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Encapsulation of Fragrances in Micro- and Nano-Capsules, Polymeric Micelles, and Polymersomes

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Dedicated to Prof. Wolfgang Meier (1964–2022), mentor, friend, and pioneer in the field of biomimetic block copolymer membranes and polymersomes

Fragrances are ubiquitously and extensively used in everyday life and several industrial applications, including perfumes, textiles, laundry formulations, hygiene household products, and food products. However, the intrinsic volatility of these small organic molecules leaves them particularly susceptible to fast depletion from a product or from the surface they have been applied to. Encapsulation is a very effective method to limit the loss of fragrance during their use and to sustain their release. This review gives an overview of the different materials and techniques used for the encapsulation of fragrances, scents, and aromas, as well as the methods used to characterize the resulting encapsulation systems, with a particular focus on cyclodextrins, polymer microcapsules, inorganic microcapsules, block copolymer micelles, and polymersomes for fragrance encapsulation, sustained release, and controlled release.

1. Introduction

Usually, an enjoyable smell or aroma is associated with pleasure and has positive connotations. A product's competence or ability to perform effectively is often judged by the impression and longevity of its scent. Furthermore, many individuals are attracted to good smells and will be influenced to purchase or use a particular product based on how it smells. Therefore, many manufacturers of perfumes, textile finishes, household items, cosmetics, personal care items, detergents, cleaning products, foods, and beverages rely on fragrances within their products to ensure an excellent impression. Fragrances are mixtures of small, volatile organic molecules that produce an olfactory response (**Figure 1**). The molecules responsible for creating scent within these volatile mixtures usually have a molecular weight of <300 g mol^{-1} and have high vapor pressures.[1] Consequently, they evaporate readily and diffuse into the air, allowing them to be perceived by receptors in the nose as certain smells. Commonly, these fragrances are composed of alcohols, aldehydes, esters, terpenes, ketones, and other naturally occurring organic molecules—as well as a growing number of synthetic fragrance molecules.[2,3] Although a certain degree of volatility in fragrance molecules is essential for creating their scent, this causes fragrances to evaporate quickly and, as such, creates challenges by limiting effectiveness within products due to premature depletion of the fragrance molecules upon storage and use. One challenge researchers face within academia and industry is finding ways to mitigate this volatility and preserve the longevity of fragrances within their products. A prominent technique employed to achieve this are profragrances.[4] They are utilized as a method of fragrance preservation whereby the volatile fragrance molecules are covalently bound to a larger substrate to produce a new species with increased molecular weight and, thereby, decreased volatility. The fragrance is subsequently released from the substrate through cleavage of the covalent bond under specific environmental conditions such as heat, light irradiation, or pH changes.[5] However, the use of profragrances is limited by the availability of functional groups on the fragrance molecule to bind to a particular substrate.[6] Another very effective method used to preserve fragrances is through encapsulation.[7–15] Encapsulation in, for example, polymeric microcapsules provides a diffusion barrier that retains the fragrance molecules on the product for longer periods of time. Moreover, it allows for a triggered release, for example, by mechanically opening the capsules.[7,13] Furthermore, capsules can provide a protective barrier between the fragrance and outside influences such as heat, atmospheric oxygen, and light, creating enhanced thermal, oxidative, and UV stability. Thus, encapsulation can overcome some of the main limitations of fragrances in their applications. Here, we review the state-of-the-art of fragrance encapsulation and discuss the advantages and challenges of the various

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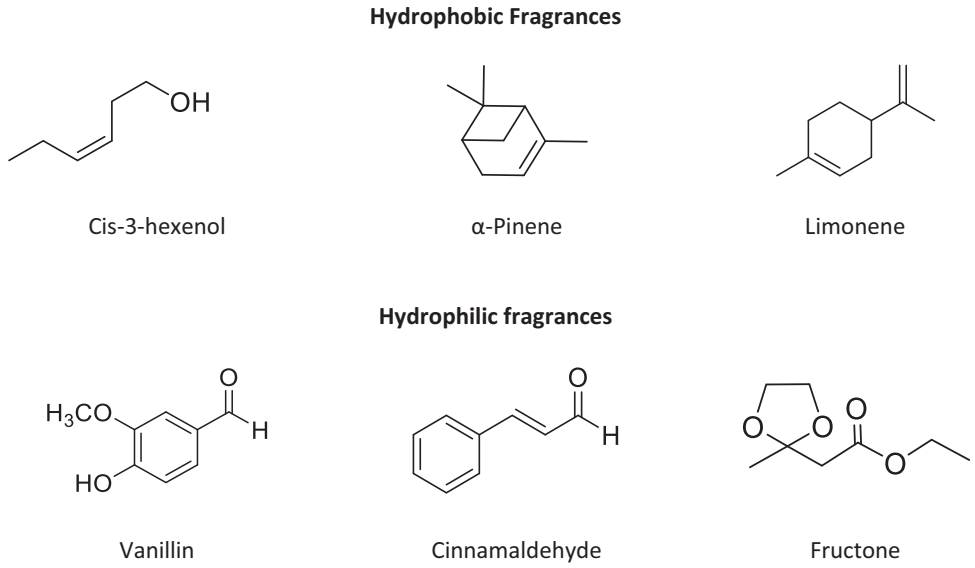

Figure 1. Selection of typical hydrophobic and hydrophilic fragrance molecules.

encapsulation systems that have been explored, ranging from inclusion complexes in cyclodextrins[12,16–18] to inorganic and polymeric microcapsules[8,11,12] to block copolymer micelles and polymersomes.

2. Fragrance Encapsulation

Encapsulation processes involve encasing one or a mixture of substances within a protective coating material, usually termed the wall or shell material, which serves as a functional barrier—shielding the core material from its surrounding environment and providing a diffusion barrier that inhibits or slows down the release of the active compound. The core material can subsequently be released under specific controlled conditions or in response to external stimuli. The size of these capsules can vary depending on the preparation technique used, with capsule diameter sizes typically ranging from nanocapsules (<1 μm) to microcapsules (1–1000 μm). A special case, size-wise, is cyclodextrins, which can be considered molecular-scale capsules for the encapsulation of individual molecules. However, they are more commonly referred to as inclusion complexes, as discussed below.

2.1. Wall Materials

The extensive use of encapsulation technology throughout industry and academia can be attributed to the large diversity of reported wall materials. The appropriate selection of materials allows for control and selectivity over the properties of the microcapsule so that they can be designed and tailored for specific applications. Therefore, carefully selecting the wall material is crucial for developing encapsulation processes and achieving micro- or nano-capsules with desirable physiochemical properties such as biodegradability, biocompatibility, and stability.[19] The chosen material must be able to encapsulate the chosen cargo efficiently, retain the encapsulated substance within the capsule by providing a tight diffusion barrier, protect the volatile core from environmental conditions, and facilitate its controlled release at the desired site when required. Many reported materials used in microcapsule shell walls are natural and synthetic polymers. However, it should be noted that due to their microscopic size, polymeric microcapsules and similar encapsulation systems are purpose-made microplastics if they are not biodegradable. Thus, fragrance encapsulation contributes to the environmental microplastic problem as the microcapsules are readily released into the environment. Therefore, the EU has completely banned non-biodegradable intentionally added microplastics (IAMPs), including microcapsules for the delivery of fragrances, detergents, agrochemicals and cosmetics, from the European Market in 2025.[20,21] We refer the reader to excellent reviews[14,22–25] and the European Chemicals Agency's Restriction Report on IAMPs[20] that discuss this topic in great detail.

2.1.1. Natural Wall Materials

Polysaccharides and proteins are natural biopolymers and have been extensively used in encapsulation processes. There are numerous examples of encapsulation using polysaccharides, including chitosan, carrageenan, gum arabic, and alginate, as well as proteins such as gelatin, whey, albumin, silk proteins, and various plant proteins.[26–30] These materials are interesting for encapsulation due to their biogenic origin, biocompatibility, biodegradability, and other desirable attributes, such as antimicrobial properties. This section describes the materials more commonly utilized in fragrance encapsulation.

Cyclodextrins, cyclic oligosaccharides derived from starch, are widely utilized for fragrance encapsulation and delivery. They are most commonly found in nature as α, β, and γ-cyclodextrins which have 6, 7, and 8 glucopyranose units, respectively (**Figure 2**A). Cyclodextrins form a truncated conical shape with a hydrophilic outer surface and a hydrophobic cavity which allows for the formation of host-guest inclusion complexes

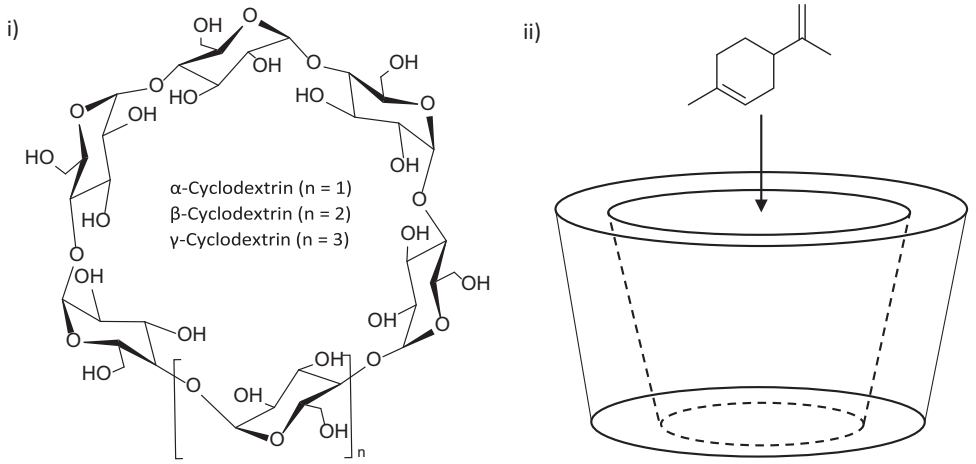

Figure 2. Cyclodextrins for the encapsulation of fragrance molecules in inclusion complexes. A) Structure of α, β and γ-cyclodextrin with either 6, 7, and 8 glucopyranose units, respectively. B) Schematic of β-cyclodextrin inclusion complex with typical nonpolar fragrance molecule, limonene. The truncated conical shape formed by cyclodextrins has a hydrophilic outer surface and a hydrophobic cavity, allowing the formation of host-guest inclusion complexes with nonpolar molecules.

with nonpolar molecules (Figure 2B).[16,31] This enables the encapsulation of hydrophobic molecules. Nui and colleagues successfully encapsulated an artificial apple fragrance, consisting of a mixture of volatile molecules, in β-cyclodextrin, which showed good fragrance retention of 34.4% after 60 days at 50 °C. The microcapsules also displayed good encapsulation efficiency of 80%, demonstrating cyclodextrin as an effective wall material for encapsulation.[32] Furthermore, cyclodextrins can be modified with various moieties to control physiochemical properties. Hydrophilic derivatives such as 2-hydroxypropyl-β-cyclodextrin (HP-β-CD) and 2,6-di-*O*-methyl-β-cyclodextrin (DM-β-CD) can be utilized to increase the aqueous solubility of poorly water-soluble molecules. For example, Ishiguro et al. have demonstrated the successful encapsulation and controlled release of several fragrances with poor aqueous solubility. The group formed inclusion complexes with citral, linalool, citronellol, linalyl acetate, and benzyl acetate using β-cyclodextrin, HP-β-CD, and DM-β-CD. The fragrance release was most effectively prolonged by DM-β-CD, followed by HP-β-CD and last by β-cyclodextrin, which released the most fragrance. The results indicate that the fragrance release can be tailored by functionalizing cyclodextrin with various moieties.[33]

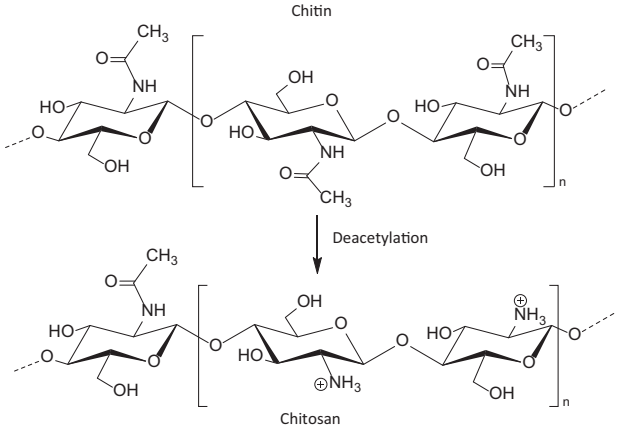

Figure 3. Schematic of the deacetylation of chitin to form chitosan, a popular bio-derived shell material for fragrance delivery capsules. Chitosan has cationic amino groups in acidic conditions, allowing electrostatic interactions with polar species. The degree of deacetylation is important as it affects the extent of the electrostatic interactions.

While the cavity of cyclodextrins can usually host only one cargo molecule, larger amounts of fragrance molecules can be encapsulated in nano- and micro-spheres made, for example, from chitosan. Chitosan is a polysaccharide produced by the deacylation of chitin (**Figure 3**), found in the shells of crustaceans and insects. Within the structure of this biopolymer are several amino and hydroxyl functional groups.[34] Chitosan is cationic in acidic conditions, which is rare as most polysaccharides are neutral or anionic at low pH values. This positive charge allows chitosan to undergo electrostatic interactions with negatively charged species. The degree of deacylation plays an important role in tailoring the properties of the chitosan wall material—as this will affect the extent of the electrostatic interaction.[35] Uses of chitosan have been extensively investigated across several different applications, and it is a popular choice of wall material for encapsulation technology, including the preservation of volatile fragrances.[36,37] Sharkawy et al. reported successful encapsulation of limonene and vanillin fragrance molecules into chitosan microcapsules which were found to have an encapsulation efficiency above 90%. These microcapsules were then bound onto cotton textiles by esterification with citric acid as a cross-linker. The resulting functionalized fabrics provided a sustained fragrance release and displayed sustained antimicrobial properties.[38] Similarly, Velmurugan and colleagues have developed scented leather by infusion of chitosan nanocapsules which contained lavender and orange essential oils. The fragrance release could be detected at ambient conditions for up to 60 days and was also retained after the leather was washed. Moreover, these chitosan capsules also displayed antimicrobial properties due to the interaction of the cationic amine groups in chitosan with the anionic bacterial cell wall causing the cells to rupture.[39] Thus, chitosan is not only a versatile wall material but also a

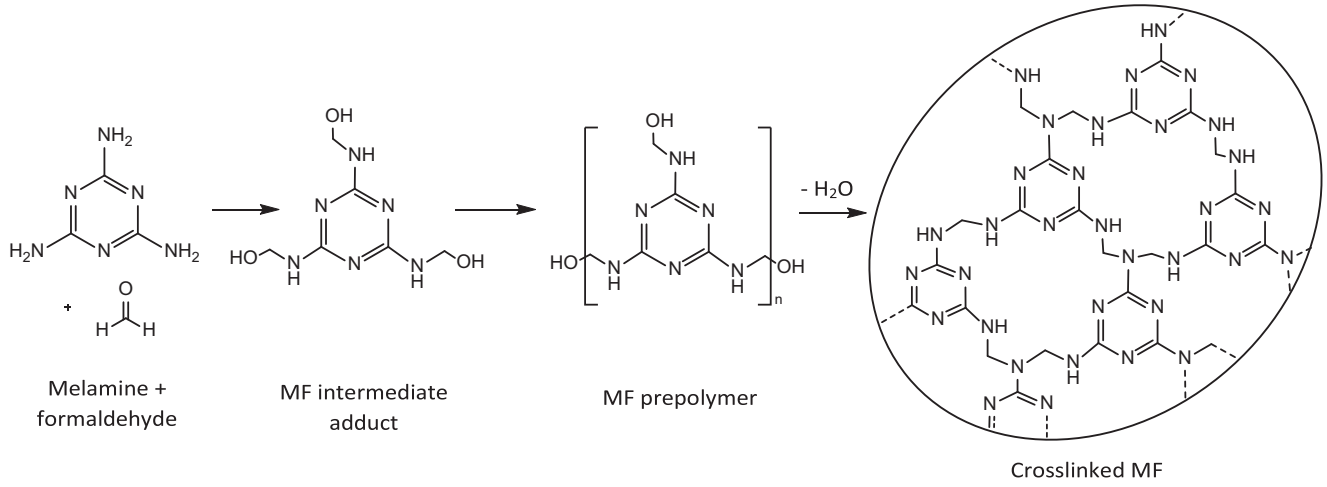

Figure 4. Schematic of the formation of melamine formaldehyde as shell wall of microcapsules for fragrance delivery. The MF resin is formed by the condensation reaction of melamine (2,4,6-triamino-1,3,5-triazine) and formaldehyde through intermediate adducts, creating a densely cross-linked melamine matrix.

powerful option for developing functional fabrics—allowing antimicrobial properties to be incorporated into textiles.

The use of proteins as wall materials has also been reported, often combined with other wall materials. For instance, Rungwasantisuk and Raibhu reported the preparation of microcapsules containing lavender oil using gelatin and gum-arabic as the wall material. The microcapsules were added to a UV-curable varnish which was subsequently applied to paper to produce functionalized scented wrapping paper. The paper released its fragrance upon application of mechanical forces, such as the friction caused by contact upon its use. However, the success of this approach was limited as only a small volume of fragrance could be deposited onto the wrapping paper due to the thin coating of varnish applied.[40] More recently, Tavares and colleagues encapsulated volatile garlic extract using a mixture of whey protein isolate and a small amount of chitosan with varying degrees of deacetylation (83%, 94%, and 96%) as wall material. The whey protein/chitosan microcapsules composed of 96% deacetylated chitosan were shown to have the highest encapsulation efficiency of the three types of microcapsules, 61%. However, the resulting microcapsule powders were very hygroscopic with a maximum moisture uptake of 28% at 75% relative humidity, significantly limiting their applications as the powders could not be stored in a humid environment.[29]

2.1.2. Synthetic Polymer Wall Materials

Synthetic polymers have become an attractive choice for use as wall materials in encapsulation due to their improved thermal and physicochemical properties and a high level of control over their macromolecular design. Moreover, synthetic polymer capsule walls can provide a tight diffusion barrier that retains the encapsulated cargo over prolonged periods of time. The synthetic nature of these materials allows the properties of micro and nanocapsules to be easily tailored and opens doors for microcapsules to be used in an even wider range of applications and challenging conditions.[11] For instance, synthetic aminoplast resins such as melamine and urea-formaldehyde are widely used as robust encapsulation wall materials that can be used in harsh environments such as laundry applications.[25] Melamine formaldehyde (MF) is an aminoplast resin that is a popular choice of wall material in encapsulation technology due to the low cost of raw materials and favorable physical and thermal properties, and its use in fragrance microcapsules is well reported in the literature.[41,42] MF resin is a thermosetting polymer formed by a condensation reaction of melamine (2,4,6-triamino-1,3,5-triazine) and formaldehyde, creating a densely cross-linked melamine matrix resulting in excellent durability and high thermal stability (**Figure 4**).[43] For example, industry-leading fragrance and flavor company Givaudan has developed MF microcapsules for fragrance preservation and sustained release called "Mechacaps," which increased the longevity of olfactory response over several weeks of storage.[42]

The fragrance encapsulation process using MF resins involves forming an emulsion with an aqueous phase and an organic phase containing the fragrance and prepolymers. The condensation polymerization is then activated by lowering the pH. When the MF polymers reach a certain molecular weight, they begin to precipitate from the solution and form the microcapsule wall, which is then further cross-linked by heat. More recently, efforts have been made to apply these microcapsules to functional fabrics. For example, Elesini et al. have demonstrated the use of MF microcapsules to produce functional fabrics used in a bow tie with sustained release of two fragrance types, targeted at both males and females.[44] The male-targeted fragrance microcapsules were slightly larger (23.5 μm) than those containing the female-targeted fragrance (15.5 μm). The larger size of the male-targeted capsules resulted in a shorter-lasting scent due to the increased surface area of the individual capsules being more prone to rupturing and release of the core material compared to the surface area of the smaller, female-targeted capsules. In addition, Zhao and colleagues have demonstrated the ability to control the size of fragrance-containing MF microcapsules using agitator paddles. This work showed that smaller microcapsules could be prepared by increasing the stirring rate within the

reaction vessel, increasing the potential applications of MF microcapsules containing fragrances.[45] Unfortunately, the reaction of formaldehyde to melamine is reversible under acidic conditions, leading to the release of formaldehyde during the encapsulation process or upon storage. This is a significant drawback, as formaldehyde is a known carcinogen.[25,46] Some efforts have been made to reduce the amount of residual formaldehyde by using ammonia or urea as scavengers to neutralize any remaining formaldehyde.[44] There have also been some attempts to completely remove formaldehyde from the encapsulation processes. For instance, Leon et al. reported formaldehyde-free melamine microcapsules using glyoxal as an alternative aldehyde. It was shown that formaldehyde could be successfully replaced with glyoxal through an alternative mechanism using a separate crosslinking agent that is significantly less toxic and yielded microcapsules with improved and more diverse mechanical properties.[47]

Another synthetic polymer wall material used for encapsulating volatile fragrance molecules is poly(methyl methacrylate) (PMMA). Teeka et al. reported the encapsulation of jasmine oil using PMMA as the wall material. The microcapsules were prepared by creating an oil-in-water emulsion with a mixture of toluene, jasmine oil, and PMMA as the hydrophobic phase in an aqueous solution containing polyvinyl alcohol as a stabilizer, followed by evaporation of the solvent. Using a ratio of 2:1 PMMA:jasmine oil resulted in spherical PMMA microcapsules with a high fragrance encapsulation efficiency of 72%. However, the release of fragrance from the prepared microcapsules was not discussed.[48] Additionally, Tasker and colleagues prepared PMMA microcapsules by this emulsion-solvent evaporation method containing hexadecane as a solvent in addition to common fragrance oils used in perfumes. By calculating the interaction between the different phases during the encapsulation process in the presence of surfactants, the group successfully predicted the morphology of the resulting PMMA microcapsules, which ranged from core–shell structures to multi-core–shell morphologies and acorn morphologies.[49] These results allow researchers to reduce or remove time-consuming experiments to probe capsule morphology resulting from the solvent evaporation method.

In a different context, Rezvanpour et al. reported similar PMMA microcapsules that encapsulated *n*-eicosane. These microcapsules were not intended for fragrance delivery but as phase change material due to the temperature-dependent phase transition of *n*-eicosane. However, *n*-eicosane provides an example of a compound showing increased stability upon encapsulation. The degradation of unencapsulated *n*-eicosane started at 55 °C, while encapsulated *n*-eicosane began to degrade at 110 °C, as shown by thermogravimetric analysis (TGA).[50]

PMMA can also be copolymerized with several different monomers to improve the process's encapsulation efficiency and the physiochemical properties of the microcapsule wall. Recently, Ouyang and colleagues have demonstrated in situ copolymerization of PMMA and trimethylolpropane triacrylate in an emulsion to prepare poly(MMA-*co*-TPMPA) copolymer microcapsules that encapsulated lavender essence fragrance. The resulting microcapsules ranged in size from 10 to 20 μm and showed increased thermal stability. The unencapsulated lavender fragrance began to volatilize at 62 °C, whereas the volatilization of the encapsulated fragrance did not start below 116 °C. The prepared microcapsules were also shown to have a high encapsulation efficiency of 91% and sustained release properties for more than 90 days.[51]

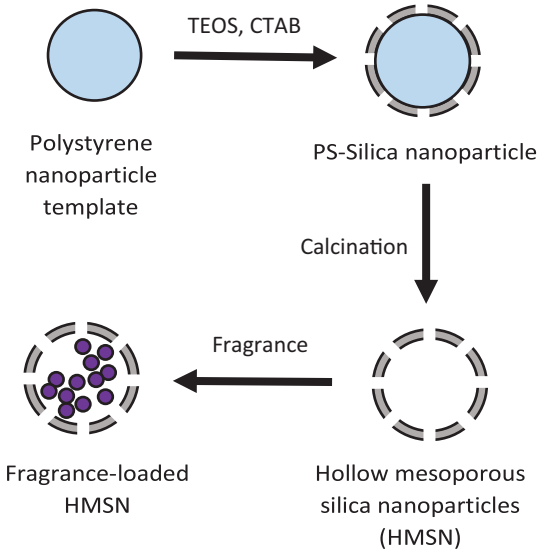

Figure 5. Preparation of fragrance-loaded silica nanocapsules using polystyrene (PS) templates, as described in ref. [53]. First, PS nanoparticles around 200 nm in size were prepared, which were used as a template to subsequently prepare PS-SiO_2 core–shell particles using tetraethoxysilane (TEOS) and hexadecyl trimethyl ammonium bromide (CTAB). The PS was subsequently removed by calcination to prepare mesoporous hollow silica microcapsules. They were loaded with the fragrance by simple incubation in an essential oil.

2.1.3. Inorganic Wall Materials

Inorganic materials can also be used in encapsulation processes and provide advantageous properties. Silica has been extensively explored as inorganic wall material due to its ability to create robust microcapsules with good control over microcapsule size.[52] The surface of silica is hydrophilic due to the presence of hydroxyl groups affording colloidal stability. This also allows for a high degree of functionalization as different moieties can be covalently linked to the surface to modify the physiochemical properties of the capsules. Mesoporous silica capsules are well suited to fragrance encapsulation due to the slow release of core material through pores in the shell wall. Xue and colleagues have developed superhydrophobic aromatic cotton fabrics that have shown sustained release of lemon essential oil from mesoporous silica nanoparticles, which were applied to the fabric coating. First, polystyrene (PS) nanoparticles around 200 nm in size were prepared, which were used as a template to subsequently prepare PS-SiO_2 core–shell particles using tetraethoxysilane and hexadecyl trimethyl ammonium bromide. The PS was subsequently removed by calcination to prepare mesoporous hollow silica microcapsules. They were loaded with the fragrance by simply incubating the essential oil (**Figure 5**). The loading capacity of the microcapsules was very high and was found to be 86%. (It should be noted that loading capacity in the context of encapsulation technologies is often noted as the weight of the encapsulated cargo over the weight of the cargo-filled capsules.)

The microcapsules exhibited good storage stability, releasing less than 10% of fragrance after six days at ambient conditions. Furthermore, sustained fragrance release could be achieved at 50 °C for over 30 h.[53]

Various release mechanisms have been reported to facilitate the controlled and sustained release of cargo from silica microcapsules. For instance, Radulova et al. reported the encapsulation of various fragrances within pH-responsive silica microcapsules with a mean diameter of 20 µm. The capsules were produced through a particle-stabilized Pickering emulsion route by assembling colloidal silica particles, polymers, and surfactants around oil droplets in water, which yielded so-called colloidosomes. Passive release of the fragrances through the mesoporous silica was blocked by a mixture of polymers and surfactants. The microcapsules remained stable upon storage in the aqueous phase at a pH range of 3–6 for 8 months. However, above pH 6, the capsules broke, and the fragrances were released—most likely due to the desorption of the polymer from the gaps between the wall material. A limitation of these microcapsules is that successful encapsulation could only be achieved if the cargo material had moderate aqueous solubility, as no stable microcapsules were obtained using cargo materials for the oil core with either high solubility or zero solubility in water.[54] In a subsequent study from the same group, the system was further developed through the preparation of nanocapsules, also through a Pickering emulsion, yielding smaller microcapsules with higher dispersity with a mean radius ranging from 2 to 11 µm. These microcapsules displayed improved stability across a larger pH range between pH 3 and 10, with the release of core material triggered at pH ≥ 11. However, the effect of the solubility of the core material on successful encapsulation was not discussed further.[55] The surfactants in these processes can have harmful effects once released into the environment. Fortunately, Zhao and colleagues have developed a method of forming silica capsules without using surfactants, instead relying on methyl-functionalized silica nanoparticles to catalyze the formation of silica microcapsules, facilitating a much greener process.[56] More recently, Ali et al. have developed graphene oxide-silica hybrid capsules through a one-step, surfactant-free process using the resulting microcapsules to encapsulate vanillin. The mechanically induced release resulted in sustained release for up to 2 months.[57]

Beyond silica as inorganic capsule material, Wu and colleagues have developed a biocompatible magnetic nanoporous carbon metal–organic framework (Fe-MNPC) and used it to encapsulate and control the release of fragrances. The group demonstrated prolonged release of various fragrance molecules—isobutyraldehyde, ethyl acetate, benzaldehyde, and methoxybenzene. Ethyl acetate and benzaldehyde were most effectively retained by the material due to hydrogen bonding with hydroxyl functional groups—with 60% released after seven days at ambient conditions.[58]

2.2. Methods of Encapsulation

Microcapsules can be prepared through various routes. The reported encapsulation methods can be broadly categorized as either physical or chemical encapsulation processes. Physical methods use mechanical processes such as spray-drying, freeze-drying, and electrochemical processes. Alternatively, microcapsules can be prepared through chemical means such as coacervation, gelation, formation of molecular inclusion complexes, and various types of polymerizations.

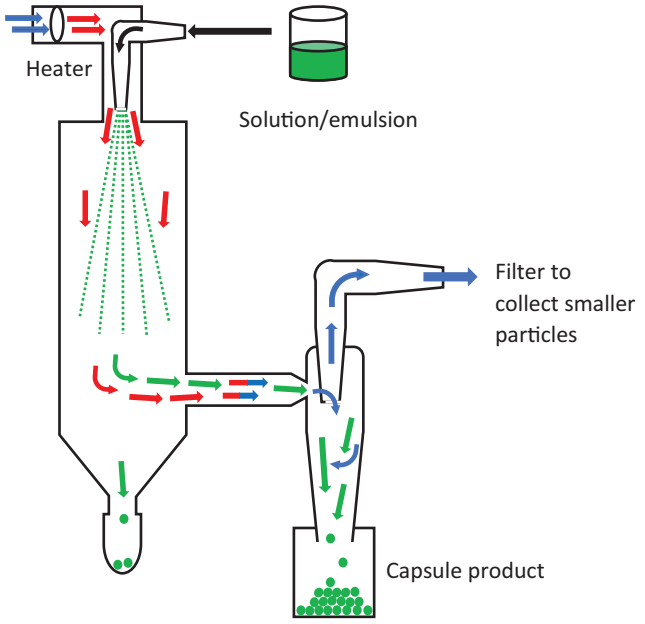

Figure 6. Schematic of a typical spray drying process for the formation of encapsulated fragrances. First, the emulsion/solution of wall and core material is sprayed through a nozzle and rapidly heated to evaporate the solvent, leaving dry capsules. The capsules are then collected and filtered to maintain the desired size.

2.2.1. Physical Encapsulation Methods

Physical encapsulation processes are commonly used with natural wall materials to encapsulate volatile substances.[10] Among these processes, spray drying is a well-known technique that converts a mixture of liquids, usually in the form of an emulsion, into a dry powder. Spray drying is simple and fast and is typically a single-step process. Encapsulating materials through spray drying is an attractive route, commonly used in industry due to its low costs and easy scalability. Emulsions of wall and core material in a solvent are sprayed through a nozzle and rapidly heated to evaporate the solvent, leaving dry capsules (**Figure 6**).[59]

For example, Li and colleagues used spray drying to prepare osmanthus flower fragrance microcapsules with gum arabic and maltodextrin as wall materials. The resulting microcapsules demonstrated excellent thermal stability, showing 95% retention of the fragrance after a week at 60 °C with sustained-release properties.[60] Similarly, Ordonez et al. demonstrated the encapsulation of limonene within microcapsules with a mixture of gum arabic, cassava starch and whey protein as wall materials. The capsules generated showed good fragrance retention but with moderate encapsulation efficiency above 40%.[61] More recently, Yingngam et al. prepared citronella oil microcapsules with acacia gum as wall material using a spray drying method that could be easily incorporated into fabrics. First, an oil-in-water emulsion was prepared with citronella oil, acacia gum, and water,

which was subsequently spray-dried. It was shown that the spray drying temperature significantly impacted the resulting microcapsules. Higher temperatures during the process increased microcapsule size and yield. However, the high temperature had a detrimental effect on the encapsulation efficiency, causing premature and unwanted volatilization. Therefore, a balance must be struck to optimize the process to produce microcapsules with good size and encapsulation efficiency.[62]

Free freeze-drying processes can be implemented to eliminate the risk of volatilizing core fragrance materials at high temperatures. For instance, De Araújo and colleagues reported the preparation of microcapsules that used maltodextrin and maltodextrin/gelatin mixtures to encapsulate sweet orange essential oil using a freeze-drying method. An emulsion of the core and wall materials was prepared with water and surfactants. The emulsion was subsequently lyophilized to form the microcapsules with an encapsulation efficiency of up to 75.5%.[63] In another recent study, Xiao et al. encapsulated watermelon flavor and its various fragrance compounds with γ-cyclodextrin using a freeze-drying method. The watermelon flavor was successfully encapsulated and preserved until release. However, the associated fragrance molecules—isoamyl acetate/butyrate, melonal, linalool, cinnamaldehyde, γ-undecalactone, and α-terpineol were not as effectively encapsulated due to interactions with the γ-cyclodextrin wall material. The molecular structures of the fragrance molecules significantly affected the inclusion and release behavior due to varying hydrophilic interactions with γ-CD. The inclusion efficiency decreased from alcohols > aldehyde > ester. The release decreased with increasing hydrophobicity, demonstrating the varying interactions with the CD wall material.[64]

Electrospraying techniques can also remove the risk of high temperatures causing premature and undesired volatilization of fragrance molecules and could mitigate core-wall interactions. In a recent study, Kose et al. encapsulated labdanum essential oil in a β-cyclodextrin inclusion complex via an electrospraying method. This method allowed selectivity with the interactions between the cyclodextrin and volatile core molecules by varying the electric field during spraying.[65] In a recent study, Ye and colleagues reported encapsulation of menthol in silk fibroin capsules with a mean diameter of 1–2 µm, using electrospinning and electrospraying techniques. The resulting microcapsules showed a moderate encapsulation efficiency of around 46% for the electrospinning technique and 14% using electrospraying. However, this method had the added advantage of good control over the microcapsules' morphology, size, and wall thickness.[66]

Sonication-aided methods have also recently been reported for the encapsulation of fragrances. Siva et al. encapsulated cumin aldehyde and isoeugenol within a methyl-β-cyclodextrin inclusion complex using ultrasonication followed by freeze-drying to produce an inclusion complex which increased the stability of the volatile core materials as well as improved antioxidant and antibacterial activity. The encapsulation efficiency and release behavior were not discussed.[67]

2.2.2. Chemical Encapsulation Methods

Chemical encapsulation methods are versatile and can be used with natural and synthetic wall materials. Coacervation is used widely across the pharmaceutical, food and textile industries due to high encapsulation efficiency, relatively low cost, scalability, and biocompatibility of the materials typically used.[68] There are two types of coacervation—simple and complex. Simple coacervation processes involve a single polymer, and coacervates are formed by adding a salt or desolvation liquid into the reaction medium. Complex coacervation processes proceed through ionic interactions between two or more oppositely charged polymers, usually proteins and polysaccharides, leading to coacervate formation and phase separation (**Figure 7**). The complex coacervation encapsulation process starts with an emulsion of core material and oppositely charged wall materials. A change in temperature or pH then triggers the coacervation of the wall materials. Finally, the polymer matrix is hardened by elevated temperature or the addition of a cross-linking agent.[69] This technique was first used to make carbonless copy paper and scratch-and-sniff technology.[70] Complex coacervation for fragrance encapsulation can be done with various wall materials, both natural and synthetic. For instance, Lv et al. used complex coacervation to form highly stable gelatin/gum arabic nanocapsules containing jasmine oil which could withstand heating to 80 °C for up to 5 h.[71] In the previously mentioned study by Rungwasasntisuk and Raibhu, gelatin/gum arabic microcapsules containing lavender oil were investigated for use in functional wrapping paper.[40] The microcapsules were prepared via complex coacervation as the fragrance was easily degraded at high temperatures. High encapsulation efficiency was achieved between 67% and 85%.[40] Zhang and coworkers used mixtures of chitosan, gum arabic and maltodextrin to encapsulate peppermint oil in a two-step process comprising complex coacervation followed by spray drying, which resulted in an encapsulation efficiency of 19–29%[72] as well as chitosan and gum Arabic to encapsulate the fragrances hexyl salicylate[73] and limonene[74] with encapsulation efficiencies of ≈60% and 29–44%, respectively. In another study conducted by Hernandez-Nava and colleagues, oregano essential oil was encapsulated by complex coacervation using gelatin and chia mucilage as wall material. The highest encapsulation efficiency obtained was around 91%, and this sample was subsequently spray-dried before characterization.[75]

Gelation can also be used for encapsulation. In a recent study by Hadidi et al., the group extracted the essential oil of clove buds for encapsulation in chitosan capsules using an ionic gelation technique. Sodium tripolyphosphate was employed to induce the gelation of chitosan in a previously prepared emulsion. The resulting nanocapsules had a reasonable encapsulation efficiency of (56–73%) and the dispersity of capsule size ranged from 220 to 445 nm.[76]

Chemical encapsulation includes the synthesis of the encapsulants in the presence of the cargo, for example, through a variety of polymerization reactions. These reactions are usually free radical polymerizations such as in situ, interfacial, and suspension polymerizations. Interfacial polymerizations have been well explored as an encapsulation technique. The process involves dissolving monomers or prepolymers into immiscible phases where polymerization can occur at the interface between these two phases.[77] For example, Berthier, Hermann, and coworkers prepared poly(urea-urethane) core–shell microcapsules in an interfacial polyaddition of polyisocyanates, added to the oil phase, and diamines in the water phase.[78] The capsules

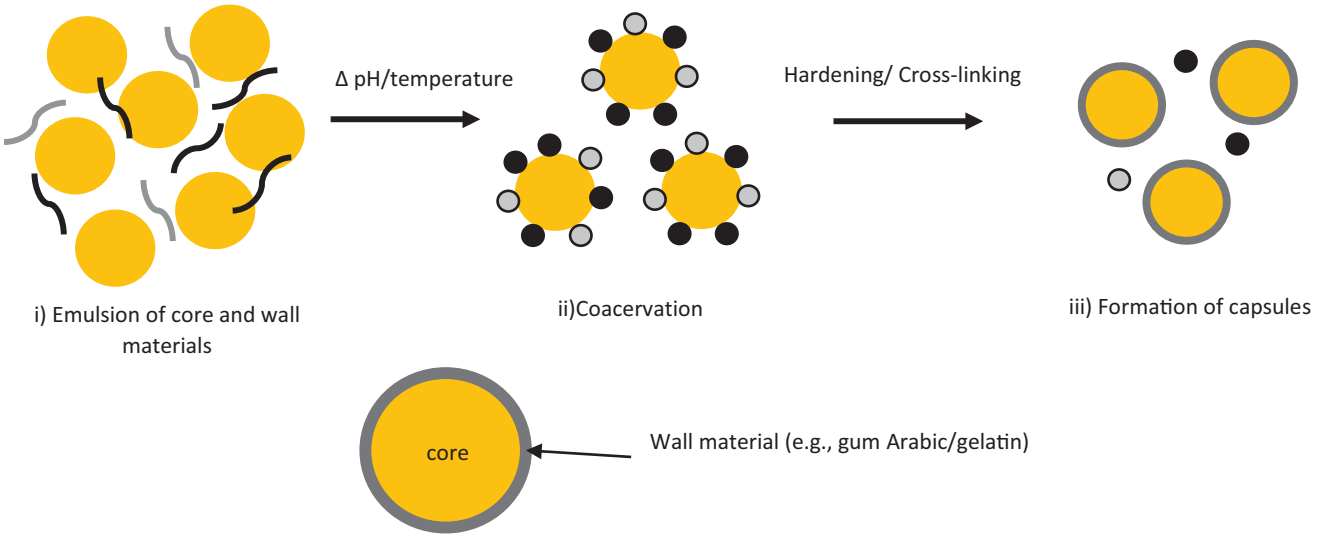

Figure 7. Schematic of complex coacervation process. A) First, a stable emulsion of the oppositely charged polymers and core material is obtained. B) A change in pH or temperature triggers the coacervation process. C) Microcapsules are formed at elevated temperatures or by adding a cross-linking agent.

contained light-responsive pro-fragrances, commercial fragrances, and 2-oxoacetates that decompose upon UV irradiation into a carbonyl compound and CO_2 or CO. The formation of the gas led to pressure build-up in the capsules and their subsequent rupture, which led to the release of the olfactory compounds. Thus, UV-light responsive fragrance microcapsules were created. In another example, Zhao et al. reported the preparation of poly(1,4-butanediol dimethyl acrylate) microcapsules that contained peppermint oil using interfacial polymerization. Interestingly, the microcapsule surface was broken when fully loaded with peppermint oil fragrance. Even when the peppermint oil content was decreased to 75 wt% in the core material, the capsules were of irregular morphology. Uniform spherical capsules were obtained only when fragrance content was further reduced to 50 wt%. The resulting microcapsules were easily impregnated onto fabrics, showed good thermal stability, and prevented fragrance loss up to 100 °C. It was also found that the fragrance was slowly released from the microcapsules, and release was sustained even across 15 wash cycles.[79] Viriyakitpattana and Sunintaboon demonstrated the encapsulation of sunflower oil in poly(methacrylic acid) (PMAA) capsules via interfacial polymerization. The resulting microcapsules were pH-responsive due to the presence of carboxylic acid groups within the cross-linked PMAA in the shell. The polarity of the PMAA chains could be controlled by varying the pH of the system allowing the microcapsules to be in a collapsed state at low pH, where the carboxylic acid groups are protonated, and induce encapsulation as the pH is raised. The degree of pH responsiveness could also be controlled by varying the methacrylic acid (MAA) monomer content during the polymerization.[80] As demonstrated by Wang et al., interfacial polymerization can also be facilitated by Pickering emulsions. The group prepared methyl laurate-loaded polyurethane microcapsules by interfacial polymerization in Pickering emulsion stabilized by TiO_2 nanoparticles.[81] However, encapsulation via interfacial polymerization has some drawbacks, as polymerization occurs at the interface between phases. As such, a polymer layer can form, blocking reagents from interacting and preventing further reaction.[77]

In situ polymerization methods are also commonly used in encapsulation technology.[82] An in situ polymerization is very similar to an interfacial polymerization, with the distinguishing factor being that the polymerization is carried with all the reactants present in the same phase. This technique is commonly used in making melamine or urea formaldehyde aminoplast resins. For instance, He and colleagues prepared MF microcapsules containing clove oil, sunflower oil, or hexyl salicylate by a combination of solvent evaporation and in situ polymerization. First, the essential oil and poly(methyl methacrylate-*co*-butyl acrylate-*co*-acrylic acid) random copolymers were dissolved in dichloromethane. The resulting solution was emulsified in an aqueous phase. The solvent evaporated upon heating, which induced phase separation between the polymer and the oil. As a result, the polymer accumulated at the interphase of the oil core and the water phase. In the next step, these pre-encapsulated oil droplets served as a template for in situ polymerization of MF precondensates which were added to the aqueous phase. The polyacrylate separated the essential oil from the precondensates, thus avoiding reactions between the core oil and the shell material. Moreover, it acted as a template for the MF polycondensation through electrostatic interactions between the carboxylic acid groups of the acrylic acid units and the amine groups of the melamine prepolymer. The resulting microcapsules showed a moderate encapsulation efficiency of around 49% and exhibited good thermal stability, with loss of clove oil from the microcapsule at an onset of 120 °C.[83]

Another avenue of in situ methods for the preparation of microcapsules is suspension polymerization. For example, Al-Shannaq and colleagues used suspension polymerization to prepare PMMA microcapsules containing paraffin as an example volatile material. Encapsulation was performed over two steps. First, an emulsion was prepared by a combination of surfactant

in an aqueous phase and a mixture of methyl methacrylate, pentaerythritol tetraacrylate (PETRA) as a cross-linking agent, the initiator benzoyl peroxide (BPO) and paraffin in an organic phase. Once the emulsion was obtained, polymerization was induced. The resulting microcapsules contained up to 85 wt% paraffin—demonstrating good potential for use as a fragrance encapsulation method.[84] Zhang et al. prepared polyacrylate/paraffin microcapsules using a similar suspension polymerization method. Pickering emulsion was used to facilitate the suspension polymerization with the aqueous phase containing a paraffin/β-CD inclusion complex and the organic phase comprising various methacrylate monomers (MMA, butyl methacrylate [BMA], and lauryl methacrylate [LMA]), paraffin core material, cross-linking agent PETRA and initiator BPO. The emulsion was prepared by adding the aqueous phase dropwise to the organic phase, followed by the polymerization step. The various acrylate monomers yielded three distinct microcapsules—cross-linked PMMA, P(MMA-*co*-LMA), and P(MMA-*co*-BMA) microcapsules. A number of the P(MMA-*co*-LMA) microcapsules were broken, suggesting that adding LMA caused the microcapsules to have weakened shells. The P(MMA-*co*-BMA) microcapsules exhibited the highest thermal stability, withstanding temperatures up to 284 °C. The resulting microcapsules also showed excellent cargo retention with minimal loss over 3 months of exposure to air.[85] Hofmeister et al. prepared pH-responsive nanocapsules containing α-pinene with encapsulation efficiencies of more than 90%. This was achieved using a mixture of MMA, BMA, MMA, and the cross-linker 1,4-butanediol dimethacrylate in a miniemulsion polymerization. The miniemulsion droplets contained the monomers, cross-linker, and core material. After a free radical polymerization was initiated, polymerization-induced phase separation of the polymers from the hydrophobic fragrance occurred. Cross-linked polymer nanocapsules with an average particle size of 150–200 nm and an adjustable MAA content were obtained. The nanocapsules exhibited high storage stability over several months and possessed the added benefit of pH-responsive release. The nanocapsules were "closed" under typical fabric conditioner conditions (pH 3). As the pH was increased above 9, the capsule walls were deprotonated, which increased water absorption and caused the microcapsules to swell, consequently allowing diffusion of the fragrance through the capsule wall.[86]

While encapsulated fragrances for textile or food applications usually need to be delivered in aqueous environments, perfumes represent a situation in which the hydrophobic fragrance molecules are directly dissolved in a lipophilic solvent. Thus, any sustained-release perfume capsule must be readily dispersed in the perfumatory solvent. To solve this challenge, and in contrast to most of the examples discussed above, hydrophobic capsules must be prepared. Therefore, Stasse and colleagues encapsulated fragrances in oil-in-water-in-oil (O/W/O) double emulsions using two surfactants with opposing polarity (**Figure 8**). The intermediate aqueous phase serves as a diffusion barrier for the hydrophobic fragrance molecules between the core and the outside. A hydrophilic surfactant was used to contain a mixture of industry-relevant fragrances in the water, while a lipophilic surfactant was used to stabilize the aqueous "globules" dispersed in the perfumery solvent. This method has shown extremely high encapsulation efficiency of up to 99%.[87]

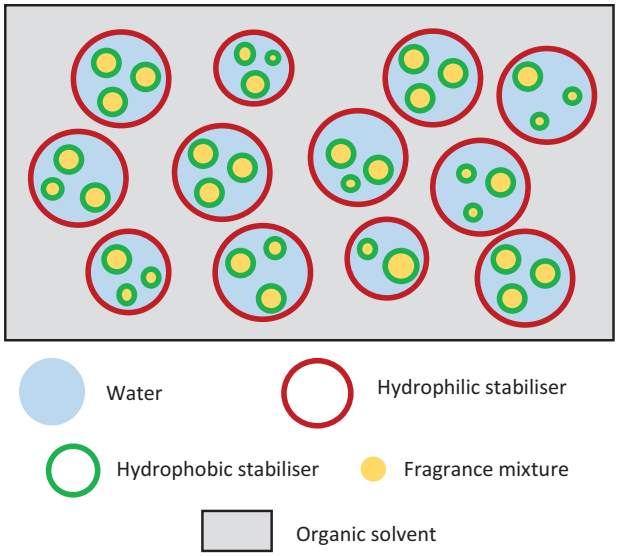

Figure 8. Schematic of oil-in-water-in-oil (O/W/O) double emulsions for fragrance encapsulation in perfume applications as described in ref. [87]. The fragrance mixture (yellow) is encapsulated by a hydrophobic stabilizer (green). This system is then further encapsulated in an aqueous solution by a hydrophilic stabilizer (red) in an organic solvent.

The group developed the concept further, describing a method to use these double O/W/O emulsions in conjunction with a cross-linking copolymerization within the water phase to synthesize capsules for the controlled release of fragrances. Double emulsions were prepared with the fragrance in the inner phase and the monomer and cross-linker in the aqueous phase. Four combinations of the monomers methacrylamide (MAM) or oligo(ethylene glycol) methacrylate (OEGMA), as well as the cross-linkers tetra(ethylene glycol) diacrylate (TEGDA) or *N,N*-methylene-bis-acrylamide (MbA), were subsequently polymerized to form microcapsules. After polymerization, the encapsulation efficiencies were more than 70% for all four types of capsules. Release, measured after 150 days at 20 °C, ranged from 18% for poly(OEGMA-*co*-TEGDA) capsules, to 93% for poly(MAM-*co*-MbA) capsules. Therefore, a range of release profiles could be obtained depending on the choice of monomer and cross-linker. In addition, premature fragrance release was prevented upon storage, and desired fragrance release could be induced using mechanical stress.[88]

3. Liposomes, Polymeric Micelles, and Polymersomes

Natural and synthetic lipids can self-assemble into various structures, including micelles and vesicles. A lipid bilayer membrane encloses a water-filled lumen in such vesicles, which are called liposomes. These nanostructures are well-suited to encapsulate and deliver cargo molecules.[89] Micelles can carry hydrophobic substances in their core, and liposomes can encapsulate water-soluble molecules in their interior and hydrophobic molecules in their membrane. Given their biocompatible nature and biological origin, lipids have been well-studied for fragrance encapsulation. For example, Sebaaly et al. prepared soybean-based phospholipid

liposomes to encapsulate eugenol—a volatile component of clove essential oil.[90] In another recent study, Ji and colleagues used soya lecithin-based liposomes to encapsulate lily fragrance. The resulting liposomes showed a low encapsulation efficiency of 22%. However, the liposomes prolonged the release of the fragrance.[91] In addition, Gonçalves and colleagues reported the use of liposomes and proteins in functionalized cotton for the preservation and controlled release of fragrances.[92] The group described two approaches for releasing β-citronellol fragrance from functionalized cotton using carbohydrate-binding modules (CMB)—protein domains that bind to cotton surfaces. First, the fragrance was complexed to a so-called odorant-binding protein (OBP) fused to the CMB. In the second approach, the fragrance was loaded into liposomes functionalized with the CMB attached to a peptide. The release of the fragrance was triggered by acidic conditions designed to simulate sweat. It was shown that the release of β-citronellol was more rapid from the complex, with up to 32% released after 1.5 h, whereas the liposomes facilitated a more sustained release of 6% after 1.5 h.

Although liposomes have been well studied, they usually have poor chemical and mechanical stability and are not easily functionalized.[93] The desire to improve the physiochemical properties of micelles and vesicles has driven extensive research into polymeric analogues.[93–98] Amphiphilic block copolymers are a polymeric analogue to lipids and have several advantages over lipids, most notably, the diversity and versatility of the chemical building blocks, which results in a broad range of functionalization possibilities. This opens up many opportunities to tailor the polymers' physiochemical, mechanical, and electronic properties—influencing important factors such as thermal stability, surface activity, solubility, and viscosity. Polymer micelles and polymersomes can be functionalized with a large variety of moieties which can bestow them with highly desired controlled release properties causing the micelles and vesicles to be responsive to several environmental triggers such as temperature, pH, light irradiation, and mechanical forces.[99,100]

In the realm of fragrance delivery, Lui et al. investigated fragrance-loaded pH-responsive polymeric micelles. The group synthesized a poly(5-aminopentyl-2-oxazoline)-*b*-poly(2-ethyl-2-oxazoline) block copolymer. Amine side groups on the first block were functionalized with *p*-anisaldehyde via Schiff base formation, which not only connected the fragrance molecule to the polymer through an acid-labile functional group but also rendered the block hydrophobic. The resulting polymer–fragrance conjugates were self-assembled in water into micelles. Upon lowering the pH, the imine groups linking the fragrance to the polymer slowly hydrolyzed, releasing the aldehyde fragrance. The profragrance micelles showed sustained release properties, with up to 39% of fragrance released after 120 h under acidic conditions. The polymer–fragrance conjugates were also easily deposited onto cotton due to positively charged ammonia groups on the polymer chain.[101]

In another study published by Zhang et al., amphiphilic polymer–lipid conjugates were synthesized using poly(carboxyl beanie) (PCB) as the hydrophilic polymer and distearoylphosphoethanol amine (DSPE) as the hydrophobic part. They self-assembled into micelles in water, which were used to encapsulate linalool. The presence of the zwitterionic side chains of PCB produced more densely packed micelles than micelles formed by DSPE-PEG polymer–lipid conjugates. Also, it provided an extra barrier to prevent the loss of fragrance. The encapsulation efficiency of the DSPE-PCB micelles was 1.5 times higher than those formed by PEG-DSPE. In addition, the DSPE-PCB micelles showed a slower release, with only 17% of linalool released after 24 h compared to 25% from the DSPE-PEG micelles.[102]

Poloxamers, also known under their commercial name Pluronics, are triblock copolymers consisting of a hydrophobic poly(propylene oxide) block between two hydrophilic poly(ethylene oxide) blocks (PEO-*b*-PPO-*b*-PEO). These amphiphilic copolymers can self-assemble into micelles and be used for fragrance encapsulation. For instance, Suzuki et al. used PEO-*b*-PPO-*b*-PEO micelles to facilitate the sustained release of three fragrances, 2-phenyl ethyl acetate, linalool, and benzyl acetate.[103] Similarly, Vauthey et al. used such block copolymers to encapsulate the hydrophilic aroma compounds diacetyl, 2-methyl pyrazine, pyrrole, furfural, and guaiacol. The results indicate that the polarity of the encapsulated cargo dictated its preferential location within the micelle structure. The more hydrophilic molecules were encapsulated within the corona of the micelles, whereas more hydrophobic compounds were found within the core.[104] More recently, Grillo and colleagues investigated the effect of encapsulated fragrances on the structure of PEO-*b*-PPO-*b*-PEO micelles. The micelles did swell upon loading with fragrances. The swelling of the micelles highly depended on the hydrophobicity of the fragrance molecules and on their chemical functionalities.[105]

In another study, Baglioni and coworkers reported the formation of unimeric micelles from poly(ethylene glycol)–poly(vinyl acetate) graft copolymers (PEG-*g*-PVA) that were used to encapsulate limonene, terpinyl acetate, and *p*-anisaldehyde. Similar to the study discussed above, the degree of swelling of the micelles depended on the hydrophobicity of the fragrances. Hydrophobic molecules were fully solubilized in the micelle core and did not cause swelling. Conversely, hydrophilic molecules aggregated in bulky structures, causing the micelles to swell.[106] In a subsequent study, the group investigated the effects of the hydrophobicity of the fragrances 2-phenyl ethanol, *L*-carvone and α-pinene on the structure adopted by the copolymers, as well as the effect of different solvent systems. It was found that a variety of structures could be obtained. 2-Phenyl ethanol was encapsulated in a so-called matrix capsule, in which the polymer and the fragrance form a homogeneous microparticle, and *L*-carvone caused the assembly of giant polymersomes. However, α-pinene was found to phase-separate from the assemblies as it was too hydrophobic.[107] Baglioni and coworkers also investigated the interplay of fragrances and the amphiphilic graft copolymer poly(ethylene glycol)-*graft*-(poly(vinyl acetate)-*co*-poly(vinyl caprolactam)) (PEG-*g*-(PVAc-*co*-PVCL)), also known under its commercial name Soluplus. Compared to PEG-*g*-PVA, it is more hydrophilic due to the presence of the VCL units and, therefore, better suitable to encapsulate more hydrophilic molecules. Moreover, the grafted chains are longer than in PEG-*g*-PVA, which should give the polymer more conformational freedom to interact with the encapsulated cargo. The phase behavior of the polymer in the presence of seven fragrance molecules was studied over a wide range of concentrations. 2-phenyl ethanol was the most hydrophilic encapsulant tested and was taken up into polymeric micelles that slightly increased in size due to the

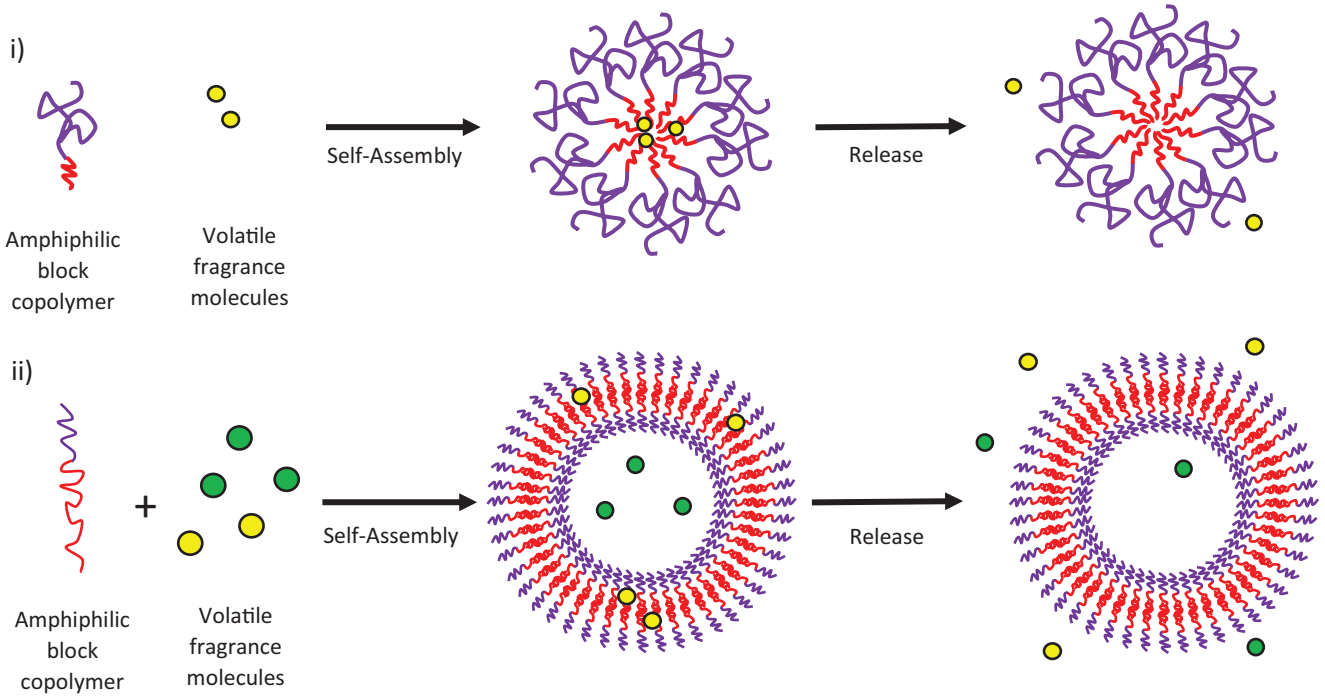

Figure 9. Schematic of encapsulation and release A) of hydrophobic fragrance molecules in/from the core of polymer micelles, and B) of hydrophilic and hydrophobic fragrance molecules in/from the interior and the membrane of polymersomes. Hydrophilic blocks of the copolymers are depicted in dark purple and hydrophobic blocks in red. Hydrophobic fragrance molecules are depicted as yellow spheres and hydrophilic fragrance molecules as green spheres.

encapsulated cargo. Florhydral and *L*-carvone resulted in matrix-like capsules, that is, the polymer and the fragrance were homogeneously distributed throughout the nanoparticle. Linalool and *β*-citronellol resulted in giant polymersomes in which the cargo resided in the polymer shell. *α*-pinene and *R*-limonene resulted in an emulsion in which polymeric micelles surrounded and stabilized fragrance microdroplets.[108] Thus, the solubilization and encapsulation of fragrance molecules, at least by this polymer, is not only governed by fragrance's octanol/water partition coefficient but also by the molecular structure and functional groups of the encapsulated molecules and their interaction with the encapsulating polymer, which raises the need for further in-depth studies of the phase behavior of polymers commonly used in fragrance formulations.

Polymersomes are synthetic analogues of liposomes.[93] They consist of amphiphilic block copolymers, which are, in the simplest case, a hydrophilic polymer block covalently linked to a hydrophobic polymer block. Due to the difference in polarity between the two blocks, and if the ratio between hydrophilic and hydrophobic blocks favours assembly into planar membranes, these amphiphilic block copolymers can self-assemble into hollow spherical vesicles (**Figure 9**), which offer vastly improved stability over liposomes—partly due to the greater degree of entanglement of the copolymers within the structure and because of the lower solubility of polymers in aqueous solutions. Polymersomes are very similar in structure to liposomes, with the main difference being the increased wall thickness of polymersomes due to the macromolecular nature of the block copolymers.

Polymersomes are excellent encapsulation systems for several applications, including targeted drug delivery—most notably in the delivery of anti-cancer drugs[109,110] and therapeutic proteins as well in other medical applications such as controllable insulin delivery systems.[111] However, there are only very few reported examples of the use of polymersomes for fragrance encapsulation, which is surprising given the excellent physicochemical properties of polymeric vesicles and their great propensity for encapsulation. One reason is that most fragrances are hydrophobic or amphiphilic molecules that can only be accommodated in the polymersome membrane but not in the much larger lumen of the vesicles. A report on polymersomes that contain fragrances is the study mentioned above on PEG-*g*-PVA unimeric micelles,[107] in which the encapsulation of carvone could also result in giant polymersomes with a shell thickness of 4 µm an average radius of 15 µm. The relatively thick membrane indicates that aggregated micelles formed the shell of the giant polymersomes. Moreover, giant polymersomes were also observed for PEG-*g*-(PVAc-*co*-PVCL) in the presence of linalool and *β*-citronellol. In these micrometer-sized vesicles, the fragrance resided in the shell of the polymersomes but was not detected in the interior water phase or on the outside of the capsules.[108]

4. Characterization Techniques for Fragrance Encapsulation Systems

The effective characterization of nano- and micro-capsules is essential to study encapsulation systems. Several aspects must be analyzed, such as wall morphology, thermal and structural

stability, encapsulation efficiency, and release profiles. Following the synthesis of monomers and the subsequent polymerization reaction, the resulting macromolecules must be fully characterized by NMR spectroscopy, gel permeation chromatography, mass spectrometry (MS), IR spectrometry, and other methods. Several techniques can be used to determine the size and morphology of nano- and micro-capsules. Confocal laser scanning microscopy, other types of light microscopy, scanning electron microscopy, and transmission electron microscopy are powerful techniques to analyze the size and morphology of capsules and self-assemblies, gaining important information about their structure and shape, as well as about their surface. Other methods complementary to microscopy are dynamic light scattering and static light scattering, which give information about the particle size, size dispersity, and particle structure. Furthermore, small-angle neutron scattering, differential scanning calorimetry, and rheology are used to characterize the phase morphology of fragrance–polymer–water systems.[107,108] Encapsulation efficiency and loading capacity can be determined by various methods, including thermogravimetric methods, as well as gas chromatography (GC) and HPLC. One of the most important aspects of fragrance encapsulation technology is the release behavior of fragrance molecules from the encapsulating material. The intrinsic volatility of encapsulated fragrances makes analysis by GC, often coupled to MS (GC-MS), a very effective method to quantify fragrance release. For instance, Zhao and colleagues prepared fragrance-containing melamine-formaldehyde microcapsules, which were impregnated into fabric. The group then used solid phase microextraction-GC-MS (SPME-GC-MS) to study the controlled release of the fragrance from the impregnated fabric.[112] Analysis of the thermal properties of microcapsules is also crucial in understanding the thermal stability of wall materials. TGA allows study the thermal stability of microcapsules.[84] TGA is a type of thermal analysis that measures a sample's mass as a temperature function. This yields important information about the thermal stability of the material and of the encapsulated cargo, for example, to determine the temperatures at which the wall material decomposes. In addition, unexpected mass losses in the TGA trace could indicate premature release of the encapsulated material. For instance, Lopes and colleagues prepared chitosan-cellulose capsules to facilitate the prolonged release of limonene, using TGA analysis to investigate the interaction between the two wall materials.[113] Often, the combination of several methods yields even deeper insights into the fragrance release properties of the formulation. For example, Lopes and coworkers used TGA and GC to probe the release behavior from the capsules.

5. Conclusions

The fast evaporation of fragrances under ambient conditions presents a substantial challenge to industrial manufacturers that rely on pleasant scents and aromas in their product formulation for a range of applications, including perfumery, textile modifications, laundry formulations, cosmetics, and hygiene products. As highlighted, many materials, encapsulation methods, and types of capsules are used to facilitate the preservation, sustained release, and controlled release of fragrances. Inorganic capsules have high physical stability and good release properties. However, these capsules are limited to only a few materials, and the release relies on pores in the capsule wall or the physical breaking of the capsules. Various natural polymers have been used for fragrance encapsulation which have the advantage of being intrinsically bioavailable, showing good encapsulation efficiency, with some materials even showing additional benefits such as antimicrobial properties. Compared with natural polymers, synthetic materials are much more versatile in scope for functionalization and have the advantage of fine-tuning important aspects of the material, such as the release properties from the resulting capsules. Polymer capsules used for fragrance preservation include microcapsules and block copolymer micelles. However, the use of polymersomes for encapsulation and sustained release of fragrances needs to be further explored and presents a promising avenue.

One aspect that will require further studies is to elucidate in more detail the influence of hydrophobic and amphiphilic fragrance molecules on the self-assembly of amphiphilic block copolymers and graft copolymers to obtain a predictive understanding of the molecular interplay between fragrance molecules and polymers, and therefore, of the resulting capsule morphologies. Moreover, the high level of customizability afforded by polymers in fragrance encapsulation means that the permeability of the polymer shell can be facilitated by a number of different triggers—allowing for control over the release behavior of the encapsulated fragrances. However, even though the stimuli-responsive release is well-established for the controlled release of therapeutic molecules from polymeric drug delivery systems, this aspect is yet vastly unexplored in fragrance delivery. Therefore, it leaves plenty of room for innovative ideas to create controlled release systems tailored toward delivering fragrances, perfumes, aromas, and scents. Finally, any encapsulation system used in everyday products will readily find its way into the environment. Thus, the selection of capsule materials should be limited to those that readily degrade under biological conditions. Otherwise, the microcapsules will significantly contribute to microplastic pollution of the environment, including water streams and the ocean.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

S.R.: Conceptualization, writing—original draft, and visualization. N.B.: Conceptualization, writing—review and editing, supervision, project administration, and funding acquisition.

Keywords

block copolymer vesicles, cyclodextrin inclusion complexes, fragrances, microcapsules, perfumes, polymer micelles, polymersomes, scents

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