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Viewpoint

Pickering Emulsions as Templates for Architecting Composite Structures

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EMULSIONS

The most common emulsions are comprised of oil and water, with droplets of one in a continuous phase of the other. This includes oil-in-water (o/w) and water-in-oil (w/o) systems (Figure 1A), where the emulsions are commonly formed by mixing the two liquids by shaking or shear. The identity of the continuous and discontinuous phases depends on the ratio of the two liquids, the method of formulation, and most notably the identity of the surfactant or surface-active agent.[1] Small molecules, polymers, and particles can all stabilize emulsions.[2,3] For small molecules, the hydrophilic−lipophilic nature of surfactants greatly impacts the identity and stability of the emulsion. For nonionic surfactants, the hydrophilic−lipophilic balance (HLB) is commonly used to predict what emulsifier is suitable for a particular system.[4] A more lipophilic surfactant is assigned a lower HLB number, while a more hydrophilic compound would have a higher HLB. In general, the range of HLB values is classified with respect to the surfactant solubility in water and/or its application as a w/o emulsifier (HLB 4−6), wetting agent (HLB 7−9), o/w emulsifier (HLB 8−18), detergent (HLB 13−15), or solubilizer (HLB 10−18). For ionic surfactants, the calculated HLB usually underestimates the hydrophilic character since this value only considers the molecular-weight-average of the hydrophilic and lipophilic parts of the surfactant and not ionization. Instead, other approximations such as the surfactant packing parameter at the oil−water interface, the hydrophilic−lipophilic deviation, and the Winsor ratio are used to predict a stable system.[5−7] Regardless, small molecule surfactants stabilize emulsions by lowering the interfacial tension of a system; for example, the canonical small molecule surfactant, sodium dodecyl sulfate (SDS), decreases the interfacial tension of the water−oil interface from ∼40 mN/m to ∼20 mN/m, with the hydrophilic charged headgroup being exposed to the water and a hydrophobic hydrocarbon tail in the oil.[8] Polymeric surfactants are also of great interest since they can be designed to have a responsive behavior to different external conditions such as pH, temperature, ionic strength, and UV radiation. Polymeric surfactants show solvent-dependent self-assembled structures that can be leveraged for the design of smart materials.[9,10]

In complement to the common o/w and w/o emulsions, multiemulsions contain multiple internal phases. For example, double emulsions can have a core−shell or multicore configuration (Figure 1A) with compositions that classically involve [water-in-oil]-in-water (w/o/w) or [oil-in-water]-in-oil (o/w/o) emulsions. However, there are complex configurations such as w/o/o, o/o/w, w/w/o, and o/w/w.[11] Traditionally, multiple emulsions are obtained through a two-step emulsification method: an initial emulsion, stabilized by surfactant A, is emulsified with a new phase (stabilized by surfactant B) with special care taken to avoid disruption of the initial droplets.[12] For example, in a w/o/w emulsion the inner w/o interface is stabilized by a hydrophobic surfactant and the external o/w interface is stabilized by a hydrophilic surfactant, in agreement with their respective HLB values. Nonetheless, multiple emulsions stabilized only by small molecule surfactants tend to be unstable against coalescence and Ostwald ripening.[13] As such, the introduction of solid surfactant particles, in combination with conventional surfactants or alone, can overcome destabilization issues.[14,15]

Pickering emulsions, those stabilized by solid particles, are a distinct class of emulsions in which a particle surfactant provides a steric barrier to the fluid−fluid interface and prevents the coalescence of droplets in an emulsion. Whereas small molecule or polymeric surfactants stabilize emulsions by decreasing interfacial tension, Pickering surfactants do not have this explicit requirement (though this may occur). Pickering surfactants include surface-modified silica particles, clay nanosheets, and cellulose nanocrystals, among others; of these, 2D particle surfactants are attractive from the standpoint that a single particle covers a larger amount of surface area than the spherical analog and the overlap of nanosheets at the interface can lead to enhanced stability.[16] Notably, the interfacial activity of the particles is dictated by their wettability to both phases, and the particle itself may have a functional property, such as conductivity or catalytic activity. The ability to expand the composition of emulsions, in both the liquid/liquid composition and surfactant identity, provides a distinct opportunity to tailor structures and composites for a variety of applications: from energy harvesting and management, to foodstuffs and cosmetics, to controlled payload release.

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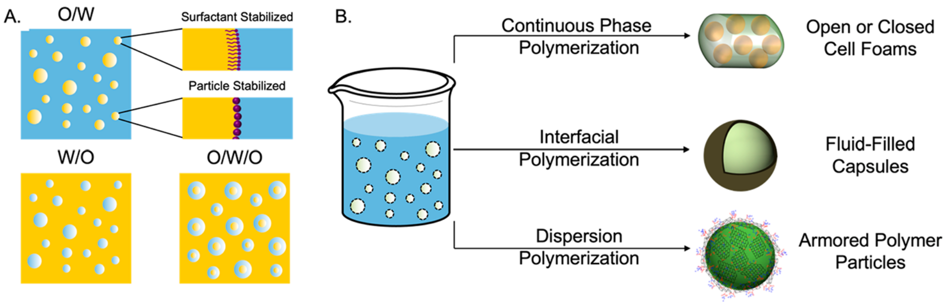

Figure 1. (A) Different emulsions (w/o, o/w, o/o, and multi-) stabilized by small molecule or polymeric surfactants. (B) Cartoon with routes of polymerization to produce of foams (open/closed cell), capsules, and armored particles.

TEMPLATING COMPOSITES BY POLYMERIZATIONS IN PICKERING EMULSIONS

Performing polymerizations in Pickering emulsions provides a scalable and rapid approach to producing composite materials of particle surfactant and polymer. Selective choice of the continuous and discontinuous phases as well as solubility of monomers and initiators/catalysts can give rise to (i) open or closed-cell foams by the polymerization of the continuous phase; (ii) composite capsule shells encasing droplets of the discontinuous phase by interfacial polymerization; or (iii) polymer particles armored by surfactant particle by polymerization of the discontinuous phase (Figure 1B). Polymerizations applied in these emulsions may be step growth or chain growth, and monomers can serve as one of the phases or an additive. Polymerization techniques applied to o/w and w/o emulsions are powerful but also limited to components that are compatible with water. As such, monomers must not undesirably react with water and must be selectively miscible or immiscible with water, as partition of components across the two phases can result in the poor control of composite formation.

Emulsions stabilized by nanosheets, coupled with polymerization, can give composite structures which incorporate the functional properties of the nanosheet, at low nanosheet concentration. For example, dispersion polymerization of emulsions stabilized by transition metal carbide nanosheets (i.e., MXenes) produce MXene-armored polystyrene particles that can be hot pressed into composite films for use in electromagnetic interference (EMI) shielding.[17] Alternatively, cobalt oxide nanosheets surfactants and dispersion polymerization gives nanosheet-armored polybenzyl methacrylate particles that can activate catalysts for the degradation of bisphenol A.[18] In complement, polymerization of the continuous phase of MXene-stabilized emulsions yields foams with pores lined with the nanosheets. Applying this approach to high internal phase emulsions (HIPES, in which the emulsion is >74 vol % discontinuous phase) yields open-cell foams with pores lined with MXenes. Here, the concentration of the nanosheets dictates the size of the pores, degree of connectivity, and the architecture of the composite structure which mitigates the oxidation of the sensitive MXene nanosheets.[19]

Emulsions can also be used to encapsulate liquids in a single step, with the discontinuous phase serving as the core liquid. For example, emulsions can be formed at elevated temperatures to prepare droplets of an organic solid−liquid phase change material (PCM); then cooling the emulsion to ambient temperature leads to solidification of the core. This produces solid particles coated with the particle surfactants that can then be cross-linked to form a robust shell. Such an encapsulation strategy gives structures that accommodate the volume change associated with solid−liquid phase transition and prevents leakage of the liquid, enabling the storage and release of thermal energy.[20] In complement, interfacial polymerization in emulsions can lead to capsules with cores of poly(α-olefin) (PAO), a low volatility hydrocarbon oil. These core−shell capsules can be used to remove BTEX (benzene, toluene, ethylbenzene, and xylene) from water.[21] Alternatively, ionic liquids (IL) can be encapsulated by interfacial polymerization of a IL/w emulsion to give capsules with applications in CO_2 uptake,[22] electrochemical energy storage,[23] and separations.[24] Notably, encapsulation of PAO or IL via this so-called soft template method not only transforms the viscous liquids into a more easily handled powder but also increases the active surface area, supporting application in separations.[25] This overcomes the need for agitation, which is required for bulk liquid/liquid systems, and the capsules can even be incorporated into column/flow systems. In these pioneering systems, the composition of the composites produced is limited by the use of water as the continuous phase. The ability to stabilize nonaqueous emulsions would significantly expand the composites accessible and enable better tailoring of composition and structure for enhanced technology-relevant properties.

NONAQUEOUS EMULSIONS

A critical challenge to stabilizing oil-in-oil (o/o) emulsions is the lower interfacial tension of o/o systems,[26] compared to oil and water. For example, the interfacial tension of hexane and water is ∼42 mN/m, whereas that of hexane and *N*,*N*-dimethylformamide (DMF) is ∼19 mN/m.[27] Traditional surfactants for o/o emulsions are block copolymers, where the relative block length and Hansen solubility parameter of each block are tailored for the two liquids, and the polymer chains entangle at the interface for enhanced stability.[28] Molecular brush surfactants have also been reported to stabilize o/o emulsions, even at high internal phase through interfacial jamming of the polymeric brushes.[29] Recently, Pickering surfactants have emerged for the stabilization of o/o emulsions, again imparting steric stabilization to the interface, and not solely relying on decreasing the interfacial tension.[26,30] For example, fumed silica particles, with hydrocarbon groups or fluorocarbon chains, fluoro-silicone particles,[31] plate-like fluorinated calcium lauryl taurate particles,[32] Shigaite-like clay,[33] polystyrene particles,[34] silica particles,[35] diblock copolymer particles,[36,37] alkylated cellulose,[38] and magnetic particles have been reported to stabilize these nonaqueous interfaces.[39]

The Pentzer lab developed alkylated graphene oxide (GO) nanosheets for the stabilization of o/o emulsions (Figure 2).

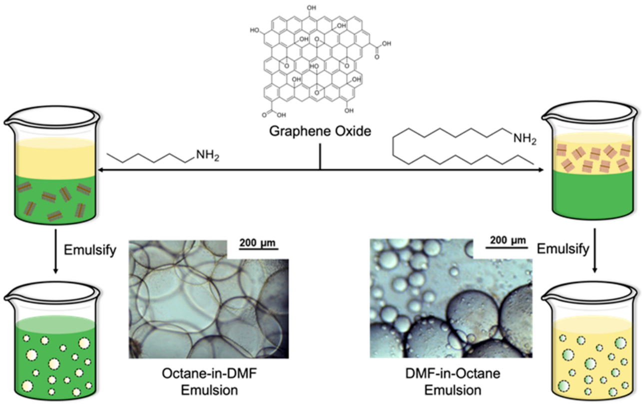

Figure 2. Modification of graphene oxide (GO) by reaction with primary alkyl amines to give nanosheets of different wettability for stabilization of nonaqueous emulsions. Functionalization of GO with hexyl amine gives nanosheets dispersible in DMF and capable of stabilizing octane-in-DMF o/o emulsions (left). Functionalization of GO with octadecyl amine gives nanosheets dispersible in octane and capable of stabilizing DMF-in-octane o/o emulsions (right). Optical microscope images reproduced with permission from ref 40. Copyright 2017 American Chemical Society.

To prepare these surfactants, GO nanosheets are dispersed in DMF and then modified with primary alkyl amines (such as hexyl amine or octadecyl amine). Functionalization occurs by ring opening of epoxides on the basal plane of the nanosheets, as well as acid−base chemistry with the carboxylic acids on the edges. Unlike GO, the alkylated nanosheets are not dispersible in water, with the length of the alkyl chain dictating the polarity of the oil that the nanosheets can be dispersed in. Hexyl amine modified GO are dispersible in polar oils, such as DMF and acetonitrile (ACN), and octadecyl amine modified nanosheets are dispersible in nonpolar oils, such as hexane and octane (Figure 2).[40] By adding an immiscible oil to either of these dispersions and agitating, o/o emulsions that are stable for weeks are produced, with the nanosheets residing at the fluid−fluid interface. Thus, hexyl amine-modified nanosheets stabilize octane-in-DMF emulsions, whereas octadecyl amine-modified nanosheets stabilize DMF-in-octane emulsions. Notably, the octadecyl amine-modified nanosheets can also stabilize w/o emulsions. Polymerization of the continuous or discontinuous phase or interfacial polymerization in these o/o emulsions readily gives access to foams, armored particles, or capsules, respectively.[41] For example, if the droplets are composed of an isocyanate-bearing methacrylate monomer, dispersion free radical polymerization yields armored polymer particles. In this case, the isocyanate groups of the polymer particles can then be modified. This is not possible if a traditional o/w emulsion is used since the isocyanate group would hydrolyze by reaction with water to give an amine that could then lead to cross-linking.

Alkylated GO nanosheets can stabilize more than o/o emulsions provided that the nanosheets are dispersible in the liquid that becomes the continuous phase and that the two emulsion phases are immiscible with each other (e.g., Bancroft rule). This extends beyond o/o systems to include IL and salt hydrates, as well as gases (e.g., for the formation of Pickering bubbles).[42,43] We term these nonaqueous emulsions, as water does not serve as one of the phases, yet water does not need to be strictly excluded from the system (as in the case of salt hydrates). Ready access to such phase-separated systems significantly expands the types of emulsions that can be formed and integration of more diverse components. Thus, the ability to stabilize nonaqueous emulsions is not only critical to using reagents that could react undesirably with water (such as isocyanates) but also for tailoring the composition. Specifically, many ILs are water-immiscible or hygroscopic, and their physical properties (viscosity, capacity for small molecules) are dictated by composition. In a similar vein, the thermal energy management performance of solid−liquid salt hydrate phase change materials is highly sensitive to composition, where small changes in stoichiometry leads to detrimental consequences for the selected application.[44]

A single-step encapsulation of IL can be realized by interfacial step growth polymerization in an emulsion, provided orthogonal solubility of two monomers.[45] For example, a GO-stabilized emulsion can be prepared with ethylenediamine in the continuous water phase and hexamethylene diisocyanate in droplets of an IL, such that interfacial polymerization yields capsules with a core of the IL and composite shell of nanosheets and polyurea.[46] This approach was used to encapsulate the generic IL [BMIM][BF_4] and give capsules with applications in CO_2 uptake and separations. The capsule shell contributed to performance in CO_2 uptake, attributed to adsorption and possibly reaction of any residual amines with CO_2. Upon accounting for the contribution of the shell, it was found that the encapsulated IL reached full capacity of CO_2 in a shorter amount of time than the bulk IL, and without the need for agitation, thus greatly simplifying the system (Figure 3A). In complement, the same type of capsule was loaded into a column and then a phenol-contaminated oil was passed through; here, the phenol was sequestered by the encapsulated IL, giving an eluent of phenol-free, pure oil.[24] Comparison of the fluid-filled capsules to the capsule shell alone highlighted the critical performance of the IL in the separation. In both applications, the capsules could be regenerated by mild heating (e.g., to release the small molecule sequestered).

In preparation of capsules in an IL/oil emulsion, the diisocyanate in the IL may react with water that has partitioned into the IL, thereby producing a primary amine which reacts with other isocyanate groups. Thus, nonaqueous emulsions present an opportunity to better control the composition of the product. A task-specific IL which both chemisorbs and physisorbs CO_2 was encapsulated using a nonaqueous emulsion and interfacial polymerization, giving capsules with a core of 1-ethyl-3-methylimidazolium 2-cyanopyrolide ([EMIM][2-CNpyr]) and composite shell of alkylated GO and polyurea.[46] For the IL, the anion can reversibly react with CO_2, enhancing capacity and performance compared to generic ILs. Detailed characterization of the performance of these capsules for CO_2 uptake, using breakthrough experiments and under varied humidity, highlights the distinct properties and opportunities of these structures. Importantly, the capsules are stable to multiple CO_2 uptake and thermal release profiles (Figure 3Aiii) and are stable under humid conditions, without detriment to performance. Further, at low pressures, these capsules outperform canonical porous inorganic materials (i.e., zeolites). Taken together, these data suggest that encapsulated ILs, as prepared from nonaqueous emulsion templates, may be useful in capture of CO_2 at low concentrations, such as direct air capture (DAC). Oppor-

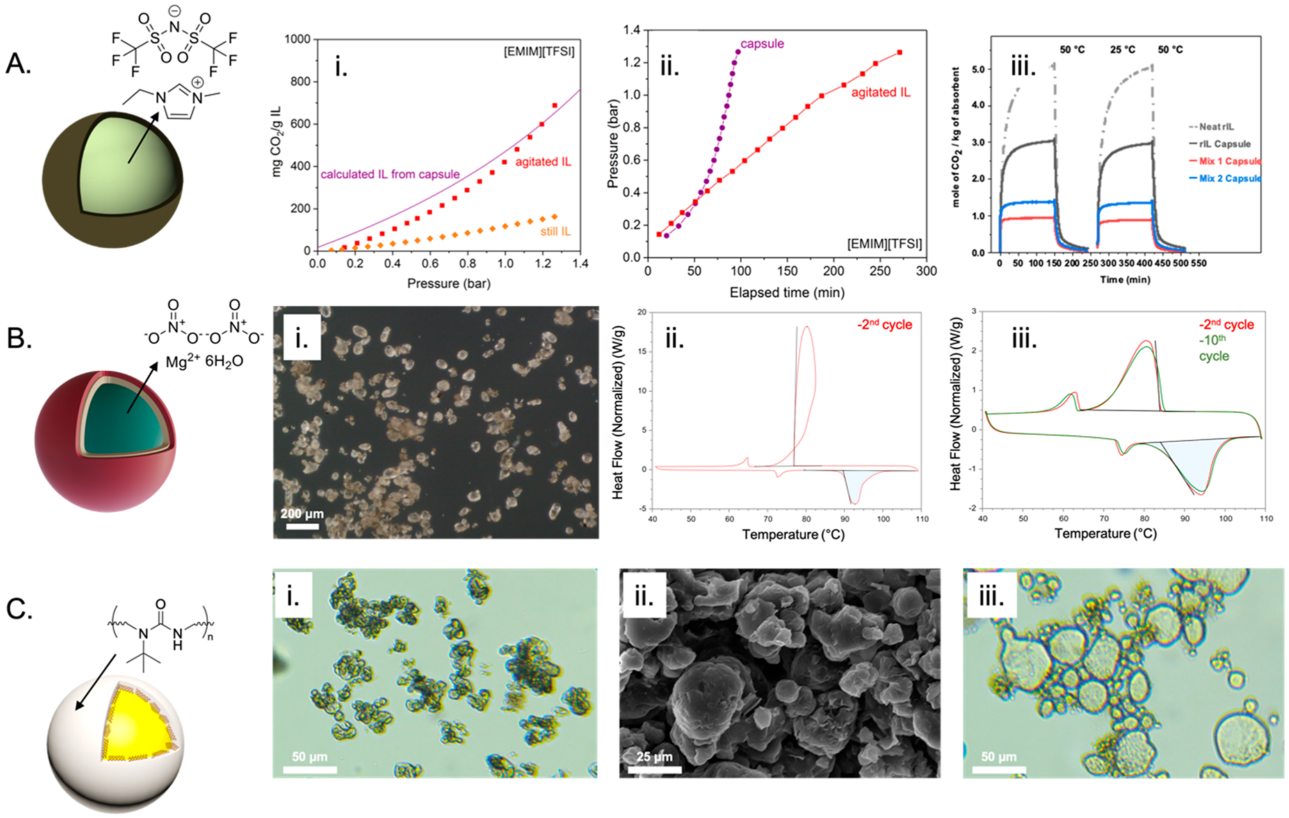

Figure 3. Examples of the performance of composite structures produced from Pickering emulsions: (A) Capsules of ionic liquid (IL) and their performance in uptake of CO_2: (i) comparison of capacity of still IL, agitated IL, and encapsulated IL, (ii) time for equilibration of CO_2 uptake for agitated IL and encapsulated IL, and (iii) CO_2 uptake and release profiles for capsules with core of task specific IL. (3Ai-3Aii) reproduced with permission from ref 22. Copyright 2019 American Chemical Society. (3Aiii) reproduced with permission from ref 46. Copyright 2019 American Chemical Society. (B) Capsules with core of salt hydrate phase change material (PCM): (i) optical microscopy image of capsules when heated about the melting point of the PCM, (ii) DSC curve of bulk PCM, and (iii) DSC trace of encapsulated PCM. Reproduced from ref 48 with permission. Copyright 2022 Elsevier. (C) Capsules with a shell that contains hindered urea bonds: (i) optical microscopy image of as prepared capsules, (ii) SEM image of capsules after shell fusion, and (iii) optical microscopy image of the emulsion formed after destruction of shells. Reproduced with permission from ref 50. Copyright 2022 American Chemical Society.

tunities for advances center on tailoring the shape and size of the capsules, as well as the composition of the shell and core.

Encapsulation of salt hydrate PCMs can enable them to be handled as a solid when they are in liquid form and can also address undercooling by integration of nucleating agents. Prior approaches to encapsulating salt hydrate PCMs leveraged excess water to access liquidous salt hydrate and required selective evaporation to access ideal compositions, a time-consuming and challenging task.[47] Interfacial polymerization, with one monomer in the continuous phase and the other in the discontinuous phase (e.g., diisocyanate and diamine), is undesirable for encapsulating these PCMs because this would lead to an impure core (e.g., presence of residual monomer). Thus, an alternative route is required to access capsules with a pristine core of salt hydrate PCM, with a nonaqueous emulsion enabling encapsulation. Lak and co-workers utilized alkylated GO nanosheets dispersed in toluene to prepare emulsions with droplets of the salt hydrate PCM $MgNO_3 \cdot 6H_2O$ (Figure 3B).[48] The PCM/oil emulsion was formed above the melting point of the PCM (90 °C), then allowed to cool to ambient temperatures, which resulted in solidification of the salt hydrate. A solution of polymer in, e.g., dichloromethane, was then added; the change in the solvating environment led to precipitation of the polymer onto the salt hydrate particles, thus forming a core–shell–shell structure (PCM-nanosheet-polymer). This approach to encapsulation was also demonstrated for an IL which melted above room temperature (80 °C) and for different commodity polymers, including polystyrene, polyethylene, and poly(methyl methacrylate). The capsules of PCM were stable to multiple heating–cooling cycles, in which the PCM melted and resolidified. Perhaps surprisingly, the alkylated nanosheets served as a nucleating agent for the salt hydrate and significantly decreased undercooling compared to the bulk (compare Figure 3Bii and Biii). This approach of polymer deposition onto the emulsion droplet in nonaqueous emulsions is promising for accelerating composite formation, specifically for producing capsules with pristine core compositions.

Nonaqueous emulsions offer the opportunity to integrate new polymer chemistries into Pickering emulsion templated composites, specifically those that are incompatible with water. This includes catalysts that traditionally require stringent exclusion of water, as well as the formation of bonds that are water sensitive. Wang and co-workers leveraged nonaqueous emulsions stabilized by alkylated GO nanosheets to integrate hindered urea bonds (HUBs) into capsules shells. Urea bonds formed by the reaction of a primary amine with an isocyanate are robust and thermally stable; in contrast, HUBs prepared by the reaction of a secondary amine and an isocyanate have a thermally accessible reverse reaction (i.e., to yield the secondary amine and isocyanate). This is due to the poor planarity of the HUBs imparted by steric constraints. Notably, if HUBs are formed in the presence of water, liberated isocyanate can react with water, expel CO_2, and form a primary amine that can react with other isocyanates, giving undesired and thermally irreversible urea bonds. Hence, o/o emulsions were used to prepare shells of an HUB-containing polyurea-polyurethane (using chain extenders).[49] These capsules were stable at ambient temperature but underwent transformations with gentle heating: (i) upon compaction, bond exchange between neighboring capsule shells led to the formation of a monolith; or (ii) in the presence of hexyl amine in an octane dispersion, capsule shells were destroyed due to production of the isocyanates which irreversibly reacted with the primary amine. The temperature required to access the thermal bond reversion was similar to that observed for the bulk polymer and dictated by the bulkiness of the amine system for *N*,*N*-di-*tert*-butyl ethylenediamine (35 °C), *N*,*N*-di-isopropyl ethylenediamine (55 °C), and *N*,*N*-diethyl ethylenediamine (80 °C).[49,50] Notably, this system could not be used to prepare room-stable capsules with cores of pure IL; stable capsules were obtained with a maximum of 45 wt % IL in DMF, and even then bond exchange was observed at 8 °C.[50] These studies support that the polymer capsule shell prepared by interfacial polymerization is plasticized with the liquid of the core, such that intermediates and/or transition states for the HUB transformation are stabilized.

OUTLOOK

Emulsions are an attractive platform for which to template different structures, including capsules, foams, and armored particles, and the use of particle surfactants gives access to composite structures. Nonaqueous emulsions are emerging systems, both for the fundamental understanding of stabilization of microphase separated systems and for the fabrication of new compositions and architectures not possible by other approaches. Researchers should consider how to develop new functional particles as surfactants, so that the properties of the particles are integrated into the composites formed. Such advances would benefit by moving beyond a simple formulation approach and the use of high throughput experimentation and characterization, possibly integrating data science approaches, and integrating the application of machine learning. This would support the rapid design, fabrication, and application of new material constructs for a broad range of technologies. Further, the particle surfactants themselves can be made reactive by selective modification to further enhance, and perhaps simplify, composite formation. In addition to traditional emulsions, high internal phase emulsions (HIPEs) and bicontinuous emulsions should be developed, such that monoliths with a high interfacial area and surface area of the functional particles are produced, in a scalable and rapid method and using nearly any liquid−liquid combination. In addition to oils, IL, and salt hydrates, new liquid compositions can be used which include hydrogen bonded solvents or deep eutectic solvents (DESs)[51] as well as reactive or volatile liquids. Performance of the produced composites may be further enhanced by emulsification under a controlled environment (such as nitrogen or water-free air). The application-oriented properties of the composites fabricated must also be better delineated; for example, how does shell composition impact mass transfer across the barrier—both for desirable transfer of, e.g., CO_2 for direct air capture, and for undesirable transfer of, e.g., water in salt hydrate PCMs for thermal energy management.[52] Nonaqueous and/or water-free emulsion compositions are ideal for tailoring composition to include components that have traditionally been considered impractical due to solubility or water incompatibility issues, as these systems may lead to unexpected applications, such as feedstocks in additive manufacturing or reconfigurable structures.

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Notes

The authors declare no competing financial interest.

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Nicholas Starvaggi received his B.S. in chemistry and biochemistry from Mount St. Mary's University in 2021. He is currently pursuing his PhD in Chemistry in the Pentzer lab at Texas A&M University, where he is an NSF graduate research fellow. His research interests focus on functionalized soft materials and microencapsulation strategies.

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