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Oral processing of emulsion systems from a colloidal perspective

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This review discusses recent understanding of the oral destabilization of food emulsions from a colloidal perspective. The review deals mainly with the microstructural changes in emulsions and emulsion gels during oral processing at a colloidal length scale, with the key emphasis being on the role of electrostatic interactions, enzymatic modifications and surface-induced phenomena. Knowledge of these complex interactions between the emulsion droplets and the oral components, such as salivary proteins, enzymes and oral shear, might be the key to understanding the oral behaviour and sensory perception of food emulsions. Gainging insights on the interplay between interfacial engineering, oral breakdown and sensory response can serve as a reference in the designing of low fat products with a full fat sensation. Finally, the review also includes a small section on mixed hydrocolloid gel structuring, targeting populations with special oral processing needs. The combination of microstructural approaches and our understanding of the fate of structure during oral processing can help us to design new products with novel sensorial and/or textural attributes.

1. Introduction

Obesity and an aging population are the two most serious global public health challenges; they are placing ever-increasing burdens on health and social care costs. In 2014, more than 1.9 billion adults (≥ 18 years old) were overweight and, of these, 30% were obese.[1] By 2050, the proportion of the world's population over 60 years will increase from 12 to 22%;[2] thus, common geriatric conditions, such as osteoarthritis, chronic pulmonary diseases, dementia etc., are expected to increase. Interestingly, food colloid scientists have adopted a microstructural approach to the design of foods to tackle both of these challenges.

In addressing obesity, food scientists have attempted to create low fat, low sugar foods using colloidal design principles, while retaining desirable sensory attributes. In aging, the approach adopted is to design food structures with "safe swallowing" attributes, which are particularly relevant for an elderly population, to avoid malnutrition and dehydration and thereby to maintain a good level of all-round health and quality of life. There has been a gradual increase in research efforts to understand the oral processing of microstructures, as can be evidenced by the almost exponential increase in citations during the last 15 years in the domain of the oral processing of emulsions and/or gels (Fig. 1). To design such new food structures, an understanding of the underpinning principles of their interaction with oral components is essential before such knowledge can be applied.

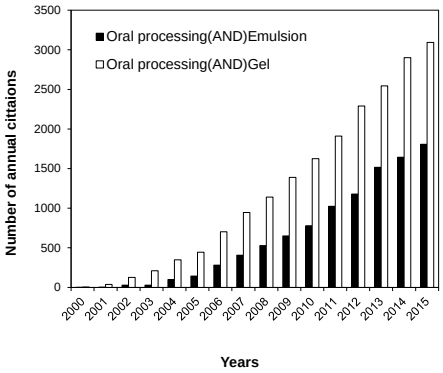

Fig. 1 Number of annual citations obtained with the search topics "(oral processing)AND(emulsion)" and "(oral processing)AND(gel)" from a search of the *Web of Science* database for the period 2000–2015 (with the most recent data downloaded on 17 June 2016).

The aim of this review is to cover the recent developments in colloidal aspects of the oral processing of food. Firstly, we discuss different mechanisms of the interactions of oil-in-water emulsions during their exposure to oral conditions. Secondly, we discuss the oral breakdown of emulsion gels. Emulsions and emulsion gels have been chosen as they broadly represent the wide spectrum of food products from liquids, such as milk, sauces to semi solids, such as yoghurts, custards to solids, such as cheese etc. However, saliva might be the most important factor in inducing microstructural changes in liquid emulsions; mechanical size reduction by shear might be more relevant for emulsion gels because of their solid-like textural attributes. The sensorial effects of these microstructural changes during oral processing are also covered. Finally, the last section deals with mixed gel structuring and how this can influence the oral residence time, with particular emphasis on designing food structures for people with special oral processing needs. Details on individual mouth components and how they influence oro-sensory perception is not covered in this review, but can be found in other recent reviews by Chen.[3,4]

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2. Oral destabilization of emulsions

The stability of emulsions during processing has attracted a lot of research attention,[5] but the destabilization of emulsions once they have been consumed and orally processed has not been investigated, until recently. Oil-in-water emulsions generally reside for a relatively short period of time (orders of seconds) in the mouth [5] but are subjected to a broad range of environmental conditions, such as exposure to body temperature, dilution with saliva, neutral pH, various ions, high shear and squeezing between oral contacting surfaces, such as teeth–teeth, tongue–teeth and tongue–oral palate. In addition to these physicochemical and mechanical aspects, emulsions also interact with salivary biopolymers, such as α-amylase and highly glycosylated negatively charged mucins.[6–12] In fact, saliva, the complex physiological fluid in the mouth, can be described as a weak colloidal gel, as observed at different length scales using cryo-scanning electron microscopy (cryo-SEM) and confocal laser scanning microscopy (CLSM) (Fig. 2).[12]

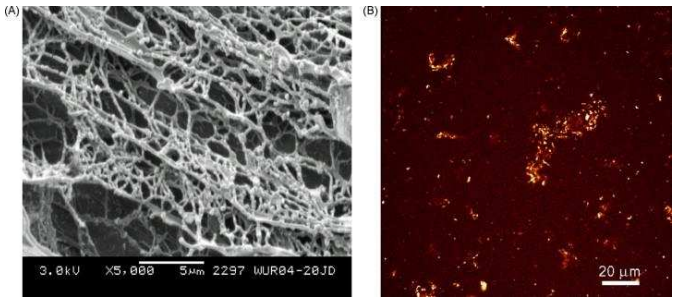

Fig. 2 Micrographs of fresh human saliva using (A) cryo-SEM and (B) CLSM; proteins stained red with Rhodamine B (reproduced with permission).[12]

From a biochemical perspective, human saliva is a complex biological fluid containing water (≈ 99.5%), various proteins (≈ 0.3%, mucins, with MUC5B and MUC7 being the prominent proteins), enzymes (α-amylase, lysozyme, lingual lipase etc.) and antibacterical compounds. The four-level colloidal model of saliva proposed by Glantz[13] includes (a) a continuous phase made up of water and electrolytes buffering the medium, (b) a scaffold-like structured gel network of highly glycosylated mucins, (c) fewer water-soluble proteins, salivary micelles and/or other salivary globular structures observed inside the saliva filamentous network and (d) dispersed droplets of water-insoluble lipoid material, bacterial cells and epithelial cells. Therefore, it would be expected that, when a food emulsion enters the mouth, the initial microstructure might not be retained because of possible colloidal interactions with saliva and such changes might influence sensory perception.[3,10,11,14,15]

Fig. 3 summarizes the different degrees and types of flocculation, which are largely driven by depletion, van der Waals' forces and/or electrostatic interactions, depending on the net charge of the emulsion droplets and the presence of other ionic molecules in the saliva, as well as by droplet coalescence, induced by shear, surface, air or saliva. [16] Table 1 presents a list of recent studies that show such interactions in emulsions stabilized by different surfactants and proteins during either *in vitro* studies or *in vivo* studies. Some of these are discussed in the following sub-sections.

2.1. Charge screening or ion binding effects

Electrostatically stabilized emulsions are known to be susceptible to aggregation, depending on the concentration of mineral ions present in the surrounding medium, because of electrostatic screening or ion binding effects.[17–19] As human saliva contains various strong and weak ions that contribute to its buffering capacity, ion-induced effects might lead to emulsion destabilization.[12,20–23] To investigate this, the behaviours of a positively charged lactoferrin-stabilized emulsion and a negatively charged β-lactoglobulin (β-lg)-stabilized emulsion were studied in the presence of artificial saliva. The composition of the latter was manipulated in terms of the presence or absence of salivary mucins.[24] On mixing with artificial saliva containing only salivary salts (no mucins), the lactoferrin-stabilized emulsion underwent extensive droplet aggregation, with a sharp decrease in ζ-potential from +50 to +27 mV, which was attributed to the screening of the positive charges of the lactoferrin molecules on the droplet surface by ions or to the binding of multivalent counter-ions, such as citrates and phosphates, to the droplet surfaces. The presence of salivary ions reduced the electrostatic repulsive forces between the droplets, and the resulting force was not sufficient to overcome the attractive forces (e.g. van der Waals' and hydrophobic forces), leading to droplet aggregation. Such "salivary-salt-induced aggregation" in lactoferrin emulsions was first reported by Sarkar et al.;[14] later, another study[24] supported this finding, showing a similar range of charge reduction ($\Delta\zeta$-potential = −28.4 mV) for lactoferrin-stabilized lipid droplets in an *in vitro* oral environment. However, such effects were not observed in the negatively charged β-lg-stabilized emulsion.[14] This can be expected as the minimum ionic strength required to cause the aggregation of a β-lg-stabilized emulsion is reported to be ≈ 150 mM NaCl[25] and the artificial saliva used in these studies had significantly low ionic strength (I = 29 mM).

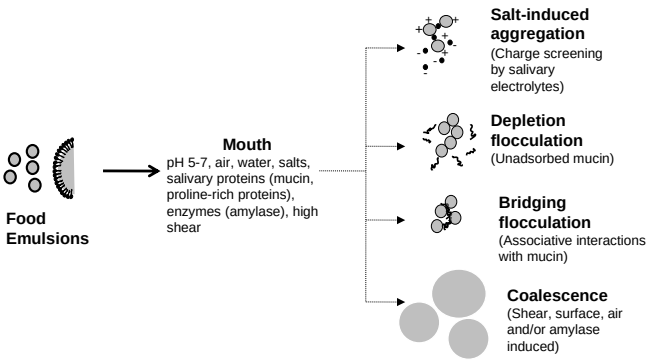

Fig. 3 Mechanisms of the oral destabilization of emulsions (reproduced with permission).[16]

Table 1 Destabilization of emulsions during oral processing and the initial interfacial layer

Oral destabilization mechanisms	Aqueous phase and/or interface*	Saliva/salivary components	References
Ionic binding and/or charge screening	Lactoferrin	Artificial saliva	[14,24]
Depletion flocculation	Whey protein isolate (WPI), *β*-lg, sodium caseinate, *β*-casein, caseinate (pH 3.0)	Whole human saliva, pig gastric mucin, artificial saliva, *in vivo*	[14,16,26–29]
Bridging flocculation	Lactoferrin, lysozyme, *β*-lg (pH 3.0), Tween 20, cetyl trimethylammonium bromide (CTAB), chitosan, caseinate (pH 3.0), WPI (pH 3.0, 3.5, 4.5)	Whole human saliva, artificial saliva, *in vivo*, mucin film, pig gastric mucin	[10,14,16,26,28–32]
Coalescence	WPI, octenyl-succinic-anhydride-modified starch (OSA starch)	Pig's tongue/glass, *in vivo*	[33,34]

Note:*only pHs < pH 6.7 are reported.

2.2. **Bridging flocculation**

Attractive interactions between food emulsions (various proteins and surfactant-stabilized emulsions) and saliva either by *in vivo* methods, i.e. by taking the emulsion in the mouth, or by *in vitro* methods, i.e. by mixing the emulsion with saliva (human or simulated saliva), have recently been well investigated.[14,26,27,30,35] Consensus that bridging flocculation occurs in positively charged emulsions in the oral environment because of the presence of mucins in saliva has now been reached. Mucins generally account for ≈ 10–25% of the total salivary protein, with molecular weights ranging from 0.5 to 20 × 10^3 kDa. Mucins are highly glycosylated proteins containing ≈ 50–80% oligosaccharides, mainly *N*-acetylgalactosamine, *N*-acetylglucosamine, fucose, galactose and sialic acid (*N*-acetylneuraminic acid), and traces of mannose and sulphate attached by *O*-glycosidic bonds to the hydroxyl groups of serine and threonine residues on the protein backbone, clustered in a "bottle brush" arrangement.[36,37] The negative charges of mucin arise mainly from the deprotonation of the carboxylate groups of sialic acid residues at physiological pH (pKa ≈ 2.6)[38,39] and in some cases from sulphated sugars.

When positively charged emulsion droplets stabilized by lysozyme, *β*-lg at pH 3 or CTAB were mixed with whole unstimulated human saliva,[26] irreversible aggregation with a marked increase in droplet size up to 100 μm was observed; this was attributed to electrostatic interactions between negatively charged mucins and positively charged interfacial layers at the droplet surface. Rheological measurements confirmed that the bridging mechanism resulted in "compact" irreversible flocs, which did not completely break up into single droplets even at high shear rates above 800 s^{-1}. However, it is worth noting that, as well as mucins, cystatins and serum albumins are also anionic at physiological pH and thus might contribute to bridging flocculation in positively charged emulsions.[40]

To understand the role of mucins in the bridging mechanism, lactoferrin-stabilized emulsions were treated with artificial saliva containing various concentrations of pig gastric mucin.[14] The lactoferrin-stabilized emulsion showed a significant charge reduction, with *ζ*-potential values close to zero in the presence of 0.2–0.3 wt% mucin, possibly because of binding with anionic mucins. Surface coverage measurements confirmed the gradual binding of anionic mucins to cationic lactoferrin molecules adsorbed at the droplet surface. As well as adsorbed layer–mucin interactions, irreversible flocs were also observed for aqueous solutions of positively charged lysozyme or chitosan or sodium caseinate at low pH in the presence of mucins.[29–31] All these studies confirm that the oral interactions in the case of positively charged species are of electrostatic origin and such irreversible flocculation can be targeted using intelligent interfacial structuring of emulsions.

In many studies, the proposed impact of the positively charged emulsion–saliva interaction was that the formation of "irreversible flocs" might result in an improved sensory perception, which could be a potential strategy in the design of low or no-fat food or fat substitutes. To better understand the role of bridging flocculation in the presence of saliva, Vingerhoeds et al.[28] compared the sensory perception of emulsions stabilized by lysozyme with that of emulsions stabilized by whey proteins at neutral pH. Interestingly, the irreversible bridging flocculation in lysozyme-stabilized emulsions was perceived orally to be astringent, dry and rough. Moreover, oil and protein retention on the surface of the tongue after oral processing and rinsing the mouth with water was shown to be much higher for the lysozyme-stabilized emulsions. This perception of oral roughness was also observed in other positively charged WPI-stabilized emulsions at pH 3.5[32] and/or in anionic chitosan–saliva interactions.[31] The sensory perception was suggested to be largely similar to that of polyphenol–saliva interactions, leading to the precipitation of lubricating mucins and the loss of elastic behaviour of the saliva, resulting in the perceived astringency, dryness and a rough mouthfeel.[41–46]

2.3. **Depletion flocculation**

Depletion flocculation occurs because of the presence of a non-adsorbing biopolymer in the continuous phase of an emulsion, which can promote high density packing of the emulsion droplets by inducing an osmotic pressure gradient within the continuous phase surrounding the droplets.[47] The depletion-induced attraction energy can be calculated by measuring the concentration of the non-adsorbing biopolymer and the radius of gyration of the biopolymer molecule, as shown by the following interaction potential $-\omega_{dep}(0)$:[48]

$$\omega\mathrm{dep}(0) = \frac{-3\mathrm{kT}}{2}\frac{\mathrm{cRv}}{\rho}\left(1+\frac{1}{2}\frac{\mathrm{cRv}}{\rho}\right)\left(\frac{\gamma\mathrm{d}}{\gamma\mathrm{g}}+\frac{2}{3}\right) \quad (1)$$

where c is the biopolymer concentration (kg/m^3), γ_d and γ_g are the radius of the emulsion droplet and the radius of gyration of the biopolymer respectively, ρ is the density of the biopolymer and R_v is given by the following expression:

$$\mathrm{Rv} = \frac{4\pi\gamma_{\mathrm{g}}{}^3\rho\mathrm{N_A}}{3\mathrm{M}} \quad (2)$$

where N_A is the Avogadro number and M is the molecular weight of the biopolymer molecule (kg/mol). Most droplets are flocculated (at a droplet–droplet separation distance h = 0) when the depletion

potential ($-\omega_{dep}(0)$) exceeds $4kT$.[48] The aggregates formed during this depletion flocculation are generally weak, reversible and flexible.[49,50]

When emulsions are stabilized by negatively charged species or when non-ionic surfactants are orally processed, the likelihood of depletion flocculation dominates because of the presence of anionic mucin molecules. Interestingly, Silletti et al.[26] reported that highly negatively charged emulsions, such as sodium dodecyl sulphate (SDS)-stabilized and Panodan-stabilized emulsions, showed no signs of aggregation in the presence of human saliva. This behaviour was attributed to the dominant repulsive forces (negative ζ-potential ≥ –75 mV), which were sufficiently high to overcome the van der Waals' attraction and depletion forces.

However, in the case of weakly negatively charged emulsions (β-lg at pH 6.7, WPIs, sodium caseinate and β-casein) and neutral emulsions (Tween 20), rapid reversible flocculation was observed, with the flocs being disrupted upon dilution and shear, which was assumed to be due to depletion flocculation.[14,26,27] Using theoretical calculations, the droplet interaction potential ($-\omega_{dep}(0)$) of β-lg emulsions in the presence of artificial saliva was found to be ≈ $11.5kT$, confirming that the observed aggregation was due to depletion interaction.[14] Interestingly, from a sensory perspective, these weak negatively charged emulsions had little retention in the mouth and revealed improved thickness, fattiness, slipperiness and a creamy mouthfeel.[28] The diametrically opposite sensorial effects of bridging flocculation and depletion flocculation emphasize the importance of choosing the appropriately charged emulsifier during food design and of predicting stability changes during oral processing to target a particular sensory perception, i.e. astringency or creamy mouthfeel.

2.4. **Coalescence**

Coalescence is hypothesized to have a positive effect on the perception of an emulsion, in terms of a creamy mouthfeel. Taking advantage of the amylase in saliva, the most common approach for inducing droplet coalescence is to design an oil–water interface using modified starch with hydrophobic groups. Emulsions containing 10 wt% sunflower oil stabilized by OSA starch underwent rapid irreversible saliva-induced coalescence, which was predominantly due to the hydrolysis of the OSA starch by salivary amylase.[34] The resulting interfacial layer was too weak to protect the droplets from gradual accretion to larger coalesced droplets (> 100 μm in size). As expected, the OSA-starch-stabilized emulsions received significantly higher scores on fat-related taste and creamy mouthfeel and low scores on friction-related attributes, such as roughness and astringency.

The incorporation of air during chewing and mastication can also induce coalescence in the mouth,[33] i.e. air can enable spreading of the emulsion droplets at the air–water interface, leading to coalescence between the neighbouring adhered droplets and resulting in subsequent oil release. In addition to saliva and air, surface- and shear-induced coalescence have also been reported for colloidal systems under controlled tribological conditions using modified polydimethylsiloxane (PDMS) or pig tongue surfaces.[51] In experiments carried out using pig tongue tissues, it was suggested that, when the radius of curvature of the microscopic asperities on the papillae of the tongue was smaller than the droplet size (radius) of the emulsion, the contact pressure between droplets and asperities could be large enough to rupture the interfacial layer. This might lead to penetration of the droplets by the surface asperities, causing (shear-induced) coalescence and oiling off. However, in reality, the filiform papillae of the tongue are approximately 320 μm long and 120 μm thick, and most of the emulsion droplets are of a micrometre length scale, i.e. the radius of curvature of a papilla is two orders of magnitude larger than the droplet size; thus, upon shearing, rupturing of the interfacial layer appears to be less likely.

However, in control experiments using CLSM, it was found that compression of the pig's tongue papillae created confined spaces in which the WPI emulsion droplets became highly concentrated, increasing their inter-droplet encounters and their susceptibility to shear-induced coalescence. Similarly, other tribological studies also provide insights into surface-induced coalescence in colloidal systems, caused by rubbing and squeezing the product between the tongue and the palate either using model PDMS surfaces or with animal tissues, but this is out of the scope of this review. Detailed information about oral tribology can be found in reviews by Stokes and his coworkers.[52,53]

Some studies suggest that a "fatty" feeling in the mouth is due to the presence of lingual lipases, which generate free fatty acids (FFAs) from lipid-rich food;[54–57] this is largely based on evidence from lipid digestion in rodents.[57] Hypothetically, if the presence of such lingual lipases does result in the generation of FFAs and mono- and/or diacylglycerols during oral processing in human adults, the *in vivo* studies as well as the *in vitro* studies done with emulsions stabilized by non-starch-based emulsifiers (Table 1) should have shown some degree of coalescence, given that lipase-digested products tend to competitively displace the parent interfacial layer.[58–60] However, no such in-mouth coalescence triggered by lipase has been reported as yet.

3. Oral breakdown of solid or semi-solid emulsions

3.1. Structures of solid and semi-solid emulsions

From the viewpoint of structural arrangements, solid and semi-solid systems containing emulsion droplets can be grouped into emulsion-filled gels and emulsion gels (Fig. 4). Because of the differences in their structural arrangements, the formation, rheological properties and fracture properties of these gels are different. An emulsion-filled gel is a gel matrix in which emulsion droplets are embedded (Fig. 4A), and its rheological and fracture properties are determined predominantly by the network properties of the spatially continuous matrix.[61] An emulsion gel is a type of particulate gel, and its rheological properties are determined mainly by the properties of the network of aggregated emulsion droplets (Fig. 4B).[62] However, in some cases, the distributions of the emulsion droplets in solid and semi-solid systems are not always as in these two typical structures. The emulsion droplets can aggregate within the biopolymer matrix and can then form their own local network as a part of the matrix (Fig. 4C); the properties will be affected by the properties of both the gel matrix and the emulsion droplets.[63] In practice, many foods, such as cheese, yoghurt, dairy desserts, tofu, sausages etc., have such a structure, which is referred to as an "emulsion gel" or an "emulsion-filled gel". A whey protein emulsion gel is a good food model that

represents these food products and has been investigated extensively.

For emulsion-filled protein gels, the gel matrix is formed by the protein in the aqueous phase; the formation and the rheological properties of these gels are dependent mainly on the properties and the concentration of the protein in the systems.[64-66] The dispersed oil droplets have less impact on the properties of the gel, which are dependent on interactions between the surface layer of oil droplets and protein in the gel matrix and the aggregation state of the oil droplets.

In protein emulsion gels, most proteins are adsorbed on the surface of the emulsion droplets, with only a very small amount of excess protein (< 1%) existing in the continuous aqueous phase.[67] The low protein concentration in the aqueous phase makes it difficult to form a gel matrix. The three-dimensional network can be formed only through direct links between protein molecules anchored on different droplet surfaces, as shown in Fig. 4B. This is different from the structure of emulsion-droplet-filled gels (Fig. 4A), where the emulsion droplets do not act as filler particles, but are the primary structural components making up the network of the gel, as reported for heat-set emulsion gels formed with a high oil concentration (> 40% oil) and in which there was very little unadsorbed protein in the aqueous phase.[62,68]

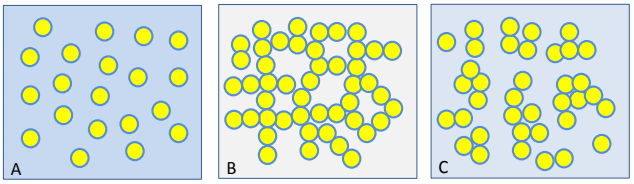

Fig. 4 Schematic presentation of the structures of (A) an emulsion-filled gel, (B) a protein-stabilized emulsion gel and (C) a mixture of both emulsion gels. The yellow circles represent the emulsified oil droplets. The blue colour outside these circles in Figs. 4(A) and 4(C) represents the gel matrix.

3.2. Formation of emulsion-filled gels and emulsion gels

An emulsion-filled gel can be generated from an emulsion by gelling the continuous phase containing protein, surfactant or polysaccharide. For a protein-stabilized emulsion with a high protein concentration in the aqueous phase, the mechanism of the formation of a solid or semi-solid network from the liquid emulsion is similar to the formation of a protein gel. The formation of a gel network can be induced by heating ($T > T_{denature}$), salting (charge screening), calcium bridging, enzyme action (rennet and transglutaminase) and acidification.[61] Therefore, for emulsion-filled gels, the rheological and fracture properties are determined predominantly by the network properties of the spatially continuous matrix. In this case, the effect of the emulsion droplets on the properties of the gel is dependent on the chemical nature of the interactions between the emulsion droplets (filler particles) and the surrounding matrix.[69] Depending on the physicochemical properties of the emulsion droplets (filler particles), they can be described as either “active” or “inactive”. Active droplets are mechanically bound to the gel matrix through physicochemical interactions. These interactions will contribute to the properties of the gel. For example, the gel stiffness may increase if the stiffness of emulsion droplets is higher than that of the gel matrix, whereas it may decrease if the stiffness of emulsion droplets is lower. [70] In contrast, inactive filler particles in a composite material behave rather like small holes in the network, leading to the matrix connecting loosely and the storage modulus decreasing monotonically with the average particle concentration.[71] Dickinson and coworkers[68,72–74] have reported much research on the contrasting effects of active and inactive fillers on the elastic modulus of heat-set whey protein emulsion gels. They found that the interaction between the protein matrix and the oil droplets was a key factor in determining the gel strength. The protein-coated oil droplets had strong cross-links with the protein matrix through disulphide bonds, hydrophobic interactions and hydrogen bonds. These links could reinforce the connections of protein aggregates, thereby leading to an increase in gel strength. In contrast, as Tween-coated (small molecular weight surfactant) oil droplets had almost no cross-linking with the protein matrix, the gel strength decreased. However, when oil droplets stabilised with a surfactant that interacted strongly with the protein was added to the gel, it had a positive effect on the elastic modulus.

In the case of emulsion gels, structural formation of the gel occurs mainly because of the aggregation of emulsion droplets, which is due to the attractive force between the droplet surfaces that is induced by some processes, e.g. heat treatment, change in pH, increase in ionic strength and enzyme action.[62,73,75] As the aggregation of emulsion droplets involves the formation of structural bonds, the surface layer, the volume and the size of the emulsion droplets influence the structure and the rheological properties of emulsion gels markedly. For example, the strength of heat-set whey protein emulsion gels increases with the oil volume fraction[68] and decreases with the size of the oil droplets (Fig. 5).[62,74,75] Increasing the salt concentration (e.g. NaCl and $CaCl_2$) reduced the surface charge of the emulsion droplets and caused calcium bridging between the droplets; this resulted in an increase in the strength of the protein emulsion gel and made the structure of the gel change from homogeneous at the micro scale to porous in both heat-set and cold-set whey protein emulsion gels.[62,76,77] A prior heating of the protein solution to denature the protein that stabilizes the emulsion or of the protein-stabilized emulsion to denature the surface protein can enhance the acid-induced gelation of whey-protein-stabilized emulsions.[62,64,65,77]

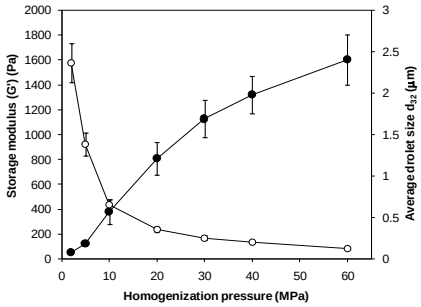

Fig. 5 Maximum storage modulus (●) of gels made with 3 wt% WPI and 20 wt% fat emulsions as a function of the homogenization pressure. Gels were formed from preheated (90 °C for 30 min) emulsions with different average sizes (d_{32}) (○) through acidification by the addition of 0.6% glucono-δ-lactone. Reproduced with permission from Ye and Taylor.[62]

3.3. Large deformation rheological properties and oral processing

When an emulsion gel is eaten, the structure of the gel is first broken down in the mouth, and relates to the perception of texture in the

mouth. As the gel structure may be reprocessed and modified during oral processing, the large deformation and fracture properties of gels containing emulsion droplets have been considered to be important in oral processing.[78]

Young's modulus has been correlated with the perceived hardness of gels.[79] Fracture stress correlates with the hardness perception of cheeses.[80,81] In emulsion gels, the attributes toughness and elastic are related to high fracture stress and high fracture strain, whereas lumpy and grainy are related to high fracture stress and low fracture strain. Recoverable energy and water-holding capacity have a marked impact on the breakdown properties of gels and are highly correlated with particle size distribution, cohesiveness, adhesiveness and moisture release. Pure polymer gels have a high fracture strain, because of their stranded network cross-link structure. When emulsion droplets are incorporated into polymer gels, the structure becomes close to that of particulate gels and the fracture strain reduces significantly, suggesting that the structure is a major factor in determining the fracture properties of emulsion gels.

The structure is influenced by several properties of the emulsion droplets. Firstly, the effects of oil droplets on the large deformation and fracture properties are dependent mainly on the interactions of the oil droplets with the gel matrix (bound and unbound). A change in the interaction between the oil droplets and the gel matrix, by varying the surface properties of the emulsion droplets, can have an impact on the effect of the oil droplets on both the fracture properties and the rheological properties. With increasing oil content, the fracture strain decreases for gels with bound droplets and is unaffected for gels with unbound droplets. The fracture stress is unaffected by an increase in the concentration of bound droplets when the strength of the gel matrix is close to that of the droplets and decreases with an increase in the concentration of unbound droplets.[82–86]

The state of the oil droplets, such as shape and aggregation state, in the gel matrix can markedly influence both the small and the large deformation rheological properties of emulsion-filled gels. Aggregated emulsion droplets in gelatin and WPI gels enhanced Young's modulus but did not affect the fracture properties.[87] However, the effect of aggregation is also dependent on the size, the stiffness and the concentration of the oil droplets in the gel matrix.[70] An increase in the solid fat content in emulsion gels increases Young's modulus, compared with gels containing medium chain triglyceride oil droplets.[86] However, enhancement of the strength of gels by solid fat content is also dependent on the bound and unbound oil droplets in the gel matrix. Gels with unbound droplets and high solid fat cannot be strengthened by fat crystals as much as gels with bound fat droplets. In contrast, an increase in solid fat content leads to a decrease in fracture strain.

3.4. Fragmentation of solid and semi-solid emulsions in the mouth

Mechanical breakdown (fragmentation) is a core part of oral processing,[88] in which the particle size is reduced and the bolus is formed. The influence of food characteristics on oral processing has been reviewed extensively by Chen.[87] Within the human mouth, a bolus is formed by the mechanical action of chewing and biochemical processing by enzymes in the saliva, enabling safe swallowing of the food. The degree of fragmentation of a food product is critically dependent on the structural and mechanical properties of the food consumed.[89,90] In general, harder foods require more chewing cycles and masticatory force, and lead to a higher degree of fragmentation during mastication.[88] However, foods with the same hardness may have totally different degrees of fragmentation, demonstrating the importance of the original structures of the food on the fragmentation process.[91,92] Agrawal et al.[89] and Lucas et al.[90] found that the breakdown of food in the mouth is highly correlated with the mechanical property index: toughness and Young's modulus. Toughness is defined as the energy consumed in growing a crack of a given area. Young's modulus represents the rigidity of the food material.

Recently, Guo et al.[93] examined the oral behaviour of whey-protein-based emulsion gels with different gel strengths and reported that higher gel hardness led to a greater degree of gel fragmentation in the human mouth. The degree of fragmentation of the gel was highly correlated with measurements of the mechanical properties. The hardness and the Young's modulus of the gels increased with an increase in ionic strength, which had an impact on the breakdown patterns in the mouth. The median size of the particles in the masticated gels decreased when the gels were higher in hardness and Young's modulus (Fig. 6). This suggests that higher hardness leads to greater fragmentation in the human mouth. In contrast, sensory experiments showed that gels with low hardness required a significantly lower number of chewing cycles than gels with higher hardness.

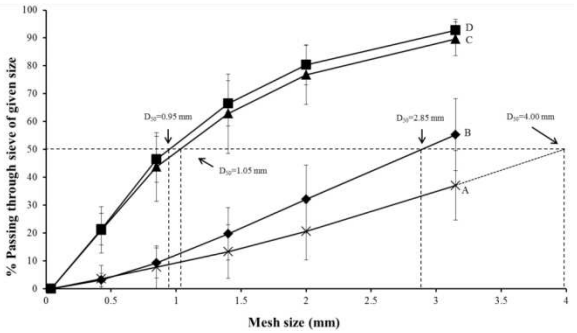

Fig. 6 Average particle size distributions of fragments of heat-set whey protein emulsion gels (A: 10, B: 25, C: 100 and D: 200 mM NaCl) upon chewing, obtained from eight human subjects. The points represent the amounts of material passing through a sieve of a given size. Reproduced with permission from Guo et al.[93]

In another experiment, Guo et al.[94] investigated the effect of the oil droplet size in emulsion gels on the degree of fragmentation and the release of oil droplets from the gel matrix. The shear storage modulus (i.e. the mechanical property in the linear viscoelastic region), the fracture force and the fracture strain of the emulsion gels decreased significantly with an increase in the size of the oil droplets in the gels. From CLSM, gels containing small oil droplets can be regarded as a type of aggregated particle gel, whereas gels containing large oil droplets can be regarded as a type of particle-filled gel with a spatially continuous protein matrix. Since the emulsion droplets are stabilized by whey protein, interactions occurred between the surface of the droplets and gel matrix during the formation of gel. For a given system, small oil droplets induced strong bonding between the oil droplets and the protein matrix because of the higher interfacial surface area to which protein was

adsorbed compared with large oil droplets. This strong bonding can effectively transfer the applied stress from the protein matrix to the emulsion droplets and improve the gel strength,[95] which explains the decrease in storage modulus with increasing oil droplet size. Similarly, the fracture force and fracture strain decreased significantly with an increase in droplet size, indicating that large oil droplets may act as defects in the fracture test.[96] The decrease in storage modulus and fracture force led to a slight increase in the mean particle size of the gel boluses after mastication[94] , which may be because of the low fracture stress of gel, the lower number of chews and the shorter chew duration.

For emulsion-filled gels and emulsion gels, the release of fat or oil droplets from the gel matrix under shearing and melting of the gel matrix during oral processing has been considered to be an important property, which relates to the sensory properties of emulsion gels, such as creamy and fatty,[97] and to further digestion behaviours of lipids in the gastrointestinal tract.[94,98] The release of oil droplets is dependent on the interactions between the oil droplets and the gel matrix and the melting behaviour of the gelling agents in emulsion-filled gels. The extent of breakdown during oral processing determines the release of the oil droplets, which is also affected by the bound or unbound oil droplets in the gel matrix. Oil droplets not bound to the gel matrix are released in amounts that are related to the size of the particles in the gel that is broken down. For oil droplets bound to the matrix, their release relies on the melting of the gel matrix at the oral processing temperature. The fracture properties of gels slightly influence the oil release. Gels with a low fracture strain tended to release more oil than gels with a high fracture strain. An emulsion made with WPI released half the oil from the WPI gel compared with an emulsion made with Tween 20, suggesting that the emulsifier has an impact on oil release.[85]

After mastication, for emulsion gels containing oil droplets with different sizes, only a few oil droplets were released from gels containing small oil droplets whereas large quantities of oil droplets were released from the protein matrices of gels containing large oil droplets (Fig. 7).[94] The difference in oil droplet release could be attributed to the differences in gel structure caused by the oil droplet size. Oil droplet release is difficult in the oral processing of aggregated particle gels, because of the protection of the thick protein coating around them and the strong interactions between protein-coated oil droplets under low electrostatic repulsion. However, for particle-filled gels, the oil droplets are released easily upon deformation or cutting because of the low stress transfer capacity across the oil–protein interface, thereby leading to cracking of the interface, which is supported by the decreases in fracture force and strain with increasing oil droplet size. The size of the oil droplets increased after release from the gel matrix, indicating that coalescence occurs in the released oil droplets in oral processing. A similar phenomenon has also been observed in the oral behaviour of liquid emulsions, as discussed in the previous section.

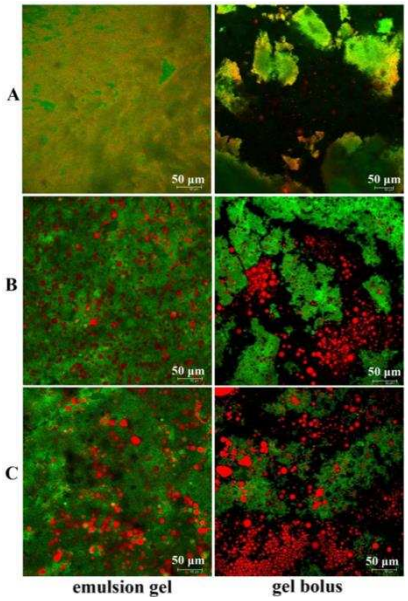

Fig. 7 CLSM images of boluses of a whey protein emulsion gel after human mastication (A, B and C: gels containing 1, 6 and 12 μm oil droplets respectively). Green colour represents the protein, red colour represents the oil phase and black colour represents air or water. Reproduced with permission from Guo et al.[94]

4. Structuring of mixed gels for special oral processing needs

Designing optimally textured foods for populations that are at risk of swallowing disorders is now one of the most critical challenges faced by the food industry. The importance of food texture to safe swallowing has recently received attention.[99] For the design of a food with special oral processing attributes, the rheological properties of the food and thus the bolus play a key role. In comparison with a thin bolus, a cohesive and thicker bolus tends to reside for a relatively longer time in the mouth.[100,101] This sensory feedback of slow bolus flow through the oropharynx can protect airways and lower the chances of aspiration and pneumonia. In addition, increasing the viscosity and thereby thickening the food, either by flocculation or by the addition of hydrocolloids as thickening agents such as starch, xanthan gum, guar gum and carrageenan, and thus varying the textural attributes of fluid and semi-solid foods[28,34,102–105] and mixed gel structures for “safe” swallowing has captured recent research attention. Readers may refer to recent reviews [106-107] which focus on essential elements for formulation design and rheological aspects of safer and better foods for elderly. Although this review is not focused on hydrocolloid gel design, we include a small section on three mixed gel structuring studies in which the approach was to increase the oral processing time using rheology-based design strategies.

To prolong the mastication time, the development of highly elastic gels, based on *κ*-carrageenan in the presence of *ι*-carrageenan, xanthan gum and konjac glucomannan, was investigated.[108] The addition of xanthan gum to *κ*-carrageenan or *κ*-carrageenan/*ι*-carrageenan mixtures in the absence of konjac glucomannan led to an initial increase in the elastic modulus, followed by a maximum and a weak subsequent decrease because of the onset of anisotropic arranging of the xanthan chains. In contrast, the same gel mixtures in the presence of konjac glucomannan led to

clear global and local maxima and minima of the Young's modulus and the fracture strain and fracture stress. Another interesting study with 20 different hydrocolloids was conducted,[109] in which the authors presented an interesting map of textural attributes and eating difficulties versus rheological properties. A synergistic interaction between κ-carrageenan and locust bean gum resulted in high sensory firmness and sensory elasticity, which essentially meant longer mastication times but also greater eating difficulties for the κ-carrageenan/locust bean gum mixed gel.

Recently, Laguna and Sarkar[110] designed model mixed biopolymer gels with initially different degrees of inhomogeneity (i.e. the inclusion of different sizes of calcium alginate microgel particles to a κ-carrageenan continuous network)**.** Overall, SEM images and small deformation rheology results confirmed that the inclusion of calcium alginate microgel particles (1–2 wt%) altered the surface regularity of κ-carrageenan by introducing defects that were due particularly to the presence of "inactive filler particles" and resulted in a less defined network because of incompatibilities between the biopolymers.[111,112] Interestingly, such inactive calcium alginate microgel particles significantly increased the oral residence time in young adults[109] (Fig. 8) as well as the elderly[113] compared with a single continuous gel system made up of corresponding κ-carrageenan concentrations. Also, such an increase in oral residence time was achieved without a significant increase in eating difficulty perception; this is an important consideration when designing food for the elderly.

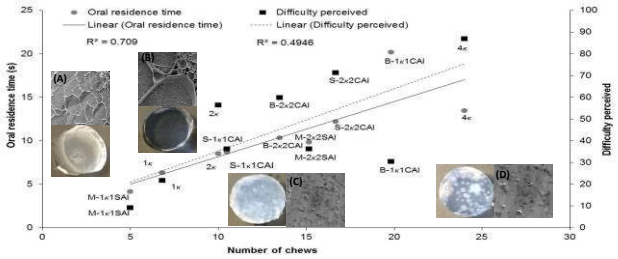

Fig. 8 Number of chews (young participant average) in relation to the oral processing time of the different gels and the difficulty perceived. M: mixed; SAl: sodium alginate; κ: κ-carrageenan; CAl: calcium alginate; B–: big calcium alginate microgel particle (1210–2380 μm), S–, small calcium alginate microgel particle (57–185 μm); numbers indicated in the sample codes are the corresponding biopolymer concentrations. Insets indicate the visual image and the electron micrographs of (A) mixed 2 wt% κ-carrageenan 2 wt% sodium alginate gel, (B) 2 wt% κ-carrageenan gel, (C) 1 wt% κ-carrageenan gel with 1 wt% small calcium alginate microgel particles and (D) 1 wt% κ-carrageenan gel with 1 wt% big calcium alginate microgel particles. Reproduced with permission from Laguna and Sarkar. [110]

As such, the behaviours of these mixtures are in many ways similar to those of emulsion gels with oil droplets as "fillers". Thus, much can be learnt from applying our existing knowledge of the material properties of biopolymer mixtures and filler–matrix interactions to the design of mixed gels with novel textural attributes, which can result in a homogeneous, cohesive bolus with increased oral processing time, and thereby beneficial for people with special oral processing needs.

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