing particles are much more complex than traditional Pickering stabilizers. Dombrowski et al. [24,25] have studied the foaming properties of soluble heat-induced aggregates of pure β-lactoglobulin up to sizes of 1 μm. In general, foam stability increased with aggregate size, due to increased protein surface hydrophobicity, and correlated with maxima in the ε and κ. Hu et al. [26] reported similar findings with β-lactoglobulin aggregates of different size and shape - more fibrillar aggregates gave the highest values of

ε and foam stability. The effects of steam pressure and nozzle design on barista-style milk foams as noted by Jimenez-Junca et al. [27] are undoubtedly related to the different extents of milk protein aggregation induced.

Protein-based nanoparticles and microgels

Another way of improving the foaming properties of EWP is to convert the protein into protein microgels [28-30] For example, Li et al. [31] created submicron (360 nm) EWP microgel (EWPM) particles by homogenization of a thermally cross-linked EWP bulk gel and showed that the EWPM-stabilized aqueous foams via a Pickering-type mechanism. Foamability was less good than EWP-stabilized foams but the EWPM stabilized foams exhibited higher stability to disproportionation and coalescence, in agreement with higher interfacial shear viscosity (η_i) of adsorbed films of EWPM, that were less brittle and liable to fracture. Further work [32]● showed that combinations of EWP and EWPM could achieve the same foamability as EWP alone, whilst still improving stability to bubble shrinkage and coalescence. At the same time, the higher the ratio of EWPM to EWP in the mixtures, the more stable were the foams to freeze-thaw, oven-heating and even microwave heating. The improvement with the mixtures is similar to that obtained with mixtures of gluten hydrolysate and EWP referred to above [20], although here the EWP was not present as microgels but natural aggregates. One might ask what is the difference between a large fractal-type aggregate formed by bottom-up self-assembly of protein molecules and a microgel particle? However, a particle formed by top-down fragmentation of a bulk gel might be expected to retain *internally* the percolating network structure of its parent gel, whilst fractal aggregates do not necessarily have a percolating structure or hold large quantities of solvent. In this review we have reserved the term microgel for those particles that are specifically referred to as such by the authors. The deliberate formation of biopolymer-based particles and aggregates, including microgels, as stabilizing agents of foams (and emulsions) has been reviewed by Dickinson [30]. Microgels in particular have also been reviewed by Murray [29].

The use of protein microgel particles as foam stabilizers exploits the natural superiority of Pickering stabilization, whilst microgels may have other advantages (and disadvantages) compared to traditional solid Pickering stabilizers [28-30,33]. At the same time, other workers have sought to create or exploit other novel protein-based particles as stabilizers that may be considered insoluble in water, or have re-appraised existing proteins as particulate stabilizers. The latter include casein micelles, that may form structures in thin films that significantly curtail drainage [33] and hydrophobin, which is able to form extremely stable small bubbles that can also block drainage of water through the Plateau borders [34]●. The only barrier to use of hydrophobins in foods might be whether or not it represents as significant allergenic potential [35]. Peng et al. [36] created gliadin nanoparticles (diameter ≈ 100 – 200 nm) and showed that foaming decreased as the particles became more charged, due to slower adsorption and weaker dynamic dilatational moduli at the A-W interface, whilst effects of varying particle size were negligible. This highlights again the importance of obtaining adequate bubble coverage fast enough with particles

In terms of the minimum bubble surface coverage required for Pickering stabilization, it is well known that particles with a higher aspect ratio than spheres are far more effective. Self-assembly of protein fibrils produced by heating dilute solutions of proteins at low pH have been investigated by various workers and reviewed recently by Mohammadian and

Madadlou [37]●. Thus Peng et al. [38] have investigated β-lactoglobulin fibrils and found that film strength and bubble stability is a maximum close the pI, where the absorbed films have highest dilatational moduli but at the expense of foamability. Raising the pH slightly above the pI and re-introducing some charge to the fibrils improved foamability whist maintaining good foam stability.

One protein that naturally forms very water-insoluble particles (diameter ≈ 100 nm) is the maize storage protein zein and various workers have investigated zein as a natural Pickering stabilizer. Zou et al. [39] found that foams stabilized by zein alone broke down completely in less than 24 h, but if the anionic surfactant sodium dodecyl sulfate (SDS) was added the zein formed fractal clusters of much larger size that give much improved foam stability. Excess SDS reduced stability as adsorption became totally dominated by the LMWS, illustrating another generic difficulty with particle stabilizers. Wouters et al. [40]● also studied zein nanoparticles (size *ca.* 100 to 150 nm) and also when mixed with wheat gliadin nanoparticles (size *ca.* 130 to 140 nm), both produced via antisolvent precipitation. In agreement with Zou et al. [39], zein on its own showed very poor foaming, whilst the gliadin on its own was excellent and exhibited much higher surface dilatational moduli. Mixtures were generally worse than the equivalent gliadin concentration alone. This points to the fact that highly hydrophobic and insoluble particles, like the zein, may adsorb strongly, but if there are no cohesive forces between the particles, then the film has little resistance to expansion, as noted earlier for hydrophobins [41].

Modified proteins (physical and chemical)

Physical modification

In this section we will discuss work that has been done to deliberately modify the foaming properties of proteins by physical and chemical means. We have tried to separate out studies of mixtures of proteins with other non-proteinaceous materials, discussed in the following section, although non-covalent complex formation between proteins and other ingredients can still be thought of as a physical modification. We note again that only physical modification is likely to be accepted by regulatory bodies and consumers and also that, much of the work on modified proteins involves plant proteins, in the search for replacements for animal-derived proteins.

Tran et al. [42] have summarized the effects of high-pressure-jet processing on milk proteins in relation to their foaming properties. Apparently this can dissociate casein micelles and denature whey proteins, affecting the bulk viscosity and increasing, in particular, the foamability of whole milk. There is debate about how far the hydrodynamic forces exerted on proteins during their passage through high pressure homogenization can irreversibly affect their conformation [43]●● and therefore how this might affect their ensuing emulsification or foaming properties. It seems obvious that the larger the starting protein aggregates, the more likely it is that such aggregates will be disrupted. Djemaoune et al. [44] have shown that microfluidization only seems to affect the surface activity of pea albumin aggregates when the pH is such that the proteins are in a more compact form. It should always be remembered that the effect of high shear forces on emulsions can sometimes be related to minute contamination with the free-radical inducing transition metal elements in stainless steel.

Ultrasound treatment can also be used to effect physical modifications to proteins, although this can also induce chemical changes due free radical initiation at high power (i.e., sonochemistry). In this respect, there is a similarity with the effects of very high shear (see above), in that both physical and chemical changes might be induced. Sheng et al. [45] and Chen et al. [46] showed significant improvement in EWP foaming properties on sonication, ascribed to formation of aggregates via increased free sulfhydryl content and surface hydrophobicity. Martinez-Velasco et al. [47] used high-intensity ultrasound to increase the solubility and surface activity of faba bean protein isolate which led to improved foam stability but decreased protein digestibility.

Shao, Y. Y., et al. [48] and Wang et al. [49] showed that high quality foaming properties can be obtained by the action of much more simple physical processing, namely heating, of soy protein isolate solutions, again due to opening up of the proteins and exposing more hydrophobic groups. Ossa et al. [50] have shown that pH and temperature treatment are critical in determining the foaming properties of tofu-whey concentrates, an important 'waste' stream of tofu processing. Acidic pH values gave the best foamability and stability, ascribed to the adsorption of more aggregated protein as well as higher concentrations of soluble bean polysaccharides in the aqueous phase.

Chemical modification

Corzo-Martinez et al. [51] studied the effect of limited hydrolysis followed by glycation with galactose (via dry Maillard conjugation), and vice versa, on interfacial and foaming (foamability and foam stability) properties of β-lactoglobulin at pH 7 and pH 5. In particular, the system obtained after glycation followed by limited hydrolysis gave foams with exceptional stability, which might be related to the increase in elastic character and cohesion of the interfacial film, indicated by the increase of the surface dilatational modulus ε. Hardly any effect on foaming capacity was observed with the two treatments: hydrolysis followed by glycation, or *vice versa*.

Enzymes, although natural agents themselves, can be used to introduce new covalent cross-links between proteins and create new types of 'unnatural' aggregates. So, although these new aggregates may have improved foaming properties there are doubts about how easily their acceptance might be obtained for use in foods. Thus Dhayal et al. [52] have used transglutaminase or horseradish peroxidase (HRP) to cross-link α-lactalbumin to produce particles with hydrodynamic radii = 20 to 100 nm that gave improved foam stability cf. monomeric α-lactalbumin. However, the stability depended upon which enzyme was used, indicating that the location of the cross-links, i.e., the internal structure of the particles was also important (as might be expected) in terms of surface hydrophobicity, surface area. Kunarayakul et al. [53] have used a glutaminase enzyme to deamidate and improve the foaming properties of coconut protein.

The opposite approach, i.e., cleaving proteins into smaller fragment via enzymes, also continues to be extensively investigated. This has proved particularly useful for plant proteins, which tend to be relatively aggregated and water-insoluble, as demonstrated by Martinez and Pilosof [47] for sunflower protein. As a general rule any enzyme treatment of plant proteins that results in an improvement in aqueous solubility improves foaming properties, but as Bruckner-

Guhmann et al. [54]● showed with oat protein enzymatic hydrolysates, the efficacy depends on the type of enzyme via the different the cleavage patterns and subsequent effects on the (mixed) peptide solubility versus pH. One might also expect that with more extensive hydrolysis the smaller peptides become less effective as steric stabilizers, but this may be mitigated by low molecular weight peptide self-assembly. Li, T., et al. [55] have shown synthetically modified dipeptides to be very effective foam stabilizers, either via the peptides self-assembling (via metal ions) into fibre-like networks at the A-W interface or in the continuous phase to form a gel.

Commercial food grade proteins may contain a range of species with different susceptibilities to the same enzyme conditions compared to native proteins. For example, Pein et al. [56] showed that limited hydrolysis of β-lactoglobulin (fractionated from a whey protein isolate) with pepsin or alcalase, increased both foamability and/or foam stability. It was suggested this was due a combination of non-hydrolysed, native β-lactoglobulin plus more surface active peptides derived from denatured β-lactoglobulin. The denatured β-lactoglobulin was presumably a result of the drying of the whey protein isolate, which made it more accessible to the protease enzymes.

The use of food enzymes to modify food proteins still presents regulatory challenges but recently Jiang et al. [57] have applied natural lactic acid fermentation to EWP and showed a modest but significant foamability, presumably due to the opening up of the proteins and exposing more hydrophobic groups. Such 'traditional' enzymatic treatments may be more acceptable.

Other Novel Plant Proteins

Plant-based, non-modified proteins that have received relatively little attention to date include algal proteins [58]. Suitably extracted protein was reportedly superior to a whey protein isolate. In addition to the large amount of work done on soy protein [48,49], other legumes and pulses have been investigated, e.g., lentil protein aggregates [59] and mung bean proteins [60]. Lonchamp et al. [61] have investigated the properties of a currently unexploited bi-product from the Quorn® fermentation process. One fraction, isolated via ultrafiltration, displayed good foamability and foam stability, although the fraction contained a wide range of metabolites and cell fragments, so that is difficult to be sure which were the key components. It is noted that, like most plant proteins, considerable physical processing is required to improve the solubility and functionality of such proteins, whilst further enzymatic and/or chemical modification might improve this further, if permissible.

Complexes

Another way to improve the foaming properties of proteins is to combine them with other ingredients that may improve the protein solubility or moderate it's surface hydrophobicity – although the two things are obviously connected. If surface hydrophobicity is too high, proteins will self-aggregate in the aqueous phase rather than adsorb; if surface hydrophobicity is too low then there is little driving force for adsorption. Of course the concept of surface hydrophobicity is of little use if the proteins change their conformation significantly during adsorption, as most do. Complexes between different proteins or proteins or polysaccharides can arise from electrostatic attraction and hydrogen bonding, whereas hydrophobic bonding may also operate between different proteins or proteins and lipids and surfactants. One can distinguish soluble complexes of dimensions similar to the constituent molecules and much larger coacervates, the latter appearing as colloidal particles in their own right. Here we also ignore any effects of proteins and polysaccharides where the polysaccharide merely acts as an independent thickening agent or induces depletion flocculation of the protein.

Jarpa-Parra et al. [62] demonstrated coacervate formation at mildly acidic pH between lentil proteins and guar gum, xanthan gum and pectin that gave much enhanced foam stability, due to an electrostatically cross-linked gel-like interfacial network. The aggregates also plugged the junctions of the Plateau borders in the same way as noted above with EWP aggregates [10] and with casein micelles [34]. Significantly, the proteins and polysaccharides phase separated segregatively at neutral pH and this led to a loss of foam stability.

Even more complicated foaming mixtures involve proteins and synthetically modified polysaccharides, such as starches modified with octenyl succinic anhydride (OSA-starches) [63,64], the latter also being surface active. Asghari et al. [63]● suggest waxy maize OSA-starch adsorption can exclude pea protein from the interface when the latter is still sufficiently aggregated to prevent enough hydrophobic protein residues accessing the interface. Zhan et al. [64]● studied an even more complex system of an OSA-starch, tannic acid and sodium caseinate, the latter being more surface active than pea protein or EWP. Tannic acid cross-links the caseinate films and makes them more rigid. Measurements of ε over a range of strains suggested that the OSA-starch increased the degree of strain softening on interfacial extension via more isolated adsorbed OSA-starch domains in between protein/tannic acid domains. With EWP, Asghari et al. [63]● suggested OSA co-adsorbs but de-mixing in the interface forces the EWP to form more closely packed regions that increases stability. These workers also compared the effect of the OSA-starches with dry heated (non-OSA treated) rice starch granules. Such dry-heating seems to make the granule surface more hydrophobic in some way [65], though it is not clear if this makes them sufficiently surface active to compete with protein adsorption. The dry-heated granules slowed down the drainage of EWP foams via some mechanism but they were not as effective as the OSA starches.

Wang et al. [66] showed that heating WPI with λ-carageenan in solution under neutral or near neutral pH can induce the formation of soluble complexes with improved functional properties compared to heating WPI then adding the carageenan afterwards. The explanation proposed was that heating the two components together resulted in enhanced electrostatic interactions between them, due to their more open molecular configurations. Xu et al. [67] have investigated similar complexes between WPI and sodium alginate. Foam stability was particularly improved (at low overall protein concentrations) at pH values where surface active soluble electrostatic complexes were formed between the oppositely net charged components at a relatively narrow (2:1 to 1:1) range of weight ratios of WPI to alginate.

All the above studies highlight the complexity of the different effects on foaming properties when there are different adsorbing and non-adsorbing macromolecules and/or particles present, although this is always likely to be the case in real food systems.

Novel, non-protein based systems

Two types of novel non-protein based foaming agents have been mainly investigated: polysaccharides that are modified to make them surface active and non-protein based particle (Pickering) stabilizers. Of the former, OSA-starch has already been mentioned above, though this has largely been used in admixture with other foaming agents, whilst with regard to the latter, polysaccharides are also relevant, in terms of water-insoluble cellulose and chitin particles.

Cellulose & chitin

Tzoumaki et al. [68]● have investigated the foaming of chitin nanocrystals. As with many Pickering foams, the importance of structuring of particles both at the interface and within the thin films between bubbles (affectively forming thin layers of a 'bulk' particle gel) was also considered. Even more work has been done on cellulose as a Pickering foam stabilizer, though debate continues how the cellulose can be made hydrophobic enough to adsorb efficiently enough at the A-W interface, or the reason for any apparent natural surface activity of cellulose nanocrystals.[69,70] Beatrice et al. [71] required free radical-oxidized nanocellulose in combination with various water-soluble (polysaccharide) thickening agents to produce adequate foaming properties. Another important observation was that, the effect of shear in these systems caused the cellulose nanofibres to flocculate and accumulate at bubble surfaces, though this depended on the attractive interaction between the cellulose and the polysaccharide thickening agents. Such aggregates can potentially act as *defoaming* agents, plus the more aggregated the particles become, the lower the surface area they can cover and so the coarser will be the foam produced. Ahmadzadeh et al. [72] combined chemically modified clay particles to improve the foaming properties of cellulose-based Pickering foams, for foam packing with enhanced physical properties.

Saponins

A relatively new set of Pickering particles that has emerged is based on the natural class of surface active molecules named saponins. Saponins have long been known to be highly surface active and excellent foaming agents in their own right, but Wan et al. [73] have shown that nanofibrils of glycyrrhizic acid can form networks at the A-W and O-W interfaces of oil droplets and bubbles as the system is emulsified and aerated simultaneously, i.e., an emulsion foam, much like whipped dairy cream. The jamming of the emulsion droplets in thin liquid films also enhances foam stability. On cooling the nanofibrils form a three-dimensional net (gel) that prevents coalescence of the droplets and bubbles within. The foam system could be destroyed rapidly on heating because of the melting of the bulk gel. In later work Ma et al. [74] showed that nanofibrils of glycyrrhizic acid alone can form multilayer networks at the A-W interface and also in the bulk aqueous phase, leading to extremely stable foams. Similarly, the foams could be rapidly destabilized by heating, via break-up of the fibrillar networks. This emulsion foam work is related to the findings of Chen et al. [75], who reported that aqueous foams stabilized by Quillaja saponin-coated 'nanodroplets' were far more stable than foams stabilized by the saponin alone, presumably because the droplets created thicker films between adjacent bubbles. The nanodroplets were of sunflower oil, prepared by sonication and with a mean size ca. 150 nm. Santini et al. [76] also investigated Quillaja saponin and mixed saponin-chitosan solutions. The results substantiated the high surface activity of the saponin and showed that it produced the high values of dilatational viscoelasticity. Another effect emphasized was that the highly charged chitosan molecules + saponin-induced aggregates may prevent thinning of the thin liquid films between bubbles. This therefore prevents coalescence during foam formation, aiding the subsequent saponin adsorption and stabilization of the bubbles. In addition, there is the possibility of electrostatic complex formation of chitosan with adsorbed saponin, increasing electrosteric stabilization of the bubbles. Gonzalez and Sorensen [77]● have recently reviewed work on saponins and investigated the foaming behaviour of those extracted from Soapwort (*Saponaria officinalis*) in the presence other common food ingredients (salt, sugar, ethanol) and conditions (pH and temperature). In general the foams were resistant to such formulation variations, apart from ethanol.

Whether such systems can overcome the potential toxicity (albeit in large quantities) of saponins remains to be seen, although saponins may have some health benefits in sequestering bile salts and so lowering blood cholesterol [78].

Bacteria-stabilized

It may seem odd to think of bacteria as particulate stabilizers, but it is well known that the high bacterial cell load in fermented products like yoghurt, along with the mucilages they produce, make a significant contribution to the texture and physical stability of such products. Only recently, however, have workers turned to the idea of bacterial cells themselves acting as Pickering-style particles [79,80]. Jiang et al. [81] have taken this a step further in chemically modifying the 'surface' of lactic acid bacteria (using the same octenyl succinic anhydride commonly used for starch modification) to improve their foaming properties. Although a low level of modification maintained cell viability, it is doubtful if such ingredients would be encouraged in real food stuffs. Foaming is a serious problem during anaerobic digestion of food waste and sewage streams He et al. [82], where it is believed that fatty acids generated are the main foaming agent [83]. It remains to be seen if certain bacterial cells themselves contribute to the foam stability by acting as Pickering stabilizers.

Combinations of particles and other foam stabilizing agents

The problem of particles adsorbing fast enough to the surface of gas bubbles in order to reach a high enough coverage to stabilize them [4,5] was touched upon in the Introduction. At the same time, there is the difficulty of finding native particles that have the correct wetting characteristics without resorting to chemical modification of their surfaces. Both these difficulties may be overcome via physical means by combining particles with other materials that also adsorb to the bubble surfaces and/or that adsorb to the particle surface and advantageously alter the particle contact angle at the bubble surface. In this way, particles may be made to be more strongly adsorbing or less strongly aggregating in solution and therefore more available for adsorption. Alternatively, combinations of particles with other surface active agents may impart the optimum characteristics to the absorbed film that give rise to high foamability and foam stability. In this way, Ellis et al. [84] used the unusual cationic surfactant lauric arginate to partially neutralize the charge on k-carageenan microgel particles so that this adsorbed more strongly but did not aggregate in solution, to improve their foaming characteristics. Similarly Binks et al. [85] used combinations of hydrophilic calcium carbonate particles and the LMWS sodium stearoyl-2-lactylate to improve the stability of foams to coalescence and disproportionation. The same technique was applied [86]● to other, more acceptable food surfactants, including β-lactoglobulin, sodium caseinate, sodium dodecanoate and the Quillaja saponins mentioned earlier. However, it was found that the higher molecular weight, structurally more complex proteins and Quillaja did not increase foam stability, only the LMWS. This is presumably because the latter adsorb 'head-down' on the inorganic particles and give 'clean' hydrophobic patches and the correct hydrophobic-hydrophilic balance for strong adsorption and a high barrier to particle desorption.

Novel applications of foams in foods

Foam mat drying

There has been increasing research into foam mat drying, where material is foamed and moisture removed by application of heat in some way. The higher surface area of the foam can have the advantage of accelerating the drying process, but mitigating against this are the low thermal conductivity of foam and also the increasing viscosity of the aqueous phase if thickening agents are employed or naturally present. Sangamithra et al. [87] have reviewed this technique, which may be particularly useful for drying fruit juices and pulps that are naturally very sticky due to the sugars they contain' but which also contain valuable colours and antioxidants [88-90] that may be easily damaged and lost in spray drying or prolonged heating. Heat may be applied in a number of ways: freezing stable foams then freeze-drying [88,89] or by application of microwave energy [91] to the wet foam, for example. The bubble size distribution, bubble packing and viscoelasticity of the thin liquid films all play a role in determining the efficiency of drying, all of which also depend on the original foam formulation.

Foam fractionation

Foam fractionation exploits the natural tendency of surface active material to accumulate at bubble surfaces and to become trapped in thin film lamellae as the foam drains. The mining industry has exploited this technique for many years in froth flotation, where foaming is used to accumulate and separate out valuable inorganic particulates via their natural tendency to adsorb at the gas-water interface or via introduction of froth floatation agents that deliberately make them do so. However, the technique potentially also has a number of food-related uses.

An interesting case is the work of Ayetigbo et al. [92] who added glycerol monostearate and sodium carboxymethyl cellulose to aid foaming of cassava pulp. In this case the foamed pulp had a significantly lower concentration of toxic cyanogens. In the opposite sense, Larson et al. [93] have shown that foaming concentrates perfluorinated surfactants that may be harmful to the environment. This alters the site-specific impact of such surfactants but potentially might be exploited to remove them from waste streams. Turing this round again, Le Toquin et al. [94]● have shown that foamed disinfectant agents are at least as effective as liquid solutions at the same concertation but generate far less toxic effluent due to lower run off. This has the potential for cleaning in place of food equipment as well as many other scenarios for disinfecting surfaces.

Foam fractionation of surface active material from a high viscosity bulk liquid is clearly more difficult and slow, but Li et al. [95] have developed a novel foam fractionation column with vertical sieve trays. This was applied to recovering yam mucilage from yam starch processing wastewater and resulted in significant enrichment. Li et al. [96] have pointed out that recovery of functionally useful protein from soy processing waste water, via foam fractionation, relies on preventing irreversible aggregation of the protein. Interestingly, their results suggested that most insoluble aggregates were formed in the *desorption* of protein from the A-W interface, i.e., aggregation was effectively induced via protein adsorption in the first place, similar to EWP. Addition of a defoaming agent based on LMWS therefore reduced the formation of aggregates. Liu et al. [97] used foam fractionation to recover lycopene from the tomato-based processing wastewater via tomato proteins as the collectors. Moreover natural rhamnolipids could be used to enhance foam stabilization via formation of a protein-lycopene complex.

Oleogels and oleofoams

Another way of reducing the overall calorie content of a fatty product is to incorporate gas bubbles directly into the lipid phase, i.e., an oleofoam. This can be achieved by stabilizing the bubbles with oil-dispersible particles, i.e., Pickering stabilization, or via gelation of the oil-phase, i.e., physically trapping the bubbles in a network with sufficient strength to resist movement of the bubbles via gravity or Brownian motion. In the latter case, termed an oleogel [2]●, the network may be provided by fat crystals inherent to the lipid itself, or other oil-insoluble particles introduced into the system. With oleogels there may also be some adsorption of the gelling particles the bubble surfaces, so that it may not always be clear which mechanism is dominant, analogous to water droplet stabilization in margarines via fat crystals. Binks et al. [98] have provided a clear example of pure Pickering stabilization of air-in-oil (A/O) foams via fluorinated inorganic particles (clays and zinc oxide). Stability depended upon both particle wettability and the amount of shear applied, so that some systems broke down or even inverted to O/A systems. If fluorinated particles could be avoided the latter might provide some interesting opportunities for flavour oil release from the dry powders.

Solely Pickering stabilization of A/O dispersions seems to rare - highlighting the difficulty of finding food-grade particles that easily disperse in oils but that are also sufficiently surface active at the A-O interface – much more work has been done on oleogels. Fameau et al. [99] have produced A/O foams (mean bubble diameter < 200 μm) based on an oleogel of fatty alcohols in sunflower oil. The foams are also most indefinitely stable as long as the fatty alcohol crystals do not melt. An interesting idea therefore, was to make the foams light responsive by also incorporating carbon black particles. On application of UV radiation the gel rapidly warmed, the crystals melted and the foam collapsed. Fameau et al. [100]● have reviewed these and other such responsive foams, where the switch from stability to instability can be induced by changes in the bulk or interfacial material on exposure to light, temperature, and magnetic fields. Heymans et al. [101] have produced a similar A/O system but based on monoglyceride crystals.

In all the above oleogel-stabilized foams, successful stabilization depends upon the size, shape and form of the crystals, which in turn depends on the time-temperature history any other physical processing of the system, the chemical composition of the crystals and their solubility in the continuous oil phase. In other words, the fat crystallization kinetics, which is difficult to control and an area that is still not fully understood. In addition, by analogy with aqueous foams, the bulk viscosity of the continuous phase and the effect of the crystallization on this viscosity determines the ease of incorporation of gas. Higher viscosity makes incorporation more difficult (lower foamability), but once incorporated the bubbles will be more stable. Some these issues have been nicely discussed in a recent contributions from Mishra et al.[102]

New methods of studying foam formation and stability

As outlined at the outset, foams are relatively unstable compared to many other dispersions in food and this, combined with the relatively large size of bubbles, the tendency for bubbles to cream and pack closely together separated via very thin films, makes them particularly tricky beasts to study. It is therefore of interest to highlight some new methods and techniques that have been developed to improve our understanding of foam formation and destruction.

Many of these new methods centre around the development of microfluidic devices for production of dispersions under controlled and observable conditions, as reviewed recently by Deng et al. [103]●. Labarre and Vigolo [104]●● have developed a method for evaluation of foam stability after a deformation in a microfluidic device. Whether one or more row of bubbles forms in the channels and the size of these bubbles depends on: the gas and liquid pressure drop as bubbles are formed from the flow focussing nozzle; the viscosity of the liquid phase; the surface tension; the ease of bubble deformation at the channel walls. Laporte, M., et al. [105]● applied microfluidics to produce foams stabilized by combinations of whey protein isolate and xanthan gum, showing how on a minute scale this could be used to test and predict the effects of bubble size, bubble volume faction, continuous phase viscoelasticity and other solution conditions on bulk foam stability. Clarke et al. [106] have studied isolated foam channels created by withdrawing a specific frame geometry from surfactant solutions and using image analysis to monitor film thickness and drainage across the model Plateau borders created. Drainage for aqueous solutions of food grade LMWS, hydroxypropyl methylcellulose and hydrolyzed pea protein were studied. Novel distortions in the border thickness profiles were exhibited with the polymeric surfactants, ascribed to the much higher η_i produced with such stabilizers. In similar ways, the flow of bulk foam down microchannels can be tested, where wall slip or 'partial coalescence' with the wall are key factors controlling the flow, particularly for bubbles stabilized by particles [107]. Increasing particle coverage creates a more rigid and rough bubble surface that increases the frictional resistance to slip at the microchannel wall. Such effects can also be used to inhibit liquid ingress into narrow channels and capillaries [108].

Zhang et al. [109]●● reported a 'new' type of particle-stabilized foam material, capillary foam, which is stabilized by the synergistic action of particles and a small amount of an immiscible liquid - typically an oil for aqueous-based foams. The stabilization mechanism relies on the wetting of particles by the oil to some extent, which results in them sticking together via capillary bridges. The capillary foam is then formed by aeration of the flocculated dispersion. Alternatively, a particle stabilized foam can be formed first, then the oil added and the system re-agitated to distribute the oil to the particles. In this way, one indirectly tunes the capacity of the particles to stabilize the air-water interface via the particle affinity for the air-oil and oil-water interfaces and the spreading of a thin oil film around the bubbles. This results in foams that are then extremely stable. Oil soluble dyes can be added to make the foam appear highly coloured, or the oil film cured (solidified) to produce highly stiff, load-bearing dry foams. Whilst such systems have been deliberately designed, the effects are also important because of the inadvertent interaction of Pickering foams with oils in their potential usage as enhanced (crude) oil recovery agents and their sealing of capillaries and cracks as discussed above [107,108]. Simulating and visualizing the flow behaviour of such complex systems in order to understand them better also remains a great challenge, as discussed by Lipsa et al. [110].

Conclusions

Research into novel stabilizers of food foams continues apace, particularly with regard to particulate stabilizers (Pickering foams). Most of these systems still employ proteins as the key stabilizing ingredient, either in the form of particles of some type, or as modifiers of the surface properties of other particulate material. Many of these studies seek to include stable air bubbles as bulking agents and calorie-lowering agents, at the same time seeking to find replacements for traditional stabilizers based on animal proteins (e.g., dairy and egg proteins). Whilst in most food foams the bulk liquid phase is aqueous, interesting work on air-in-oil foams (oleofoams and oleogels) represent additional novel ways of influencing food texture and stability for the benefit of consumers.

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●● 109. Zhang Y, Allen MC, Zhao RY, Deheyn DD, Behrens SH, Meredith JC: **Capillary Foams: Stabilization and Functionalization of Porous Liquids and Solids**. *Langmuir* 2015, **31**:2669-2676.

Lovely explanation of this new type of foam system, with either an aqueous or non-aqueous based continuous phase.

110. Lipsa DR, Roberts RC, Laramee RS: **FoamVis, A Visualization System for Foam Research: Design and Implementation**. *Computers* 2015, **4**:39-60.

Conflict of Interest Statement

Regarding the manuscript: “Recent Developments in Food Foams”, authored by myself, Brent S. Murray

I declare there are no conflicts of interest.

Dear Editor, Thank you for the positive response to our review. I note your minor editorial comment and have inserted any missing page numbers or article numbers in the references where these are available. I also thank the Reviewer for their suggestions, which I have addressed as follows, allowing the opportunity to improve the MS further. Below I repeat Reviewer 1's comments/suggestions, followed by my response, in italics for clarity.

It is not really clear where the Introduction ends and the material specific discussion starts.
In the Introduction I have focused almost exclusively on the generic problems of stabilizing foams, though I have introduced Pickering foams as a special case. At the end of the Introduction I introduced Table 1, a sort of classification summary of the different types of stabilizer as a lead into the following sections, which discuss most of these in turn. However, to make this more clear, I have changed the last sentence of the Introduction to "The main classes and sub-class of foam stabilizer covered in this review are summarized in Table 1 and these will be discussed in the following sections."

The Abstract features abbreviations and parentheses, which impairs the optical and reading pleasure. Later on also some sentences are placed parentheses: In my opinion, the parentheses are not needed.
There is only one abbreviation in the Abstract, for egg white protein (EWP), which I subsequently used only once. I think this was introduced this mainly to keep the word count down. Nevertheless, I have removed this. There is one set of parentheses, around "Pickering foams". I think this is justified because the term is not entirely widespread yet, unlike Pickering emulsions.

On page 7 there is a valid comment on the often-claimed link between foam stability and interfacial properties. I think the comment is important and should be extended to interfacial shear rheology as well (right now only interfacial dilatational rheo is mentioned).
We agree entirely and so have extended the 4th sentence already there in paragraph 2 of page 7, so that this now reads "Once adsorbed, most proteins are also able to form a thin, viscoelastic, crossed-linked network that can resist further bubble deformation, up to a point, often more reflected in measurements of the interfacial shear rheological properties."

For cellulose (page 13) one could also mention some of the recent published reviews on cellulose at interfaces (https://doi.org/10.1021/acs.chemmater.7b00531, https://doi.org/10.1016/j.cocis.2017.04.001, https://doi.org/10.1016/j.cis.2019.102089). These reviews not entirely focus on foams but might help the reader to understand cellulose interfaces better.
There have been a huge number of recent publications relating to cellulose and various colloidal systems so that it is impossible to know which to select unless they specifically relate to foams, the subject of this review. In addition, there is a lot of confusion between interfacial and network stabilization, which we have discussed. In the light of this, the best of Reviewer 1's recommendations seem to be the 2nd and 3rd (Capron et al., 2017 and Bertsch & Fischer, 2020), which discuss the nature of cellulose surface activity and foams: we have therefore included these two in the revised MS, in the 3rd sentence of the section of cellulose and chitin, which now ends …" or the reason for any apparent natural surface activity of cellulose nanocrystals" with these references inserted.
The first recommendation (De France et al, 2017), relates to aerogels and NOT foams, so we have not included it since the above two cover the required topic adequately.

Page 14: Heading "Combinations of particles and other foaming agents". What do you mean by foaming agents? The foam stabilizing surface-active materials or the gas? In engineering nomenclature the foaming agent would be the gas. Just to avoid confusion.
I was not aware of this engineering nomenclature, so thanks to the Reviewer for bringing this to my attention. I have clarified this by changing the title heading to ""Combinations of particles and other foam stabilizing agents"

Page 16: Section on oleogel. It might be worth to check with two super-recent publications by Mishra et al. on fat foam generation (https://pubs.acs.org/doi/abs/10.1021/acs.cgd.9b01558) and the interfacial aggregation of differently treated triglycerides (https://pubs.acs.org/doi/10.1021/acs.langmuir.0c01195).
Again this is an area that is expanding rapidly, so that it is hard to keep up, so the recommendations of Reviewer 1 are very welcome. The second (Langmuir paper) actually refers to the work in the first (Crystal Growth and Design) paper, so we have included just the second, adding the sentence: " Some these issues have been nicely discussed in a recent contributions from Mishra et al. [inserted] at the end of the "Oleogels and oleofoams" section.

[Inclusion of these additional reference has obviously activated some reference re-numbering].

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