



Pickering stabilization of foams and emulsions with particles of biological origin



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ABSTRACT

The focus in the study of Pickering foams and emulsions has recently been shifting from using inorganic particles to adopting particles of biological origin for stabilization. This shift is motivated by the incompatibility of some inorganic particles for food and biomedical applications, as well as their poor sustainability. This review focuses on major developments in foams and emulsions stabilized by particles of biological origin from the last 5 years. Recent reports in the literature have demonstrated the ability of particles derived from cellulose, lignin, chitin, starch, proteins (soy, zein, ferritin), as well as hydrophobic cells to stabilize biphasic dispersions. We review the use of such nano- and micron-sized particles of biological origin for the stabilization of foams and emulsions, summarize the current knowledge of how such particles stabilize these dispersions, provide an outlook for future work to improve our understanding of bio-derived particle-stabilized foams and emulsions, and touch upon how these systems can be used to create novel materials.

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1. Introduction

Biphasic dispersions, such as foam and emulsion systems are thermodynamically metastable systems that over time tend to separate into the individual components of which they are composed. A foam can be defined as a gas-in-liquid dispersion, while an emulsion can be defined as a liquid-in-liquid dispersion; typically, the dispersed and continuous phases in foams and emulsions are immiscible. Amphiphilic molecules are traditionally used to prevent or delay phase separation and to reduce the energy of the air-liquid or liquid-liquid interfaces in these systems. In the past two decades, scientists have started examining the use of partially hydrophobic particles for the stabilization of foams and emulsions due to their ability to adsorb strongly at the air-liquid and liquid-liquid interfaces to sterically hinder coarsening, as well as to slow down drainage/syneresis by structuring in the continuous phase [1–3,4,5].

Much of the research into particle-stabilized (or "Pickering-Ramsden") systems until the past few years has been focused on using

inorganic particles such as silicas as a result of their well-defined shape, availability in different sizes and at narrow size distributions, as well as the chemical tunability of their surfaces [6,7]. While this work has revealed a great deal of information about the mechanisms by which particles stabilize foams and emulsions, and defined the conditions necessary for improved stability in Pickering systems, such inorganic particles are limited in their relevance to applications requiring biocompatibility and biodegradability. Thus, in the past few years, there has been a shift toward studying materials of biological origin for the stabilization of foam and emulsion systems with the goal of utilizing them in food and drug delivery applications [8–11].

Many biomacromolecules exhibit surface activity at air-liquid and liquid-liquid interfaces. The activity and solubility of these materials in water can be easily affected by changes in pH, temperature, ionic strength, and age [11,12,13,14]. While this susceptibility to environmental change may not be very attractive from the perspective of robust molecular stabilization of biphasic systems against variable environmental factors; it can be utilized as a favorable trait for the creation of tuneable biphasic dispersions [11,12,13,14]. However, not all biopolymeric materials are susceptible to changes in solution environment. For example, emulsions stabilized by fibrillated cellulose as well as native starch granules above a certain critical concentration tend to resist changes in pH, ionic strength, as well as increases in temperature [15,16,17]. Bio-derived particles may also improve the transdermal

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transport of emulsions for applications in topical drug delivery as well as prevent lipid oxidation in food grade emulsions [9,11*,18]. Enhanced transdermal transport of lipophilic drugs has also been previously demonstrated for Pickering systems stabilized by silica nanoparticles [19]. Table 1 summarizes examples in the literature pertaining to the use of biologically derived particles for the stabilization of foams and emulsions.

1.1. Prerequisites for Stabilization of Foams by Particles

The design of biologically derived stabilizers begins with analysis of the specific properties desired by these particles. Since the beginning of the 20th century, scientists have known about the ability of partially hydrophobic particles to impart greater stability onto foams and emulsions than molecular surfactant stabilizers [1,2]. Not all particles, however, serve as good stabilizers and in many cases their surfaces need to be modified to adsorb at fluid interfaces. Particles with specific surface properties can irreversibly adsorb at the air–liquid or liquid–liquid interface with high energy gain as described by the following equation [63,64]:

$$G = \gamma_{1S}A_{1S} + \gamma_{2S}A_{2S} + \gamma_{12}A_{12} \quad (1)$$

Here, G is the surface free energy for a particle adsorbed at an interface; γ_{1S} , γ_{2S} , and γ_{12} are the interfacial tensions between phase 1 and the particle, phase 2 and the particle, and immiscible phases 1 and 2, respectively; A_{1S} and A_{2S} the contact area between phase 1 and the adsorbed particle and phase 2 and the adsorbed particle; and, A_{12}

the contact area between the immiscible phases eliminated by the adsorption of the particle at the interface. This expression can be used to calculate the energy needed to remove a particle from the interface between two fluids. For a spherical particle, Eq. (1) can be expressed as [3*,14*]:

$$G = -\Delta E = \pi r^2 \gamma_{12} (1 - |\cos \theta_{12}|)^2 \quad (2)$$

where r is the radius of the particle, γ_{12} the interfacial tension between the immiscible phases, and θ_{12} the three phase contact angle. This expression for spheres asserts that the closer the contact angle of the particle at the interface to 90° and the larger the particle, the more energetically favorable the adsorption. Solving Eq. (2) for a $1 \mu\text{m}$ sphere adsorbed at an air–liquid interface ($\gamma_{12} = 72.8 \text{ mN/m}$) gives $E_s \sim 10^7 kT$ at $\theta \approx 90^\circ$, which is several orders of magnitude greater than the thermal energy kT . The particle cannot be displaced from the interface by random fluctuations and is adsorbed more or less irreversibly at the A/W or O/W interface. Although Eq. (2) states that the energy required to remove a particle from the interface between two fluids is highest when the particle is equally wetted by the two phases, experimental results have shown better dispersion stability for systems where slightly more than 50% of the stabilizing particle is situated in the continuous phase. This means $CA < 90^\circ$ for water-continuous dispersions and $CA > 90^\circ$ for oil or air continuous dispersions [3*,4,14*]. This discrepancy can be explained by accounting for the capillary pressure between two bubbles/droplets, which is not taken into consideration in Eq. (1) or (2) [3*]. Particles can stabilize biphasic systems not only by adsorbing and packing at the air–liquid or liquid–liquid interface, but

Table 1

Summary of literature reports on the utilization of particles from biopolymers and of biological origin for creation and stabilization of foams and emulsions.

Material	Surface Modification	Particle Shape	Particle Size Range (d = diameter, l = length, h = height)	Type of System (E = emulsion, F = foam)
Polysaccharides (Crystalline)				
Cellulose nanocrystals (bacterial) [20,21*,22*]; (cotton) [21*,22*,23,24]; (green algae) [22*]; (ramie fiber) [25*]	PNIPAm [25*]	Fiber-like [20,21*,22*,25]; rod/elongated [21*,22*,23]	3 nm < d < 20 nm; 50 nm < l < 4000 nm; 6 nm < h < 15 nm [21*,22*,23]	E [20,21*,22*,23,24,25*]
Microcrystalline cellulose			300 nm < d < 10 μm	E [10,26,27]
Chitin nanocrystals		Rod [18,28*]	(240 nm \times 18 nm) [18,28*]	E [18,28*,29*]
Starch (nanocrystals) [30,31]; (nanoplatelets) [32]		Polygonal [30,31]; parallelepiped [32]	(40 nm < d < 3 μm) [30,31]; (20 nm \times 30 nm \times 4 nm) [32]	E [30–32]
Polysaccharides (Semi-crystalline)				
Bacterial cellulose fibers [26,33]; cellulose (Kraft) [34]	Silylation and acetic acid esterification [33]	Fibrils [26,34]	100 nm < d < 40 μm ; l ~ μm –mm	E [26,33] F [34]
NFC/MFC [26,35*,36] (from mangosteen) [17*]	Silylated [36]	Fibrils	4 nm < d < 20 μm ; l ~ μm –mm	E [17*,26,36] F [35*]
Hydrophobic cellulose derivatives	HPMCP [14*,37]; MCE [38]; EC [39]	Elongated/ sheet [14*,37]; spherical [38,39]	55 nm < d < 30 μm	F [14*,37–39]
Chitosan		Irregularly shaped	50 nm < d < 307.8 nm	E [12,40*]
Starch	OSA [9,10,15*,41–43]; acetylated [44]	Sphere [44,45]; various [9,10,15*,16*,41,42]	120 nm < d < 52.1 μm	E [9,10,15*,16*,41–45]
Proteins				
Soy protein		Nanoparticle aggregates [11*]; wrinkled sphere [46*]	100 nm < d < 30 μm	E [11*,46*]
Lactoferrin (Lt); Lactoferrin-polysaccharide	Polysaccharide = alginate (Alg) and carrageenan (Car)		200 nm < d < 575 nm	E [47,48]
Zein			70 nm < d < 82 nm	E [49]
Ferritin	PNIPAAm [50,51], DMIAAm [50,51]	Spherical	d = 12 nm	E [50–53]
Bovine serum albumin (BSA)			14 nm \times 4 nm \times 14 nm	E [54]
Other				
Lignin (alkaline)		Spherical	d ~ 180 nm	E [13*,55]
Hydrophobic cells and bacteria		Rod/elongated	d ~ 400 nm; l ~ 2–3 μm	E [56*,57,58]
Spore particles	DVB [59]	Round	d ~ 30 μm	E [59,60*]
Virus particles (TYMV) [61*], (CPMV) [62]		Icosahedral	d = 30 nm	E [61*,62]

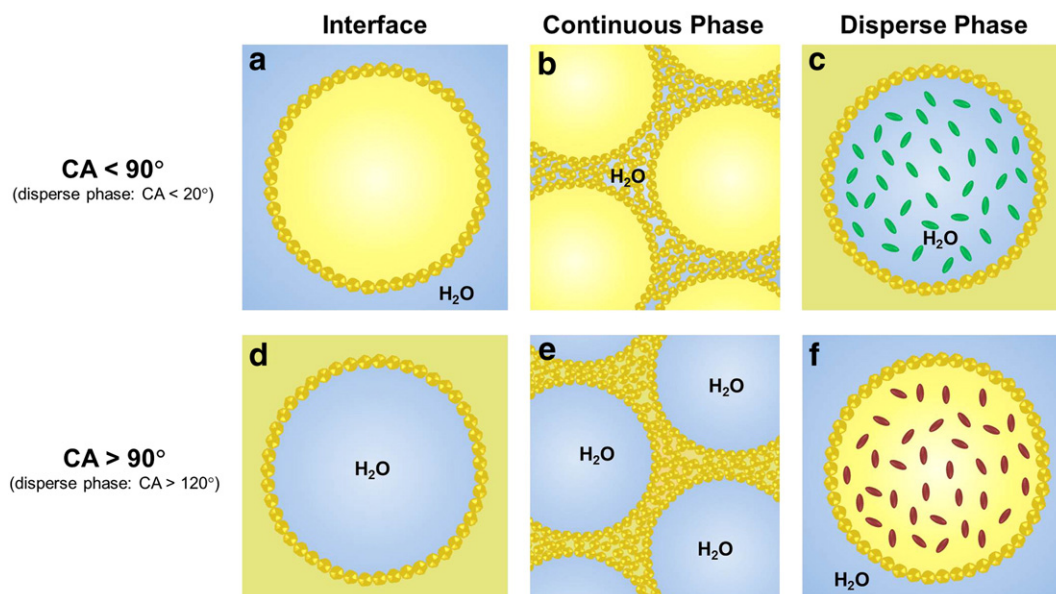


Fig. 1. Possible location and functionality of particles in foams and emulsions. (a, d) At the interface (function performed: structuring, stabilization, delivery); (b, e) in the continuous phase (function performed: structuring, stabilization); and (c, f) in the disperse phase (function performed: delivery). The second phase (not labeled “H₂O”) is the oil or air phase of the dispersion.

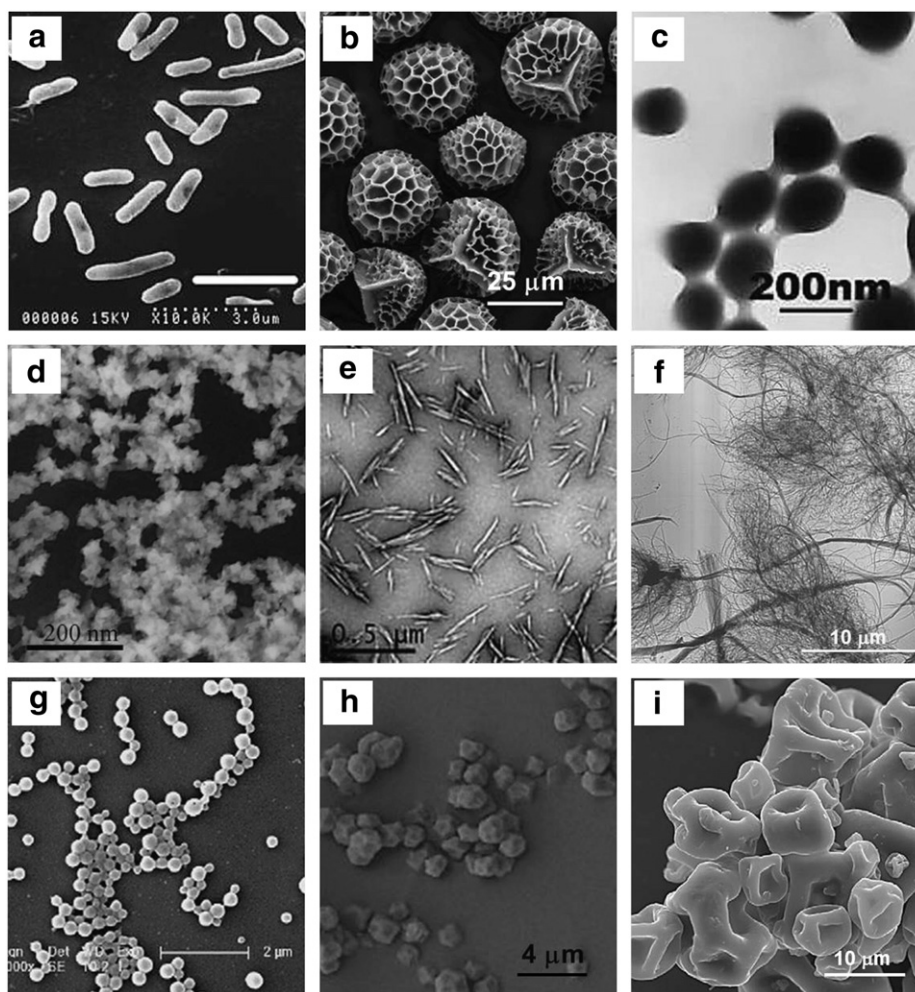


Fig. 2. Examples of bio-derived particles of various origins. The micrographs illustrate the size and shape variability between different biopolymer particles and bioparticles. (a) *E. coli* bacteria (Reprinted with permission from [56]); (b) *Lycopodium clavatum* (moss spore) (Reprinted with permission from [60]); (c) ethyl cellulose nanoparticles (Reprinted with permission from [39]); (d) chitosan nanoparticles (Reprinted with permission from [40]); (e) cellulose nanocrystals from cotton (Reprinted with permission from [22]); (f) silylated cellulose (Kraft) fibers (Reprinted with permission from [68]); (g) acetylated starch phthalic ester nanospheres (Reprinted with permission from [44]); (h) quinoa starch granules (Reprinted with permission from [31]); (i) spray-dried soy protein particles (Reprinted with permission from [46]).

also by structuring in the continuous phase (Fig. 1). In Fig. 1(c and f), we show that in emulsions, particles can also be encapsulated in the dispersed phase as the active drug or chemical agent to be delivered. Foam and emulsion stabilization by particles is discussed in multiple literature sources [3–5,8,65,66,67].

2. Biopolymer particles for stabilization of foams and emulsions

We focus this review on two classes of biologically derived materials – particles from biopolymers as well as biological organisms that can be considered as individual “particles”. The term “biopolymer” refers to polymeric compounds affiliated with live organisms; these include polysaccharides such as cellulose, chitin, chitosan, starch; aromatic macromolecules such as lignin; and, polypeptides such as soy protein, zein, lactoferrin and ferritin. Many of these materials are biocompatible as a result of their natural origin. Researchers have demonstrated the capability of particles from all these biopolymer classes to stabilize foams and emulsions in chemically modified as well as unmodified forms. Examples of various types of such particles are shown in the micrographs below (Fig. 2).

As illustrated in Fig. 2, many of these particles are irregularly shaped, polydisperse in size and morphology, and may have surface roughness. The dispersity in particle size and shape may make many of these particles and the dispersions which they stabilize difficult to characterize and compare, but it is also well known that particle shape irregularity can contribute positively to foam and emulsion stability. The outstanding ability of anisotropic particles to stabilize foams was demonstrated by Alargova et al. using microrods generated from photopolymer [69]. In terms of biologically-derived materials, shape-anisotropic particles such as cellulose nanocrystals can impart stability against creaming, coalescence and drainage at low concentrations as a result of the entanglements which form between fibers in the system. Kalashnikova et al. reported the ability of cellulose nanocrystals from green algae to stabilize an oil-in-water emulsion system at 44% disperse phase coverage as a result of the highly entangled network formed by the cellulose [22]. Capron et al. found that less than 0.1 wt% of cellulose nanocrystals from cotton was needed to form stable O/W emulsions [23]. The effect of shape anisotropy on the ability of polystyrene latex and hematite particles to stabilize emulsions was studied by Vermant et al. [70]. These authors found that particles with higher aspect ratio could stabilize biphasic systems at lower concentrations, and in certain instances were able to stabilize systems which particles of spherical shape could not. They speculated that anisotropic particles induce greater capillary deformations at the O/W interface, resulting in larger capillary attractive forces between neighboring particles adsorbed at the O/W interface. This in turn enhances the stability of the dispersion. Capillary interactions between particles protruding through fluid interfaces as well as between shape-anisotropic colloids have been studied for some time [71,72], but their effects in Pickering systems are still not completely understood. The ability of shape anisotropic particles to stabilize foams and emulsions effectively has also been reported in other studies [14,69].

In addition to engineering systems with well-controlled properties, there is also specific interest in sustainability and learning how to use biomaterials with as little modification as possible. Unlike synthetic polymers, biopolymers are often polydisperse in molecular weight, size, and chemical functionality depending on the source from which they are obtained [22,73]. The characterization of such systems is not trivial, and learning how to use biopolymers to make particles and materials with minimal chemical modification is of importance to making sustainable engineered systems from these materials.

2.1. Polysaccharides

2.1.1. Cellulose

Cellulose, a linear polysaccharide which consists of β (1,4)-linked glucopyranose units, is the most abundant biopolymer in the world,

being a structuring agent in the walls of plant cells as well as some eukaryotes [25,35]. It can also be produced by certain types of bacteria (e.g. *Acetobacter xylinum*) and algae. Bacterial cellulose and microfibrils derived from it is often touted for its high purity and potential applications in medicine since it does not exist complexed with lignin and hemicelluloses [20,26,74]. When isolated from other components of biomass such as lignin and hemicellulose, cellulose can be obtained as macroscopic fibers or as microfibrillated cellulose (MFC). Macroscopic cellulose fibers, as well as MFC (and the related nanofibrillated cellulose, NFC) are semi-crystalline in nature, meaning that the polymer contains both crystalline and amorphous domains [73]. Depending on the source from which cellulose is derived, it can have varying degrees of crystallinity. For example, cellulose derived from hemp has 44% crystallinity whereas that from algae has a degree of crystallinity higher than 80% [75]. The amorphous domains can be cleaved through treatment with acids (H_2SO_4 , HCl) to produce microcrystalline and nanocrystalline cellulose (MCC and NCC, respectively). MCC has higher crystallinity than MFC as well as cellulose microfibrils, but still contains some amorphous domains. If MCC is hydrolyzed for a longer period of time, then NCC is produced. Since the surface of cellulose contains many reactive hydroxyl groups, it can easily be chemically modified (i.e. silylation, functionalization with PNIPAm). In addition, due to the fiber-like morphology of native cellulose and high aspect ratio of hydrolyzed cellulose, cellulose particles can entangle to form physical gels in solution at low solids concentrations [73]. These characteristics, in addition to their sustainability and biocompatibility, make them ideal candidates for use in foods, cosmetics, pharmaceuticals, and lightweight porous materials.

Multiple researchers have demonstrated emulsions stabilized with macroscopic fibers, MCCs, MFC/NFC, as well as with cellulose nanocrystals (CNCs) or nanocrystalline cellulose (NCCs). Recently, Winuprasith et al. demonstrated emulsion stabilization by MFC from mangosteen rind without the aid of surfactants [17]. The authors observed an increase in emulsion stability with decreasing fiber size and increasing MFC concentration. Likewise, nanocrystalline cellulose particles and fibers have also been shown to be able to stabilize oil-in-water emulsions without the addition of surfactants [20,21,23]. This can be attributed to the somewhat amphiphilic nature of nanocrystalline cellulose. Kalashnikova et al. showed that despite the global hydrophilicity of CNCs, the edges of the nanocrystals are hydrophobic allowing for their adsorption at the O/W interface [20]. In additional work, the same authors showed that CNCs with lower surface charge density formed more stable emulsions [21]. Since cellulose is hydrophilic, it will typically stabilize water-continuous emulsions. To change this, Andresen et al. used silylation to tune the hydrophobicity of cellulose fibers for the stabilization of oil-continuous emulsions [36]. In addition, emulsions stabilized by CNCs can be made thermally responsive through the grafting of poly(*N*-isopropylacrylamide) (PNIPAm) from the surface of the nanocrystals [25].

While most forms of fibrillated cellulose have been demonstrated to be able to stabilize emulsions without the use of additional surfactants, this has not been shown for foams, possibly because the stabilization of O/W systems is easier than A/W systems for a few reasons. (1) The tension at the A/W interface is higher than at the O/W interface, resulting in larger capillary pressures in the A/W foam films than emulsion films. (2) The density difference between the dispersed and continuous phases, which drives phase separation, is higher in an air-liquid system than in a liquid-liquid system. (3) The solubility and diffusivity of a gas in H_2O is higher than that of the typical emulsion oil phase in H_2O ; this means that the driving forces causing foam destabilization are greater than those causing emulsion destabilization [3]. Thus, while relatively hydrophilic particles can still stabilize O/W dispersions, they may not be efficient in stabilizing A/W dispersions [3]. The particle properties required for foam stabilization are slightly different from those required for emulsion stabilization, for example, stable emulsions have been observed with particles having contact angles between 20° and 120°, and

sizes ranging from 5 nm to 52 μm . On the contrary, stable foam formation has only been observed for particles which form a three phase contact angle between 60° and 90°, and with sizes ranging from 10 nm to 30 μm . A comparison of the particle properties necessary for foam stabilization compared to emulsion stabilization is presented by Hunter et al. [3]. Al-Qararah et al. foamed Kraft fibers from wood pulp in the presence of sodium dodecyl sulfate (SDS) to generate foams containing cellulose fibers in the continuous phase [34]; the fibers were not adsorbed at the interface. Cervin et al. produced foams with nanofibrillated cellulose derived from wood in the presence of octylamine, which was used to reduce the surface tension at the air–liquid interface as well as the charge density of NFC, making it more hydrophobic [35]. In this system, NFC particles were “brought to the interface” by the octylamine.

Thus far, we have discussed examples of foam and emulsion systems stabilized by different types of native celluloses. However, there is a broad range of hydrophobically modified celluloses, derived from native cellulose, which have also been utilized for the stabilization of such dispersions. This class of celluloses, which encompasses methylcellulose (MCE), ethylcellulose (EC), hydroxypropyl methylcellulose (HPMC), and hydroxypropyl methylcellulose phthalate (HPMCP), is already widely used in foods as well as in drug delivery applications [14,38,39]. These biopolymers exhibit solubility in certain solvents (e.g. EC–acetone, HPMCP–water at pH > 5.6), and while chemically modified, they are still derived from natural cellulose and are both biocompatible and biodegradable. Soluble biopolymers can be precipitated into particles of various shapes and sizes, which is not the case for the non-chemically modified celluloses discussed above. The generation of particles from modified celluloses typically involves solvent attrition via solvent/anti-solvent exchange or polymer precipitation out of solution in the form of particles by adjusting solution pH or ionic strength [14,38,39,76]. Wege et al. demonstrated the ability of anisotropically shaped micron-sized HPMCP particles to form superstable foams and demonstrated the possibility of particle generation *in situ* during foam formation [14]. The ability of EC microrods and nanoparticles to stabilize food grade foams has also been demonstrated [39,76]. Another mode of utilization of cellulose-based polymers is in the form of colloidal particles based on insoluble complexes with other molecules. MCE/tannic acid colloidal complexes were shown to stabilize well both foams and emulsions [77]. Interestingly, high oil fraction “foamulsions” stabilized by MCE/tannic acid colloidal complexes exhibit a temperature dependent transition in stability [38]. The strong interactions between another polyphenol, epigallocatechin gallate (found in green tea), with MCE and HPMC have been exploited in the fabrication of novel beads with controllable core–shell morphology [78].

2.1.2. Chitin/chitosan

Another linear polysaccharide found in nature is chitin. It is derived mainly from the shells of crustaceans, insects, and microorganisms and is the second most abundant polysaccharide found in nature [28,29]. Chitin, similar to cellulose, also contains hydroxyl groups along its backbone. However, due to the presence of amine groups, the variation of its surface charge with pH is opposite that of cellulose. The presence of amine groups also enables the pH dependent solubility of chitosan, a deacetylated form of chitin which is water soluble at low pHs (<6) but precipitates out of solution at high pHs [12]. At low pHs, chitosan is (positively) charged but at higher pHs, the amino groups along the chitosan polymer become deprotonated and the uncharged polymers associate in solution to form particles [12].

While natural chitin is semi-crystalline in structure, chitin nanocrystals which are colloiddally stable rod-like crystalline particles may be obtained through acid hydrolysis. Tzoumaki et al. demonstrated the ability of chitin nanocrystals to form stable oil-in-water emulsions and evaluated the ability of the adsorbed particle shell to protect the lipid droplets in the emulsion against lipolysis *in vitro* [18,28]. Chitosan, unlike chitin, has pH-dependent solubility in water, and due to its biocompatibility as well as antibacterial properties, is a popular material

for drug encapsulants. Wei et al. evaluated the ability of chitosan nanoparticles to stabilize emulsions and used these Pickering emulsions for the synthesis of micron-sized poly (lactic-co-glycolic acid) (PLGA) particles [40]. Since chitosan exhibits pH dependent solubility in solution, the authors also demonstrated that the O/W emulsions which were formed could be demulsified by lowering the pH of the system and that the emulsions could be recovered by subsequently increasing system pH and re-emulsifying.

2.1.3. Starch

Starch, which is derived from grains, is the most abundant carbohydrate in the human diet [32]. Depending on the source as well as preparation of starch granules, these particles are of unique shape and size (Fig. 3) [16,31]. Since starch is hydrophilic, it has mainly been shown to stabilize oil-in-water emulsions except for the case of nanoparticles produced using acetylated starch; in this study, the particles produced O/W emulsions up until an oil fraction of 0.65 after which the system inverted to form W/O dispersions [44]. Although unmodified starch granules have been shown to stabilize emulsions in some cases, many studies use octenyl succinic anhydride (OSA) to render the particles more hydrophobic for improved Pickering emulsion stability [9,10,15,31,41–43]. Starch, like cellulose, is a semi-crystalline polymer and can be hydrolyzed using strong acids to produce crystalline particles [32]. Li et al. demonstrated that starch nanocrystals can efficiently stabilize emulsions without further hydrophobization, and observed stable emulsions even after 2 months of storage [30]. Pickering emulsions stabilized by starch particles can potentially serve as drug delivery agents and as lipid encapsulants for low calorie foods.

Other polysaccharides which are important in foam and emulsion formulation include hydrocolloids such as alginate, carrageenan, and xanthan gum. These molecules are known to enhance foam and emulsion stability through modification of rheological properties in the continuous phase [79,80]. Particles from these compounds have not been demonstrated in foam and emulsion stabilization and remain a topic of potentially interesting future research. Direct complexation between xanthan gum and shellac during emulsification leading to particles from insoluble complexes, has yielded pH switchable emulsions with high stability against coalescence [81]. Shellac used in combination with gelatin was also demonstrated to form all-natural microcapsules which could be used for various bio-related applications [82].

2.2. Protein-derived particles

Proteins are amphiphilic macromolecules with a broad range of biological functions. Due to their amphiphilic nature they have long been known to be able to reduce the energy of the air–liquid or liquid–liquid interface and have been extensively studied as foam and emulsion stabilizers [83–86]. This section of the review focuses on literature reports pertaining to the synthesis and application of protein-based particles for foam and emulsion stabilization. For more information on dispersions stabilized by molecular proteins, readers can refer to literature sources such as [83–88]. Proteins are known to be capable of forming thick steric barriers against coalescence in foam and emulsion films [79,86]. In addition, it has been demonstrated that foam and emulsion stability can be enhanced by the formation of protein aggregates in solution [11,84,86]. Although such protein aggregates are in a sense particle-like stabilizers, studies of foam and emulsion stabilization using nanoparticles from proteins have not emerged until the past 2–3 years. Nanoparticle aggregates formed through the thermal treatment of soy protein have been evaluated as Pickering stabilizers of emulsions [11]. The authors found heat-treated soy protein particles to exhibit characteristics similar to conventional particle stabilizers. Spray-dried soy protein particles with calcium phosphate cores have also been demonstrated to adsorb at the oil–water interface and stabilize emulsions [46]. However, in this study, emulsion stabilization appears to be largely derived from the soluble soy protein.

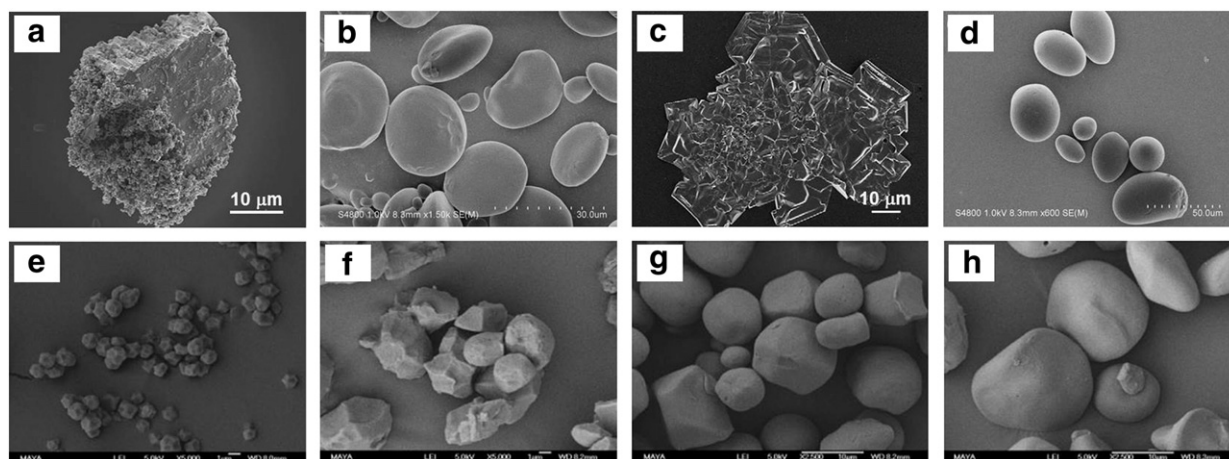


Fig. 3. Scanning electron micrographs of starch granules from different sources. (a) tapioca starch (Reprinted with permission from [41]); (b) wheat starch (Reprinted with permission from [16]); (c) waxy maize starch (Reprinted with permission from [41]); (d) potato starch (Reprinted with permission from [16]); (e) quinoa starch (Reprinted with permission from [31]); (f) rice starch (Reprinted with permission from [31]); (g) maize starch (Reprinted with permission from [31]); (h) and barley starch (Reprinted with permission from [31]).

Another recently emerging area is the use of particles from water-insoluble proteins for the formation of Pickering emulsions [49]. de Folter et al. demonstrated that particles made from zein protein through a nanoprecipitation procedure could stabilize oil-in-water emulsions. They also showed that the wettability of the particles could be tuned by varying the pH of the solution medium and that stable emulsions could be formed at zeta potentials above or below the isoelectric point of zein.

Protein-based particulate stabilizers can also be formed via coprecipitation with polysaccharides. Although not often considered to be in the Pickering class of stabilizers, protein-polysaccharide complexes are a group of foam and emulsion stabilizers which are being vigorously explored. Shimon et al. synthesized nanoparticles from lactoferrin as well as multi-component particles from lactoferrin (LF), alginate (Alg), and carrageenan (Car) [47]. The authors investigated the stability of emulsions containing LF NPs, LF-Alg NPs, and LF-Car NPs against degradation in *in vitro* gastric conditions. The effect of *in vitro* intestinal conditions on emulsions stabilized by these complexes have also been investigated [48]. Interest in using protein-polysaccharide complexes as stabilizers is also fueled by the desire to identify biodegradable, biocompatible, and sustainable materials for use in foam and emulsion systems [85].

2.3. Lignin

Lignin, an aromatic macromolecule found in the cell wall of woody plants, is the second most abundant biopolymer found in nature and the most abundant natural aromatic molecule [13]. The lignin macromolecule is composed of three monolignols (p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) and is amorphous in structure. The ratio of these three monolignols in the macromolecule varies depending on plant source [89–91]. In addition, the surface chemistry of lignin will depend on the extraction process with different extraction processes resulting in lignins of varying molecular weight (MW) and hydrophobicity. The colloidal properties of different lignins (organosolv, alkaline, and lignosulfonates) and their separation from cellulose have been investigated for many decades [91–100]. More recently, research into different forms of lignins has been fueled by the motivation to utilize this renewable “waste” to make value-added commodities by understanding the properties of lignins as molecular surfactants, particulate emulsifiers, and as replacements for petroleum-based synthetic polymers [13,55,101–103].

Lignin molecules are surface active and can adsorb at the air–liquid as well as liquid–liquid interface to provide kinetic stability to foams and emulsions [91,96,100,104]. Recently, particulate forms of lignin

have been demonstrated as emulsion stabilizers. These studies use alkaline lignin which is derived from the Kraft pulping process, and which contain additional hydroxyl and sulfur moieties as a result of this extraction process. Alkaline lignin exhibits pH dependent solubility and surface activity in aqueous media; it dissolves at high pH and aggregates to form particles in solution once pH is lowered (<10). Wei and collaborators used nanoparticles from alkaline lignin to generate pH-responsive emulsions [13]. They found that emulsion stability was greatest at low pH (~ 3 – 4) and that their system de-emulsified when the pH of the system was adjusted to a value greater than 10. In another study, Yang et al. used alkaline lignin NPs for the stabilization of high internal phase emulsions (HIPES) and utilized these emulsions to generate solid foams for the adsorption of metallic ions from solution [55]. These studies provide good examples of “green” materials and processes in which this abundant “waste” from the pulp and paper industry can be utilized.

2.4. Discrete bioentities — single cells, viruses & spores

For decades, foams stabilized by hydrophobic bacteria have plagued wastewater and sewage treatment plants. In fact, many papers pertaining to bacteria-stabilized foams discuss how to defoam or prevent foam formation by these microorganisms [58,105,106]. Recently, however, researchers have utilized the hydrophobicity of such organisms to their advantage [57,60,62,107]. Biological particulates such as bacteria, viruses, and spore particles have well-defined shapes and sizes in the facile range for foam and emulsion stabilization and can be obtained as species with tight size distributions. Dorobantu et al. evaluated the ability of 4 different types of hydrocarbon-degrading bacteria to stabilize emulsions [57]. They observed formation of O/W as well as W/O Pickering emulsions depending on the hydrophobicity of the bacterial species, and found species that were partially hydrophobic to exhibit the best ability to stabilize emulsions. Rosenberg et al. also observed the same dependence of foam stability on cell surface hydrophobicity in a study pertaining to the ability of different strains of *Acinetobacter calcoaceticus* to adsorb to the oil/water interface [108]. These findings for the influence of bio-particle hydrophobicity on emulsion stability correlate well with knowledge previously elucidated from examining conventional Pickering systems stabilized by spherical silica and latex particles. Binks et al. as well as Ballard et al. reported Pickering stabilization of liquid–liquid dispersions by *Lycopodium clavatum* (a moss spore) [59,60]. Other examples of bacteria stabilized systems have also been described [56,58,61,62]. Such systems have potential applications in fermentation, oil recovery, as well as in microorganism assisted chemical reactions [56,57,58].

Other types of particles which have been mentioned in the literature to impart Pickering-type stability to emulsions and foams include flavonoid particles, solid lipid nanoparticles as well as fat crystals. These biocompatible Pickering-type foam and emulsion stabilizers will not be discussed in detail here as a result of their non-polymeric and non-cellular origin. They are described elsewhere in the literature [109–111,112].

3. Outlook — challenges and directions in biopolymer foam and emulsion stabilization

Most edible foams and emulsions stabilized by food-grade agents and biocompatible substances until the past few years have been primarily based on proteins and hydrocolloids [79,80,83]. Although the large molecules in both of these classes can provide sizeable barriers against destabilization, particles have been shown to stabilize foam and emulsion systems more efficiently than molecular amphiphiles [67,86].

The past few years have been an exciting time for research in foams and emulsions stabilized by biopolymers and biological particles. Not only have scientists started to learn how to make well defined partially hydrophobic particles from biopolymers (bottom up approach) [13,44,49], but they have also learned how to modify natural biopolymer particles to have the proper wettability to efficiently stabilize foams and emulsions (top down approach) [15,25,30,35,41]. In addition, researchers have identified biotic particles of varying shapes and sizes that stabilize Pickering foams and emulsions via mechanisms similar to those originally identified for synthetic silica and latex particles [28,30,41,46,57]. It has been found that partially hydrophobic particles are indeed the best stabilizers for disperse systems, and that increasing

particle concentration produces smaller emulsion droplets and results in a reduced rate of foam and emulsion creaming [10,13,30]. This is because an increase in the number of partially hydrophobic particles in the dispersion results in the capability of stabilizing a larger interfacial area. Emulsion systems stabilized by biopolymer particles have good long-term stability against coalescence and coarsening as a result of the steric barrier provided by adsorbed particles [30]. Examples of droplets and bubbles stabilized by biopolymers are shown in Figs. 4 and 5. The micrographs in Fig. 4 show the adsorption of partially hydrophobic biopolymeric particles at the interface of droplets and air bubbles. Some of the micrographs also show how particles can stabilize these systems by structuring in the continuous phase. While there has been large progress in the research of particles from naturally derived materials for the stabilization of biphasic dispersions, some of the pending challenges and areas in need of clarification include:

- (1) *Characterizing the effect of molecular adsorption on dispersion stability.* Conventional understanding of particle-stabilized interfaces postulates that the magnitude of energy reduction at the interface by particles is dependent on the concentration, size, as well as the electrostatic interactions between adsorbed particles at the fluid interface [67,87]. Some authors who have evaluated particles from biopolymers for the stabilization of foams and emulsions did not observe a lowering of interfacial tension by their particles whereas others did [26,30,39]. One possible explanation is that the lowering of interfacial or surface tension in these systems is due the adsorption of dissolved polymer or residual proteinaceous material. Better understanding of the effect of molecular and particulate biopolymer co-adsorption at the interface on system stability is important, because the presence of molecules in a particulate-stabilized system can lead to

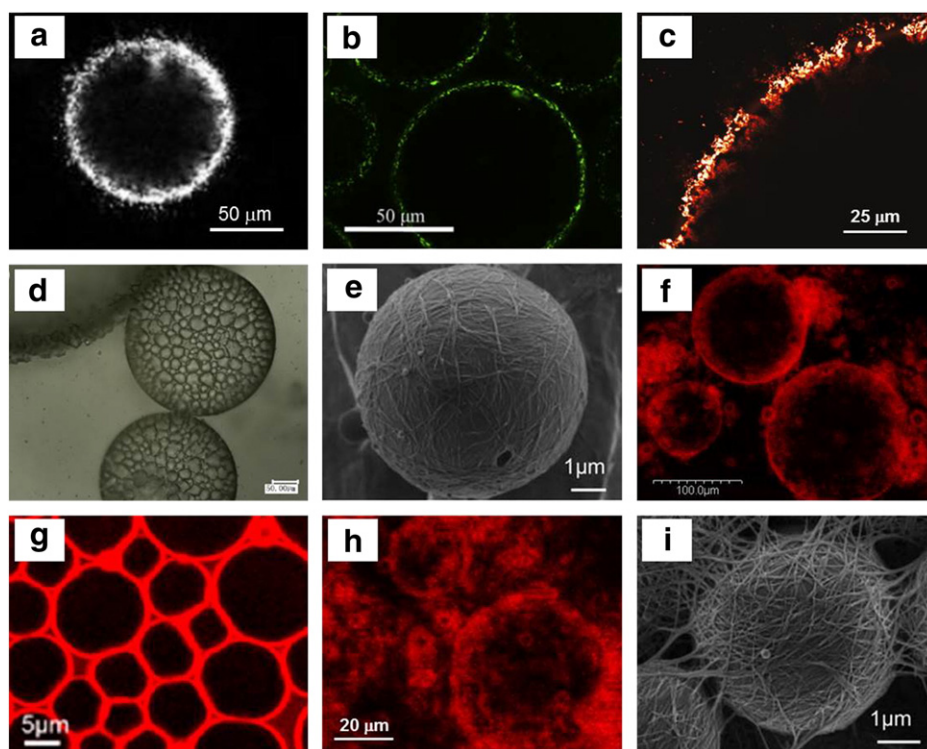


Fig. 4. Micrographs illustrating interface and continuous phase stabilization of emulsion droplets and foam bubbles by biopolymer particles. Interface stabilization: (a) confocal micrograph of *E. coli* DH5α at n-tetradecane/water interface (Reprinted with permission from [56]); (b) confocal micrograph showing chitosan NPs adsorbed at oil/water interface (Reprinted with permission from [40]); (c) confocal micrograph of flavonoid particles (tiriloxide) at n-tetradecane/water interface (Reprinted with permission from [109]); (d) optical micrograph of waxy maize starch at oil–water interface (Reprinted with permission from [16]); (e) scanning electron micrograph of bacterial cellulose nanocrystals at interface of polymerized styrene-water emulsion droplet (Reprinted with permission from [22]); and (f) confocal micrograph of HPMCP particles at interface of air bubbles. Continuous phase stabilization: (g) confocal micrograph of HIPE stabilized by CNCs from cotton (Reprinted with permission from [23]); (h) confocal stack showing interface and continuous phase stabilization of air bubbles by HPMCP; and (i) scanning electron micrograph showing ClacN (green algae) cellulose nanocrystals at interface of and bridging polymerized styrene-water emulsion droplets (Reprinted with permission from [22]). Images f and h obtained by Stephanie Lam.

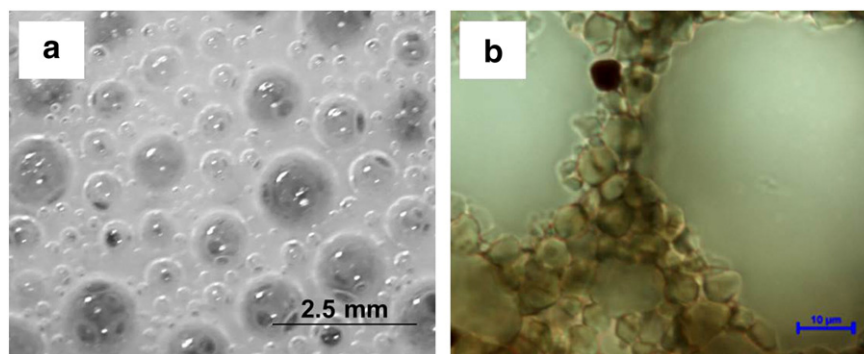


Fig. 5. Photographs illustrating the macroscopic structure of dispersions stabilized by particles in excess. (a) Foam stabilized by HPMCP particles. Image obtained by Stephanie Lam. (b) O/W emulsion stabilized by non-modified rice starch particles. Scale bar = 10 μm (Reprinted with permission from [42]). These particles sterically stabilize foams/emulsions by forming a shell around the dispersed phase and a particle network in the continuous phase.

synergistic as well as antagonistic effects [69,113].

- (2) *Quantifying the role of particle charge on system stability.* Some studies mention that particles can better stabilize foams and emulsions when the ζ -potential of the particles or emulsion droplets is low, allowing for their partial flocculation [13,21,56]. Other studies (mostly pertaining to emulsion stabilization) state that increased values of ζ -potential leading to electrostatic repulsion between droplets provides better emulsion stability [10,17,44,47,49]. It is still unclear whether this discrepancy is caused simply by a difference in how authors define stability, or if there is a physical parameter (i.e. ionic strength of dispersion, degree of emulsion droplet coverage by particles, particle size, particle concentration in dispersion) delineating these different conclusions. Better correlation between particle charge and foam and emulsion stability could be an important focus of future work.
- (3) *Exploring foam stabilization by biologically derived particles.* Table 1 illustrates that apart from hydrophobically modified celluloses, few types of biotic particles have been examined for the stabilization of foam (air–water dispersions). Comparing the adsorption and structuring of different biologically derived particles at the air–liquid versus liquid–liquid interfaces would be both interesting and important. For example, whereas cases have been reported where stable emulsions could be obtained even with incomplete coverage of the liquid–liquid interface by particles, this would be not possible in foams; partially covered air bubbles would shrink or coalesce until full surface coverage is achieved [3,114].
- (4) *Evaluating the role of non-adsorbed particles on foam and emulsion stability.* The adsorption of partially hydrophobic particles at the air–liquid or liquid–liquid interface is crucial for the formation and stabilization of Pickering foams and emulsions. However, the stability of biphasic dispersions can be enhanced by particle network formation in the continuous phase to hinder drainage, creaming, and sedimentation [5,8]. Most of the studies reviewed in this article address only the impact of adsorbed bioparticles on dispersion stability with only a few authors commenting on the effect of particle gelation in the continuous phase on the stability of their systems [10,15,17,28,30,40]. Due to the irregular shape of many of the biologically derived particles reviewed here, it would be interesting to gain a deeper understanding as to how differently-shaped particles can orient and pack in the foam film to enhance foam and emulsion stability.
- (5) *Exploring Pickering systems stabilized by biocolloids on a more fundamental basis.* Many of the papers reviewed here discuss the effects of particle wettability, ζ -potential, concentration, size, and aspect ratio on foam or emulsion stability. Although conclusions pertaining to the effect of these parameters on

dispersion stability corroborate well with observations reported for classically studied Pickering systems stabilized by synthetic particles; there seem to be very few theoretical comparisons between systems stabilized by biocolloids and those stabilized by traditional synthetic colloids. Issues which have been addressed in the current literature include: calculation of surface coverage needed for stability [20,22], evaluation of three-phase contact angle [14,36,39,49,56,57], observation of particle packing at a bubble or droplet surface [16,20,22,60,61], and calculation of coarsening rate [39]. Items which are lacking in the current literature include: estimation of adsorption energy for shape anisotropic (biologically derived) particles at A/W or O/W interfaces, estimation of maximum capillary pressure for systems stabilized by different biocolloids, modeling of drainage and coarsening/ripening in foam/emulsion systems stabilized by biologically-derived particles, and models for capillary interactions between biocolloids at interfaces.

Most of these research challenges, which were previously studied using spherical colloids may be difficult to transcribe to the systems reviewed here as a result of the shape anisotropy and size dispersity of biologically derived particles, as well as their tendency to “stick to each other”. Despite these limitations, a few papers have started to address these issues. Paunov et al. demonstrated the capability of using the gel-trapping technique (GTT) to evaluate the contact angle of irregularly-shaped particles at fluid interfaces [46,115]. A number of authors have redefined Eq. (1) for non-spherical particles with others working to elucidate the preferential orientations of non-spherical colloids at air–water and oil–water interfaces. More quantitative approaches to evaluating bulk foam and emulsion systems (e.g. fitting data for time evolution of bio-Pickering foams and emulsions to conventional drainage and coarsening equations) and more studies pertaining to particle packing and orientation at planar interfaces between immiscible fluids would not only help us learn how accurately models for spherical systems apply to more practical systems (like those reviewed here); but, would also aid in unifying the plethora of empirical data which have been generated for foam and emulsion systems stabilized by biologically derived particles.

In addition to the already mentioned uses for biopolymer particle stabilized foams (i.e. food, cosmetic, drug delivery), the potential applications of Pickering foams and emulsions span far and wide from catalysis to synthesis to everyday products like bedding and insulation [116–118]. Since the mechanical and functional properties of Pickering systems are strongly influenced by the bulk mechanical characteristics of the particle network in and functional properties of particles added to the foam, respectively, such systems can be used as a platform for

the design of functional porous materials. Kim et al. demonstrated that the pH dependent chemistry of HPMCP and a hydrophobic dye could be utilized to produce stable and selectively colored foams at pHs where the hydrophobically modified cellulose forms particles [37]. Lam et al. showed that magnetic responsiveness could be imparted to a foam through embedding magnetically responsive particles into the continuous phase of a dispersion stabilized by modified cellulose [119]. Novel hybrid materials can be created by combining particles of inorganic origin and biopolymeric particles [52,54]. The creation of solid porous materials from biopolymeric foams and emulsions has been reported by a few authors. Cervin and collaborators were able to form solid porous materials from NFC foams with greater than 98% porosity by foaming NFC from wood pulp in the presence of octylamine and then drying the aqueous foam [35^{***}]. Yang et al. generated solid lignin foams from HPIEs stabilized by lignin nanoparticles [55]. Another application for biopolymeric stabilized foams and emulsions is particle synthesis via emulsion templating [13^{*,40^{*}}]. Use of Pickering emulsions for the templating of colloidosomes had been demonstrated for systems stabilized by inorganic spherical and anisotropic particles and now has also been extended to those stabilized using biologically derived particles [120,121]. Reaction catalysis using interfaces stabilized by microorganisms has also been proposed [122]. Some of the current materials applications of Pickering foams and emulsions from biopolymers are presented in Fig. 6.

In summary, Pickering foams and emulsions stabilized by biologically derived particles are sustainable, biocompatible systems which can be applied as foods, drug delivery mediums, and as lightweight

porous materials/hybrid materials; for the synthesis of particles; as well as in catalysis. In the past few years, the scientific community has gained insight into how to (1) make particles from biopolymers for foam and emulsion stabilization, as well as (2) use naturally existent biologically derived particles to stabilize biphasic dispersions. We have also gained a better understanding of how biotic particles can stabilize foams and emulsions and have demonstrated a few ways in which these systems can be applied. Interesting directions for future work include: (1) gaining a better understanding of the effect of particle solubility (or existence of residual soluble material) and charge on foam and emulsion stability, (2) elucidating the preferential packing of and interactions between biocolloids at fluid interfaces, (3) identifying more usable materials for the stabilization of biotic Pickering systems, (4) understanding multi-component systems (containing multiple types of bio-particles or mixtures of particles and molecules), and (5) creating organic/inorganic hybrid materials from biopolymer Pickering foams/emulsions.

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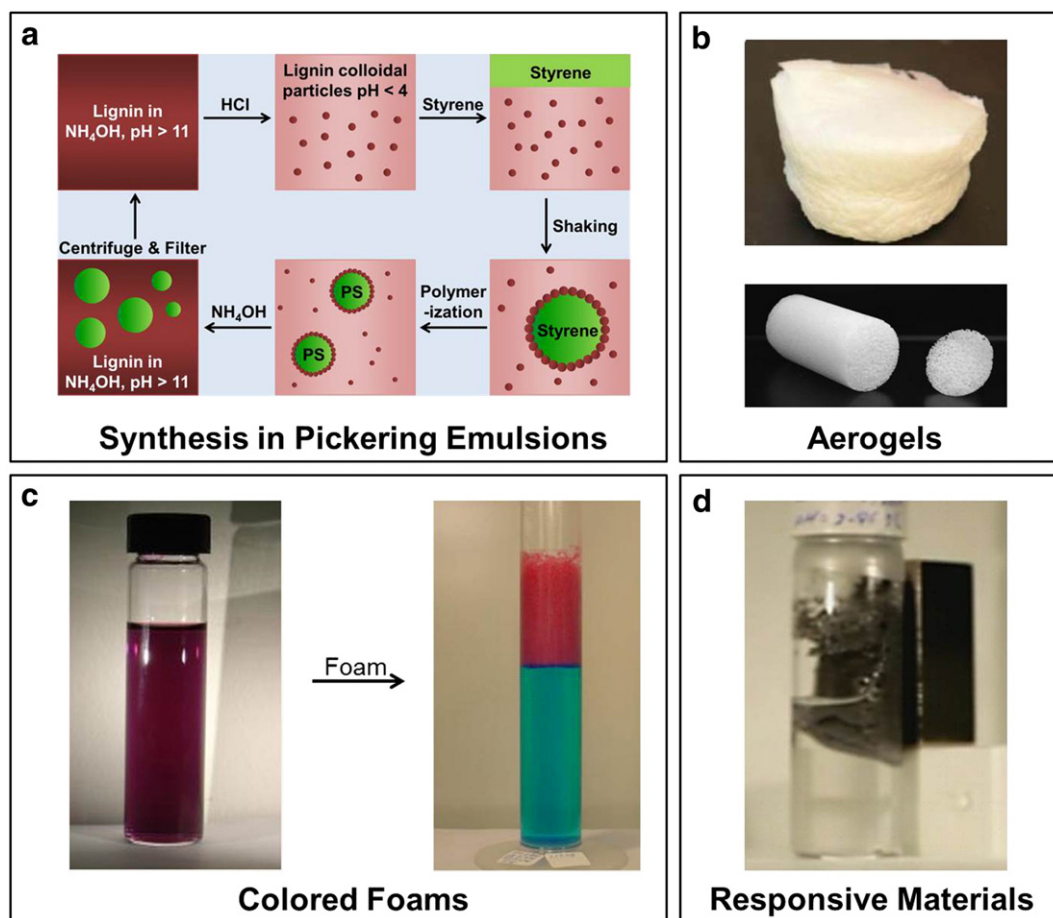


Fig. 6. Examples of applications for Pickering foams and emulsions from biopolymers (other than for foods, cosmetics and drug delivery): (a) synthesis of particles (Reprinted with permission from [13^{*}]); (b) lightweight materials with high porosity (aerogels) (Reprinted with permission from [33,35^{***}]); (c) colored porous materials or dispersions (Reprinted with permission from [37]); and (d) stimuli-responsive porous materials or dispersions (Reprinted with permission from [119]).

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