ENG. Chem. Eng. 2027, 21(3): 19
https://doi.org/10.1007/s11705-027-2725-3

REVIEW ARTICLE

Microplastic-free microcapsules for environmentally conscious formulated products: materials, performance, and industrial perspectives

Siddhant Pravin Bhutkar[1], **Daniele Baiocco**[2], **Zhibing Zhang** (✉)[3]

1 PheroSyn Ltd, Rothamsted Research, West Common, Harpenden AL5 2JQ, UK
2 Department of Chemical Engineering, School of Aeronautical, Automotive, Chemical, and Materials Engineering, Loughborough University, LE11 3TU, UK
3 School of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, UK

© The Author(s) 2027. This article is published with open access at link.springer.com and journal.hep.com.cn

Abstract Microplastic pollution poses an environmental and public health concern because persistent particles can disperse through air, water, soil, and biological systems, making recovery and long-term risk management extremely difficult. In addition to fragmented plastic waste, synthetic polymer microparticles are intentionally added to formulated products for functional benefits. Regulations such as the European Union Registration, Evaluation, Authorisation, and Restriction of Chemicals restriction on intentionally added synthetic polymer microparticles, are driving their removal or replacement. Microcapsule-based delivery systems form an important subset of this challenge in agrochemicals, detergents, personal care products, coatings, and household formulations, where polymeric shells protect active ingredients and control their release. Replacing these non-biodegradable shells is challenging because they provide desirable mechanical strength, barrier properties, high payload, and controlled release in demanding formulations. This mini-review critically examines emerging microplastic-free encapsulation strategies, including inorganic shells, biobased polymers, organic–inorganic hybrids, biodegradable aliphatic polyesters, and supramolecular assemblies formed at emulsion interfaces. These approaches show that microplastic-free encapsulation is feasible and can sometimes match conventional microcapsules, but scalability, manufacturing simplicity, and validated environmental fate remain major barriers. Future progress requires integrated design strategies that combine performance, scalable processing, environmental validation, and regulatory compliance. Direct benchmarking against conventional microcapsules and lower-energy manufacturing routes will be essential for next-generation delivery systems aligned with circular economy and net zero goals.

Keywords microplastic-free, biodegradable, microcapsules, delivery systems, formulated products

Received August 14, 2026; accepted October 13, 2026;
online November 10, 2026

E-mail: z.zhang@bham.ac.uk

1 Introduction

Today plastics have become ubiquitous in our daily lives due to their versatility, end-use adaptability, and relative robustness. However, the inherent non-biodegradability of plastics and, therefore, their long-lasting persistence is now a major environmental challenge [1]. Towards the end of their life cycle, plastics break down into sub-micron fragments that become pervasive in the environment [2]. For example, particles from automotive tyres, synthetic household and personal care products enter wastewater and sewage systems, where they are too small to be effectively filtered out in the process of wastewater treatment. These particles smaller than, 5 mm in size, are termed as microplastics (MPs), which are difficult to handle and recover due to their minute size, and can therefore cause a serious ecological problem [3]. By definition, the sources of MPs can be divided into two categories: (i) primary MPs are intentionally synthesized for use in industrial products like cosmetics, laundry detergents, and agrochemicals, and (ii) secondary MPs which are generated due to the breakdown of macroscopic plastics like tyres, packaging material, and textiles by various physical, chemical, and biological processes [4].

MPs enter the human body through various pathways, including inhalation, ingestion, dermal contact, and food intake, enabled by their widespread presence across air, water, and soil systems [5]. Over recent years, there has

been a rapid rise in reports of MPs across a wide range of human biological samples, including blood [6], cardiac tissue [7], lung tissue [8], and even in infants [9]. With the growing ecological concern, regulatory bodies worldwide started working on devising methods for mitigating microplastic pollution. Governments and non-governmental organizations have widely adopted the United Nations Sustainable Development Goals to improve their sustainability, with goal number 14 focusing specifically on phasing out and/or reducing the impact of microplastics [10]. Although, secondary MPs generated by fragmentation of larger plastic products constitute a major fraction of the global pollution [11], primary MPs intentionally incorporated into functional products such as fast-moving consumer goods, paints, and agrochemicals contribute significantly to MP pollution due to their direct and continuous release into the environment, with estimates reaching approximately 42000 tonnes annually [4]. Key examples include, microbeads added to rinse-off cosmetics for exfoliation, as well as microcapsules designed to encapsulate value-added active ingredients (VAAIs) in agrochemicals, laundry detergents, and household cleaning products [12,13].

Recognising the growing environmental concern around microplastic pollution, the European Chemicals Agency (ECHA) initiated the restriction process for intentionally added microplastics under the European Union Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) framework. This culminated in the adoption of Commission Regulation (EU) 2023/2055 in September 2023, which restricts the placing on the market of formulations that contain intentionally added synthetic polymer microparticles [14]. Under this regulation, polymers may be exempted from restriction if they demonstrate sufficient biodegradability using recognised test methods set by the Organization for Economic Cooperation and Development (OECD), such as OECD 301B–F or OECD 310, which assess ultimate mineralisation through CO_2 evolution or O_2 consumption [15,16].

Encapsulation of active ingredients within a protective microcapsule plays a critical role in improving the performance of formulated products by protecting the VAAI against external environmental factors during storage, handling and at the time of application. Additionally, encapsulation enables the controlled release of the VAAI at the target site on demand or under the action of an external stimulus. Synthetic non-biodegradable polymers such as polyurea, polyurethane, polyacrylates, and aminoplasts like urea/melamine formaldehyde are heavily petroleum-based and predominantly used in industry as the building blocks for microcapsule shells [12,17]. These polymers offer excellent mechanical strength and barrier properties and perform satisfactorily across a wide range of end-use application [18]. This is partly due to the high degree of crosslinking, which adversely affects the biodegradability of these polymers. As a result of the new regulations against MPs [14], it has become imperative for global businesses to engineer products with microplastic-free alternatives without undermining their end-use performance. In the context of encapsulation systems, 'microplastic-free' refers to microcapsules that do not contain or generate persistent synthetic polymeric particles, either by being entirely polymer-free, composed of naturally occurring unmodified polymers which are biodegradable, or by employing materials that fully meet biodegradability criteria under relevant environmental conditions [13,15].

To date, relevant scientific reviews have explored specific aspects of the field, including the implications of microplastic-free regulations on formulated products [19], formulation strategies for sustainable consumer products [12], and the broader challenges associated with encapsulation technologies [13]. In addition, recent reviews have begun to address the relationship between microencapsulation and the regulatory microplastic classification by evaluating whether microcapsules should be labelled as microplastics based on their shell chemistry [4]. In parallel, reviews focusing on biodegradable or sustainable encapsulation have also emerged, but these are typically framed around specific application areas such as laundry and fragrance formulations [12,17], food systems [20], and cosmetics [11]. These studies provide valuable insights, but a comprehensive assessment of shell-forming technologies, fabrication methods, performance limitations, and scalability potential across materials is still lacking.

In this mini-review, we provide a focused and critical overview of the principal approaches explored for microplastic-free encapsulation, including inorganic shell materials, biobased polymers and derivatives, inorganic-organic hybrid microcapsules, biodegradable polyesters, and supramolecular shells via interfacial self-assembly, evaluating their advantages and limitations in terms of performance, scalability, and industrial feasibility. Microencapsulation also has significant biomedical applications, including drug delivery, cell encapsulation, tissue engineering, and delivery of biologics and vaccines [21]. These delivery systems operate within distinct regulatory and application contexts, with requirements related to safety, efficacy, biocompatibility, and clinical evaluations established by regulatory agencies such as the United States Food and Drug Administration [22]. However, the present review focuses on sectors directly impacted by the emerging EU REACH restrictions on intentionally added synthetic polymer microparticles [14], particularly agrochemicals, detergents, household care, and personal care [11−13,17,19].

2 Inorganic shell materials

Inorganic shell materials like phosphates, carbonates, and

silicates have recently garnered interest for encapsulation of VAAI [23−25]. These inorganic materials represent one of the most direct routes towards microplastic-free encapsulation because they avoid the use of persistent synthetic polymeric shell networks. Their chemical inertness, biocompatibility, and thermal stability make them attractive candidates for applications where regulatory compliance and environmental persistence are key concerns [26]. A range of facile synthesis strategies have been reported for the fabrication of inorganic microcapsules [27]. Among them, template-based approaches are particularly relevant for commercial formulations that need to align with increasingly tight regulations on microplastics. In these systems, emulsion droplets of the VAAI serve as soft templates, around which the inorganic shell is formed at the oil-water interface [24].

2.1 Silica

Silica-based microcapsules are among the most explored inorganic systems, largely because the sol-gel chemistry enables shell formation under relatively mild conditions and allows control over shell morphology through parameters, such as precursor concentration, pH, and temperature [23,28]. For instance, Yeom et al. [25,29] synthesized core-shell fragrance microcapsules by premixing tetraethyl orthosilicate (TEOS) with the VAAI to create a homogeneous lipophilic phase which was emulsified in an aqueous phase to create an oil-in-water (O/W) emulsion. The hydrolysis and condensation of the TEOS at the oil-water interface led to the formation of a silica shell around the droplets. However, silica shell formation is strongly governed by relatively slow hydrolysis-condensation kinetics, with the initial formation of the shell requiring approximately 2 days. Moreover, the inherent mesoporosity of silica can compromise barrier properties, allowing fragrance leakage through residual pores in the shell. To mitigate this, additional TEOS was introduced to promote seeded silica growth, increasing shell thickness and reducing pore area/volume, thereby improving fragrance retention [25,29]. While effective, this additional densification step increases both duration and complexity of the process and must be balanced out against encapsulation performance, barrier properties, and potential scalability.

An alternative strategy is to use colloidal silica nanoparticles as Pickering emulsifiers, where the interfacial particle layer both stabilises the emulsion droplets and provides a scaffold for subsequent silica mineralisation, enabling the formation of surfactant-free silica microcapsules (Fig. 1) [30,31]. This method was initially formulated by Cardoso et al. [32] and later optimized at Procter & Gamble, Brussels Innovation Centre in Belgium, to encapsulate a variety of VAAI including fragrances for laundry applications. In the patent, shell permeability was evaluated using a verdyl acetate tracer test, where only ~12% of the encapsulated tracer was detected outside the capsule after 7 days at 35 °C in a 15 wt% sodium dodecyl sulphate medium, indicating strong barrier performance under accelerated testing and surfactant-rich conditions. However, stable Pickering emulsions are highly sensitive to nanoparticle wettability and often require surface modification to achieve appropriate interfacial activity, adding processing complexity, and potential variability during scale-up [31,33]. Moreover, because shell hardening and densification still rely on sol-gel hydrolysis and condensation of silica precursors, these systems can retain the kinetic limitations of TEOS-based routes, requiring extended curing times to form a dense, low-permeability shell [32].

Another unique approach to create silica microcapsules was developed by Brossault et al. [34], which involved destabilizing and aggregating colloidal silica nanoparticles in aqueous dispersions via addition of electrolytes (e.g. calcium chloride). By using an oil in water in oil double emulsions, hydrophobic VAAI (in the inner oil phase) were successfully encapsulated in a silica shell formed by destabilizing the silica nanoparticles in the middle aqueous phase [35]. However, this process involves the use of double emulsions which are thermodynamically unstable, with a large tendency for coalescence, creaming, and flocculation [35]. Additionally, the reported payloads of the VAAI were below 20% [36].

Overall, silica microcapsules provide one of the clearest and environmentally benign, polymer-free routes towards microplastic-free encapsulation with inherent biocompa-

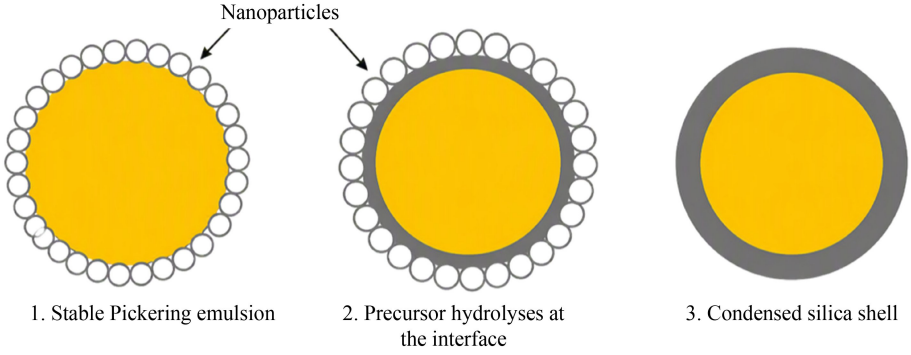


Fig. 1 Forming silica microcapsules using Pickering emulsions stabilized by colloidal silica nanoparticles. Adapted from Ref. [32].

tibility and low toxicity. Furthermore, the industrial relevance of silica microcapsules is evident from industrial investigations available in patent literature [32,37,38]. However, their broader applicability remains constrained by the mesoporous nature which can compromise long-term active retention [36]. Moreover, the rigid inorganic network can make these microcapsules brittle and susceptible to rupture under stress [39].

2.2 Calcium carbonate ($CaCO_3$)

$CaCO_3$ represents another inorganic material that can be used for synthesizing microplastic-free microcapsules. Industrially, $CaCO_3$ is generated by bubbling carbon dioxide (CO_2) through a dispersion of slaked lime ($Ca(OH)_2$) [40]. Wang et al. [41] combined this method of carbon dioxide bubbling to fabricate a $CaCO_3$ shell on a Pickering emulsion template. Stable O/W emulsions were prepared using pristine $CaCO_3$ nanoparticles as Pickering emulsifier. Carbon dioxide was introduced into the aqueous emulsion to generate carbonate ions, and controlled addition of calcium chloride into the continuous phase led to the crystallization of $CaCO_3$ onto the interface of the emulsion droplets. A dense $CaCO_3$ shell was generated with excellent mechanical properties (nominal rupture tension = 175 $N \cdot m^{-1}$).

Ionic reactions involving Ca^{2+} and CO_3^{2-} have also been used to generate $CaCO_3$ shells at the interface of an emulsion [42]. In these systems, water-in-oil-in-water (W/O/W) double emulsions are typically used as templates, where the inner and outer aqueous phases contain either calcium or carbonate ions. Their subsequent diffusion and interfacial reaction result in the formation of a $CaCO_3$ shell surrounding the inner aqueous droplets. Nevertheless, stabilizing double emulsions is extremely challenging and this method is only useful for specific biomacromoleules [43].

Hettiarachchi et al. [44] demonstrated the use of a cationic surfactant to aid the interfacial crystallization of $CaCO_3$ onto an emulsion template. Using cetyltrimethylammonium chloride, as a surfactant, an epoxy core was emulsified in water. Subsequently, calcium chloride and sodium carbonate solutions were added dropwise to the emulsion to spontaneously precipitate $CaCO_3$ shell at the interface. Presumably, the positively charged surfactant holds the negatively charged CO_3^{2-} at the interface and acts as a pre-nucleation site for the generation of $CaCO_3$ crystal (Fig. 2). Although this process appears more straightforward than using double emulsions, uncontrolled nucleation and growth of $CaCO_3$ crystals in the bulk can lead to significant loss of raw materials [45], which consequently leads to the formation of an incomplete shell and unencapsulated oil.

Similar to silica systems, microcapsules fabricated using $CaCO_3$ exhibit inherent porosity and brittleness, which negatively affects their mechanical performance and barrier properties [46]. As a result, their use may be limited and not suitable for encapsulating small and volatile active ingredients, such as those used in laundry, personal care, and fragrance formulations, which require long-term stability under harsh conditions and extended shelf life [12,47]. Moreover, the intrinsic sensitivity of $CaCO_3$ to acidic pH should also be taken into account, which can result in premature degradation of the shell [39,46].

3 Biobased polymers and derivatives

Till date, biobased polymers derived from natural sources, have been widely investigated for fabricating microcapsules, primarily due to their inherent biocompatibility and biodegradability [48]. The majority of these polymers and the corresponding encapsulation techniques have been established well within multiple industrial sectors, like pharmaceuticals, cosmeceuticals, and food technology, to name a few [20]. However, their translation to consumer products, such as laundry detergents and agrochemicals remains limited, as microcapsules in these applications must withstand significantly harsher physicochemical conditions to ensure controlled release [12]. This section highlights recent efforts to extend the use of emerging biobased polymers to such non-biological applications.

3.1 Chitosan and complex coacervates

Chitosan is one of the most extensively studied biobased polymers for microencapsulation, owing to its biodegradability, biocompatibility, and inherent cationic

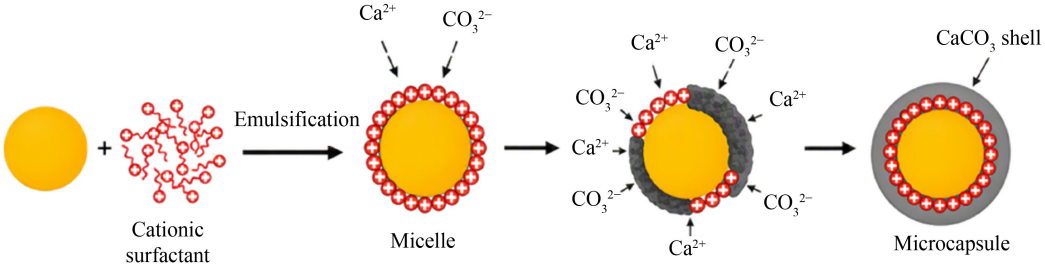


Fig. 2 *In-situ* emulsion and interfacial mineralization of $CaCO_3$. Reproduced from Ref. [44], licensed under Creative Commons Attribution 4.0 International License (CC BY 4.0).

nature arising from protonatable amino groups [49]. These functional groups enable a wide range of encapsulation strategies, including ionic gelation, covalent crosslinking, and complex coacervation, making chitosan highly versatile for forming microcapsule shells [49,50]. Most of these techniques rely on the phase separation of chitosan from aqueous solution, where oleophilic VAAI are first emulsified in dilute acidic chitosan solutions. Microcapsule formation is then driven by interfacial self-assembly and solidification at the oil-water interface, typically triggered by pH adjustment, addition of anionic species, or changes in temperature [49,51].

Complex coacervation is a widely preferred technique to fabricate microcapsules in an aqueous medium under ambient conditions, achieving high encapsulation efficiencies [52,53]. Various natural proteins and polysaccharides, including gelatine, alginate, gum Arabic, and chitosan, have been employed for encapsulating oleophilic VAAIs via this approach [52,54−56]. Other naturally derived polymers have also been investigated but to a lesser extent including pea proteins [57], soy proteins [58], whey proteins [59], and silk fibroins [60]. Overall, complex coacervation offers a wide range of biopolymers to choose from for encapsulating VAAI. However, the process is extremely sensitive to pH [61]. For every polyelectrolyte combination, a narrow range of pH exists wherein both components carry opposite charges, necessary for the coacervation [51]. Therefore, encapsulating VAAI sensitive to low pH is challenging. Furthermore, the coacervate shells lack long term stability as the structure is governed by weak electrostatic interactions, often necessitating crosslinking for practical applications [62]. Common crosslinkers include glutaraldehyde [54,55], transglutaminase enzyme [63], tannic acid [64], and ionic crosslinkers like sodium tripolyphophate [65]. Although crosslinking improves the shell stability, it can also adversely affect the biodegradability of the coacervates.

3.2 Cellulose derivatives

Cellulose-based materials represent a widely explored class of biobased encapsulation systems due to their abundance, biocompatibility, and favourable film-forming properties [66]. However, native cellulose is rarely used directly because of its intrinsic insolubility arising from its highly crystalline hydrogen-bonded structure [67]. Instead, chemically modified derivatives such as ethyl cellulose [68], cellulose acetate [69], cellulose acetate butyrate [70], and cellulose sulphate [71] are more commonly employed as shell precursors for microcapsules. Methyl cellulose is often used as an emulsifier rather than a structural component, owing to its amphiphilic and water-soluble nature, which enables effective stabilisation of oil-water interfaces but limits its ability to form dense, mechanically robust films required for continuous microcapsule shells [72]. Among available fabrication techniques, solvent evaporation remains the most commonly used route [73]. While this approach is versatile and well established, the use of halogenated organic solvents such as dichloromethane raises environmental and safety concerns [74]. Ethyl acetate, has been used as an alternative with a better toxicology profile, which is less harmful than other halogenated solvents [75]. However, phase separation and solvent removal can induce porosity in the resulting shell, thereby compromising barrier properties [12]. Additionally, the biodegradability of cellulose derivatives is highly dependent on the degree of chemical substitution, meaning that not all systems can be unequivocally classified as microplastic-free [76,77].

3.3 Proteins

Protein-based microcapsules represent another versatile and inherently biodegradable class of encapsulation systems, owing to their excellent film-forming ability and widespread availability from both animal (e.g. gelatine, whey, casein) and plant-based proteinaceous sources (e.g. soy, pea, and zein) [78,79]. Bovine serum albumin [80], pea protein isolates [81], soy protein isolate [82], and a variety of legume proteins [83], have been utilized for encapsulating oleophilic VAAI using sonochemical emulsification. However, ultrasonication is difficult to scale because cavitation is spatially localized and sensitive to reactor geometry, energy input, and temperature control, which can affect droplet size distribution and reproducibility [84]. Spray drying is therefore commonly used as a more scalable alternative for producing protein-based microcapsules [85]. In addition to conventional protein systems, silk fibroin has recently emerged as a promising biocompatible material for microencapsulation, wherein its inherent polymorphism, allows transitions between hydrophilic coil and hydrophobic β-sheet structures, enabling control over shell morphology and properties [86]. This behaviour has been exploited to fabricate silk fibroin microcapsules with tuneable structures for encapsulating hydrophobic active ingredients such as herbicides [87].

Despite these advances, single protein microcapsules are known to be sensitive to external environmental conditions like pH or temperature and may also lack the mechanical strength required to withstand physical stresses generated in processing equipment [88,89]. As a result, complex proteins are used in combination with other natural materials (e.g. polysaccharides) to produce microcapsules with enhanced characteristics [88]. The intrinsic charge of proteins enables their interaction with oppositely charged polymers, promoting the formation of hybrid microcapsules via ionic interactions. Structural reinforcement is typically achieved through covalent or enzymatic crosslinking of amino groups, using agents

such as glutaraldehyde and transglutaminase, although these modifications can increase complexity and adversely affect biodegradability [88,90].

4 Inorganic-organic hybrid materials

Nature-inspired organic-inorganic hybrid microcapsules offer a promising strategy for overcoming the limitations of single-component shell materials. In many biomineralised systems, a soft organic matrix directs the formation of a rigid inorganic phase, producing structures with enhanced strength, toughness, adhesion, thermal resistance, and barrier properties [91−94]. Similarly, combining inorganic materials with organic components in hybrid microcapsule shells has demonstrated to overcome drawbacks like porosity and brittleness associated with purely inorganic shell materials [46,91]. Consequently, these composite materials have been investigated to leverage the synergistic properties of both organic and inorganic components. For instance, Shchukin et al. [92] employed a layer-by-layer (LbL) approach to fabricate alternating layers of poly(allylamine hydrochloride) and poly(styrene sulfonate) on sacrificial $CaCO_3$ templates, followed by ion exchange and mineralization steps to deposit inorganic phases such as calcium phosphate. Similar approaches have been extended to construct hybrid shells incorporating silica, titania, or polydopamine via electrostatic assembly and subsequent inorganic deposition [93,95,96]. These strategies highlight the ability of oppositely charged polyelectrolytes to form interfacial templates that facilitate controlled inorganic growth, enabling the fabrication of structurally integrated hybrid shells. However, because each LbL coating is typically very thin, multiple sequential deposition and washing cycles are required to build a mechanically robust shell, making the process time consuming, operationally complex, and difficult to scale up industrially.

As explained before (Fig. 1), Pickering emulsions can be used for stabilizing O/W emulsions by leveraging the ability of nanoparticles to adsorb at liquid-liquid interfaces. For instance, Baiocco et al. [97] used pristine $CaCO_3$ nanoparticles at the emulsion interface as nucleation sites for controlled mineralisation, followed by the deposition of secondary polymeric or polydopamine layers, yielding hybrid microcapsules with enhanced mechanical strength and barrier performance. The process was further improved, by the use of silica nanoparticles modified using a cationic surfactant, cetyltrimethylammonium bromide (CTAB), to stabilize O/W emulsions [39]. The positively charged emulsion was further modified using negatively charged poly(acrylic acid). Then, using calcium chloride and sodium carbonate, a primary $CaCO_3$ layer was formed onto the interface. Finally, a polydopamine layer was coated onto the primary inorganic shell (Fig. 3(a)). The resulting composite shell combined an inorganic $CaCO_3$-rich layer with an outer polydopamine coating (Figs. 3(b) and 3(c)), which led to the formation of extremely strong microcapsules (nominal rupture tension 486 ± 29 $N \cdot m^{-1}$).

However, these performance gains come at the expense of increased process complexity. Multilayer hybrid capsules typically require several sequential operations, including nanoparticle surface modification, adsorption of charged polymers, controlled mineralisation, pH adjustment, and secondary coating deposition. Each step introduces additional formulation variables and potential batch-to-batch variability, which can complicate scale-up and process reproducibility [39]. A related strategy is the deposition of superhydrophilic polyelectrolyte multilayers onto capsule surfaces to reduce the diffusion rate through the shell for hydrophobic or semi-hydrophobic actives [98]. However, this again relies on LbL assembly and adds further processing complexity. Moreover, from a regulatory perspective, although the individual components used in hybrid microcapsules may be biodegradable or compliant with emerging microplastic-free requirements, their integration into complex architectures can alter interfacial properties and potentially slow the overall degradability process [47]. Furthermore, although polydopamine is largely claimed to fully degrade, the underlying biodegradation mechanisms still remain to be investigated [99].

5 Biodegradable aliphatic polyesters

Biodegradable polymers developed using naturally occurring compounds (e.g., lactic acid) have long been employed for sustainable encapsulation of VAAI [100]. Particularly aliphatic polyesters such as polylactide [101], poly(lactide-co-glycolide) (PLGA) [102], polyhydroxyalkanoates (PHAs) [103], and polycaprolactone (PCL) [104], have been widely explored as microplastic-free alternatives due to their hydrolysable backbones and established use in encapsulation applications. These materials enable tuneable degradation behaviour and have been successfully employed for controlled release systems, with encapsulation typically achieved via emulsion-based techniques such as solvent evaporation and phase separation [100].

A wide variety of functional VAAIs including fragrances [105,106], essential oils [101,102,107], fertilizers [104], herbicides [103,108], and pharmaceutical molecules [109] have been encapsulated within these synthetic biodegradable polymers with encapsulation efficiencies reaching as high as 83% [101]. However, solvent evaporation, commonly used for preparing microcapsules from synthetic biodegradable polymers,

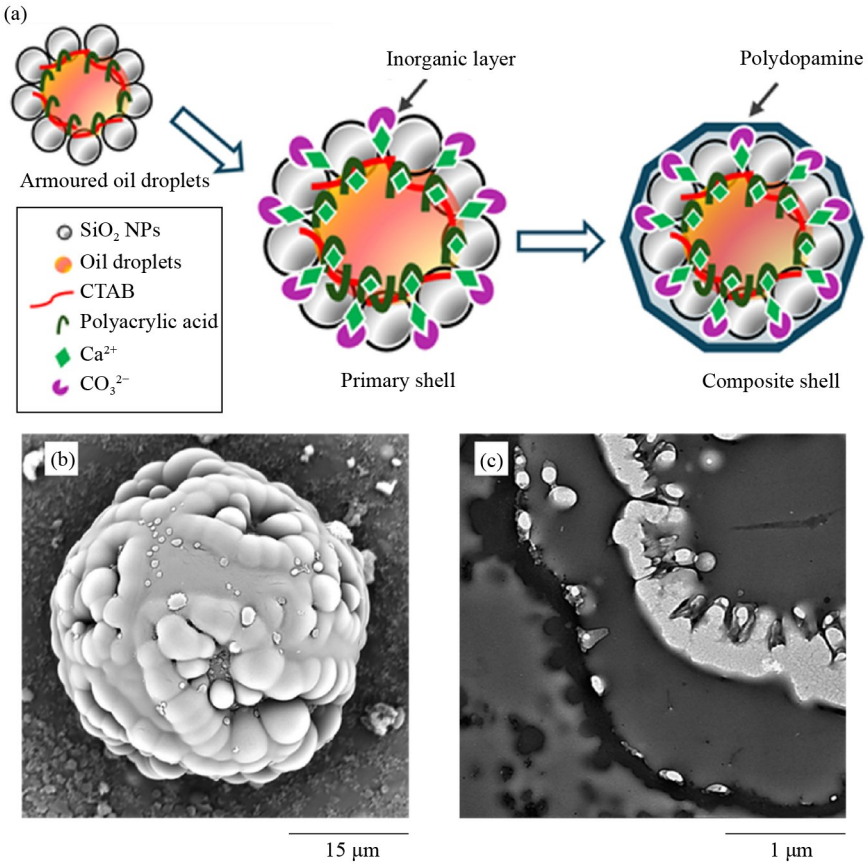


Fig. 3 Formation and morphology of inorganic–organic multilayer microcapsules (a) schematic of multilayer shell formation, (b) scanning electron microscopy (SEM) image of the resulting polydopamine-coated composite microcapsule, and (c) TEM cross-section showing the multilayer shell structure, with inorganic and organic regions visible across the capsule wall. Reproduced from Ref. [39], licensed under Creative Commons Attribution 4.0 International License (CC BY 4.0).

requires substantial amounts of organic solvents. These solvents must be handled under controlled conditions to minimise exposure to potentially harmful vapours, followed by recovery and appropriate reuse or disposal, all of which add to the operational complexity and cost [12]. Additionally, solvent removal and phase separation processes can introduce porosity into the capsule shell, potentially resulting in rapid leakage of the encapsulated active ingredient [33].

6 Supramolecular shells via interfacial self-assembly

Interfacial polymerization is widely regarded as the most established route for the large-scale industrial production of microcapsules [18,48,110]. It involves the rapid reaction of complementary monomers at the interface between two immiscible phases, resulting in the formation of a thin, crosslinked polymeric film around dispersed droplets. Owing to its robustness, scalability, and compatibility with emulsion-based processing, this technique has been extensively adopted to produce microcapsules used in many commercial formulations [110−112]. Consequently, using this technique as a basis for developing microplastic-free microcapsules can present a significant advantage for industrial implementation, as it enables compatibility with existing processing infrastructure, thereby facilitating scale-up without requiring substantial changes to established manufacturing practices [33].

Wilson-Whitford et al. [113] demonstrated that small molecules bearing hydrogen-bonding motifs can self-assemble at oil-water interfaces to form supramolecular shells capable of encapsulating fragrances. Despite requiring multiple processing steps and volatile organic solvents, this approach demonstrates the feasibility of producing fully microplastic-free microcapsules using exclusively hydrogen-bonded assemblies. Building on this concept, Bhutkar et al. [33] developed a one-pot in-situ process in which bis-urea molecules form at the O/W interface and spontaneously self-assemble into a supramolecular shell. Inspired by the process methodology of interfacial polymerization, the functionality of one reacting precursor was restricted to one to prevent long-chain polymer formation, thereby generating discrete bis-urea molecules *in situ* at the oil-water interface (Fig. 4(a)). By varying the precursors, the

molecular structure of the bis-urea could be systematically modified, which in turn controlled its amphiphilicity, interfacial localisation, and tendency to self-assemble into a continuous shell rather than crystallise in the bulk. This strategy enabled capsule morphology, mechanical strength, and barrier properties to be adjusted through molecular design, while aromatic bis-urea systems further allowed encapsulation of a commercial herbicide [114]. The SEM comparison also illustrates the distinct shell morphologies, wherein aromatic bis-urea capsules formed a rough uneven surface (Fig. 4(b)), and the polyurea capsules showed a smoother morphology typical of a conventional polymeric film (Fig. 4(c)). Despite this non-polymeric shell structure, the bis-urea capsules achieved > 99% encapsulation efficiency, higher nominal rupture tensions than the benchmark polyurea capsules, and comparable herbicide release performance under accelerated thermal testing conditions (130 °C for 3 h). However, their long-term stability under harsh conditions that disrupt hydrogen bonding (e.g., solvents or high surfactant concentrations) remains uncertain, and application-specific safety and toxicological profiles still need to be investigated.

7 Encapsulation of hydrophilic active ingredients

While the encapsulation strategies discussed thus far have been extensively developed for hydrophobic VAAIs, their application to hydrophilic actives remains challenging. This arises primarily from the high aqueous solubility and low molecular weight and size of these compounds, which promote rapid diffusion through most microcapsule shells. Unlike hydrophobic systems, where retention is governed largely by interfacial compatibility and shell permeability, hydrophilic actives are inherently more difficult to confine, often resulting in premature leakage, low encapsulation efficiency, and poor sustained release performance [115]. These challenges, compounded by increasing regulatory pressure to replace non-degradable polymers, have intensified efforts to develop alternative encapsulation strategies that can provide both effective retention and environmental compliance [116].

Hydrophilic VAAIs are typically encapsulated using water-in-oil (W/O) or W/O/W emulsion templates, which allow confinement of the active within an internal

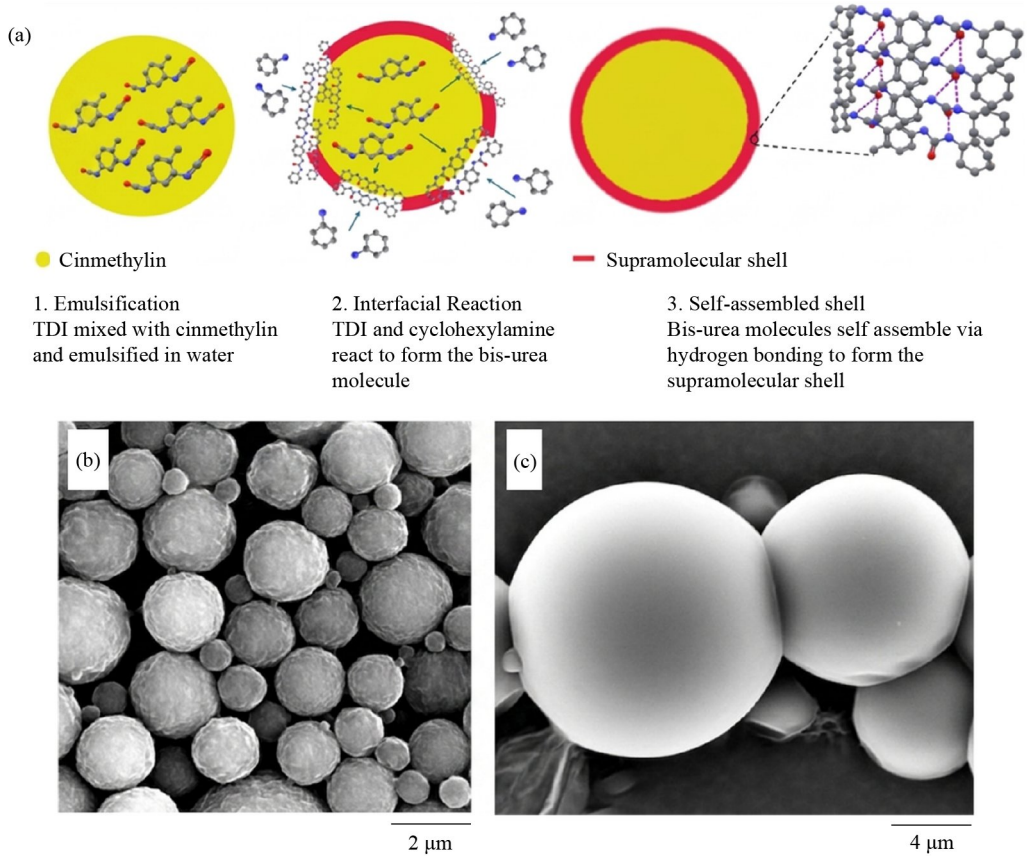


Fig. 4 Supramolecular microcapsules using bis-urea molecules. (a) Schematic representation of shell formation via interfacial reaction between toluene diisocyanate (TDI) and cyclohexylamine; (b) supramolecular bis-urea microcapsules; (c) conventional polyurea microcapsules. Reproduced from Ref. [114], licensed under Creative Commons Attribution 4.0 International License (CC BY 4.0).

aqueous phase. In some systems, water-water interfaces formed between aqueous polymer phases can also be exploited as templates for microcapsule formation. Li et al. [117] demonstrated this approach using microfluidic-assisted self-assembly of hydrazone-based hydrogelators at water–water interfaces, enabling the continuous fabrication of supramolecular microcapsules and the encapsulation of glucose oxidase as an aqueous biomolecular VAAI. However, reported applications of these supramolecular hydrogel-based systems have so far been predominantly focused on biomedical applications, such as enzyme and cell encapsulation, rather than formulated consumer products [118,119]. Moreover, while microfluidic fabrication provides good control over capsule size and shell structure, production throughput, device complexity and scale-up remain important challenges for translation to large-scale formulated products [119].

The encapsulation of hydrophilic VAAIs using emulsion-based approaches, however, is highly dependent on the physicochemical properties of the VAAI. For example, Fujiwara et al. [43] fabricated $CaCO_3$ microcapsules for biomacromolecule encapsulation via interfacial ionic reactions, where encapsulation efficiency varied significantly with molecular size. Bovine serum albumin (66 kDa) achieved ~93% encapsulation, whereas lysozyme (14 kDa) exhibited only 1%. This strong molecular weight dependence highlights a fundamental limitation of porous inorganic shells, which are unable to effectively retain small, highly diffusive hydrophilic molecules. To address this limitation, secondary stabilization strategies using biodegradable polymers have often been combined with W/O/W emulsions to improve the retention of hydrophilic VAAI. For instance, Hu et al. [120] prepared vitamin C microcapsules using W/O/W emulsion followed by spray drying using chitosan and hydroxypropyl methyl cellulose as gelling agents in the internal aqueous phase. The formation of ionic interactions between vitamin C and the protonated amino groups of chitosan significantly improved encapsulation efficiency (~92%). Wang et al. [121] used a W/O/W double emulsion-complex coacervation process to co-encapsulate vitamin C and hydrophobic xanthoxylin to improve transdermal delivery achieving encapsulation efficiencies of 70%. However, these biodegradable systems, which are mainly targeted toward food and skin-care applications, typically provide controlled release over relatively short time scales, generally on the order of a few hours [120,121].

For small hydrophilic molecules requiring prolonged retention, effective encapsulation remains a considerable challenge. Sui et al. [122] addressed this by developing a process to fabricate melamine-formaldehyde (MF) microcapsules to encapsulate potassium chloride and allura red dye. By introducing the MF precondensate in the internal aqueous phase of a W/O emulsion together with the VAAI, encapsulation efficiencies up to 82% and sustained release profiles over 10 h were realized. Further improvement was achieved by inserting a superhydrophobic octadecyltrichlorosilane interlayer between two MF shells, enabling retention of potassium chloride and Allura Red for up to one month without detectable release [123]. The introduction of a superhydrophobic interlayer provides an effective strategy for confining hydrophilic actives and markedly improving retention. However, the MF shell employed in this system is non-degradable, which has hindered further development of the technology. Furthermore, the multilayer architecture requires multiple fabrication steps, thereby increasing process complexity and limiting scalability. Nevertheless, the underlying concept of introducing low-permeability or superhydrophobic barrier layer within the capsule shell may provide useful basis for future exploration, particularly if the shell can be fabricated using microplastic-free components.

8 Conclusions and outlook

Against the backdrop of the EU restriction on intentionally added synthetic polymer microparticles, particularly in agrochemicals, cosmetics, personal care, and cleaning products [14], the development of robust microplastic-free encapsulation technologies represents both a regulatory necessity and a significant commercial opportunity. Companies capable of replacing conventional high-performance encapsulation technologies with microplastic-free alternatives are likely to gain a competitive advantage, particularly if that combines regulatory compliance with competitive cost, release performance, and formulation stability.

Overall, the transition from conventional microplastic-based shells, such as polyurea, polyurethane, and MF chemistries [12,17], towards reduced-microplastic and fully microplastic-free encapsulation systems is gradual and technically challenging. While crosslinked natural polymers, inorganic shells, organic-inorganic hybrids, and supramolecular assemblies each represent important steps in this direction, none yet provides a universal replacement for conventional polymeric microcapsules [31,33,39,57,63,90]. As discussed throughout this review, each approach presents distinct trade-offs in terms of barrier properties, biodegradability, process complexity, and scalability.

Commercially, interfacial polymerization remains the most established techniques for microcapsule production, and several emerging biodegradable systems retain this process architecture by combining natural polymers with synthetic crosslinkers [111,112,124–126]. For example, biopolymers such as chitosan, which contain reactive amino groups, can be crosslinked with synthetic

oligomers such as polyisocyanates or acrylates at the oil–water interface [111,112,124], while complex coacervate shells can be reinforced using multifunctional crosslinkers (e.g., trifunctional isocyanate) [125,126]. These systems may be more appropriately described as reduced-microplastic rather than fully microplastic-free, because their biodegradability is enhanced by the natural polymer but their shell structure may still contain synthetic or highly crosslinked domains.

Although such formulations are designed to exceed the regulatory threshold of >60% mineralisation within 28 days in OECD biodegradability tests [14,15], this does not necessarily confirm complete degradation of the capsule shell or absence of persistent residues. Lobel et al. [13] outlined a framework for assessing microcapsules in the context of microplastic regulation, emphasising that the biodegradability of the constituent polymer does not necessarily reflect that of the complete microcapsule. Crosslinking, chemical modification, and capsule architecture can substantially influence the degradation behaviour of the resulting capsule. Moreover, Karagianni et al. [16] showed that biodegradation values for fragrance microcapsules can vary from approximately 0% to 91% in 60 days depending on the purification method, because residual fragrance oil, soluble additives, and non-bound materials can give false-positive biodegradation results. Standardised methods are available for assessing degradation in different environmental compartments, including seawater (OECD 306) and soil (ISO 17556), using complementary measures such as CO_2 evolution, oxygen consumption, dissolved organic carbon, and physicochemical changes in the capsule or shell material [13]. Therefore, environmental validation should be performed on the final capsule or isolated shell under application-specific conditions, with appropriate reporting of test-specimen composition and analytical verification to support robust biodegradability claims.

Importantly, ‘microplastic-free’ and ‘biodegradable’ should not be treated as synonyms under the EU REACH restriction on synthetic polymer microparticles [14]. Polymer-free systems, such as purely inorganic or small-molecule supramolecular capsules, may fall outside the definition of synthetic polymer microparticles and therefore may not require biodegradability testing to comply with the microplastic regulations. However, the safety and toxicological profiles of the shell materials, degradation products, residual reactants, and final formulations must still be evaluated to ensure their safe use in the intended application and to assess their environmental impact. Additionally, complying with the regulatory frameworks does not guarantee that the encapsulation technology will be industrially viable. Emerging alternatives should be directly benchmarked against conventional MF, polyurea, or polyurethane microcapsules in terms of mechanical strength, barrier properties, payload, release control, and end-use efficacy.

Future development should also focus on nature-inspired shell architectures that combine complementary functions, such as the mechanical robustness of inorganic materials with the flexibility of organic components. The organic-inorganic hybrid microcapsules are particularly promising in this regard, provided that their fabrication can be simplified and the degradation behaviour of the entire composite shell can be validated. A key challenge is to provide sufficient stability during formulation and storage while enabling release of the active under the required conditions. Following application, the spent microcapsule should then degrade within a regulatorily acceptable timeframe. For instance, biodegradable PCL microcapsules were shown to remain stable under hydrophobic or dry static storage conditions; conversely, the release rate of the encapsulated VAAI increased upon exposure water, particularly under strongly acidic condition (pH < 5) [100]. Such systems could therefore be designed to maintain shell integrity during formulation and storage, while enabling degradation or burst/sustained release upon exposure to a specific environmental stimulus, such as changes in pH, ionic strength, temperature, or enzymatic activity following application [13,116].

Because emulsions underpin many microencapsulation processes, the sustainability of formulation ingredient should also be considered. Renewable surfactants from natural sources and oleochemical feedstocks, such as plant oils and sugars, can reduce reliance of petroleum-based chemicals. Examples include alkyl polyglucosides, sucrose esters, sulfosuccinates, and other sugar- or plant oil-based surfactants, such as coconut fatty acids [127]. However, these alternatives are only useful if they still produce stable emulsions and effective microcapsules.

In the future, impactful next-generation delivery systems will need to demonstrate performance comparable to, or exceeding, that of current commercial microcapsules while meeting the requirements for large-scale manufacture. For example, in larger stirred-tank and emulsion-based processes, perfect mixing conditions may be challenging. Larger tanks can affect mixing and shear conditions, leading to stagnant or dead volumes, which affects droplet size, size distribution, morphology, and aggregation. With that being said, uniform mixing is critical for reproducible production [128]. Microfluidic approaches provide precise and sequential control over capsule size and configuration at small scale; however, scaling up to industrially relevant throughputs remains challenging due to technological constraints and the substantial increase in both capital and operating costs [119].

Where shell formation involves chemical reactions, maintaining consistent temperature, concentration and mixing conditions during scale-up is also important as local variations in these parameters can affect shell formation and thickness [18,128,129]. Wet-chemistry

approaches may be adapted to established industrial processes, such as interfacial polymerization, utilising existing manufacturing infrastructure, minimising new capital investments associated with plant upscaling [33,114]. These considerations should be aligned with sustainability and Net Zero goals minimising waste and energy consumption, supporting circular economy.

Competing interests The authors declare that they have no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution, and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not pemitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit https://creativecommons.org/licenses/by/4.0/.

References

1. Borrelle S B, Ringma J, Law K L, Monnahan C C, Lebreton L, McGivern A, Murphy E, Jambeck J, Leonard G H, Hilleary M A, et al. Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. Science, 2020, 369(6510): 1515–1518
2. Lamichhane G, Acharya A, Marahatha R, Modi B, Paudel R, Adhikari A, Raut B K, Aryal S, Parajuli N. Microplastics in environment: global concern, challenges, and controlling measures. International Journal of Environmental Science and Technology, 2023, 20(4): 4673–4694
3. Thompson R C, Olsen Y, Mitchell R P, Davis A, Rowland S J, John A W G, McGonigle D, Russell A E. Lost at sea: where is all the plastic? Science, 2004, 304(5672): 838
4. Woźniak-Budych M, Staszak K, Wieszczycka K, Bajek A, Staszak M, Roszkowski S, Giamberini M, Tylkowski B. Microplastic label in microencapsulation field—consequence of shell material selection. Journal of Hazardous Materials, 2024, 465: 133000
5. Nawab A, Ahmad M, Khan M T, Nafees M, Khan I, Ihsanullah I. Human exposure to microplastics: a review on exposure routes and public health impacts. Journal of Hazardous Materials Advances, 2024, 16: 100487
6. Leslie H A, van Velzen M J M, Brandsma S H, Vethaak A D, Garcia-Vallejo J J, Lamoree M H. Discovery and quantification of plastic particle pollution in human blood. Environment International, 2022, 163: 107199
7. Gu E, Devorkin B, Chu M. Emerging links between cardiovascular disease and microplastics exposure—a narrative review. Hellenic Journal of Cardiology, 2026 (in press)
8. Saha S C, Saha G. Effect of microplastics deposition on human lung airways: a review with computational benefits and challenges. Heliyon, 2024, 10(2): e24355
9. Mišľanová C, Valachovičová M, Slezáková Z. An overview of the possible exposure of infants to microplastics. Life, 2024, 14(3): 371
10. Walker T R. (Micro)plastics and the UN sustainable development goals. Current Opinion in Green and Sustainable Chemistry, 2021, 30: 100497
11. Anagnosti L, Varvaresou A, Pavlou P, Protopapa E, Carayanni V. Worldwide actions against plastic pollution from microbeads and microplastics in cosmetics focusing on European policies, has the issue been handled effectively? Marine Pollution Bulletin, 2021, 162: 111883
12. Bruyninckx K, Dusselier M. Sustainable chemistry considerations for the encapsulation of volatile compounds in laundry-type applications. ACS Sustainable Chemistry & Engineering, 2019, 7(9): 8041–8054
13. Lobel B T, Baiocco D, Al-Sharabi M, Routh A F, Zhang Z B, Cayre O J. Current challenges in microcapsule designs and microencapsulation processes: a review. ACS Applied Materials & Interfaces, 2024, 16(31): 40326–40355
14. ECHA. Amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) as regards synthetic polymer microparticles. 2023
15. OECD. Test No. 301: Ready Biodegradability. 1992
16. Karagianni K, Kuntzmann-Dembele F, Bocokic V, Charbonnier A, Harrison I, Kreutzer G, Mendoza A, Jenner K. Fragrance encapsulates: effect of polymeric shell purification method on the accuracy of biodegradability testing. Environmental Toxicology and Chemistry, 2024, 43(6): 1242–1249
17. Mamusa M, Resta C, Sofroniou C, Baglioni P. Encapsulation of volatile compounds in liquid media: fragrances, flavors, and essential oils in commercial formulations. Advances in Colloid and Interface Science, 2021, 298: 102544
18. Ricardo F, Pradilla D, Luiz R, Alvarez Solano O A. A multi-scale approach to microencapsulation by interfacial polymerization. Polymers, 2021, 13(4): 644
19. Amberg S, Mitrano D M. Exploring the essential use concept for primary microplastics regulation in the EU. Environmental Science & Technology, 2025, 59(16): 7799–7809
20. Timilsena Y P, Haque M A, Adhikari B. Encapsulation in the food industry: a brief historical overview to recent developments. Food and Nutrition Sciences, 2020, 11(6): 481–508
21. Salerno A, Causa F, Di Natale C, Domingo C, Vecchione R. Editorial: microencapsulation for biomedical applications. Frontiers in Bioengineering and Biotechnology, 2022, 10: 891981
22. Yu Q, Tian Z X, Li G Y, Yang Y F, Chen X M, Wang D, Peng W X, Liu R Q, Gu H P, Yue X C. Multifunctional composite capsules in drug delivery systems: bridging pharmaceutical and biomedical applications. Advanced Composites and Hybrid Materials, 2025, 8(1): 118
23. Leon M. Si-based inorganic microencapsulation. Physical Sciences Reviews, 2016, 1(3): 20150008
24. Bell R V, Rochford L A, de Rosales R T M, Stevens M, Weaver J V M, Bon S A F. Fabrication of calcium phosphate

microcapsules using emulsion droplets stabilized with branched copolymers as templates. Journal of Materials Chemistry B, 2015, 3(27): 5544–5552

25. Yeom J, Shim W S, Kang N G. Eco-friendly silica microcapsules with improved fragrance retention. Applied Sciences, 2022, 12(13): 6759
26. Liu S P, Li J J, Zhang Y C, Zhang X F, Ding Y, Zhang W R, Rao J S, Zhang Y X. Progress in the preparation and applications of microcapsules for protective coatings against corrosion. International Journal of Molecular Sciences, 2025, 26(4): 1473
27. Su Y C, Zong W, Zhao X L, Ma S H, Han X J. Inorganic microcapsules mineralized at the interface of water droplets in ethanol solution and their application as drug carriers. RSC Advances, 2015, 5(100): 82247–82251
28. Han Y D, Zhang L, Yang W S. Synthesis of mesoporous silica using the sol-gel approach: adjusting architecture and composition for novel applications. Nanomaterials, 2024, 14(11): 903
29. Yeom J, Kang M, Goh A, Jeon J, Shim W S, Kang N G. Timed-release silica microcapsules for consistent fragrance release in topical formulations. Applied Sciences, 2024, 14(23): 11308
30. Bago Rodriguez A M, Binks B P. Capsules from Pickering emulsion templates. Current Opinion in Colloid & Interface Science, 2019, 44: 107–129
31. Dhiman A, Gupta A, Sethi S K, Manik G, Agrawal G. Encapsulation of wax in complete silica microcapsules. Journal of Materials Research, 2023, 38(3): 814–827
32. Cardoso M, Barros A M, De Nies P, Verstraete P D, Wong V, Smith S D, Smets J. WIPO, WO2020214877A1, 2020
33. Bhutkar S P, Millard P E, Preece J A, Zhang Z B. Microplastic-free microcapsules using supramolecular self-assembly of bis-urea molecules at an emulsion interface. Langmuir, 2024, 40(29): 14798–14810
34. Brossault D F F, McCoy T M, Routh A F. Preparation of multicore colloidosomes: nanoparticle-assembled capsules with adjustable size, internal structure, and functionalities for oil encapsulation. ACS Applied Materials & Interfaces, 2021, 13(43): 51495–51503
35. Ficheux M F, Bonakdar L, Leal-Calderon F, Bibette J. Some stability criteria for double emulsions. Langmuir, 1998, 14(10): 2702–2706
36. Al-Sharabi M, Lobel B T, Baiocco D, Cayre O J, Zhang Z B, Routh A F. Multicore silica microcapsules containing α-tocopherol for potential consumer product applications. Materials Advances, 2025, 6(4): 1468–1477
37. Traynor D H, Markowitz S M, Comptonm D L, Traynor H G, Dulak M. US Patent, 7226582B2, 2007
38. Lei Y, Popplewell L M, Huang X. US Patent, 9532933B2, 2017
39. Baiocco D, Lobel B T, Al-Sharabi M, Cayre O J, Routh A F, Zhang Z B. Organic-inorganic multilayer microcarriers with superior mechanical properties for potential active delivery in fast-moving consumer goods. Industrial & Engineering Chemistry. 2025, 64 (9), 4917–4931
40. Boyjoo Y, Pareek V K, Liu J. Synthesis of micro and nano-sized calcium carbonate particles and their applications. Journal of Materials Chemistry A, 2014, 2(35): 14270–14288
41. Wang X L, Zhou W Z, Cao J, Liu W C, Zhu S P. Preparation of core-shell $CaCO_3$ capsules via Pickering emulsion templates. Journal of Colloid and Interface Science, 2012, 372(1): 24–31
42. Nakahara Y, Mizuguchi M, Miyata K I. Effects of surfactants on $CaCO_3$ spheres prepared by interfacial reaction method. Journal of Colloid and Interface Science, 1979, 68(3): 401–407
43. Fujiwara M, Shiokawa K, Morigaki K, Zhu Y C, Nakahara Y. Calcium carbonate microcapsules encapsulating biomacromolecules. Chemical Engineering Journal, 2008, 137(1): 14–22
44. Hettiarachchi N M, De Silva R T, Gayanath Mantilaka M M M G P, Pasbakhsh P, De Silva K M N, Amaratunga G A J. Synthesis of calcium carbonate microcapsules as self-healing containers. RSC Advances, 2019, 9(41): 23666–23677
45. Niu Y Q, Liu J H, Aymonier C, Fermani S, Kralj D, Falini G, Zhou C H. Calcium carbonate: controlled synthesis, surface functionalization, and nanostructured materials. Chemical Society Reviews, 2022, 51(18): 7883–7943
46. Long Y, Song K, York D, Zhang Z B, Preece J A. Composite microcapsules with enhanced mechanical stability and reduced active ingredient leakage. Particuology, 2016, 26: 40–46
47. Baiocco D, Al-Sharabi M, Lobel B T, Cayre O J, Routh A F, Zhang Z B. Eco-friendly fungal chitosan-silica dual-shell microcapsules with tailored mechanical and barrier properties for potential consumer product applications. ACS Omega, 2024, 9(26): 28385–28396
48. Bhutkar S, Shanmuganathan K. Polymer based microcapsules for encapsulation. In: Micro- and Nano-containers for Smart Applications. Singapore: Springer, 2022: 1–37
49. Meng Q Y, Zhong S L, Wang J, Gao Y, Cui X J. Advances in chitosan-based microcapsules and their applications. Carbohydrate Polymers, 2023, 300: 120265
50. Negm N A, Hefni H H H, Abd-Elaal A A A, Badr E A, Abou Kana M T H. Advancement on modification of chitosan biopolymer and its potential applications. International Journal of Biological Macromolecules, 2020, 152: 681–702
51. Baiocco D. Fabrication and characterisation of vegetable chitosan derived microcapsules. Dissertation for the Doctoral Degree. Birmingham: University of Birmingham, 2021
52. Timilsena Y P, Akanbi T O, Khalid N, Adhikari B, Barrow C J. Complex coacervation: principles, mechanisms, and applications in microencapsulation. International Journal of Biological Macromolecules, 2019, 121: 1276–1286
53. Raza Z A, Khalil S, Ayub A, Banat I M. Recent developments in chitosan encapsulation of various active ingredients for multifunctional applications. Carbohydrate Research, 2020, 492: 108004
54. Leclercq S, Harlander K R, Reineccius G A. Formation and characterization of microcapsules by complex coacervation with liquid or solid aroma cores. Flavour and Fragrance Journal, 2009, 24(1): 17–24
55. Ach D, Briançon S, Broze G, Puel F, Rivoire A, Galvan J M, Chevalier Y. Formation of microcapsules by complex coacervation. The Canadian Journal of Chemical Engineering, 2015, 93(2): 183–191
56. Zhao W D, Baiocco D, Boussahel A, Grover L, Zhang Z B, Roudaut A. Bio-interfacial engineering of electrophoretic

coacervate microcapsules for cytocompatible on-skin displays. Journal of the Royal Society Interface, 2026, 23(242): 20260105

57. Kornet R, Roozalipour S L, Venema P, van der Goot A J, Meinders M B J, van der Linden E. Coacervation in pea protein solutions: the effect of pH, salt, and fractionation processing steps. Food Hydrocolloids, 2022, 125: 107379
58. Bordón M G, Paredes A J, Camacho N M, Penci M C, González A, Palma S D, Ribotta P D, Martinez M L. Formulation, spray-drying, and physicochemical characterization of functional powders loaded with chia seed oil and prepared by complex coacervation. Powder Technology, 2021, 391: 479–493
59. Yu Y T, Liu L N, Zhu X L, Kong X Z. Microencapsulation of dodecyl acetate by complex coacervation of whey protein with acacia gum and its release behavior. Chinese Chemical Letters, 2012, 23(7): 847–850
60. Deveci S S, Basal G. Preparation of PCM microcapsules by complex coacervation of silk fibroin and chitosan. Colloid and Polymer Science, 2009, 287(12): 1455–1467
61. Nezamdoost-Sani N, Amiri S, Mousavi Khaneghah A. The application of the coacervation technique for microencapsulation bioactive ingredients: a critical review. Journal of Agriculture and Food Research, 2024, 18: 101431
62. Ballesteros L F, Ramirez M J, Orrego C E, Teixeira J A, Mussatto S I. Encapsulation of antioxidant phenolic compounds extracted from spent coffee grounds by freeze-drying and spray-drying using different coating materials. Food Chemistry, 2017, 237: 623–631
63. Baiocco D, Preece J A, Zhang Z B. Microcapsules with a fungal chitosan-gum Arabic-maltodextrin shell to encapsulate health-beneficial peppermint oil. Food Hydrocolloids for Health, 2021, 1: 100016
64. Xiao Z B, Liu W L, Zhu G Y, Zhou R J, Niu Y W. Production and characterization of multinuclear microcapsules encapsulating lavender oil by complex coacervation. Flavour and Fragrance Journal, 2014, 29(3): 166–172
65. Butstraen C, Salaün F. Preparation of microcapsules by complex coacervation of gum Arabic and chitosan. Carbohydrate Polymers, 2014, 99: 608–616
66. Carrick C, Ruda M, Pettersson B, Larsson P T, Wågberg L. Hollow cellulose capsules from CO_2 saturated cellulose solutions—their preparation and characterization. RSC Advances, 2013, 3(7): 2462
67. Seddiqi H, Oliaei E, Honarkar H, Jin J F, Geonzon L C, Bacabac R G, Klein-Nulend J. Cellulose and its derivatives: towards biomedical applications. Cellulose, 2021, 28(4): 1893–1931
68. Zou Y, Zhang R, Li Y. Analysis of wall materials and preparation methods of microcapsules. Journal of Research in Agriculture and Animal Science, 2021, 8(12): 32–35
69. Simões M G, Coimbra P, Carreira A S, Figueiredo M M, Gil M H, Simões P N. Eugenol-loaded microspheres incorporated into textile substrates. Cellulose, 2020, 27(7): 4109–4121
70. Huang A M, Li X H, Liang X T, Zhang Y J, Hu H Y, Yin Y Z, Huang Z Q. Solid-phase synthesis of cellulose acetate butyrate as microsphere wall materials for sustained release of emamectin benzoate. Polymers, 2018, 10(12): 1381
71. Wu Q X, Lin D Q, Yao S J. Fabrication and formation studies on single-walled CA/NaCS-WSC microcapsules. Materials Science and Engineering: C, 2016, 59: 909–915
72. Zhou Y, Yin X Q, Chen J, Feng D C, Zhu L. Encapsulation efficiency and release of citral using methylcellulose as emulsifier and interior wall material in composite polysaccharide microcapsules. Advances in Polymer Technology, 2018, 37(8): 3199–3209
73. Carvalho J P F, Silva A C Q, Silvestre A J D, Freire C S R, Vilela C. Spherical cellulose micro and nanoparticles: a review of recent developments and applications. Nanomaterials, 2021, 11(10): 2744
74. Shim H, Sah H. Qualification of non-halogenated organic solvents applied to microsphere manufacturing process. Pharmaceutics, 2020, 12(5): 425
75. Song X C, Yu Y L, Yang G Y, Jiang A L, Ruan Y J, Fan S H. One-step emulsification for controllable preparation of ethyl cellulose microcapsules and their sustained release performance. Colloids and Surfaces B: Biointerfaces, 2022, 216: 112560
76. Bading M L, Olsson O, Kümmerer K. Analysis of environmental biodegradability of cellulose-based pharmaceutical excipients in aqueous media. Chemosphere, 2024, 352: 141298
77. Entwistle K, Moise S, Guler F, Smart K A, Crow M, Chuck C J. Determining the biodegradation of functionalised cellulose esters. Faraday Discussions, 2026, 262: 414–431
78. Li M J, Guo Q Y, Lin Y C, Bao H R, Miao S. Recent progress in microencapsulation of active peptides—wall material, preparation, and application: a review. Foods, 2023, 12(4): 896
79. Kent R M, Doherty S B. Probiotic bacteria in infant formula and follow-up formula: microencapsulation using milk and pea proteins to improve microbiological quality. Food Research International, 2014, 64: 567–576
80. Cui X J, Wang B N, Zhong S L, Li Z F, Han Y S, Wang H Y, Moehwald H. Preparation of protein microcapsules with narrow size distribution by sonochemical method. Colloid and Polymer Science, 2013, 291(10): 2271–2278
81. Ye Q Y, Biviano M, Mettu S, Zhou M F, Dagastine R, Ashokkumar M. Modification of pea protein isolate for ultrasonic encapsulation of functional liquids. RSC Advances, 2016, 6(108): 106130–106140
82. Wang T, Chen K R, Zhang X Z, Yu Y J, Yu D Y, Jiang L Z, Wang L Q. Effect of ultrasound on the preparation of soy protein isolate-maltodextrin embedded hemp seed oil microcapsules and the establishment of oxidation kinetics models. Ultrasonics Sonochemistry, 2021, 77: 105700
83. Sridhar K, Bouhallab S, Croguennec T, Renard D, Lechevalier V. Application of high-pressure and ultrasound technologies for legume proteins as wall material in microencapsulation: new insights and advances. Trends in Food Science & Technology, 2022, 127: 49–62
84. Taha A, Ahmed E, Ismaiel A, Ashokkumar M, Xu X Y, Pan S Y, Hu H. Ultrasonic emulsification: an overview on the preparation of different emulsifiers-stabilized emulsions. Trends in Food Science & Technology, 2020, 105: 363–377
85. Samborska K, Boostani S, Geranpour M, Hosseini H, Dima C, Khoshnoudi-Nia S, Rostamabadi H, Falsafi S R, Shaddel R,

Akbari-Alavijeh S, et al. Green biopolymers from by-products as wall materials for spray drying microencapsulation of phytochemicals. Trends in Food Science & Technology, 2021, 108: 297–325

86. Wang Y F, Cheng Q Q, Liu J, Tariq Z, Zheng Z Z, Li G, Kaplan D L, Wang X Q. Tuning microcapsule shell thickness and structure with silk fibroin and nanoparticles for sustained release. ACS Biomaterials Science & Engineering, 2020, 6(8): 4583–4594
87. Liu M C, Millard P E, Urch H, Zeyons O, Findley D, Konradi R, Marelli B. Microencapsulation of high-content actives using biodegradable silk materials. Small, 2022, 18(31): 2201487
88. Ma D H, Yang B J, Zhao J, Yuan D D, Li Q H. Advances in protein-based microcapsules and their applications: a review. International Journal of Biological Macromolecules, 2024, 263: 129742
89. Shi P Z, Qin J H, Luo S, Hao P Y, Li N, Zan X J. Effect of the stiffness of one-layer protein-based microcapsules on dendritic cell uptake and endocytic mechanism. Biomaterials Science, 2021, 10(1): 178–188
90. Muhoza B, Xia S Q, Zhang X M. Gelatin and high methyl pectin coacervates crosslinked with tannic acid: the characterization, rheological properties, and application for peppermint oil microencapsulation. Food Hydrocolloids, 2019, 97: 105174
91. White A L, Javier H A, Withey S, Biggs S R, Rose S, Puttick S G, Whittaker A K. Deposition of non-porous calcium phosphate shells onto liquid filled microcapsules. Journal of Colloid and Interface Science, 2022, 609: 575–583
92. Shchukin D G, Sukhorukov G B, Möhwald H. Smart inorganic/organic nanocomposite hollow microcapsules. Angewandte Chemie International Edition, 2003, 42(37): 4472–4475
93. Zhang S H, Jiang Z Y, Zhang W Y, Wang X L, Shi J F. Polymer-inorganic microcapsules fabricated by combining biomimetic adhesion and bioinspired mineralization and their use for catalase immobilization. Biochemical Engineering Journal, 2015, 93: 281–288
94. Jagtap S B, Mohan M S, Shukla P G. Improved performance of microcapsules with polymer nanocomposite wall: preparation and characterization. Polymer, 2016, 83: 27–33
95. Zhang L, Shi J F, Jiang Z Y, Jiang Y J, Meng R J, Zhu Y Y, Liang Y P, Zheng Y. Facile preparation of robust microcapsules by manipulating metal-coordination interaction between biomineral layer and bioadhesive layer. ACS Applied Materials & Interfaces, 2011, 3(2): 597–605
96. Wang X L, Jiang Z Y, Shi J F, Liang Y P, Zhang C H, Wu H. Metal-organic coordination-enabled layer-by-layer self-assembly to prepare hybrid microcapsules for efficient enzyme immobilization. ACS Applied Materials & Interfaces, 2012, 4(7): 3476–3483
97. Baiocco D, Lobel B T, Al-Sharabi M, Cayre O J, Routh A F, Zhang Z B. Environmentally friendly calcium carbonate-polydopamine microcapsules with superior mechanical, barrier, and adhesive properties. Sustainable Materials and Technologies, 2024, 41: e01001
98. Bergek J, Andersson Trojer M, Uhr H, Nordstierna L. Controlled release of a microencapsulated arduous semi-hydrophobic active from coatings: superhydrophilic polyelectrolyte shells as globally rate-determining barriers. Journal of Controlled Release, 2016, 225: 31–39
99. Sun T, Li Z J, Wang H G, Bao D, Meng F L, Zhang X B. A biodegradable polydopamine-derived electrode material for high-capacity and long-life lithium-ion and sodium-ion batteries. Angewandte Chemie International Edition, 2016, 55(36): 10662–10666
100. Parente J F, Sousa V I, Marques J F, Forte M A, Tavares C J. Biodegradable polymers for microencapsulation systems. Advances in Polymer Technology, 2022, 2022: 4640379
101. Martins I M, Rodrigues S N, Barreiro M F, Rodrigues A E. Release studies of thymol and *p*-cymene from polylactide microcapsules. Industrial & Engineering Chemistry Research, 2012, 51(35): 11565–11571
102. Moreira A C G, Martins I M, Fernandes I, Barreiro M F, Rodrigues A E. Microencapsulation of red and white thyme oil in poly(lactic-co-glycolic) acid: assessment of encapsulation efficiency and antimicrobial capacity of the produced microcapsules. The Canadian Journal of Chemical Engineering, 2016, 94(3): 469–475
103. Ahmadi A N, Ganjeali A, Mohassel M H R, Mashreghi M. Controlled release of trifluralin herbicide using luminescent *Vibrio*-derived polyhydroxyalkanoate (PHA) microcapsules. International Journal of Biological Macromolecules, 2025, 289: 138845
104. McQuillan R V, Stevens G W, Mumford K A. Implementation of biodegradable liquid marbles as a novel controlled release fertilizer. ACS Sustainable Chemistry & Engineering, 2023, 11(1): 122–132
105. Kim S T, Heo J Y, Lee S Y, Kim S B. WIPO, WO2025005535, 2025
106. Cortial A, Vocanson M, Bourdon M, Agusti G, Briançon S. Encapsulation of fragrance mixture I into poly-ε-caprolactone nanoparticles by nanoprecipitation process. Journal of Colloid Science and Biotechnology, 2015, 4(2): 160–169
107. Akolade J O, Balogun M, Swanepoel A, Ibrahim R B, Yusuf A A, Labuschagne P. Microencapsulation of eucalyptol in polyethylene glycol and polycaprolactone using particles from gas-saturated solutions. RSC Advances, 2019, 9(58): 34039–34049
108. Diyanat M, Saeidian H, Baziar S, Mirjafary Z. Preparation and characterization of polycaprolactone nanocapsules containing pretilachlor as a herbicide nanocarrier. Environmental Science and Pollution Research, 2019, 26(21): 21579–21588
109. Deepika M S, Thangam R, Sheena T S, Vimala R T V, Sivasubramanian S, Jeganathan K, Thirumurugan R. Dual drug loaded PLGA nanospheres for synergistic efficacy in breast cancer therapy. Materials Science and Engineering: C, 2019, 103: 109716
110. Zhang Y F, Rochefort D. Characterisation and applications of microcapsules obtained by interfacial polycondensation. Journal of Microencapsulation, 2012, 29(7): 636–649
111. Harrison I M, Aussant E. WIPO, WO2024017931 A1, 2024
112. Wu Y, Shen J J. WIPO, WO2021116306 A1, 2021
113. Wilson-Whitford S R, Jaggers R W, Longbottom B W, Donald

M K, Clarkson G J, Bon S A F. Textured microcapsules through crystallization. ACS Applied Materials & Interfaces, 2021, 13(4): 5887–5894

114. Bhutkar S P, Millard P E, Urch H, Preece J A, Zhang Z B. Self-assembled microplastic-free microcapsules using aromatic bis-ureas with improved strength and tunable barrier properties for encapsulating cinmethylin. ACS Applied Materials & Interfaces, 2025, 17(21): 31522–31533
115. Li Q, Li X S, Zhao C. Strategies to obtain encapsulation and controlled release of small hydrophilic molecules. Frontiers in Bioengineering and Biotechnology, 2020, 8: 437
116. Guan Z R, Baiocco D, Barros A, Zhang Z. Microscale delivery systems for hydrophilic active ingredients in functional consumer goods. WIREs Nanomedicine and Nanobiotechnology, 2025, 17(2): e70009
117. Li Z Q, Wang H C, Gao Y L, Chen J J, Gu G Y, Liu J, Chen Y Q, Guo X H, Wang Y M. Microfluidic-assisted self-assembly of molecular hydrogelator at water-water interfaces for continuous fabrication of supramolecular microcapsules. Small, 2024, 20(45): e2403085
118. Zhang J H, Jin K Y, Feng Y F, Lu D, Chen M, Wang H C, Jin C, Wang D Y, Li Z L, Wang Y M. Injectable self-healing and anti-dissolving low-molecular-weight hydrogels enabled by ionic cross-linking for cell encapsulation. ACS Macro Letters, 2025, 14(1): 20–25
119. Lee J, Kim J W, Kim S H. Microfluidic production of hydrogel-shelled microcapsules and their applications. Current Opinion in Colloid & Interface Science, 2025, 78: 101936
120. Hu S H, Ding Z, Zhang G, Wang X, Zhao Y N, Fan Z P, Liu M, Han J, Wang Z P. Fabrication and spray-drying microencapsulation of vitamin C-loaded W1/O/W2 emulsions: influence of gel polymers in the internal water phase on encapsulation efficiency, reconstituted stability, and controlled release properties. LWT: Food Science and Technology, 2022, 170: 114113
121. Wang R J, Ma C L, Yan H T, Wang P, Yu S Y, Zhang T Y, Yin Z G. Preparation and characterization of GX-50 and vitamin C co-encapsulated microcapsules by a water-in-oil-in-water (W1/O/W2) double emulsion-complex coacervation method. Langmuir, 2023, 39(39): 13863–13875
122. Sui C, Preece J A, Yu S H, Zhang Z B. Novel encapsulation of water soluble inorganic or organic ingredients in melamine formaldehyde microcapsules to achieve their sustained release in an aqueous environment. RSC Advances, 2018, 8(52): 29495–29498
123. Sui C, Preece J A, Zhang Z B, Yu S H. Efficient encapsulation of water soluble inorganic and organic actives in melamine formaldehyde based microcapsules for control release into an aqueous environment. Chemical Engineering Science, 2021, 229: 116103
124. Fernandez Prieto S, Hans Eykens V F, Nijakowski T R, Smets J, Feng L, Ian Bardsley T, Chakar F S, Bobnock R S. US Patent, 20220152572 A1, 2022
125. Elabbadi A, Erni P, Ouali L. WIPO, WO2024018014 A1, 2024
126. Aussant E. WIPO, WO2021239742A1, 2021
127. Patil H V, Badgujar N P, Suresh Kulkarni R D, Nagaraj K. Sustainable bio-based surfactants: advances in green chemistry and environmental applications. Materials Today Communications, 2025, 48: 113583
128. Jacobs I C. Process scale-up considerations for microencapsulation processes. In: Microencapsulation in the Food Industry. Amsterdam: Elsevier, 2014: 391–398
129. Patterson G. Modeling and scale-up of mixing- and temperature-sensitive chemical reactions. Industrial & Engineering Chemistry Research, 2005, 44(14): 5325–5341