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Pickering emulsions in foods - opportunities and limitations

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Abstract

In order to critically discuss the potential of Pickering-type emulsions in food applications this review provides the theoretical background of the stabilizing mechanisms, the resulting requirements for particles to stabilize these systems and the limitations resulting from these fundamental considerations. Food grade particle systems investigated in the past are presented. It becomes obvious that with a proper choice of a particle, oil-in-water as well as water-in-oil emulsions can be achieved. For highly viscous products, products with a high internal phase volume and foams Pickering particles offer alternatives to commonly used surfactants. Pickering emulsions might be able to offer new approaches for fat reduction as well as encapsulation and sustained release of active ingredients. Nevertheless, a major part of successful systems have been achieved with silica or modified particles, which is not in line with the consumer demand for clean label, natural systems or not even food grade. However, the intriguing possibilities motivate and justify future research on the identification of new suitable ingredients, improvement of existing formulations and identification of new fields of application.

Keywords

Pickering emulsions, food, particles, stability

Subject classification codes: include these here if the journal requires them

Introduction

Emulsions generally consist of small spherical droplets of one liquid dispersed in another immiscible liquid stabilized through a surface active compound. These systems are thermodynamically unstable and tend to breakdown over time through aggregation and coalescence of the dispersed phase (McClements 2012). Other limitations inherent to conventional emulsions include limited stability to pH, salt, heating, dehydration, freezing and chilling (Guzey et al. 2006).

Pickering emulsions date back to 1903 when Ramsden first discovered the stabilizing effect of particles in emulsions and bubbles (Ramsden, 1903). Named after Pickering, who found similar results a few years later (Pickering 1907) it took a while before scientists regained interest in particles at interfaces (Chevalier et al. 2013). They came into focus when researchers tried to overcome the limitations of conventional emulsions and extensive research was performed during the past ten years (Binks & Horozov 2006; Leal-Calderon & Schmitt, 2008). Main advantage of particle-stabilized systems is their superior stability against coalescence (Frelichowska et al. 2009). Another intriguing idea behind these systems is their surfactant free character (Leal-Calderon & Schmitt, 2008). Surfactants known to be environmentally problematic (Braisch et al. 2009) or showing adverse effects (Chevalier et al. 2013) can be replaced, which is highly relevant for medical and skincare applications (Sadeghpour et al. 2013). With respect to food applications, surfactant-free formulations meet the demand associated with the clean label trend to create environmentally friendly solutions and a commercial need to make food labels 'green' (Green et al. 2013; Kalashnikova et al. 2011). Two review articles have recently been published on Pickering emulsions in foods, which either focus on the physical chemistry of Pickering emulsions or on food-grade particles with a potential to serve as Pickering particle (Dickinson 2012, Tavernier et al. 2016). We feel that there is a need to combine these approaches and thus focus on a critical discussion of the possibilities and limitations of the usage of Pickering particles for the food industry. To get a better understanding the physics behind Pickering and the mechanisms of stabilization are discussed in detail. Based on these considerations the influence of other surfactants in particles stabilized systems is outlined, since food systems are usually complex systems and particles and surfactants may coexist (Gosh & Rousseau 2011; Dickinson 2013). Important recent developments in food grade Pickering particles, not covered by the literature cited, have been included like the recent discussion of hydrophobins. Food-grade particles are screened for their potential for Pickering stabilization and discussed with respect to possible applications for the food industry.

Stabilizing mechanisms in Pickering emulsions

Particles are able to stabilize emulsions by providing a physical barrier to droplet coalescence (Tambe & Sharma 1994b). If the particles are neither soluble in water nor in oil they will accumulate at the interface. Depending on the wettability of the particles they either immerse more into one phase than into the other (Binks 2002; Aveyard et al. 2003; Dickinson 2012b). The Young equation, found in Eq. 1, for the determination of the contact angle θ between the three phases describes the situation:

$$\cos \theta = (\gamma_{p/o} - \gamma_{p/w}) / \gamma_{o/w} \quad (1)$$

where $\gamma_{p/o}$ is the particle-oil interfacial tension, $\gamma_{p/w}$ is the particle-water interfacial tension and $\gamma_{o/w}$ is the oil-water interfacial tension (Owens 1969; Binks & Clint 2002). At a contact angle of 90° a particle is immersed in equal shares into each phase as demonstrated in Fig. 1. If the particle is more hydrophilic the particle is predominantly wetted by the aqueous phase and the contact angle is below 90° (Binks 2002; Aveyard 2003; Hunter et al. 2008; Leal-Calderon & Schmitt, 2008). Because of the large contact area of particles with water the interface will get a curvature towards the oil phase, which means that rather an oil-in-water emulsion will be formed (Binks 2002; Binks & Clint, 2002). If the particle is more lipophilic the immersion preferentially occurs into the oil phase and the interface bends towards the aqueous phase, which will result in a water-in-oil emulsion. Once attached to the interface, the energy needed to remove a particle is given by the free energy of desorption (ΔG_D):

$$\Delta G_D = \pi r^2 * \gamma_{o/w} * (1 - \cos \theta)^2 \quad (2)$$

with r being the radius of the Pickering particle. From equation 2 it can be derived that the most important factor is particle size as $\Delta G_D \sim r^2$. With increasing particle size, the binding energy increases. Nevertheless even for nano-sized particles ($r \sim 5 - 10$ nm) the free energy of desorption ΔG_D is well above 10 kT, with k being the Boltzmann's constant and T the absolute temperature, and particle absorption can be considered irreversible (Binks 2002; Leal-Calderon & Schmitt 2008; Dickinson 2010; Sadeghpour et al. 2013). Because of the high binding energy of the particles at the interface emulsions with large droplet size can be stabilized against coalescence. Pickering emulsions with an oil drop diameter of 100 μm or even larger are reported to be stable against coalescence for several months (Timgren, 2013; Li et al., 2013; Binks & Lumsdon 2000).

The above explained mechanism mainly governs Pickering stabilization, but other effects add to the stabilization as well. Lopetinsky et al. (2006) recapitulates possible configurations of particles at solids-stabilized interfaces. As can be seen in Figure 2(a) one possibility is the complete coverage of the droplet surface with particles. In this case a bilayer of particles prevents coalescence of the droplets upon collision. The stabilizing effects are depicted in Figure 2 (i) -- (iv) with (i) and (ii) both being sterical and (iii) and (iv) describing effects based on thin film properties.

Fig. 2(i) depicts suppression of coalescence as a result of the balance between the gain in free energy upon desorption of particles and the reduction of free energy through shrinkage of the surface area upon coalescence. In case two droplets show coalescence the interfacial area decreases. This implies that particles need to be removed from the interface. The free energy of desorption is far greater than the thermal energy released upon reduction of the interface. This is an important reason why particles represent such a strong barrier against coalescence. The mechanism was very well demonstrated in experiments of pending drops. Visual observation of inflated and deflated pending silicone oil drops covered with hydrophobized silica revealed the virtually irreversible particle attachment. No particles

were released but the interface crumpled together with contraction of the drop volume (Asekomhe et al.; 2005). Xu et al. (2005) obtained similar results for a sessile water drop covered with polystyrene particles against decane.

Fig 2(ii) depicts the particle strength of aggregation preventing lateral displacement of particles at the interface. The force to laterally displace a particle along the interface is much smaller than to remove it from the interface and is strongly dependent from particle concentration (Tambe & Sharma, 1995). It was found that loosely packed particles provide little resistance to lateral displacement, which may result in emulsions susceptible to shear induced coalescence (Stancik et al. 2003; Whitby et al. 2011). Another stabilizing mechanism is the capillary pressure of the thin film of continuous phase between particles shown in Fig 2(iii). Since the force to displace the particles from the interface is too high, particles will approach and contact each other when droplets collide due to Brownian motion. A thin film of continuous phase will be held between the particles pores. The thin film is stable as long as the pressure inside the film does not exceed the maximum capillary pressure. This only applies under the assumption of complete particle coverage. Another point not everyone aware of is contact angle hysteresis (Yan & Masliyah 1996). This is the difference between the contact angle formed by a liquid advancing, ϑ_a , and receding, ϑ_r , over a solid surface (i.e. $\vartheta_h = \vartheta_a - \vartheta_r$). Since the capillary pressure is dependent on the contact angle the pressure needed for thin film rupture changes with different contact angles. Depending on the type of liquids and particles these differences determine which type of emulsion will be formed. This hysteresis is caused by several phenomena including surface roughness, surface chemical heterogeneity and adsorption of impurities from the liquid phases (Lopetinsky et al. 2006). Contact angle hysteresis might be the driving factor for those cases where the mixing protocol, and accordingly initial particle location was the driving factor for the generated emulsion type.

Fig 2(iv) represents the rheological properties of the interface influencing thin film drainage. Tambe & Sharma (1994a) found, that the rheological properties of the interface change with increasing particle concentration. With increasing particle concentration film drainage is not only influenced by hydrodynamic (viscous) effects but more and more by interparticle interactions (elastic effects). This leads to an interface with viscoelastic properties, which positively affects film drainage, coalescence and steric hindrance. This again is only valid for dense particle layers.

Other stable interfaces with lower particle occupation were observed and are depicted in Fig 2b-d. A typical phenomenon reported is bridging as demonstrated in Figure 2(b) where a single particle layer stabilizes the interface between two droplets. Ashby et al. (2004), Stancik & Fuller (2004), Stancik et al. (2004), Fuller et al. (2006) and Xu et al. (2007) presented images of a water drop covered completely by polystyrene particles pendant in decane approaching a planar decane-water interface. The two liquid surfaces were virtually irreversibly bridged together by a particle monolayer. The pendant drop could not be detached without breaking it up and in doing so forming a small particle stabilized water droplet which resided at the interface. Horozov et al. (2005) suggested that bridging is a bilayer to monolayer transition, which occurs when the capillary pressure exceeds the strength to

withstand lateral movement at the interface. But French et al. (2012) came to the conclusion that bridging mainly depends on the factor whether there are enough particles to cover the created surface. This is also supported by Bon & Colver (2007). The degree of bridging increased with increasing shear rate (smaller oil droplets, more surface to cover) and decreased with increasing particle volume fraction. Lee et al. (2012) were able to form a gel-like emulsion solely stabilized by bridged monolayers of silica microspheres demonstrating that bridging does not impair stability.

Figure 2(c) shows the formation of a 2D network of particles on the droplet surface. The steric hindrance is sufficient to stabilize an emulsion if the strength of aggregation of the particles prevents displacement at the interface and the energy of adsorption prevents removal from the interface. Alternatively, particle cluster formation at the interface may occur as depicted in Figure 2(d). Electrostatic interactions and steric hindrance are mainly responsible but are not fully understood yet (Velev et al. 1996). Aveyard et al. (2000) observed clustering of polystyrene spheres upon addition of anionic, cationic and non-ionic surfactants. The authors conclude that neutralization of charge cannot cause the effect and give the change in interfacial tension as reason for cluster formation.

Last but not least 3-D network formation (Figure 2(e)) extending through the continuous phase was observed improving stability by preventing droplet to droplet contact (Torres et al. 2007; Chen et al. 2011; Juárez & Whitby 2012; Lee et al. 2012; Nesterenko et al. 2014; Fuma et al. 2015). If particle charge allows aggregation, this formation is mainly driven by particle concentration. In such cases usually a dense layer of particles at the interface exists stabilizing through above explained mechanisms (i)-(iv). Excess particles provide additional stabilization by preventing contact between droplets and increasing viscosity of the continuous phase.

Factors influencing formation and stability of Pickering emulsions

From the mechanisms outlined above the factors influencing the formation and stability can be derived. The majority of studies have been performed using silica particles and results of these studies can be used to derive a summary of factors affecting the performance of a Pickering system. Formation of particle stabilized emulsions depends on the particle wettability, -concentration, -size, on the packing density and shape of particles, on the pH of the aqueous phase and presence of additives (Tambe & Sharma 1993).

Suitable particle wettability as a requirement for successful Pickering stabilization is already described above. Different approaches have been described to modify the wettability to generate particles with the defined properties. For example mild drying changed the wettability of silica particles (White et al. 2011). However, the majority of work has been done through combination of particles with other surfactants, which will be discussed in more detail in another chapter.

Another pre-requisite, in order to form a layer around a droplet, the particles need to be smaller than the oil droplets. To form a stable emulsion the particles need to be at least one magnitude smaller

than the droplets. Thus, the particle size determines the minimum oil droplet diameter. It is well demonstrated that smaller oil drops can be stabilized by smaller primary particle size. Köhler et al. (2010) prepared an emulsion with 3% hydrophilic silica particles and 20% corn oil. The focus was on primary particle size and homogenization. Non-creaming emulsions from 12 nm sized particles with resulting droplet sizes of $90.3 \sim 10 \mu\text{m}$ were produced compared to $\sim 100 \mu\text{m}$ with 200 nm sized particles.

Particle concentration affects the particle packing at the interface, which is crucial for emulsion stabilization. Juárez & Whitby (2012) defined a minimum particle concentration needed to prevent Ostwald ripening, if partly water soluble substances are in the oil phase. Binks & Whitby (2004) demonstrated that the particle concentration also influences the average drop diameter in the emulsion. With increasing particle concentration emulsion droplet size decreased. Frelichowska et al. (2010) found a similar correlation and concluded that for predicting success in emulsification the particle to oil ratio is more useful than only particle concentration. The interfacial stabilization also depends on the density of packing of the adsorbed layers of nano- or microparticles (Capron & Cathala 2013). As outlined above most scenarios assume ideal packing of the particles. For complete surface coverage, the packing of the colloidal particles on the surface would have perfect hexagonal symmetry. Topological constraints imposed by the curved surface, however, require a minimum of 12 five-fold disclinations, like the pentagons on a soccer ball (Bowick et al. 2005; Dinsmore et al. 2005). These assumptions apply for perfectly spherical particles. Packing density is therefore dependent on particle shape. The maximum possible particle density decreases with decreasing aspect ratio of the particles. However, successful stabilization with particles other than spherical particles is possible. E.g. Alargova et al. (2004) and Tzoumaki et al. (2011) demonstrated Pickering stabilization with rod-like particles.

While the functionality of surfactant stabilized emulsions heavily depends on the ability of the surfactant to reduce the interfacial tension, this is not the case for solid particles (Lo-petinsky et al. 2006). Even though Zartgartlebi et al. 2013 reported that silanized silica particle reduce the interfacial tension of kerosene and water to half its original value, the majority of reports document no or only little interfacial tension reduction for particles at the oil-water interfaces (Brian 1987; Aveyard et al. 2000b; Vignati et al. 2003; Wang et al. 2004; Gouchi Eskandar 2007; Ravera et al. 2008; Whitby et al. 2008; Drelich et al. 2010 and Hu et al. 2015). Perino et al. 2013 even report higher interfacial tension. Analytical methods used need to be considered in this context, since particles show sedimentation and thus several techniques are not reliable like e.g. the pendant drop technique, where particle sedimentation occurs.

The influence of pH and ions on Pickering stabilization is correlated with the conductivity of the continuous phase and therefore particle charge and state of aggregation (Binks & Whitby 2005). Whitby et al. (2012) demonstrated the influence of salt concentration and accordingly zeta potential on the stabilization of Pickering emulsions. With decreasing zeta potential, the repulsive forces decrease, which allows the particles to mildly aggregate to form a dense layer around the oil drops (Reynaert et al.

2006). Flocculation is commonly found at a zeta potential of approximately zero (iso electric point) (Köhler, 2010).

It was shown that silica is able to stabilize emulsions best when it is partly hydrophobized (Binks & Lumsdon 2000; Persson et al. 2014). Emulsions with 1.5% Aerosil R816, a hydrophobized silica, and 30% dodecane were reported to be stable over several months even though the Sauter mean diameter was 25 μm (Whitby et al., 2012). Flocculation may transform the Pickering particles into larger aggregates thereby reducing their ability to reside at the oil-water interface (Binks and Lumsdon, 1999). In contrast, deflocculation may disrupt the network of particles and will thus reduce the energy required to laterally displace particles from the drop-drop contact region (Tambe & Sharma 1994b). These considerations hold true for particles with low zeta potential or no charge. As mentioned above they form closely packed structures with the ability to stabilize emulsions. In addition, Nikolaides et al. describe attractive forces between like-charged particles at interfaces as the deformation causes capillary forces that attract neighboring particles to each other (Nikolaides et al., 2002).

Even though many researchers emphasize the superior stability of Pickering systems, in most cases this only refers to droplet coalescence. However, a system stable to coalescence is not necessarily stable against creaming or sedimentation. Creaming is tolerated in some applications as unavoidable and the height of the cream layer is a characteristic parameter, which is used for comparing emulsion stability (Frith et al. 2008; Braisch et al. 2009; Morishita et al. 2009; French et al. 2012; Lee et al. 2014). However, creaming or sedimentation is in general not acceptable for a food product. Stability issues may also arise from a change of the composition of the surrounding medium. Frequently, food compounds are produced, which are incorporated by another manufacturer in specific foods. One example is dilution of aroma concentrates or clouding agents in non-alcoholic beverages. The particle interactions change upon dilution because the surrounding of the droplets change (Mishchuk 2004). So far, no publication focused on the dilution of Pickering emulsions. But several authors (Binks & Lumsdon (2001), Köhler et al. (2010), Varka et al. (2010) and Arditty et al. (2005)) reported aggregation or flocculation when diluting samples for oil droplet size analysis by laser diffraction. Possible applications must be reviewed carefully considering stability during all steps of processing and in all dimensions. To improve stability, one may combine particles with surfactants (Tambe, Paulis & Sharma 1995) which will be discussed in the following chapter.

Surfactants as co-stabilizers

The primary role of co-stabilizers is to control the wettability of the particles towards a 90° contact angle for maximum particle adsorption (Midmore 1999; Mendoza et al. 2014). Small surfactants are also supposed to reduce the initial interfacial tension for better droplet breakup upon homogenization (Pichot et al. 2009; French et al. 2015). In the case of hydrophilic silica it was demonstrated, that a cationic surfactant absorbs to the particle surface and renders them more hydrophobic. Resulting oil in water emulsions were most stable when particles had little to no charge and were most flocculated (Midmore 1998; Binks & Whitby 2005; Ravera et al. 2006; Lan et al. 2007;

Binks & Rodrigues 2007; Sugita et al. 2008; Limage et al. 2010). According to this concept, the performance of positively charged silica particles could be optimized by addition of anionic surfactant (Binks & Rodrigues 2007b; Whitby 2009) or non-ionic surfactant (Nesterenko et al. 2014). The positive stabilization effect is usually linked to the surfactant concentration (Binks & Rodrigues 2007a; Santini et al. 2014). Above a critical surfactant concentration desorption of particles from the interface may be observed (Lan et al. 2015).

A question linked to the combined use of particles and surfactants is whether they compete at the interface (Drelich et al. 2010). In this context it is noteworthy that special attention should be given to the mixing protocol. Binks & Desforges (2007) highlight the difference whether particles are added to a surfactant stabilized emulsion, surfactant is added to a particle stabilized emulsion or both are added simultaneously and conclude that only the latter approach is successful.

Hu et al. (2015) demonstrated with confocal laser scanning micrographs of fluorescent cellulose nanocrystals that addition of a cationic surfactant before homogenization prevents surface occupation by particles with increasing surfactant concentration. Drelich et al. (2010) for example observed a slow destabilization of an initially stable particle stabilized emulsion upon addition of surfactant. Whitby et al. (2009) prepared stable oil-in-water emulsions with partially hydrophobized silica and diluted them into sodium dodecyl sulfate solutions. Above the critical micelle concentration the emulsions creamed and flocculated rapidly indicating that the surfactant displaces particles from the interface. Pichot et al. (2010) found lipophilic silica removed from the interface by polysorbate with increasing concentration whereas this was not the case for lecithin. Guzman et al. (2012) on the other hand found palmitic acid removed from the interface because of adsorption on the silica particle surface. Gouchi Eskandar et al. (2007) emphasize that stability is governed by initial particle location for emulsions composed of hydrophilic silica and lecithin or oleylamine as co-surfactant. Coalescence was greatly reduced when silica was incorporated through the oil phase. It becomes obvious that co-stabilized systems are as well strongly influenced if not driven by the mixing protocol.

This chapter highlights the importance of particle charge for successful stabilization. Emulsions usually were most stable around zero charge. On one hand, by using a co-surfactant the surfactant free character is lost, which was one of the drivers for the food industry. On the other hand this is a suitable strategy to bring particles to the interface and tailor desirable properties. The surfactant level in such systems would still be greatly reduced.

Food grade approaches

As becomes obvious from the previous chapter, extensive work has been done for emulsions stabilized by silica particles. As silica is only approved as anti-caking additive (E551) other materials are needed for the food industry. In the food industry many products are emulsion based (Guzey et al. 2006; Atares et al. 2012). As mentioned above, the surfactant-free character of Pickering emulsions is very intriguing, since the food industry is very interested in food-grade approaches for clean label products

(Green et al. 2013). Consequently, extensive research has been done to investigate the possibilities of food grade approaches to Pickering emulsions. Apart from specific individual studies on flavonoids, phytosterols, lactoferrin, shellac, cellulose or chitin nanocrystals (Campbell et al. 2008; Habibi et al. 2010; Kargar et al. 2012; Atares et al. 2012; Dhar et al.; 2012; Tzoumaki et al. 2011; Luo et al. 2011, 2012; Zoppe et al. 2012; Shimoni et al. 2013; Capron & Cathala 2013; Liu et al. 2014; Salas et al. 2014),,, main focus in the last decade was to derive stabilizing particles from one of the three major food constituents protein, starch or fat. The latter are reviewed in more detail below.

Protein

Proteins are composed of amino acids with different side chains and therefore exhibit an amphiphilic character (Hoffmann & Reger 2014). Particularly, dairy and soy proteins are well known for their emulsifying properties (Dickinson & Parkinson 2004). Proteins aggregates dissociate and unfold upon adsorption at an interface, (Gao et al. 2013). Furthermore the molecular structure is sensitive to heat and pH (Leal-Calderon et al. 2007). This is why Dickinson (2012a) stated, that proteins per se cannot be considered typical Pickering particles. As a consequence researchers tried to strengthen the structure of proteins for example by cross-linking (Dhayal et al. 2014; Wu et al. 2015) or heat treatment (Timgren et al. 2013) to inhibit unfolding at the interface. De Folter et al. (2012) prepared emulsions with zein, an insoluble corn protein with high hydrophobic acid content. Gao et al. (2014) prepared zein particles by ultrasonification with stearic acid, both considering zein as Pickering particles. However, either the emulsions were only stable under very defined pH conditions, which limits their usage (De Folter et al. 2012) or stability was mainly achieved by gel formation of excess protein in the continuous phase (Gao et al. 2014). Bressy et al. (2003) come to the conclusion that sodium caseinate forms one soft elastic shells around the stabilized oil droplets rather than single particles. All of these considerations put the Pickering character of proteins and their suitability for emulsion stabilization into question. Finally, another limiting factor is that protein stabilized droplets may behave as sticky droplets (Hoffmann & Reger, 2014). This implies that droplets, even though they may not show coalescence, aggregate and therefore show creaming or sedimentation. Consequently only emulsions with very high internal phases (≥ 0.6) may be stabilized by some proteins, which is for example the case for soy protein aggregates (Liu et al. (2013).

Recently, extensive research focused on a newly discovered class of proteins: hydrophobins. Hydrophobins are relatively small proteins expressed by filamentous fungi. They consist of 100 ± 25 amino acids with a distinctive eight cysteine motif forming four disulfide bonds (Blijdenstein 2010). The characteristic disulfide bonds result in a tight core, which prevents hydrophobins from unfolding at the interface (Blijdenstein 2010) which is why they are traded as Pickering particles. Hydrophobins may adhere to any surface due to their amphiphilic character and therefore invert the hydrophobicity of this surface (Lumsdon et al. 2005; Sunde et al. 2008, Zampieri et al. 2010). In nature they serve as coatings around spores to facilitate their adhesion on surfaces or to colonize hosts (Grünbacher et al. 2014). On

one hand they prevent desiccation on the other hand they prevent air channels in fruiting bodies to get blocked by rain water (Wösten 2001).

The amphiphilic character makes them highly surface active and contributes to their self-assembling properties (Cheung 2012; Green et al. 2013). Depending on the concentration hydrophobins exist as mono-, di- or tetramers. They quickly adsorb to the interface where they form strong elastic and dynamic films (Wohlleben et al. 2010). Thus, hydrophobins are comparable to so-called Janus particles, which are compartmentalized colloids with two different sides of chemistry or polarity (Walther & Müller 2008). Hydrophobins may be classified into two groups based on differences in solubility and stability: class I and class II. Class I hydrophobins are poorly water soluble, while class II hydrophobins show good solubility in an aqueous environment. Class I hydrophobins resist 2% sodium dodecyl sulfate (SDS) at 100°C and can only be dissociated by trifluoroacetic acid, class II hydrophobins dissociate in 60% ethanol and 2% SDS (Vocht et al. 1998; Askolin 2006; Stanimirova et al. 2014). Class I hydrophobins lower the air/water surface tension from 72 mN/m to 24 mN/m at concentrations of 50 µg/L, making them the most surface-active molecules known (Wösten & Vocht 2000). Upon self-assembly at an interface they form a visible, light-reflecting membrane, which resists washes with water (Linder 2009; Wösten 2001; Zhang et al. 2011; Lienemann et al. 2015). This film solidifies over time and is irreversibly adsorbed (Alexandrov et al. 2012). On a microscopic scale a holey grid becomes visible which can be picked up as a discrete film (Wösten 2001). The stability of hydrophobin membranes and their particle like character may be demonstrated upon compression of the film where the compressed layer shows wrinkles (Blijdenstein 2010, Knoche & Kierfeld 2015). Because of their unique properties hydrophobins are investigated in the context of a wide range of possible applications. In medicine they are studied for their possibility to stabilize emulsions with fluoruous fluids, as fusion proteins to encourage the binding of human fibroblasts on implant surfaces and to prevent bacterial growth on catheter surfaces (Scholtmijer 2001; Milani et al. 2013). A similar approach is the usage in biosensor applications to immobilize molecules or enzymes on surfaces (Wang et al. 2010). The grid-like membrane may also be used for membrane ultrafiltration or for chiral separation (Oude Vrielink et al. 2015). Applications in the field of consumer and diversified products are eco-friendly dirt repellent, antifouling coatings for windows, cars and ships, eco-friendly surfactant for laundry detergents and heat protecting hair care products (Hektor & Scholtmijer 2005; Wohlleben et al. 2010). BASF patented hydrophobins as an additive to glue in bookbinding with improved flexibility (Baus et al. 2009).

Widely used in research is H Star protein B (HPB), which belongs to class I hydrophobins. It is soluble up to 5 g/100 mL at pH 7.54 and lowers the interfacial tension of the decane - water interface from 50 mN/m to 15 mN/m (Reger et al. 2011a). Reger et al. (2011a; 2011b; 2012a; 2012b) demonstrated that emulsions with HPB alone are not stable against creaming, if the phase volume of the dispersed phase is below 65%. Addition of bohemite or laponite clay allows to minimize the phase volume down to 30%. Furthermore, the authors verified a 3D-network and bridging between drops upon drying of the emulsion. The usage is therefore again limited to very viscous systems, which must not undergo dilution upon final preparation. Other researchers report extraordinary foam stability of so

called air-filled emulsions, even from just shaking the sample (Cox et al. 2009; Tchuenbou-Magaia et al. 2011; Blijdenstein et al. 2010; Basheva et al. 2011a). It could be shown that hydrophobins effectively stop disproportionation in foams (Blijdenstein et al. 2010). The use of hydrophobins as a foaming agent for aerated and aerated frozen food as fat replacer has been patented e.g. for ice cream, sorbets and low-fat whipping cream (Tchuenbou-Magaia et al. 2009; Cox et al. 2009; Baus et al. 2009; Aumaitre et al. 2009; Bot et al. 2013; Cox et al. 2014). Thus, on one hand hydrophobins offer new possibilities in aerated systems like milk shakes, mousses and creams, but on the other hand they have been identified as a major factor responsible for gushing in beer. As a consequence use of hydrophobins cannot be recommended for carbonated beverages (Khalesi et al 2012; Shokribousjein et al. 2015). From an industrial perspective, the rather long time-scale required for assembling at interfaces along with the partly low solubility of hydrophobins raises concerns with respect to processing of these proteins on a large scale (Tchuenbou-Magaia et al. 2009; Green et al. 2013). Furthermore the high affinity for surfaces taken together with their ability to form biofilms may cause hygienic problems (Rieder et al. 2011).

In summary it becomes obvious that proteins itself might not easily be utilized for Pickering stabilization. Their susceptibility towards pH and their tendency to unfold, makes structural modification necessary. The range of applications seems to be limited to systems with high internal phase volume and high viscosity, where particle aggregation is part of the physical stabilization or at least not disadvantageous. Hydrophobins exhibit the potential for a wider range of dispersed systems. However, future research should focus on challenges related to large scale industrial processing.

Starch

The use of starch granules as Pickering particles bears several advantages. Starch is considered as a natural ingredient, is abundant in nature, renewable, biodegradable, thus sustainable, and inexpensive (Timgren et al 2011; Dufresne 2014). Timgren et al. (2013) and Li et al. (2013) compared the functionality of starch granules from different botanical sources as Pickering particles. The authors reported that Quinoa starch exhibits the smallest granules with a volume weighted mean diameter of 2 μm . With particles of that size, oil droplets in emulsions could be stabilized at a mean oil droplet size of approximately 200 μm . Since native starch is not hydrophobic, attempts have been made to improve the wetting properties by partial hydrophobization with octenyl succinic anhydride (OSA) (Nilsson & Bergenst hl 2007; Rayner et al. 2012; Timgren et al. 2013; Miao et al. 2014). For commercially available OSA-starch this is an established procedure where esterification of depolymerized or hydrolyzed starch takes place under alkaline conditions (Bao et al. 2003). In this commercially available type of OSA-modified starch, due to depolymerisation and hydrolysis starch granules are disintegrated and the stabilisation is therefore not Pickering-type stabilization. For Pickering purposes only the surface of intact starch granules is modified. However, the processing may cause partial breakdown of the starch granule. With this modification the oil droplet size of the emulsions could be reduced from 320 μm to 27 μm (Marku et al. 2012).

Another approach to use starch as Pickering particle is based on the use of starch nanocrystals ranging from 10 -- 300 nm. Dispersions of starch nanocrystals were studied by Wei et al. (2013) and show sufficiently low zeta potential at low pH. Tan et al. (2012) created hydrophobized starch nanospheres by modification with acetic aldehyde and phthalic anhydride. Emulsions prepared using these nanospheres were only stable at a tricaprylin phase volume of 50% or higher (Tan et al. 2014). Song et al. (2014) prepared OSA-modified particles from rice starch and prepared emulsions with 16% - 75% soybean oil. Emulsions were stable against coalescence, but not against creaming even at very high phase volume (Song et al. 2015).

Several questions remain to be clarified to draw a final conclusion on the suitability of starch-based nanoparticles for food-grade Pickering applications. At first, depending on the process of modification it is not clear whether these particles are still food grade. On the other hand Yusoff et al. (2011) express concern whether OSA-modified starch nanocrystals can still be considered particles as the surface tension measurements for cryo-milled OSA-modified starches decreases to values typical for low molecular weight surfactants. The milling process has the same effect like a heating step and will lead to particle disintegration and increase amorphous structures (Belitz & Grosch 2001). Starch particles may disintegrate and gel at the interface as observed by Marefati et al. (2013) and Sjöo et al. (2015) who use this effect to improve freeze-thaw stability and barrier properties. All of these findings question, whether starch can be considered as Pickering particle and demonstrate that starch performed best when slightly hydrophobized. This is per se not a new approach and would not deliver a solution for the food industry to get more label friendly ingredients as OSA-starch needs to be labelled as modified starch E 1450 in Europe and is not permitted in other countries as for example India.

Fat

Rousseau extensively reviewed the role of fat crystals in food emulsions (Rousseau 2000; 2013). He concludes that fat crystals can either stabilize or destabilize an emulsion depending on the localization. Crystals in the continuous phase may adsorb to an interface and add to the stabilization. In contrast, crystals in the dispersed phase may protrude through the interface and lead to droplet aggregation. The first proof of successful Pickering stabilization with fat particles was demonstrated with tristearin by Lucassen-Reynders and van den Tempel in 1963 (Lucassen-Reynders & van den Tempel, 1963). It is well demonstrated that fat crystals partially or wholly stabilize oil continuous emulsions as for example butter, margarines and low fat spreads (Juriaanse & Heertje 1988; Bergenstahl & Aalander 1997; Rousseau & Gosh 2009; Gosh, Tran & Rousseau 2011). Lots of studies deal with the optimization of the crystallization or the effect other present emulsifiers impart on the stability of water-in-oil emulsions (Rousseau 2000; Coupland 2002; Gosh & Rousseau 2011; Douaire et al. 2014). Paunov et al. (2007) demonstrated that unmodified fat crystal particles of hardened rape seed oil were only able to stabilize water-in-oil emulsions. For oil-in-water emulsions a combination of carbonate particles coated with stearic acid was successful. This resembles the findings for starch particles which only gain the wanted properties via modifications.

Recently, there has been growing interest in creating so-called solid lipid particles for pharmaceutical applications (Svilenov & Tzachev 2014). These systems are usually fat-in-water dispersions prepared from high melting emulsifiers such as phospholipids. Aim is to create a dense solid structure through crystallization of the lipid phase starting from the interface. The resulting structure facilitates encapsulation and protection of lipophilic active ingredients and is thus also interesting for the food industry. Kurukij et al. (2013) demonstrated the successful preparation of emulsions stabilized by sodium stearyl lactylate (SSL) which has a melting point of 49°C. Via differential scanning calorimetry (DSC) it was demonstrated that at room temperature SSL was in solid state at the interface. Salminen et al. (2013) were able to produce dispersions stabilized by high melting phospholipids. A well-known low melting phospholipid is lecithin which needs to be declared as food additive. The same applies to SSL. Despite the promising results, there might be a challenge in finding a suitable food grade ingredient which will be label friendly. Another interesting fact is that upon crystallization fats usually undergo an increase in density due to the closer packing in the crystal lattice. This may positively affect the buoyancy of the oil phase and thus the stability of the emulsion against creaming. Since creaming is a very prominent issue, this makes fat particles intriguing candidates for particle stabilized emulsions.

It can be concluded that fat particles are prominent stabilizers in water-in-oil food emulsions. Recent results for solid lipid particles, makes fat particles interesting candidates as well for oil-in-water systems, especially under the presumption that they additionally can improve stability by increasing the density of the oil phase. Further research should focus on finding suitable and label-friendly solutions.

Concluding remarks on Pickering emulsions in food-related applications

As previously mentioned dispersed systems are very common among foodstuffs (Guzey et al. 2006). Products such as soft drinks, milk, coffee whitener, cream, whipped cream, ice cream, salad dressings, mayonnaise, soups, sauces, dips, butter and margarine are only few examples of emulsion-based systems in the food sector (McClements 1999; Guzey et al 2006; Atares et al. 2012). As a consequence, there are tremendous differences in physical structure and consumer-related requirements e.g. towards specific properties like texture, shelf life and so forth.

One of the most important factors for successful Pickering stabilization is minimization of the attractive forces between the particles to form a dense layer at the interface. These may be adjusted as could be demonstrated for starch nanocrystals (Murray et al. 2011; Gao et al. 2014; Hu et al. 2015) and silica particles (Midmore 1998; Binks & Desforges 2007; Gouchi Eskandar et al. 2007; Maas et al. 2010; Whitby et al. 2012; Sadeghpour et al. 2013; Santini et al. 2014) upon the addition of non-ionic surfactants and fatty acids like oleic or palmitic acid.

Lack of electrostatic repulsion inevitably leads to aggregation of the stabilized dispersed phase. Systems exhibit extraordinary stability towards coalescence, but creaming or sedimentation can only be avoided when a 3D network in the continuous phase is formed. Another important factor is the dependency of the stability from the phase volume. Only systems with high internal phase volume

(starting from 50%) can successfully be stabilized against creaming. Lagaly et al. (1997) pointed out that the network formation is linked to the phase volume. Typically focus on research of Pickering systems is the stability against coalescence whereas for a stable food application stability against coalescence and creaming must be guaranteed. The need for aggregation to yield stability is as well the limiting factor for the minimum phase volume. For a wide range of applications it is sensational to be able to stabilize high internal phase volumes by a small amount of particles. The same applies for paste like water-in-oil emulsions like confectionary creams with high viscosity.

High density of Pickering particles can help to adjust density differences between the phases and thus increase physical stability of the system. Binks & Lumsdon (2001) prepared emulsions, in which the dispersed oil phase showed sedimentation. Particle adsorption altered the overall density of the dispersed phase. Large density differences e.g. occur in non-alcoholic beverages. The continuous phase is high in sugar and shows a rather high density, while aroma oils have typically a low density especially citrus oils and need weighting agents for density adjustment.

Pickering particles may also be used to alter the optical properties of a dispersed system. Velev et al. (2000) stated that closely packed crystals display a number of potentially usable characteristics such as light diffraction. Due to closer packing of molecules in highly ordered structures and the birefringence effects caused by different spacing between the atoms, crystalline structures inhibit stronger light scattering properties than amorphous substances (McClements, 1999). As a consequence the optical properties of an emulsion are not only affected by the oil phase, but also by the composition of the interface. Particles may be used to adjust difference in the refractive index between dispersed and continuous phase. This effect is highly relevant for applications where turbidity is a desired property, like in beverage emulsions. Typical values for the refractive index of polysaccharides are about 1.46 (Kasárova et al. 2007), which is lower than the refractive index of most of the oil phases used for beverage emulsions. Because of their crystal structure fats should exhibit a higher refractive index than oil and might be a promising choice in this context. On the other hand one has to keep in mind that aggregation and network formation is detrimental for dilute systems like beverages with near water viscosity or intermediate products, which undergo further dilution before consumption. Since the initial particle structure will be destroyed during the process, those emulsions will be instable against creaming.

Superior stability of Pickering stabilized foams offers good opportunities for application and fat reduction in aerated creams, ice-cream, desserts and shakes. In own studies it was observed that emulsions immediately after preparation contain a high proportion of occluded air and therefore represent very fine foams. This foam stays stable for more than two weeks. In this state it appears that there is a single expanded network of particle stabilized bubbles and droplets as described by others (Juarez & Whitby 2012), which even measure a yield stress (Braisch et al. 2009; Chen et al. 2012). Upon mechanical agitation foam settles and emulsions did not show yield stress or any shear thinning behavior. Still the emulsions did not separate in visually detectable phases for several months. Highly

stable foams are desirable in a wide variety of applications, e.g. for milk froth of coffee drinks, milk shakes and ice cream. Very fine foams can probably add to the mouthfeel of fat reduced variety of whipping creams, spray cream, cream cheese, mayonnaise, ice cream, sauces, vegetarian spreads or meat paste. As mentioned above, first patents using hydrophobin to create fat reduced foods have been filed. Fat replacement may also be achieved through reduction of the oil load by using double emulsions. Matos et al. (2013) stabilized double emulsions with OSA-modified Quinoa starch granules and recommend this system for fat replacement or as vehicle for hydrophilic nutrients.

Encapsulation and release of lipophilic ingredients via Pickering emulsions has also been investigated. Tikekar et al. (2013) demonstrated sustained release of curcumin over an extended time period from silica stabilized emulsions. Kargar et al. (2011) and Zhao et al. (2015) prepared emulsions with enhanced oxidative barrier properties using silica and silica--polymer microparticles. Controlled release and improved encapsulation of lipophilic ingredients seem to be tunable, but to the best of the author's knowledge no food grade approaches have been published yet.

In summary, this review of food grade Pickering approaches demonstrates the possibilities and limitations of particle stabilization in the food sector. With a proper choice of a particle, oil-in-water as well as water-in-oil emulsions can be achieved. For highly viscous products, products with a high internal phase volume and foams Pickering particles offer alternatives to commonly used surfactants. Pickering emulsions might be able to offer new approaches for fat reduction as well as encapsulation and sustained release of active ingredients. Nevertheless, a major part of successful systems have been achieved with silica or modified particles, which is not in line with the consumer demand for clean label, natural systems or not even food grade. However, the intriguing possibilities motivate and justify future research on the identification of new suitable ingredients, improvement of existing formulations and identification of new fields of application.

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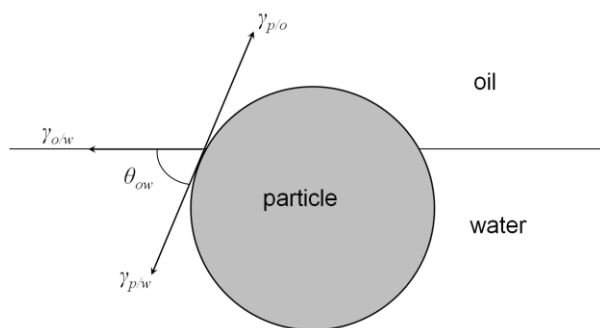


Figure 1: Schematic diagram of a spherical solid particle at an oil-water interface showing the various interfacial energies and the contact angle measured into the water phase with the particle-oil interfacial tension, the particle-water interfacial tension and the oil-water interfacial tension the oil-water contact angle θ_{ow} (adapted with permission from Binks, B. P.; Clint, J. H. (2002): Solid Wettability from Surface Energy Components. Relevance to Pickering Emulsions. In *Langmuir* 18 (4), pp. 1270--1273. Copyright 2002 American Chemical Society.).

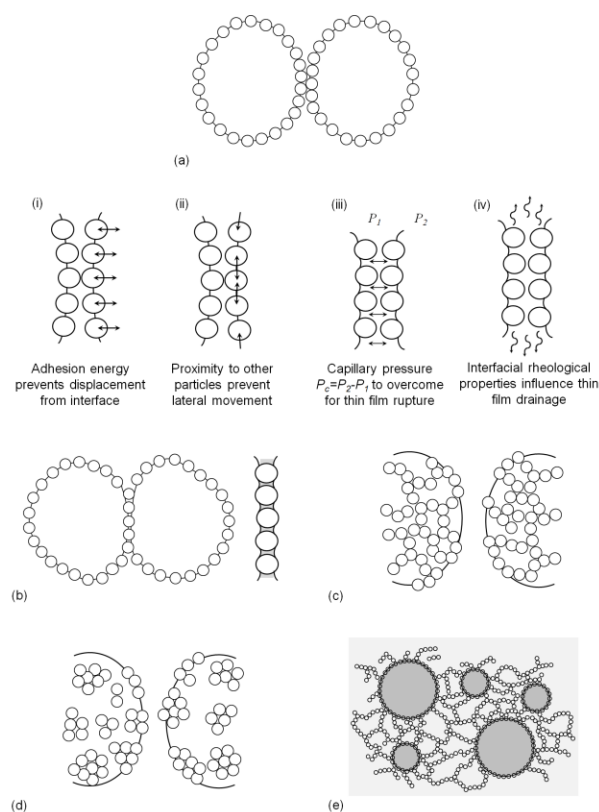


Figure 2: Possible configurations of particles in solids-stabilized emulsions, (a)–(e), and the underlying mechanisms responsible for stability (i)–(iv), (adapted with permission from Lopetinsky, Robert J.G.; Masliyah, Jacob H.; Xu, Zhenghe (2006): Solids-Stabilized Emulsions: A Review. In Bernard P. Binks, Tommy (edt) Horozov (Eds.): Colloidal Particles at Liquid Interfaces: Camebridge University Press, p.194.)