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Murray, BS orcid.org/0000-0002-6493-1547 (2019) Microgels at fluid-fluid interfaces for food and drinks. Advances in Colloid and Interface Science, 271. 101990. ISSN 0001-8686

https://doi.org/10.1016/j.cis.2019.101990

Microgels at fluid-fluid interfaces for food and drinks

Brent S. Murray

Food Colloids & Bioprocessing Group, School of Food Science & Nutrition
University of Leeds, Leeds LS2 9JT, UK
Tel. 44 (0)113 3432962
E-mail b.s.murray@leeds.ac.uk

Submitted to
Advances in Colloid & Interface Science
Virtual Special Issue (VSI)
"Food Colloids: Application of Soft Matter Concepts"

Abstract

Various aspects of microgel adsorption at fluid-fluid interfaces of relevance to emulsion and foam stabilization have been reviewed. The emphasis is on the wider non-food literature, with a view to highlighting how this understanding can be applied to food-based systems. The various different types of microgel, their methods of formation and their fundamental behavioral traits at interfaces are covered. The latter includes the aspects of microgel deformation and packing at interfaces, their deformability, size, swelling and de-swelling and how this affect their surface activity and stabilizing properties. Experimental and theoretical methods for measuring and modelling their behaviour are surveyed, including interactions between microgels themselves at interfaces but also other surface active species. It is concluded that challenges still remain in translating all the possibilities synthetic microgels offer to microgels based on food-grade materials only, but Nature's rich tool box of biopolymers and biosurfactants suggests this field still opens up important new avenues of food microstructure development and control.

Keywords: microgels; biopolymers; interfaces; emulsions; foams

1. Introduction

Microgels, or microgel particles, may be defined as systems where each particle is a network, i.e., a gel, of some sort of material, formed by either controlled network growth ('bottom-up' formation) or controlled fragmentation of a bulk gel into the particles ('top-down' formation). Microgels are a fascinating class of material that form a very active area of research in food (Farjami and Madadlou, 2017) and non-food (Plamper and Richtering, 2017) systems (Dickinson, 2016), since they have great potential as novel rheology modifiers and also as 'particulate' stabilizers of other colloids, such as emulsions an foams. It is the deformability of microgels that, on close packing in the bulk or at interfaces, is responsible for this novelty. As such, it has been proposed that emulsions stabilized by microgels (so-called Mickering emulsions (Gong et al., 2014)) should be distinguished from emulsions stabilized by 'true' solid particles, the classic Pickering emulsions (Binks, 2017), (Linke and Drusch, 2018). The structure and dynamics of layers of solid particles at interfaces has been reviewed by a number of authors, e.g., see (Maestro et al., 2018b). Surface pressures rise only when particles are in very close proximity and are related to inter-particle interactions and consequent intra-layer particle clustering and structuring. Interfacial rheology of such layers is highly non-linear except at very low particle coverages, whereas at the higher coverages relevant to emulsion stabilization, the behaviour of particle layers is more akin to that of 'soft glasses' (Maestro et al., 2018a). The deformability of microgels – as result of interfacial tension forces or changes in environmental conditions (such as temperature, concentration, pH, etc.) – further complicates the understanding of the behaviour of microgels at interfaces, as discussed below and recently elsewhere (Murray, 2019).

Although various workers have produced microgels possessing a cross-link density that, by accident or design, varies throughout the particles, e.g., from a more densely cross-linked core to a more loosely cross-linked outer corona (Gong et al., 2014), microgels should still be distinguished from colloidal particles with a truly solid hard core but covered by thick polymer layers. The polymer configurations in of these outer layers may bear some resemblance to the outer layers of a microgel, but the fact that the core of a microgel is still deformable to a significant extent is used in this review to distinguish microgels from sterically stabilized solid particles.

This review also mainly confines itself to fluid-fluid interfaces, i.e., systems relevant to emulsions and foams and, in view of the food soft matter theme, the emphasis is on reaching an understanding of biopolymer-based microgels (Farjami and Madadlou, 2017) that have some hope of application in real food stuffs. Thus, studies of interactions of microgels with solid surfaces are largely excluded, except where this teaches us significantly more about the microgel properties in general.

Drying of microgels onto solid surfaces and the factors that control the structure of the films that form and their barrier properties is an interesting area discussed elsewhere (Horigome and Suzuki, 2012); (Mayarani et al., 2018) . Similarly, there are many studies investigating microgel absorption into gels or release from them (Yaroslavov et al., 2017), plus adsorption of biopolymers and bioactive compounds onto (Kumar and Singh, 2010), (Kureha et al., 2017), (Liu et al., 2014), (Morisada et al., 2010) and absorption into microgels, such as enzymes (Sigolaeva et al., 2014, Sigolaeva et al., 2015), beta-carotene (Tan et al., 2014) and DNA (Ozdemir et al., 2006), including the interaction of microgels and their payloads with membranes (Nordstrom et al., 2018); (Mihut et al., 2013) and cells (Vihola et al., 2007). Of particular importance to foods is the ease of enzymatic digestion of materials encapsulated within the microgel particles (Mansson et al., 2013), (Torres et al., 2016). Such studies are not comprehensively reviewed here, but rather aspects of the direct interaction of microgels with fluid-fluid interfaces in general, principally air-water (A-W), oil-water (O-W) and their effects of bubble(foam) and emulsion stability, respectively. Consequently, the majority of the studies reviewed are not directly food-related, but the intention is to highlight the findings that are potentially most relevant to food-users of microgels.

The key advantages of any particulate stabilizer are that they can impart very high stability to coalescence (at least in the absence of shear) and to ripening. This is due to the high desorption energies of Pickering particles and the fact that the adsorbed layer is often much thicker than that of most other stabilizers, imparting strong steric or electrosteric stabilization. There are many other excellent reviews (Dickinson, 2016, Dickinson, 2017) of particulate stabilizers in general. This increased thickness may also have some uses in modifying the rate and extent of enzymatic digestion of either the stabilizing layer or the enclosed droplet material (Sarkar et al., 2017b, Sarkar et al., 2018) (Torres et al., 2016) (Sarkar et al., 2019). One perceived advantage of particulate stabilizers in food and drink is the replacement of low molecular weight surfactants as emulsifiers, which may cause irritation to skin and that are seen as more ‘chemical’. With respect to microgels, however, there are further advantages in terms of the responsiveness of the microgels to environmental conditions: they may swell or shrink depending the temperature, pH (Liu et al., 2014), ionic strength, presences of osmolytes, etc., as well as the type of interface. This is turn may change their surface activity (Ito et al., 2018) and or induce the localized (interfacial) release of their contents or uptake of other species. Some of these unique aspects of microgels at interfaces are discussed in the following sections.

2. Types of microgel

In principal any type of gelling material could be made into a microgel particle, but the majority of systems studied to date are composed of either synthetic or natural polymers. By the far the most widely investigated synthetic microgels are based on poly-(N-isopropylacrylamide) (PNIPAM) (Wellert et al., 2015) or its derivatives. PNIPAM microgels have a volume phase transition temperature in the convenient region of 32 °C. Cooling just a few degrees above/below this temperature can cause significant shrinkage/expansion of PNIPAM microgels, depending upon their degree of cross-linking. Thus loosely cross linked PNIPAM microgels and their derivatives (Zhou and Chu, 1998) may change their radius by a factor more than 5 (and therefore volume more than 125), for example, whilst more highly cross linked microgels may hardly change at all. Shrinkage of PNIPAM microgels is accompanied by increased hydrophobicity of the particles overall, as well as their increased stiffness, due to the higher cross-link density and polymer volume fraction at the 'surface' of the particles. Increased stiffness also reduces the tendency for spreading at the interface, which has implications for microgel surface activity (see below). A key advantage of synthetic microgels is that they can be made 'to order' of different mean sizes (generally sub-micron) with a very narrow size distribution and related properties. There is an interesting cross-over between classic polymer latices, which when highly swollen by solvent begin to resemble microgels. Indeed much of the first synthetic microgel work stems from Pelton and Chibante (Pelton and Chibante, 1986) (on NIPAM) and later Obey and Vincent (Obey and Vincent, 1994) on monodisperse polydimethylsiloxane (PDMS) liquid droplets. The distinction between microgels and polymer colloids really depends on how high the solvent content of the particle must be, plus how deformable the particle must be, to be considered gel-like. Most materials considered as microgels in the current literature have solids contents less than ca. 10% and have shear and tensile moduli moduli > 0.1 MPa.

Many types of synthetic microgel have been produced and although they would not be permitted in foods they are good model systems for understanding how biopolymer-based microgels might behave. Thus, one key issue is the variation in cross-link density from the centre to the outside. Microgels that are formed via polymerization from a fixed concentration of monomers and cross-linking agent via nucleation naturally have a density that falls off radially, simply due to the increase in surface area to volume ratio as the particles grow, unless the reactivity (or reactant concentration) is varied throughout their formation. The latter is a more complex process, but can be achieved (Fernandez-Nieves, 2011) to produce more uniformly cross-linked material. On the other hand, workers (e.g., (Welsch et al., 2012)) have deliberately produced core-shell type microgels which have different core and shell strengths, from the same or different polymeric materials. The behaviour of such microgels at interfaces will obviously be more complex, but such model systems may help to understand the behaviour of more complex food-grade microgels based on combinations (Gtari et al., 2016) of different biopolymers and other materials. Further complexity has been explored involving Janus-like (Destribats et al., 2013) and also worm-like (Thompson et al., 2015) microgels.

Most microgels that could be considered food-grade are based on the two main classes of biopolymer proteins and polysaccharides. Since proteins are generally highly surface active, most protein microgels are surface active, combining the high desorption energies of Pickering particles with the ability of proteins to adsorb to almost any interface, whilst the adsorbed layer is much thicker than a protein monolayer. Microgels can also be formed from any polysaccharide that gels. Although polysaccharides are generally non-surface active, polysaccharide microgels can be combined with other ingredients, such as proteins or lipids, to make them so. For example a protein layer or lipid (Ellis et al., 2019) or protein-stabilized droplets (Ma et al., 2017) adsorbed to the surface of the polysaccharide microgel. Another advantage from the food point of view is that surface active particles of reasonably well-controlled size can be formed from complicated mixtures of biopolymers (Dickinson, 2017). Thus one can convert natural protein sources that have a wide range of molecular weights and/or molecular aggregate sizes, into a more uniform surface active entity. At the same time, this may greatly improve the functional properties of the original proteinaceous material overall. This is most promising for plant proteins (Matsumiya and Murray, 2016) (Jiao et al., 2018), (Tang, 2017), which tend to be relatively insoluble compared to milk proteins, for example, but also for the huge amounts of insoluble plant polysaccharides available, such as cellulose (Zhu et al., 2017).

3. Methods of preparation of microgels

There are many recipes for the formation of synthetic microgels (Pich and Richtering, 2010), (Fernandez-Nieves, 2011). Generally methods are based on micellar solubilization of the monomer where initiation takes place. Production of more complex microgel structures may involve templating and change of solvent and monomers to add additional layers. All such methods may therefore be described as ‘bottom-up’, in that the microgels grow via continuous growth of polymer chains and their incorporation into the larger particle.

For biopolymer-based microgels bottom-up synthesis is more complex in that the building block is already polymeric, but the approach can still be used to cause controlled aggregation of the biopolymers into microgel entities. This has been most studied with proteins (Schmitt et al., 2010), (Destribats et al., 2014b), where activation of cross-linking can be induced by higher temperature, opening up globular structures to expose hydrophobic residues. In this respect the approach is much the same as bulk gelation of proteins, but by performing the processing at low protein concentrations and/or where there is significant electrostatic repulsion between the protein molecules, aggregation can be slowed and controlled to form fractal gel particles of high solvent content very similar to the synthetic microgels discussed above (Schmitt et al., 2010). The natural cross-linking that forms is a combination of (mainly) hydrogen bonding between the chains on cooling back to room temperature, plus some covalent cross-links than can form via disulphide cross-linking. Obviously, it is more difficult to control the variation in cross-linking density for such microgels, which ultimately depends on the conformation and reactivity of the protein sub-units at each point in the process.

Producing adequate quantities of protein microgels via these methods may appear problematic, but with more research into practical processing methods this is likely be solved. Indeed, Chen et al. (Chen et al., 2017b) have even shown that soy protein microgels can form ‘spontaneously’ from raw materials on simple changes in solution conditions. Thermally induced cross-linking can be supplemented by further chemical (Kang and Kim, 2010) or enzymatic (Guo et al., 2016) cross-linking, but this runs the risk of decreasing the acceptability of such materials in foods.

An alternative to slow heating methods is reactive precipitation, where protein solutions are rapidly mixed with a low concentration of natural cross-linking agent, like Ca^{2+}, i.e., cold gelation (Beaulieu et al., 2002). This method has been applied to whey protein isolate to produce microgel particles (Torres et al., 2017a) with mean sizes ranging between ca. 40 and 200 nm. The reactive precipitation method also lends itself well to the production of polysaccharide-based microgels, since many polysaccharides gel on addition of Ca^{2+} ions, e.g., pectins, alginates, carageenans. This has been pursued by Pravinata et al., including Ca-alginate microgels decorated with lactoferrin (Pravinata et al., 2016, Pravinata and Murray, 2019). However, so far there seems to be little knowledge of how the cross-link density might vary within microgel particles produced via this method.

The ‘top-down’ process can be applied to any biopolymer or other gelling material. Here a bulk gel is formed via some cross-linking process and then the gel is broken into microgel particles usually via mechanical action. This simple method has been surprisingly successful, in that very small particles of relatively narrow size distribution can be produced, albeit not as narrow as with synthetic microgels and so far it seems difficult to produce sizes < 100 nm diameter. Microscopy of microgels produced via homogenization, for example (Sarkar et al., 2016, Matsumiya and Murray, 2016), shows that they are globular in shape, suggesting almost ‘emulsification’ of bulk gel pieces under the extreme shear stresses applied. Thus protein (Sarkar et al., 2016, Matsumiya and Murray, 2016) and polysaccharide microgels as small as ca. 80 nm diameter have been produced via this method, including larger microgel particles with inclusions and/or surface decoration of oil droplets, produced from emulsion gels (Torres et al., 2017b) (Torres et al., 2018). Such surface inclusions are another way of modifying the surface activity of microgels, whilst it has also been shown that such particles have potential uses as tribology modifiers (Sarkar et al., 2017a),(Torres et al., 2018) in the oral cavity or elsewhere. One might imagine that the cross-link density of microgels produced via top-down approaches would reflect that within the original bulk gel, which at some length scale is expected to be fairly uniform. Thus, if the size of the microgels is significantly greater than this length scale, one would expect the cross-linking with the microgels to be similarly uniform. However, this is ignores the high shear stresses that are exerted on the bulk gels in converting them into microgels, which may result in irreversible changes in the network structure within them. Certainly the surface of such microgels probably has a more open, diffuse structure than that of the bulk gel microstructure from which it has been torn. Thus far, there does not seem to have been any systematic investigation of the properties of such microgels and their relation to the original gel rheology, although Torres et al. (Torres et al., 2017b) suggested that a higher critical fracture strain gave larger microgel particles.

One should also mention the production of so-called ‘fluid gels’ (Lazidis et al., 2016), which lies somewhere in between bottom-up and top-down in terms of processing method, in that these are dispersions of gelled particles that form as the materials are gelled *during* the application of shear. The shear disrupts the formation of a single continuous network throughout the whole system, influencing the final size (e.g., mean size 10 to 150 μm) and shape of the gelled particles that form once all the available cross-linking sites have been used up, or the cross-linking reactions are terminated by a change of conditions (e.g., temperature). Microfluidics (Kanai et al., 2011) can also be used to produce microgels, e.g., 400 to 1000 μm diameter PNIPAM as shown by these authors, i.e., in the upper size range and probably in too small quantities compared to what typical food processing lines would demand.

4. Mechanisms and features of microgel adsorption at fluid interfaces

At the core of this review is the need to examine the unique behaviour of microgels particles at interfaces, in terms of them being deformable and reactive particles (reactive to environmental conditions) and the influence that these features have on their stabilizing properties. This is not to say that all aspects of the adsorption of true (hard solid) Pickering particles are clear (Murray, 2019).

4.1 Origins of microgel surface activity

It is worth considering why microgels might prefer to adsorb at the O-W or A-W interface of emulsions and foams anyway, if they are largely composed of solvent – water in most cases. The answer is of course that the chains of linked monomers still retain some of the hydrophobicity of the original monomers and this equally applies to chains of partially unfolded protein molecules in the case of protein-based microgels. Indeed, the dangling chains of unfolded cross-linked protein molecules at the surface of protein microgels may be more surface active than the original proteins, precisely because they are trapped in a more unfolded state. Nevertheless, the ease of packing of such chains into an interface is expected to be more difficult than for free polymer molecules, unfolded or not, as a result of the more restricted mobility of the chains due to their attachment to the rest of the microgel particle. The degree to which this affects surface activity then depends on the degree to which the microgel can change its shape and packing at the interface as it begins to adsorb, further discussed below. Hegemann et al. (Hegemann et al., 2018) have reviewed this theoretically for a whole range of microgel surface elasticities and indicate the potential advantages of hollow over filled microgels in terms of increasing the adsorption energy.

Keal (Keal et al., 2017) illustrate how microgels adsorb spontaneously with little energy barrier to adsorption, like polymers. If one assumes microgels behave as objects possessing a defined surface and therefore a defined cross-sectional area occupying the interface in accordance a defined contact angle, then it easy to understand why such particles remained pinned at interfaces, since the area multiplied by the interfacial tension (energy) leads to a significant energy barrier to desorption. This would be true even for W/W systems, where the interfacial tension can be extremely low (< 10^{-3} mN m^{-1}). However, deformation of microgels on adsorption (discussed in more detail in section 4.2 below) and/or solvent penetration into microgels at interfaces (discussed in more detail in section 4.4 below) make this a tenuous assumption. There may be other reasons why the microgel particles are forced to the interface, such as incompatibility with other polymers dissolved in the aqueous phase. This has been discussed recently (Ettelaie et al., 2019) and could be the driving force for microgel stabilization of water-in-water (W/W) emulsions (Nicolai and Murray, 2017, Murray and Phisarnchananan, 2014, Murray and Phisarnchananan, 2016). In order to stabilize emulsions and foams effectively via the Pickering mechanism the microgels must be an order of magnitude smaller than the droplets or bubbles in order to achieve reasonable surface coverage of them. At least for hard (Pickering) particles, stability can be achieved at far less than close packed coverage if the particles form a rigid enough network at the interface (Destribats et al., 2014b, Kam and Rossen, 1999). Some workers suggest multilayers of microgels can form at interfaces (Zielinska et al., 2017).

4.2 Deformation of microgels on adsorption

There is ample experimental evidence (Geisel et al., 2015), (Minato et al., 2018, Zielinska et al., 2017, Zielinska et al., 2016) that microgels change their shape on adsorption, as well as simulations and theoretical models that describe this (Matsui et al., 2017), (Mourran et al., 2016), (Rumyantsev et al., 2016). Gelissen et al. (Gelissen et al., 2016) have recently used *in situ* electron and super-resolved fluorescence microscopy techniques to visualize microgel internal structure during swelling and shrinkage. The extent of change is a balance between affinity of the particle for the interface *versus* the internal resistance to deformation, which of course depends on the extent and homogeneity of cross-linking and the interaction with neighbouring microgels in the interface. The effects of microgel particle deformability (Destribats et al., 2014a) and size (Destribats et al., 2011); (Murphy et al., 2016) on adsorption and the ability to stabilize and emulsions has been studied (Chevallier et al., 2018); (Kwok and Ngai, 2018a). The outer layers of microgels tend to be less cross-linked and are therefore capable of greater distortion, giving the 'fried egg' appearance of microgels adsorbed on solids (Style et al., 2015); (Destribats et al., 2011) where the interaction with the interface can be especially pronounced, as reviewed by Wellert (Wellert et al., 2015). The balance between the rates of adsorption, spreading and inter-particle interactions (Maldonado-Valderrama et al., 2017) is important to understand in order to control the structure and properties of dried films of microgels on solid substrates (Horigome and Suzuki, 2012). Increased distortion from spherical increases the interfacial area occupied by the microgel and thus might be expected to increase the desorption energy, by analogy with classic Pickering particles. Thus, more deformable particles might be expected to adsorb more easily and be better stabilizers and this seems to be supported by several experimental (Kwok and Ngai, 2018b, Kwok and Ngai, 2018a); (Destribats et al., 2011), (Matsui et al., 2017), (Schmitt and Ravaine, 2013) and modelling studies (Mourran et al., 2016), (Style et al., 2015), (Vilgis and Stapper, 1998). On the other hand, this seems to be contradicted by other findings, i.e., more deformable particles adsorbed *less* efficiently and are *worse* stabilizers (Destribats et al., 2014a), (Keal et al., 2017), (Koh and Saunders, 2005). Probably these discrepancies arise from the balance between the facts that as microgel particles become more expanded the surface density of the remaining polymer chains capable of adsorption might actually decrease (the remainder of the 'surface' being holes, i.e., solvent), whilst increased flexibility will indeed increase the chances of these segments positioning themselves at the interface and lowering the interfacial energy. Larger and more 'floppy' microgels also tend to be more polydisperse and so lead to less well packed interfaces and bridging between emulsion droplets (Destribats et al., 2014a). These and other discrepancies have also been discussed in the review by Schmitt and Ravaine (Schmitt and Ravaine, 2013). Swelling of particles will spread out the surface density of polymer chains in the same way as spontaneous expansion at the interface, whilst if the polymer segments carry some charge, the surface charge and therefore hydrophilicity of the microgel surface will decrease as the microgel expands, making the microgel more likely to adsorb to a hydrophobic surface. PNIPAM microgel have been shown (Daly and Saunders, 2000) to possess some surface charge and therefore their swelling/de-swelling to be sensitive the ionic strength, increasing salt screening interchain repulsion.

As the microgel surface coverage increases interactions between the microgel particles becomes increasingly important and various workers have illustrated ordered structuring of microgel monolayers at interfaces, (Picard et al., 2017); (Maldonado-Valderrama et al., 2017); although the degree of ordering will depend on the size and uniformity of microgel size (Scheidegger et al., 2017), which for biopolymer-based microgels is not as great as for synthetic microgels, and also whether the microgels adsorb spontaneously or are spread (Pinaud et al., 2014). The area has been nicely reviewed by Schmitt and Ravaine (Schmitt and Ravaine, 2013). The majority of this evidence for microgel structuring comes from spread monolayers of microgels at the A-W interface, including studies of monolayer surface rheology (see section 4.5 below). Ordering suggests repulsive interactions, whilst one of the distinct advantages of microgels might be their ability to fuse together spontaneously (Sarkar et al., 2016) (Sarkar et al., 2019) to form a continuous thick layer around droplets or bubbles. Combining spread A-W monolayers and surface tensiometry of adsorbing PNIPAM microgels, Deshmukh et al. (Deshmukh et al., 2014) have illustrated an adsorption barrier at high particle coverages reminiscent of aspects of globular protein adsorption.

(Chevallier et al., 2018) have illustrated cross-linking microgels together via heating, though this decreased stability, inducing droplet aggregation. Fusion or swelling might be accelerated by other changes in environment conditions, e.g., pH, that causing microgel expansion and interpenetration at the interface or desorption (Ata et al., 2010), whilst deliberate chemical cross-linking has been used to create colloidosomes (Wang et al., 2017). (Kwok and Ngai, 2018a) have illustrated the importance of softness of PNIPAM microgels at O-W interfaces and it has been shown (Keal et al., 2017) that softer, less cross-linked PNIPAM particles are less adhesive at the A/W interface and lead to bridging of bubbles and emulsion gelation (Koh and Saunders, 2005), as already mentioned. Increased charging of microgels can lead to their desorption (Binks et al., 2006); (Mihut et al., 2013) and therefore a reduction in interfacial coverage and flocculation of the colloid stabilized by the microgels, whereas Nagai et al. (Ngai et al., 2006) have shown that the more charged, swollen state of adsorbed microgels can improve emulsion stability.

In summary swelling, surface activity and fusion are all interconnected in a complex way (Schmitt and Ravaine, 2013); (Kwok and Ngai, 2018a) and, in general, there is a relative dearth of evidence of biopolymer-based microgel structuring and deformation behaviour at interfaces compared to synthetic microgels. In addition, with respect to protein-based microgels, there is an interesting analogy with the adsorption and unfolding of globular proteins at interfaces. Many factors affect the rate and extent of protein unfolding at interfaces and the development of a coherent viscoelastic film, including the rate of adsorption: faster adsorption leaves less time for unfolding before the interface is filled up by less-unfolded molecules (Murray, 2002), (Murray, 2011). The rate of adsorption will itself depend upon the bulk concentration and the rates of diffusive and convective mass transport to the interface. Early simulations of globular protein unfolding at interfaces utilised models of the protein that are not unlike microgels themselves (Dickinson and Euston, 1990, Dickinson and Euston, 1992). Comparisons of the features of adsorption of the two types of entity have started (Pinaud et al., 2014) but much further work remains, whilst there have been a number of increasingly sophisticated models and simulations (Garbin et al., 2015), (Hegemann et al., 2018), (Mourran et al., 2016), (Rumyantsev et al., 2016), (Style et al., 2015) of microgel particle adsorption that try to take account of the internal microgel structure, mechanical properties and interactions within the adsorbed microgel particle layer. In addition, advances have been made in understanding the importance of microgel deformation in flow and how this affects microgel adsorption and stabilization of interfaces (Destribats et al., 2013) in a dynamic situation.

4.3 Characterization of microgel mechanical properties

The mechanical properties, i.e., the ease of compression, stretching, etc., of individual microgel particles is obviously key to understanding their behaviour at interfaces, when used as tribology modifiers or when subjected to shear in bulk solution. However, experimental measurements on such small particles are obviously not easy. A number of studies (Backes et al., 2017); (Backes and von Klitzing, 2018); (Aufderhorst-Roberts et al., 2018) have used atomic force microscopy (AFM) techniques to try and measure this directly for individual particles. Microgel mechanical properties can also be inferred from calorimetry (Aangenendt et al., 2017), compression isotherms of microgel monolayers at the A/W interface (Garbin et al., 2015) or O/W (Murphy et al., 2016) interface, or bulk rheological measurement of close packed microgel dispersions (Mattsson et al., 2009). In the latter, higher microgel polydispersity makes this relationship more difficult to disentangle. As mentioned earlier, for microgels formed via top-down approaches, one might expect some relationship between the original bulk gel rheology and the rheology of the individual microgel particles. In this respect, many biopolymer-based microgels created so far are probably considerably stiffer than most synthetic microgels created. Sarkar and co-workers (Sarkar et al., 2017a), (Torres et al., 2018) showed recently that whey protein and emulsion-filled starch microgels can apparently withstand significant normal and shear stresses in tribology experiments.

4.4 Solvent penetration of microgels at interfaces

Another unique characteristic of microgel particles at interfaces as opposed to impenetrable solid particles, is the ability of the solvent to penetrate *into* the particle itself. Since solvent swelling alters surface activity (see above) there can be a unique adjustment of the surface activity of the microgel particles to the type of interface at which they are adsorbing. From simulations of solvent penetration into microgels at a liquid/liquid interface Gumerov and co-workers (Gumerov et al., 2016) conclude that liquid miscibility is higher within the microgels than outside the microgels and that this internal miscibility is greater within more highly cross-linked microgels, since it is the polymer segments that screen the unfavorable interactions between the unlike liquid molecules. This further begs the question whether such porous, responsive particles should ever be considered as having a distinct contact angle at the interface in question. The same question has been asked of globular protein molecules at interfaces, where their surface area to volume ratio has been used to try and rationalize differences in their surface activity (Damodaran and Razumovsky, 2008).

For synthetic microgels, more likely to be utilized in a wide range of solvents, solvent penetration is probably more important than for biopolymer–based microgels in foods. Food-compatible microgels are almost always prepared in aqueous solution and at least one of the solvents at the fluid-fluid interface is usually water. Differences in the concentrations of ions and osmolytes during preparation versus the conditions of adsorption can obviously induce changes in microgel swelling by water migration to and from the aqueous phase, i.e., for A/W, O/W or W/W systems. It remains to be seen if oil phases of different polarity, viscosity, etc., penetrate into such microgels significantly and change their properties.

4.5 Interactions between other interfacial components

The interaction between microgel particles themselves at interfaces is a factor that is still not fully understood (Plamper and Richtering, 2017) and has been the subject of many investigations, as discussed above and also reviewed by Deshmukh (Deshmukh et al., 2015). Interactions can be probed via measurements of interfacial rheology (Mendoza et al., 2014), (Cohin et al., 2013), (Deshmukh et al., 2015); (Murphy et al., 2016), (Maldonado-Valderrama et al., 2017), (Maestro et al., 2018a). However, one also needs to recognize that in real foods microgel stabilizers will probably have to compete with a range of other surface active materials, e.g., non-microgel proteins (Chevallier et al., 2019), lipids, surfactants (Zhao et al., 2018) for the interface. These will generally adsorb more quickly and pack more efficiently at the interface due to their smaller size, whilst they may also adsorb to the surface of the microgels themselves and so alter their surface activity. (Mendoza et al., 2014) have demonstrated the importance of surfactant adsorption to, and competition with, hard particle monolayers. Classic Pickering stabilizers do not lower the experimentally measured interfacial tension until high coverage – microgel particles that do (Atta and Ismail, 2013) at apparently low coverage may also be contaminated with lower molecular weight surface active species used in their synthesis and/or formation. An additional complication with microgels is the possibility of such species absorbing *into* the microgels via the pores at the surface. Possibly this could be used as another way of enhancing or ameliorating the changes in microgel surface activity as function of the composition of the bulk phases, whilst it also obviously lends itself to design of encapsulation and release of other food components at interface (Chen et al., 2017a, Alvarez-Acevedo et al., 2019, Gu et al., 2019).

5. Examples of microgels as interfacial stabilizers in food systems

In this final section we highlight a few specific food systems that illustrate some of the above general points, also discussed recently elsewhere (Murray, 2019). Since most ‘natural’ biopolymers are more compatible with water than oil, most microgel stabilizers are suitable, or specifically designed, to stabilize oil-in-water (O/W) emulsions or foams. Thus, O/W emulsions have shown to be effectively stabilized by a range of biopolymer-based microgels, but particularly proteins. Araiza Calahorra and co-workers have recently shown (Araiza-Calahorra et al., 2018) that O/W emulsions stabilized by very small (ca. 160 nm diameter) microgels based on whey protein were efficiently able to protect curcumin release from the oil droplets, presumably due to the very close packing and high viscoelasticity of the adsorbed particle layer. Starch based microgels (100 - 300 nm) have been used to stabilize emulsions and it has been claimed that they lower the interfacial tension, (Pei et al., 2017) though this again raises the question of contamination with lower molecular weight surface active species, for example bearing the octenyl succinate group often used to make starch surface active. Starch microgels (5 – 50 μm) filled with submicron oil droplets appear to have droplets within and at the surface of the microgels (Torres et al., 2019, Torres et al., 2018), so that emulsion filling may be another way of modifying the surface activity (and lubrication properties) of these starch-based or any other microgels.

There seems to be less work on foams, i.e., A/W systems, for no obvious reasons, since the majority of the characterization of microgel behaviour is at A-W interfaces. However, some of the microgels developed have been demonstrated as good foaming agents – in aqueous (Lazidis et al., 2016); (Ellis et al., 2019), (Matsumiya and Murray, 2016), (Murphy et al., 2016) (Rayner, 2015) or non-aqueous media (Qiu et al., 2018).

There seems to be some evidence that adsorbed microgel layers can confer increased resistance to enzymatic digestion of underlying materials (Sarkar et al., 2018, Sarkar et al., 2016, Sarkar et al., 2019), although the effects of enzyme adsorption to microgels at the interface and/or excess microgels in the bulk needs to be separated from the diffusive barrier properties of the adsorbed microgel layer. Similarly, encapsulation of emulsion droplets with microgels can confer some protection against flocculation and coalescence induced by gastric conditions (Torres et al., 2019).

Water-in-water (W/W) emulsions are slightly more exotic, arising mainly where biopolymer solutions phase separate into discrete microscopic regions far richer in one component than the other (Esquena, 2016), (Nicolai and Murray, 2017) (Dickinson, 2019) and all sorts of particles that would prefer not to be in at least one of the aqueous phases can end up concentrated at the W/W interface, preventing further growth of the phase regions via fusion or migration of components between them (Nguyen et al., 2015, Gonzalez-Jordan et al., 2016, de Freitas et al., 2016, Khemissi et al., 2018, Murray and Phisarnchananan, 2016).

6. Conclusions

The behaviour of microgel particles at interfaces is a fast moving and dynamic topic, of interest to both experimentally- and theoretically-based polymer scientists. Microgels offer distinct advantages in being able to design steric stabilizers of fluid-fluid dispersions that are very effective, whilst at the same time building in added functionality. These additions can include switching the surface activity through simple and reversible physical conditions, such as temperature and pH, whilst also incorporating controlled release from, or uptake into, the microgels simultaneously. The challenge to food scientists is to match these possibilities using food grade materials only, but the wide range of natural biopolymers available, plus the work that has already started, promises significant advances to come.

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