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Trends in structuring edible emulsions with Pickering fat crystals

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ABSTRACT

The pace of development of edible Pickering emulsions has recently soared, as interest in their potential for texture modification, calorie reduction and bioactive compound encapsulation and delivery has risen. In the broadest sense, Pickering emulsions are defined as those stabilized by interfacially-adsorbed solid particles that retard and ideally prevent emulsion coalescence and phase separation. Numerous fat-based species have been explored for their propensity to stabilize edible emulsions, including triglyceride and surfactant-based crystals and solid lipid nanoparticles. This review explores three classes of fat-based Pickering stabilizers, and proposes a microstructure-based nomenclature to delineate them: Type I (surfactant-mediated interfacial crystallization), Type II (interfacially-adsorbed nano- or microparticles) and Type III (shear-crystallized droplet encapsulation matrices). Far from simply reporting the latest findings on these modes of stabilization, challenges associated with these are also highlighted. Finally, though emphasis is placed on food emulsions, the fundamental precepts herein described are equally applicable to non-food multicomponent emulsion systems.

1. Introduction

The traditional definition of a Pickering emulsion dates from the early 1900s when Ramsden [1] and Pickering [2] first explored particle-stabilized emulsions. The term 'Pickering' is now loosely used to represent any colloidal species that acts as a steric (mechanical) barrier against droplet–droplet coalescence and phase separation in oil-in-water (O/W), water-in-oil emulsions (W/O) or multiple emulsions [3••,4•,5]. Within the past decade, Pickering emulsions have been increasingly 'trending', with interest in their attributes growing in fundamental physics (e.g., interactions between nanoparticles trapped at interfaces), new materials (e.g., liquid marbles, dry water, colloidosomes, etc.) and their potential for drugs and bioactive compound encapsulation and delivery.

Since the pioneering work of Lucassen-Reynders and van den Tempel on tristearin crystal-stabilized W/O emulsions in the 1960s [6••], there have been a number of advances in the stabilization of edible emulsions using fat-based species. In this light, this review explores three types of Pickering stabilization and proposes a nomenclature to delineate them (Fig. 1). Type I is the most conventional mode of stabilization reported in the fat science literature and usually involves the direct interfacial solidification of surfactant monolayers or multilayers (Fig. 1A). Such stabilization is usually manifested as white crystalline rings surrounding dispersed droplets in polarized light microscopy images [7]. More recently, surfactant-mediated triglyceride (TG) interfacial crystallization has been developed and also falls under this umbrella. Type II stabilization results from the presence of interfacially-adsorbed nano- or micro-scale particles at the interface (Fig. 1B) [8••]. Quite surprisingly, there has been comparatively little research performed on fat-based particles compared to other food-grade micro- or nanoparticles for emulsion stabilization. Finally, Type III Pickering emulsions consist of a crystalline layer much thicker than the corresponding droplet diameter (Fig. 1C). Such interfacial crystallization takes place under rotational shear within a micro-confined gap (<1 mm), as found in a commercially-available rheometer, for example [9].

Beyond exploring their formation and properties, challenges associated with each Pickering mode are addressed, namely: i) liquid-state intermolecular compatibility and its role in TG interfacial crystallization in Type I systems; ii) use of solid lipid nanoparticles for Type II Pickering emulsions and iii) mechanistic considerations in the formation of Type III systems. Finally, though centered on edible emulsions, the mechanisms discussed in this review are clearly translatable to many fields (cosmetics, pharmaceuticals, crude oil, etc.).

2. Type I Pickering stabilization

Type I Pickering stabilization most often results from the direct solidification of high-melting, oil-tending surfactants at the oil–water interface during the post-homogenization cooling of W/O emulsions. The resulting crystal shells usually consist of sintered mono- or multilayers with thicknesses in the nm to low μm range. This mode of crystallization is effectively used in many oil-continuous foods, for example, in tablespreads where interfacially-adsorbed crystals enrobe dispersed water droplets and play a key role in emulsion stability (Fig. 2) [10,11•,12•,13•]. This approach has also been recently explored in the development of cocoa butter W/O emulsions [14•].

Surfactants are usually responsible for this type of stabilization given their inherent surface activity. In this light, most of the findings elaborated

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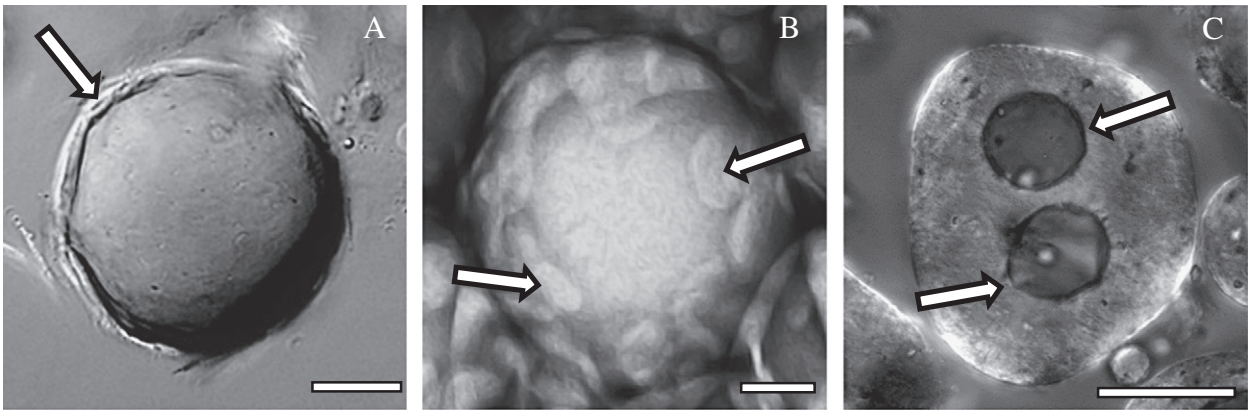

Fig. 1. Different types of Pickering stabilization in edible emulsions. (A) Type I: Polarized light micrograph of a water droplet surrounded by a GMS crystalline multilayer. Arrow shows interfacially-crystallized lipid layer <5 μm in thickness. Size bar = 10 μm. (B) Type II: Transmission electron micrograph of an oil nanodroplet partially covered by solid lipid nanoparticles (SLNs). Arrows show interfacially-adsorbed SLNs. Size bar = 50 nm. (C) Type III: Polarized light micrograph of water droplets surrounded by a hydrogenated canola fat crystalline shell following micro-confined shear crystallization. Arrows point to droplets englobed by a 10–20 μm thick shell. Size bar = 25 μm. Note different size bars.

in this section are based on oil-tending surfactants whose properties may be demarcated by their physical state at room temperature and their molecular size: the liquid-state monomer glycerol monoleate (GMO) and polymer polyglycerol polyricinoleate (PGPR) as well as the solid-state monomer glycerol monostearate (GMS). In contrast to surfactants, TGs demonstrate little surface activity as the relative contribution of the headgroup in most TGs to overall polarity is small, implying little possibility of interfacial adsorption. In this regard, Small [15] noted that lateral compression of TG Langmuir–Blodgett films on a water subphase via dilational rheology yielded a collapse pressure of ~12 mNm^{-1} implying rather weak anchoring to the aqueous phase whereas monoglycerides have been shown to adsorb much more strongly, e.g., GMS and GMO films collapse at ~50 and 40–46 mNm^{-1}, respectively [16].

A growing area of research is that of surface-templated crystallization where molecules adsorbed to the emulsion oil–water interface mediate crystallization, e.g., formation of β-hematin crystals (a detoxification by-product of malarial parasites) [17], encapsulation mechanisms in gas hydrate crystals [18] and W/O lipstick formulations [19•]. In foods, extensive knowledge gained in regard to O/W emulsions has provided clear evidence of heterogeneous nucleation via solid-state interfacial templating, as elegantly shown by the Sato and Ueno group [20].

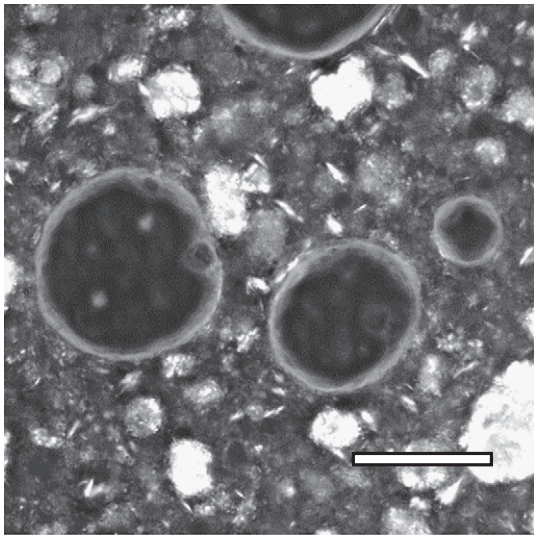

Fig. 2. Polarized light micrograph showing combined Pickering and network crystals in a model W/O emulsion consisting of vegetable oil, GMS and hydrogenated canola fat as the oil phase. The bright rings encircling the individual water droplets arise from interfacial GMS crystallization whereas their local surroundings consist of individual and aggregated hydrogenated canola fat crystals and spherulites. Size bar = 40 μm.

Recently, in an effort to create lower-fat chocolate, Norton and Fryer [14•] englobed W/O emulsion droplets with templated cocoa butter crystals thought to exist in form V (the desirable polymorph for proper chocolate sensory properties). These studies have highlighted the need for oil-soluble surfactants to initially form the W/O emulsions and interfacial crystals to stabilize them.

The importance and mechanism of surfactant interfacial crystallization in W/O emulsions are relatively well-understood. During homogenization, initially-isotropic bulk surfactants will adsorb and self-assemble at the oil–water interface where they will optimize their positional and orientational order with their polar ends (e.g., hydroxyl and/or carbonyl groups) grafted to the aqueous side of the interface and their hydrophobic groups exposed to the oil phase. In the presence of a suitable temperature drop, certain surfactants will undergo a liquid–solid phase transition thus resulting in a solid crystalline shell around dispersed droplets (Fig. 2). Such is the case for GMS which has liquid–solid phase transition temperature well-above that of GMO (48 vs. 7 °C) [21]. Thus, upon cooling GMS solidifies directly at the interface, which may then promote the heterogeneous nucleation and growth of TGs present in the continuous phase.

There is growing evidence that liquid-state surfactants can promote interfacial TG crystallization in W/O emulsions. For example, with GMO-based W/O emulsions, hydrogenated canola fat may nucleate and crystallize at the water droplet surface (Fig. 3A). As canola fat is considered surface-inactive, this suggests that GMO encourages interfacial fat crystallization thereby conferring a Pickering-like ability to TGs. By contrast, with PGPR mixed with solid fat, there is no evidence of interfacial crystallization (Fig. 3B). For polymeric surfactants such as PGPR, their true ordering at the interface still remains unknown. However, when adsorbed to the oil–water interface, the molecule likely adopts a 'spider-like' conformation, with its oxygen-containing groups embedded within the interface and the acyl moieties of the polyricinoleic acids exposed to the continuous oil phase [9]. Such a mechanism may explain its superb emulsification capacity and inability to interact with bulk phase TGs. Furthermore, in the temperature range where many foods are normally processed (e.g., margarine, confectionery), PGPR does not undergo a liquid–solid phase transition obviating the possibility of interfacial nucleation via solid-state templating. Finally, in mixed surfactant systems with both PGPR and GMO, an unusual feature arises with the appearance of clustered droplets stabilized by fat crystal spherulites (Fig. 3C). As these clusters only appear with combined surfactants, this suggests that sensible surfactant choice may be used to tailor the spatial distribution of droplets within fat-stabilized W/O emulsions.

Using GMO as an example, this author proposes the following process to explain how certain liquid-state surfactants may mediate