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Sustainable Chemistry Considerations for the Encapsulation of Volatile Compounds in Laundry-Type Applications

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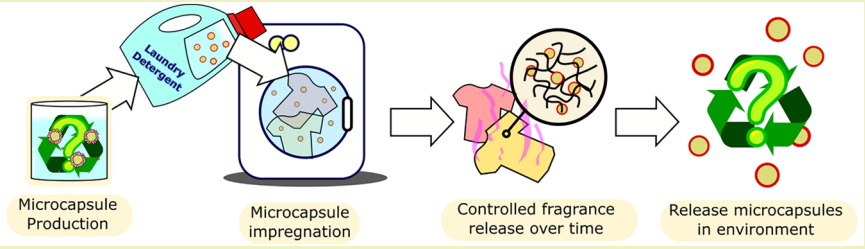

ABSTRACT: Microencapsulation of volatile compounds in fabric care products has brought extra value in a variety of laundry-type applications, allowing clothes to release pleasant scents for weeks after their last wash with minimal amounts of fragrance used. Melamine−formaldehyde is the industry standard in this regard, while polyacrylate and polyurea shells are promising candidates for use in commercial laundry-type applications. Harsh storage conditions and demanding release characteristics have limited the number of viable shell wall materials and chemistries for these kinds of applications. This renders nano- and microencapsulation of volatile compounds for laundry-type applications one of the most challenging areas in the encapsulation field. The largest drawback of the current technology is the limited biodegradability of the produced microcapsules, e.g. when leaking via wastewater. This review summarizes the search toward viable, high-performant and sustainable alternatives for the current technology. First, various techniques to encapsulate volatile compounds in this context are overviewed. Recent relevant encapsulation reports using natural and synthetic shell walls are discussed, while controlled release data are included where possible. Finally, a perspective containing insights toward sustainability in the engineering of alternative capsule chemistries is offered.

KEYWORDS: *Microcapsules, Microplastics, Fragrance Encapsulation, Bioplastics, Biodegradability*

INTRODUCTION

The controlled release of active compounds is a highly desired property in an increasing number of applications, including the cosmetic, pharmaceutical and nutritional fields.[1] In each of these fields, a number of unique and diverse requirements are imposed on microcapsules, in light of their different functions and release profiles.

A rough divide in encapsulation fields is made when considering any type of capsule containing flavor or fragrance. This entails not only all care products, textiles and leathers but also food and tobacco-related products. Recent reviews by He et al. as well as Kaur et al. discuss a variety of encapsulation applications for a wide range of these consumer goods.[2,3] In the food industry, reports on microencapsulated essential oils or preservation of flavor and fragrance have seen increased attention.[4] Food microencapsulation sets itself apart from pharmaceutical and cosmetic applications as the release rate of encapsulated food in the mouth is fast and easy due to the induced mechanical force of grinding teeth, rendering controlled release mostly unnecessary.[5] Hence, these types of shell walls are only viable for food applications as they would not be able to provide a prolonged release in environments typical for drug or general care applications. While drug encapsulation comes with the extra challenge of biocompatibility (*in vivo*) and an increased focus on timed and targeted release, some household applications (e.g., floor cleaners, liquid laundry detergents, fabric conditioners) have possibly the most demanding release requirements. On the one hand, sustained release of fragrances is a key performance parameter in many of these personal and household care items, while on the other hand the stability of the products on-shelf is crucial as well. Prolonged stability of these microcarriers, encapsulating small and volatile molecules, and the subsequent controlled release require very specific shell wall properties.[3]

Microencapsulation in the fabric care industry is one of these high-demanding microencapsulation areas where controlled release of encapsulated fragrances is driven to the extreme.[6] Fabric softeners, liquid laundry detergents and powdered laundry products often come with encapsulated fragrances with specific release profiles, preferably releasing fragrances for weeks after their last impregnation wash. Microcapsules are put to the most harsh test in liquid laundry detergents, where capsule walls are subjected to highly viscous liquids containing concentrated detergents, as they have to protect their inner

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liquid fragrance core from the oil-removing detergents for periods up to 36 months. The microcapsules are then expected to be stable during the washing cycle (with temperatures up to 60 °C) and release fragrances on fabric for prolonged periods of time (Figure 1). Due to the prolonged release of

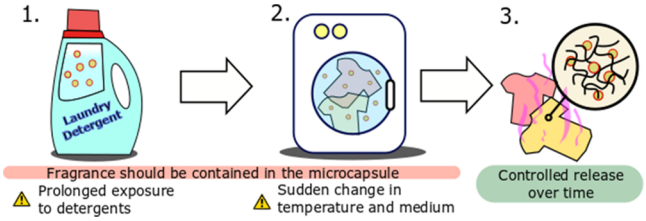

Figure 1. Critical steps of microcapsule life in the high-demanding laundry detergent application. The microcapsules are subjected to detergents for an extended period (1), exposed to increased temperature and change in medium (2), while eventually impregnated on textile for controlled release of fragrances over time (3).

microencapsulated volatile compounds, the amount of perfume used in these laundry products can be decreased significantly as its targeted release makes their use more efficient. It is due to microencapsulation that the amount of active compounds in consumer products can be decreased drastically while at the same time also improving the quality of these laundry products by protecting fragrances from oxidation caused by heat, light or moisture.[7] Moreover, it can be argued that the prolonged pleasant scent of textiles is perceived as freshness, decreasing the overall number of washing cycles, which decreases water usage and micropollution due to the decreased release of microfibers from clothing.[8]

Microcapsules found in commercial laundry applications mostly make use of aminoplast-type resins as their capsule wall. These types of structures, of which the melamine–formaldehyde (MF) is among the most popular ones, create a shell wall around an apolar perfume phase via an efficient *in situ* polymerization procedure via formaldehyde-induced methylolation and a series of complex condensation reactions (Figure 2).[9] Due to the reactivity of formaldehyde for the trifunctional melamine monomer, the resulting shell wall consists of a densely packed matrix of melamine-linked molecules with a high cross-link density. This wall chemistry exhibits exceptional shell properties as it is very durable and compatible with a wide range of applications. Part of the success of these aminoplast shell walls can also be attributed to the cheap cost of its raw materials.[10]

Although microencapsulation in textile applications can be seen as beneficial for both environmental sustainability and consumer satisfaction (on the premise of less washing cycles and more efficient use of active compounds), it is worth looking into process improvements as well as sustainable alternative solutions without compromising product quality and properties. Although current microcapsules have an excellent performance in the high-demanding laundry-type environment, improvement can still be made in terms of targeted delivery, biodegradability, toxicity and synthesis feedstock. All of these factors can improve the environmental sustainability of these products.

In terms of targeted delivery, various release mechanisms are described depending on the type of shell wall material and the external stimuli present.[3] For aminoplast-type capsules, release of active compounds is controlled by mechanical force on the stiff and brittle shell wall, which causes rupturing of the capsule on the textile.[11] It can be argued that compared to rupturing, diffusion-type release can be a more controlled and thus more efficient release mechanism. Various diffusion models are available in literature which describe the release of active compounds from a core/shell system. More so than with fractured release, capsule characteristics (thickness of shell, core/shell ratio, type of core/shell and type of external medium) all influence diffusion.[12,13] Apart from the type of release, which is ultimately controlled by the rigidity of the shell wall and its permeability properties, literature research is also focused on triggered release of active compounds which could significantly increase the efficiency of the release. Examples of these types of triggers include the inclusion of light-sensitive groups in the shell wall which decompose on irradiation of specific wavelengths, breaking bond in the shell wall[14] or even generating gas in the inner core which causes rupturing of the microcapsule.[15] The review on triggers for microcapsules by Esser-Kahn et al. gives a general overview of possibilities in this area of microencapsulation.[16]

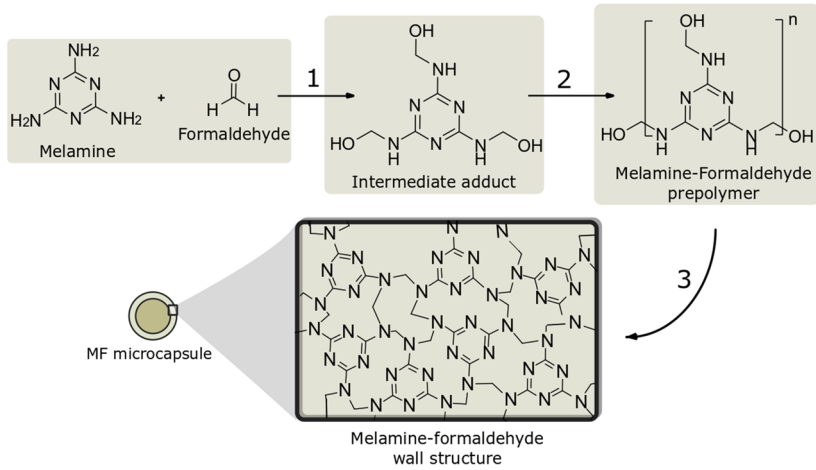

Figure 2. Synthesis of the melamine–formaldehyde (MF) microcapsule shell. Formaldehyde and melamine forms an intermediate adduct (step 1) which start forming MF oligomers which are dissolved in the continuous phase (step 2). These oligomers are ultimately deposited on the oil/water interface of the emulsified droplets and further react into a densely packed cross-linked shell (step 3).

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Apart from potential improvements on targeted release of active compounds or the good control over formaldehyde presently, the current commercial shell wall material is all petroleum-based and shows poor biodegradability. The latter is bothersome as their release into the environment is unavoidable, which results in nonbiodegradable micro- and nanoplastics polluting lakes, streams and oceans. Although the global extent of microplastic contamination is unknown, recent studies suggest that microplastic pollutants could be far more pervasive than originally thought.[17] There is increasing concern that these micropollutants, once ingested by animals, can provide possible pathways toward accumulation of hydrophobic organic contaminants, possibly leading to a variety of health concerns.[18] Although concrete numbers are not available, it is expected that a certain amount of microcapsules from laundry detergent products will find their way in the wastewater after a first washing cycle.[19,20] Microplastics are considered one of our newest emerging contaminants, with microbeads originating from consumer products being banned in the United States in 2015.[21] Moreover, a number of regulatory actions are taken worldwide to minimize future microplastic pollution. At this point it should be noted that studies investigating the extent of microplastic pollution in marine habitats rarely mention the presence of plastics normally used in microplastic shell walls as more than 90% of microplastic pollution is polyethylene or polypropylene. In one recent study which quantified the microplastic content of wild-caught Atlantic mackerel, a third of all fish contained microplastic particles Moreover, subsamples from scat of captive seals fed on these mackerels were also found to contain microplastic particles, confirming the trophic transfer of microplastics via the ingestion of whole prey, which is also relevant for humans. In this study, a minor fraction (0.5%) was found to be of the MF type.[22] It is worth mentioning that even this fraction is not solely originating from MF laundry-type microcapsules, as melamine is used in a variety of laminates, plastics, dyes and fertilizers across the globe.[23] In fact, one of the most abundant micropollutants from laundry washing are actually plastic fibers resulting from the weathering of clothes during textile washing. The magnitude of pollution from these textile fibers is thought to be orders of magnitude larger compared to any microplastic originating from microcapsule shell walls.[24]

Besides their slow biodegradability, MF and urea–formaldehyde shell walls use formaldehyde as one of their building blocks for the shell wall. Although not harmful once incorporated in the wall material, unreacted formaldehyde is classified as a known human carcinogen.[6] This puts stress on the manufacturers to comply with strict implemented regulations and even forces companies to add formaldehyde scavengers to lower and control free formaldehyde content in their products. Although it is unclear if these kind of measures are in effect in smaller companies, it seems commonplace at large consumer care companies such as Henkel and Procter & Gamble. Hence, the risk of exposure to toxic levels of formaldehyde from MF-type microcapsules with scavenger implementation is nearly nonexistent.[25] Still, consumer perception ultimately drives the market, which is troublesome for manufacturers as formaldehyde comes with negative connotations at big American retailers.[6] Some of the most recent successful alternatives, i.e. formaldehyde-free microcapsules, e.g. polyurea and polyacrylate microcapsules,[26,27] are still made from petroleum-based monomers and suffer from poor biodegradability and toxicity (Figure 3).

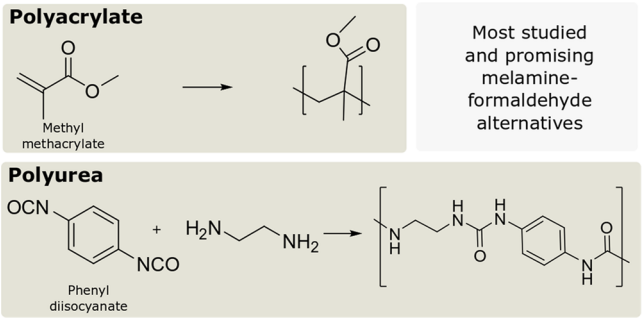

Figure 3. Two of the most studied and promising melamine–formaldehyde replacements for encapsulating fragrance compounds in laundry-type applications: polyacrylate and polyurea. A simplified synthesis scheme is shown.

The ultimate sustainable MF microcapsule replacement is made from renewable resources, consists of a shell that is made from harmless constituents and readily biodegrades when released into the environment. On top of that, the functionality should still be acceptable, i.e. maintaining a good shelf life and release profile. In regards to biodegradability, it should be mentioned that although even MF microcapsules will biodegrade after an extensive amount of time, shorter time frames are desirable to avoid accumulation in ecosystems. It should also be noted that every polymer comes with a different biodegradation profile. Although many polymers will show good biodegradation when industrially composted (compost and soil, 50–60 °C) after 3 months, this list shrinks significantly when considering biodegradation at lower temperatures (<30 °C) in (fresh) water environments via mesophilic digestion.[28] In the latter case, only some natural polymers (mostly starch-based and protein-based polymers) show substantial biodegradability after 1 month in a fresh water environment.[29,30]

The focus of the sustainability discussion of this paper is largely put on toxicity (a social-environmental concern) and biorenewability/biodegradation (an environmental concern). We should point out that, although commonly used interchangeably, a biodegradable polymer is not necessarily more sustainable compared to oil-based alternatives. Although biobased polymers, both biopolymers or synthetic polymers from biobased building blocks, are generally considered an eco-friendly alternative to petroleum-based polymers due to their renewable feedstock and presumed biodegradability, these are only contributing factors to a bigger picture in need of a complete Life Cycle Analysis (LCA).[31] When considering LCA's of biobased polymers, other factors such as the excessive usage of energy (from fossil fuel) during the agricultural, milling and production stages commonly play a major role.[31] We should therefore always be careful when labeling something as green or sustainable. Although a detailed analysis of all factors influencing the LCA in microencapsulation is far beyond the scope of this review article, we have tried to maintain a consistent approach throughout this article, giving notice to sustainability concerns, both environmentally (biodegradability, feedstock) and social-environmentally (toxicity of compounds and possible detrimental health effects).

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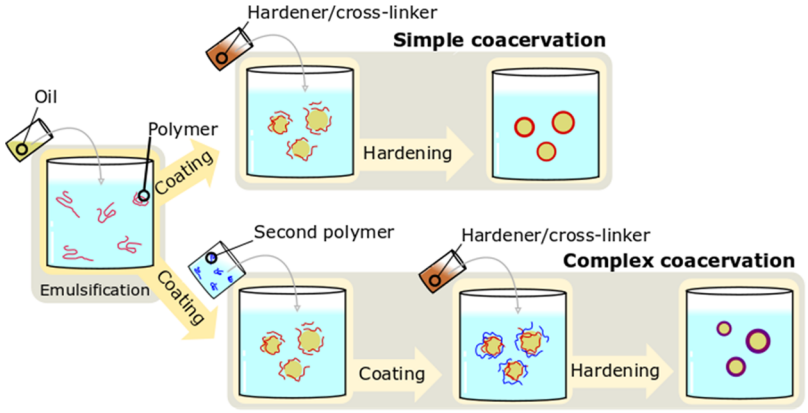

Figure 4. Simple and complex coacervation depicted, starting from emulsification of the to be encapsulated oily core.

This review focuses on the chemistry and engineering of both micro- and nanoencapsulation of volatile oils with natural and synthetic shell material in recent scientific literature and links this to the sustainability discussion. Although ideally, patents should also be part of this discussion, recent patent literature in this regard is arguably less focused (or unable to focus) on the sustainability aspect of fragrance-containing microcapsules. A large part of recent IP literature in this regard is focused on improvements of MF[32,33] or polyacrylate[34,35] shells. An increase in patents concerning polyurea[36] and polyurethane[37] shells is also noted. We have omitted discussion of these types of shells due to them not meeting the main sustainability criteria (biorenawability/biodegradability) used in this review. Reviews discussing some of the patents are available in literature for the interested readers.[1,3,38,39]

Where possible, focus is put on stability of the produced capsules in extractive detergent-containing media and their controlled release characteristics. In this light, the first part of this review discusses the most common techniques used for encapsulating these volatile compounds, irrespective of the shell wall used. The next part will discuss the most relevant reports available that make use of natural polymers as the shell wall material. In the third part, the relevant synthetic possibilities toward environmentally sustainable encapsulation are explored. Insights of the role and applicability of these natural and synthetic shell walls in specific laundry-type applications are given in the Insights section.

TECHNIQUES

Micro/nanoencapsulation is the technique where one substance or mixture of substances is coated or entrapped with or within another material. The coated material is called the active core or core material, and the coating is also called shell wall, shell material or wall material. Depending on the technique and certain parameters, capsules produced can have a varying diameter from nanocapsule (<0.1 μm) to microcapsules (0.1−1000 μm) or macrocapsules (>1000 μm). The number of techniques used for micro/nanoencapsulation is extensive, with variations within techniques still implemented. Although microencapsulation is most common for laundry-type applications, all sizes of capsules are used, depending on the needs of the application. In practice, commercially available capsules rely mostly on friction for releasing their active compounds. In this regard, the smaller the capsules the greater the covering of the product and the longer the fragrance will last, as it takes longer for the capsules to be ruptured by physical pressure due to decreased possible contact area with mechanical forces, while larger capsules release more fragrance at once.[38,40]

In general, micro/nanoencapsulation techniques can be divided into three main categories: chemical processes (focusing on polymer synthesis during encapsulation), physicochemical processes (in which the driving force is both of physical and chemical nature) and physical processes. In terms of encapsulating fragrances and oils, numerous different techniques are available. When considering sustainable alternatives for high-demanding applications, the number of reported techniques decreases significantly. In the next section, we intend to give an overview of techniques reported for the production of alternative MF-type microcapsules.

One of the most commonly used techniques when considering encapsulation of volatile compounds with a biodegradable shell is the physicochemical coacervation (or phase separation) technique (Figure 4).[41,42] This technique is divided into simple and complex coacervation, depending on the components of the shell wall. The coacervation technique starts from a stable emulsion of the core material in the continuous phase, which consists of (part of) the wall material. Through different methods, the encapsulating material is induced to precipitate as a viscous liquid (coacervate) on the encapsulated material. In simple coacervation, a single polymer is precipitated around the core material. This can be done via salting out via the addition of electrolytes, via the addition of a nonsolvent, or via temperature changes. In this step, phasing out the polymer out of the liquid phase onto the shell wall is the main purpose. While simple coacervation is induced by a change in condition that induces desolvation of the shell wall material, complex coacervation is induced via neutralization of two oppositely charged polymers, usually proteins and polysaccharides (Figure 4).[43] In the final step, the coacervate shell obtained via simple or complex coacervation can be stabilized/hardened via a number of methods to create a stable shell wall. Hardening may include chemical cross-links for an irreversible stabilization of the shell.[44] High encapsulation efficiency (%ee), one of the main parameters for evaluating microencapsulation techniques (%ee = oil encapsulated (g)/total oil (g)) and great flexibility in choice of shell wall and type of encapsulated material has made the coacervation technique one of the most studied techniques in food, pharmaceutical and personal and household encapsulation. Overall, the load of oil in the final microcapsules formed by

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coacervation is high compared to other encapsulation methods, such as spray-drying.[45] Due to the nature of the coacervation process which needs minimal or no heat, it is considered one of the best encapsulation techniques for volatile compounds.[46]

Spray-drying is another common encapsulation technique, although more so in the food industry, due to its flexibility and economic viability (Figure 5).[47] It is easily scalable and

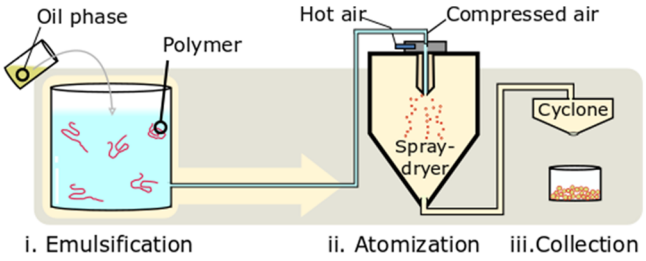

Figure 5. Spray-drying process starting from the encapsulation of the oily core which is used in an atomization process which spray-dries microcapsules.

produces high-quality products with low water activities that are easy to transport.[39,48] It is a physicochemical micro-encapsulation technique that uses an emulsion of the active component in water or an organic solvent. The selection of the wall material in this process is critical to the encapsulation process. In essence, any polymer that can be atomized is a possible wall material in the spray-drying process with proteins, polysaccharides and gums among the most heavily re-searched.[49,50] The starting emulsion controls the size distribution of the resulting microparticles and has influence on the final %ee. This emulsion is atomized into a heated compartment with hot and compressed air. The sprayed droplets quickly dry when subjected to the outlet temperature and hot gas of the spray dryer chamber. As a consequence, the solvent surrounding the emulsion quickly evaporates and a hardened particle or capsule is formed around the core material. Once dried the particles are separated and collected into the cyclone. The spray-drying and separation of the air particles is a fast process which enables continuous micro-capsule production. Apart from these advantages, the equip-ment is quite bulky and the procedure is not very thermally efficient.[51]

When considering the spray-drying of fragrances for high-demanding applications, reports are more scarce as the procedure becomes more challenging. As spray-drying forces all capsule components through a heated chamber, loss of oil to be encapsulated is common for more volatile compounds, leading to a poor %ee. Apart from unencapsulated oil, residue on the surface of the powder particle is also often observed.[52] In this regard, modifying the shell and core material and the spray-drying parameters can have a significant influence on the %ee of the process. Although many reports are available of encapsulation of volatile essential oils via spray-drying for food applications, applications requiring controlled release are less often described.

Emulsification/solvent evaporation is another common and straightforward technique for the encapsulation of a variety of active compounds in a core−shell particle. It consists of the formation of an emulsion via the use of a volatile organic solvent which dissolves the oil to be encapsulated, and the use of water with a stabilizer as the continuous phase. In this way, O/W emulsions are hardened when the volatile liquid diffuses into the continuous phase and evaporates.[53]Although widely utilized in the pharmaceutical industry for encapsulation of hydrophobic drugs, reports of this technique for the encapsulation of fragrances are less common.[54−56] The technique is quite expensive as the most efficient volatile organic liquids are most often of the halogenated type (e.g., dichloromethane). Moreover, the process is energy- and time-consuming and even in optimal conditions it provides quite low %ee compared to some of the more recent popular techniques such as coacervation.

Recently, layer-by-layer (LbL) technique carriers have received increase attention concerning their applicability in drug delivery, biosensors and bioreactors.[57] This technique is now also being explored for stabilizing volatile O/W emulsions.[58] Multilayer coatings are usually produced via electrostatic deposition of charged biopolymer onto an oil microdroplet. In this regard, the LbL technique is analogous to the complex coacervation technique as both techniques are based on polyelectrolyte complexation. But while complex coacervation is governed by a phase separation equilibrium, LbL technique creates kinetically trapped layers. Although lab-scale LbL strategies to encapsulate emulsions or droplets (with or without the use of templates) is a very common straightforward technique, upscaling is often problematic. One major concern in this regard is the time required for assembly of every separate capsule layer, which somewhat hampers the industrial viability of this process.[59]

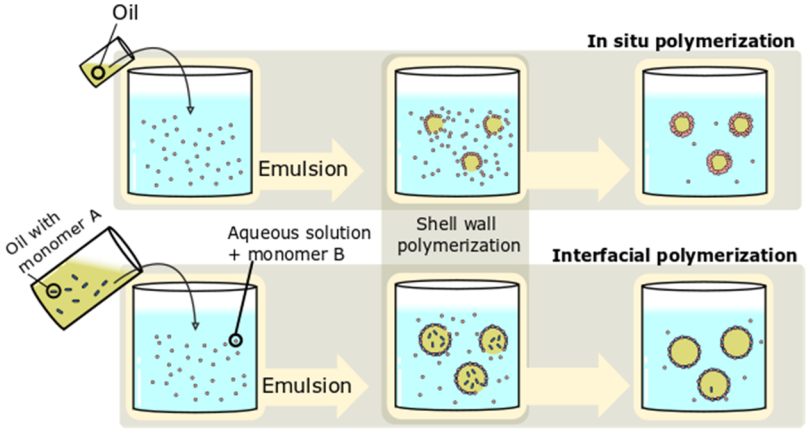

Figure 6. Scheme of *in situ* polymerization and interfacial polymerization encapsulation technique.

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Interfacial and *in situ* polymerization are two common polymerization techniques for encapsulating active compounds (Figure 6). In *in situ* polymerization, formation of the shell wall happens after the emulsification step as the monomers are located in the continuous phase.[19] A variation of this technique is the interfacial polymerization technique which occurs via dispersing two reactive monomers in alternative phases, followed by polymerization on the interface of the core phase and the continuous phase.[60] The fast reaction times, easy scale-up and generally high %ee make these polymerization encapsulation techniques highly industrially relevant. The *in situ* polymerization of melamine−formaldehyde produces one of the most forgiving shell walls, producing capsules with excellent properties with numerous volatile active cores. It is clear that the wall material of these types of techniques will likely be nonbiocompatible and more certainly nonbiodegradable. Moreover, these types of encapsulation require fast reaction kinetics to be able to cross-link the core *in situ*, which is often linked to an increase in toxicity (acrylates, aldehydes, isocyanates).

NATURAL SHELL WALL AND VOLATILE COMPOUNDS

Microencapsulation. Some reports are available of encapsulation of volatile and/or oily compounds with natural polymers via a simple coacervation procedure. Chitin, the second most abundant polysaccharide in nature, is one of the most studied biopolymers (per definition thus biobased) for use as a shell material in microencapsulation.[61−63] It is obtained from crustacean shells, composed of *N*-acetyl-D-glucosamine and D-glucosamine. Chitosan is in fact obtained by the deacetylation of chitin. This degree of deacetylation has a large influence on the properties of the resulting chitosan, as the free primary amine groups are often targeted in microencapsulation for cross-link reactions. Hsieh et al. (2006) encapsulated citronella oil via simple coacervation using 80% deacetylated chitosan as the shell wall and sodium hydroxide in various concentrations as hardener to stabilize the capsule. It was found that the concentration of sodium hydroxide was crucial. While low amounts of sodium hydroxide were not effective for total encapsulation of the oil phase, large amounts caused excessive viscosity of the entire emulsion system which resulted in bulky clusters of microcapsules. Thermal pretreatment of chitosan microcapsules at 80 °C was effective in controlling the oil release rate, as the chitosan membrane shrinks and closes its pores when heated.[64] 95% deacetylated chitosan was used to encapsulate clove oil via simple coacervation. In the hardening phase, the pH of the emulsion was adjusted to 4 and glyoxal was added as a cross-linking agent at a temperature of 10 °C to cross-link free amine groups. Addition of glyoxal was essential as there were almost no microcapsules observed after vacuum-drying when no glyoxal was added. When the glyoxal concentration was increased from 1% to 5%, serious agglomeration was observed, which was an indication that excessive cross-linking had occurred. The release of clove oil from the microcapsule was studied in an ethanol−water mixture (10%) at different temperatures. Lower release rates of clove oil were observed when the temperature of the release study was increased from 20 to 40 °C or 60 °C. This was linked to contraction of pores of the chitosan shell at higher temperatures.[65]

Gelatin is a mixture of peptides and proteins, produced via irreversible collagen hydrolysis. Due to the specific amino acid compostion of gelatin, with proline inducing close-packed chains and locking certain conformations, it is often used as a gelling agent. It is a popular biopolymer in controlled-release-type microcapsules due to these properties.[66−68] Simple coacervation was used for encapsulating *Zanthoxylum limonella* oil (ZLO). Glutaraldehyde (GA) was used as a cross-linking agent in the hardening step of the coacervation procedure. Coacervation was induced by the addition of sodium sulfate. Hardening of the shell was done with GA. Increasing concentrations of GA improved the oil retention of the gelatin microcapsule.[69] Volatile citronella oil (CO) was encapsulated via simple coacervation using gelatin as a shell wall. Sodium sulfate was added to an emulsion of CO and gelatin in purified water to induce the coacervation. Afterward, formaldehyde was added at 5 °C to cross-link the gelatin shell wall.[70] The remaining concentration of formaldehyde in the microcapsules after washing was still quite high at 0.15% (weight/weight capsule).

When considering complex coacervation, a number of successful encapsulations of volatile compounds with the classic gelatin−gum arabic system are reported. Gum arabic, a branched polysaccharide of galactose, rhamnose, arabinose and glucuronic acid, is perfectly suited for the encapsulation of lipid-based materials as it fulfils the roles of both a surface-active agent and the drying matrix.[71] Leclercq et al. (2009) reported the encapsulation of limonene and menthol powder via complex coacervation. The optimal temperature profile for the coacervation was determined starting at 45 °C (to maintain gelatin in solution). At the end of the emulsification, a decrease toward 41 °C for 10 min was deemed optimal. GA was used as a cross-linker at pH 9. The influence of temperature during cross-linking on the resulting capsule was studied. Capsules were significantly more robust when cross-linked at 25 °C compared to 8 or 15 °C. Capsules consisted of 80% core material and 20% wall material.[45] The gelatin−gum arabic system was also used to encapsulate patchouli oil, using the same GA cross-linking. Release studies of these microcapsules were performed on fabric, as the microcapsules were grafted on textile. Initially, a burst-like release rate was observed, which occurred due to a large amount of oil being on the surface of the microcapsule. After 5 days, the surface-oil was removed and the release rate was more constant, keeping a constant rate up to 30 days.[72]

Apart from gelatin, chitosan is also commonly used in complex coacervation systems due to its numerous chargeable amine groups. Butstraen et al. (2012) studied the performance of chitosan−gum arabic microcapsules with a triglyceride mixture as inner core. During the cross-link phase, the authors decided to steer away from any aldehyde-type cross-linker commonly used in combination with chitosan, mainly because of the restrictions that come with these types of toxic cross-linking agents. Sodium triphosphate (STP), a polyanion that can interact with positively charged amino groups, is a safer alternative that was studied for use as an ionic cross-linker with a gelatin−gum arabic coacervate. From spectral analysis, it was concluded that the cross-linking was effective through ionic interactions among negatively charged $P-O^-$ of STP and $-NH_3^+$ of positively charged chitosan (Figure 7).[73]

In this light, Sharkawy et al. (2017) used tannic acid during the cross-linking phase of a chitosan−gum arabic coacervation procedure with vanilllin or limonene as a volatile oily core. Tannic acid, which has the ability to bind to polymers through hydrogen bonding and hydrophobic interactions, was used

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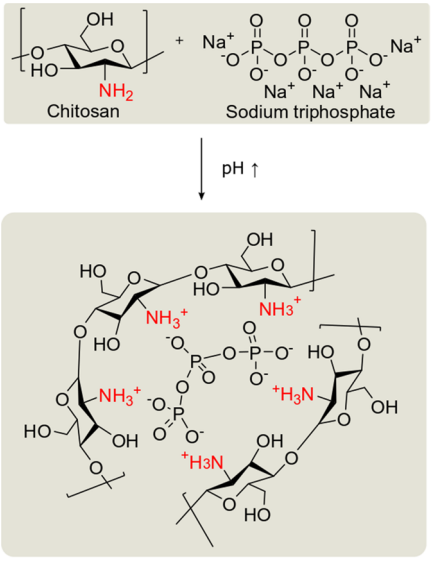

Figure 7. Sodium triphosphate used as an ionic cross-linking agent for cross-linking a chitosan network. When pH is increased, positively charged amino groups interact with sodium triphosphate.

during the hardening phase as an eco-friendly nontoxic cross-linking alternative. The produced capsules containing vanilllin or limonene were first washed and the suspensions were placed in sealed bottles containing 30 mL of *n*-hexane at 37 °C. Samples were taken from this bottle at specified times to analyze via gas chromatography to determine a release profile. Formulations containing vanillin had a higher %ee compared to limonene, attributed to the fact that vanillin was always used in combination with the viscous carrier corn oil, which might have decreased its diffusivity through the shell wall compared to limonene. Moreover, the type of surfactant used in the formulation had a significant effect on the resulting release profiles of the capsules. Sharkaway et al. used two types of surfactants: polyglycerol polyricinoleate (PGPR) and sorbitane trioleate (Span 85). Via optical microscopy it was observed that the morphology of the microcapsule can be altered by varying the surfactant, as the ones prepared with Span 85 had a mononuclear morphology while the formulations prepared with PGPR presented a polynuclear morphology. A polynuclear or multinuclear microcapsule consists of multiple cores surrounded by one (often somewhat bigger) shell. The release rate of the microcapsules produced was heavily influenced by the type of morphology obtained. It was found that a polynuclear morphology had a reduced release rate compared to mononuclear capsules. Other authors have also mentioned the superior release rate of polynuclear capsules compared to mononuclear ones.[74] Sharkaway et al. also successfully put their microcapsules to the test by thermofixating them on cotton fabrics.[46]

Although gum arabic is commonly used as a polyelectrolyte in complex coacervation, a combination of gelatin and chitosan is also reported for the encapsulation of volatile compounds. ZLO was encapsulated via a chitosan−gelatin complex. During the cross-linking phase, genipin was used as a natural cross-linker to stabilize the chitosan-gelatin shell. Genipin is a naturally occurring organic compound that reacts with primary amines and can form mono- up to tetramer cross-links at acidic or neutral pH. The amount of cross-linker and ratio of gelatin to chitosan all had a significant influence on the release rate. Release rate studies were performed in an aqueous environment with 0.3% Tween 80 as the surfactant. With a 1:1 ratio of chitosan−gelatin, a 3-fold genipin increase resulted in 15% less oil released after 100 h.[75] Lavender oil was encapsulated with a similar type of shell wall, using chitosan and collagen hydrolysate (a more hydrolyzed type of gelatin). The shell was cross-linked with GA and %ee increased with increasing concentrations of cross-linker. Release rate studies were performed in a 0.3% Tween 80 solution at room temperature. Initial burst release was observed for all capsules produced due to the oil absorbed on the surface.[76] Release after 8 h was more steady and slower, with the best performing capsules releasing 40% of their oil in 72 h in the aforementioned medium.

The most often reported polymer used for the encapsulation of volatile compounds via spray-drying is chitosan. Spray-dried chitosan microparticles are highly spherical and are characterized by a high surface area.[77] Encapsulation of orange oil was reported with a chitosan shell wall via spray-drying. The starting emulsion was prepared by adding chitosan to 1% aqueous acetic acid and adding various amounts of orange oil with surfactants to the continuous phase. After a thermal treatment, the emulsion was converted to microcapsules via a high-speed centrifugal spray-dryer. It was found that a fine emulsion and the use of compound surfactants was desirable to have the highest retention of orange oil. Interestingly, retention of orange oil in fabrics was also determined as the amount of orange oil remaining after the washing procedure to the amount of oil initially present. The release study of the microcapsules was tested by first stirring samples in a common laundry detergent medium with cotton fabric, rinsing with water and then storing. Oil retention of microcapsules on cotton fabric after 2 weeks was about 20%. It was found that smaller microcapsules are desirable in order to use the interspace between the fabric efficiently. Compared to nonencapsulated orange oil, encapsulated oil was present on the fabric for 8 days longer, 21 days in total.[77] Yang et al. encapsulated vanillin with chitosan using the emulsion/spray-drying technique. Release studies of vanillin on fabric were conducted after washing. While unencapsulated vanillin was removed after 1 washing cycle, 10% of the chitosan-encapsulated vanillin was still present after the 14th washing cycle. Still, %ee of these microcapsules often suffers from using the spray-dried technique, as is also obvious from Table 1.

The emulsion/spray-drying technique was also used for encapsulating an osmanthus flower fragrance with a blend of gum arabic and maltodextrin. Retention rate of microcapsules exceeded 90% after 100 days and was still 71% after half a year at room temperature.[78]

Prata et al. (2015) used an inventive method to encapsulate limonene with a chitosan−gelatin blend via a combination of complex coacervation and spray-drying. The cross-linking phase of the complex coacervation was performed via GA or STP after which the emulsion was fed into a laboratory scale spray-dryer. While microcapsules cross-linked with STP were easily spray-dried with minimal losses, microcapsules cross-linked with GA were joined together as a dough-mass after spray-drying, possibly due to heat activated aldehyde cross-linking.[79]

Feczkó et al. used the emulsification/solvent evaporation method to encapsulate vanillin with ethylcellulose. Vanillin was dissolved in dichloromethane, used as the volatile organic solvent, and added to a aqueous PVA solution. Microcapsules

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Table 1. Overview of Recent Literature Concerning the Microencapsulation of Volatile Oil with Natural Polymers for Fragrance-Oriented Applications

Method	Shell material	Encapsulated substance	%ee[a]	ref
Simple coacervation	Alignate complex	Eucalyptus oil	90−92	102
	Chitosan	Citronella oil	95−98	64
	Sodium alignate	Galangal oil	40	103
Complex coacervation	Gelatin/gum arabic	Patchouli oil	/	104
	Gelatin/gum arabic	Limonene	70−85	45
	Chitosan/collagen hydrolyzate	Lavender oil	44−60	76
	Chitosan/gum arabic	Triglycerides	57−67	73
Spray-drying	Gum arabic/maltodextrin	Flower fragrance	85	78
	Chitosan	Orange oil	43−56	77
	Chitosan	Vanillin	50	105
Complex coacervation + spray-drying	Gelatin/chitosan	Limonene	89	79
LbL assembly	Serum albumin/tannic acid	Fragrances	/	58
Emulsion/evaporation	Ethyl cellulose	Vanillin	15−40	53

[a]%ee is defined as the encapsulation efficiency, calculated as the percentage of oil encapsulated relative to the total oil used prior to encapsulation. When many encapsulation conditions are mentioned, range of obtained results is displayed.

were formed after 2 h of stirring and evaporation of dichloromethane. An %ee between 15 and 40% was achieved, depending on the initial vanillin concentration and 80% of encapsulated vanillin was released after 20 days at 50 °C. Still, solvent evaporation techniques are hampered by the low %ee values that can be obtained, even more so when considering the encapsulation of volatile oils.[80]

Some efforts are made to use the LbL technique for the encapsulation of fragrances. Sadovoy et al. successfully encapsulated fragrances via a bovine serum albumine (BSA)−tannic acid coating. A variety of fragrances were emulsified with sunflower oil as a base oil (1:1) added in a 90% (v/v) BSA water solution. Coating of the oil droplet was done using a filtration cell to perform quick deposition/washing cycles. Alternating layers of BSA and tannic acid were deposited on the oil droplet to obtain a stabilized LbL coating. Controlled release studies of these microcapsules at 40 °C in aqueous environment showed a correlation between water solubility of the encapsulated aroma compounds and their release rate. The release rate of the subjected aroma compounds was stable over a time span of 3 days at 40 °C, which show the viability of the LbL technique for creating a MF-alternative microcapsule.[58]

Nanoencapsulation. A modified complex coacervation technique is used for the nanoencapsulation of *Osmanthus* fragrance-loaded chitosan, produced for the application on textile applications. To create nanocapsules via coacervation, chitosan solution was mixed at 10k rpm for 10 min to reduce the size of the emulsion. STP was used to cross-link the chitosan shell after emulsification. For release tests, washing cycles were simulated with microcapsule impregnated textiles. It appeared that nanocapsules with *Osmanthus* fragrance had an excellent washing resistance. The base note was retained for over 60% after 20 washing cycles, showing the excellent retention capabilities of these cross-linked chitosan nanocapsules.[20] An adaptation of this procedure was used by Xiao et al. for the nanoencapsulation of tuberose fragrance. It was obvious from the release studies conducted that chitosan nanoparticles exhibit interesting properties for functioning as controlled-release carrier of fragrance.[81]

Solvent displacement (ethanol by water) was used for the encapsulation of six different types of fragrances. A blend of ethylcellulose (EC), hydroxypropyl methylcellulose (HPMC) and poly(vinyl alcohol) (PVA) was used as encapsulating material. The polymer particles were prepared at 70 °C in 75% (v/v) aqueous ethanol. Afterward, the blend was dialyzed against distilled water and different polymer nanoparticle suspensions were made (ranging from 2k ppm to 28k ppm). Particles were loaded by dissolving the polymer blend in aqueous ethanol and mixing fragrance compounds (e.g., camphor) in a 1:1 or 1:2 ratio of polymer to fragrance. Then the mixture was placed in a dialysis bag and dialyzed against water. Solvent displacement for encapsulation in this system works due to the insolubility of EC in water. Upon dialysis, displacement of ethanol with water induces slow precipitation of EC, with trapping of PVA and HMPC chains acting as stabilizers for the shell wall. Upon drying, PVA and HMPC are responsible for the excellent dispersibility of these particles. Although significant differences among tested volatile compounds were present, best performing compounds were still 80% encapsulated after 50 days.[82]

The sonochemical method, in which a probe is placed in the interlayer of two phases (O/W), was used by Tzhayik et al. (2012) for the nanoencapsulation of a pure fragrant oil with a BSA shell wall. Release profiles of these containers showed an initial fast release of the fragrance (amyl acetate), associated with surface oil, and a subsequent slower release rate for the encapsulated amyl acetate. BSA nanospheres showed exceptional stability at room temperature for more than six months as they were found stable in emulsions for more than 6 months, but the release rate in an open beaker with no solvent at room temperature was high at a 100% release in 40 h.[83]

Sustainability. From this overview it is clear that successful micro- and nanoencapsulation of volatile oils with biopolymers is an endeavor of many research groups, driven by an effort toward increased sustainability. However, as mentioned in the Introduction, the use of biopolymers in itself does not guarantee a more sustainable approach compared to, e.g. MF capsules. Moreover, critical thinking regarding the influence of a significant amount of cross-links on the biodegradability of resulting polymer shell and the mentioning of potential increased toxicity due to the addition of these linkers is lacking. This casts reasonable doubt on the increased sustainability of these biopolymer-based capsules, one of the primary requisites for them to be able to enter this market. It is clear that research in this field will have to be more in depth, specifically concerning biodegradation studies on the (cross-linked) end-product, which is needed in order to assess the sustainability of these microcapsules versus their commercial counterparts.

SYNTHETIC SHELL WALLS AND VOLATILE COMPOUNDS

Micro and Nanoencapsulation. Synthetic shell walls have been studied by a few groups, either focusing on biobased

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building blocks (e.g., lactic acid/lactides) or on polyesters in general, of which a certain degree of degradability via hydrolysis is sometimes asserted. Martins et al. (2009) studied the encapsulation of fragrance oils with polylactides (PLA)s extensively. Thyme oil was encapsulated with polylactide via a novel coacervation technique in which a PLA solution in DMF was added dropwise to an O/W thyme oil emulsion. In this way, precipitation of PLA was done around the thyme oil droplet. In the hardening phase, octamethylcyclotetrasiloxane was used to strengthen the PLA microcapsules. The overall encapsulation of thyme oil in this process was 30%.[84] In a subsequent report, also thymol and *p*-cymene were encapsulated via this coacervation process, giving a 55% and 83% encapsulation efficiency, respectively. Differences in %ee values between thymol and *p*-cymene can be attributed to differences in polarity influencing the encapsulation process.[85] This coacervation process was successfully tested on polylactide-*co*-glycolide (PLGA) for the encapsulation of thyme oil for antimicrobial applications, showing the versatility of this particular method.[86]

Apart from polylactide and copolymers, the use of polycaprolactone (PCL) as a fragrance carrier was reported via a solvent displacement method which resulted in both micro- and nanocarriers. Cortial et al. (2015) studied the encapsulation of a mix of 8 common fragrances with PCL. A standard procedure for the production of these nanocapsules consisted of the addition of a solution of PCL and fragrance in aceton to a continuous phase with polysorbate as a stabilizer. Nanoparticles were instantly formed when the acetone was displaced by the aqueous phase. The mean diameter of these capsules was lower than 200 nm, and the %ee values were reported between 50 and 80%, depending on the fragrance compound encapsulated. The most optimized production conditions resulted in nanoparticle suspensions which were stable for 90 days at 25 °C with no release of fragrance observed.[87] A similar solvent displacement approach was used by Mossotti et al. for the encapsulation of menthol in PCL nanocapsules. Size of PCL nanoparticles varied between 200 and 1200 nm. The fabricated PCL nano- and microcapsules were applied on cotton fabric and successfully tested on human skin for their refreshing effect.[88]

Another approach for the production of micro- and nanocarriers is via *in situ* and interfacial polymerization (Table 2). Azizi et al. (2014) produced microcapsules containing the model fragrance 2-etoxynaphthalene (neroline) from renewable materials via interfacial polymerization based on isosorbide and methylene bis(phenyl isocyanate). The interfacial polymerization was done in an O/W emulsion at 60 °C for 6 h. The resulting microcaps were used in a textile finishing experiment to check their release rate after the washing cycle. It was shown that 40% of encapsulated neroline was lost after the fifth washing cycle, while even after the twentieth cycle, 30% of nerolin was still present on the fabric, which clearly indicates the potential of these types of capsules.[19] Hedaoo et al. (2014) also used renewable monomers for the production of biobased phenol−formaldehyde microcapsules via biobased cardanol (a phenolic lipid obtained from cashew nuts) and formaldehyde in an *in situ* polymerization. Still, despite the renewable building blocks of these types of capsules, isocyanate and formaldehyde chemistry is still to be avoided due to social-environmental issues.[89] These problems can be combatted by the use of scavengers, a solution that was discussed previously for formaldehyde-based capsules, but is also shown to be possible for polyurea microcapsules. Jacquemond et al. (2009) used this strategy to decrease the amount of free isocyanates in polyurea-type via the use of ammonia, successfully encapsulating a model fragrance.[90] Still, toxic reagents or functional groups like formaldehyde or isocyanates are best to be avoided if possible. Liao et al. (2016) used interfacial thiol−ene polymerization in an effort to encapsulate fragrance oil as a replacement for MF microcapsules. A multiacrylate monomer was dissolved in the oil phased and emulsified, after which the addition of a multithiol with a base as catalyst was added to initiate the interfacial thiol−ene click reaction (Figure 8). The %ee achieved via this reaction was 91% or more depending on the acrylate monomer.[60] The resulting cross-linked thioether shell wall proved very stable as the fragrance release at 45 °C after 1 month was minimal, which shows great promise as a sustainable MF-type microcapsule replacement. Although not biobased, ester bonds are present in the acrylate monomer. A similar search toward formaldehyde-free biobased microcapsules was done by Soares-Latour et al. (2017) via interfacial polymerization of two biobased monomers: succinyl chloride and 1,4-diaminobutane. The interfacial polymerization was done by mixing jojoba oil with succinyl chloride and emulsifying this mixture with an aqueous continuous phase. The stable emulsion was then polymerized via the addition of 1,4-diaminobutane, resulting in a biobased polyamide-4,4 shell wall. The %ee or release studies of the microcapsules were not reported but preliminary experiments of polyamide microcapsule impregnation on textiles was deemed successful.[91]

Table 2. Reports of Interfacial Polymerization Technique Used for the Encapsulation of Volatile Compounds with Shells Containing Ester Bonds in Recent Literature

Shell material	Encapsulated substance	Size (μm)	%ee[a]	Reference
Thiol−ene multi cross-linked (dithiol + multiacrylate)	Model fragrance oil	10	91−96%	60
Polycodensation (methylene bis(phenyl isocyanate) + isosorbide)	2-Ethoxy naphthalene	27	30%	19
Polycondensation (acid chloride + diamine)	Jojoba oil	3	/	91

[a]%ee is defined as the encapsulation efficiency, calculated as the percentage of oil encapsulated relative to the total oil used prior to encapsulation. When many encapsulation conditions are mentioned, range of obtained results is displayed.

Sustainability. Research involving the synthetic shell for capsules mostly deals with the use of polyesters. This is not surprising as polyesters (together with polycarbonates) show high potential for use as biodegradable plastics, owing to their susceptibilities to lipolytic enzymes and microbial degradation, and to hydrolysis in general.[92] However, this potential for biodegradability is only presumed, as no efforts were noted to check for biodegradability of the end-product. To assess the possible improved sustainability of these capsules compared to commercial types completely, impact of the methods used in these examples and the impact of their shortcomings (use of DMF, acid chlorides, acrylates etc.) have to be determined. Moreover, it is clear that interfacial and *in situ* polymerizations techniques are among the most successful in producing high-performant microcapsules. Unsurprisingly, this technique is also transferred to more (potentially) biodegradable shells,

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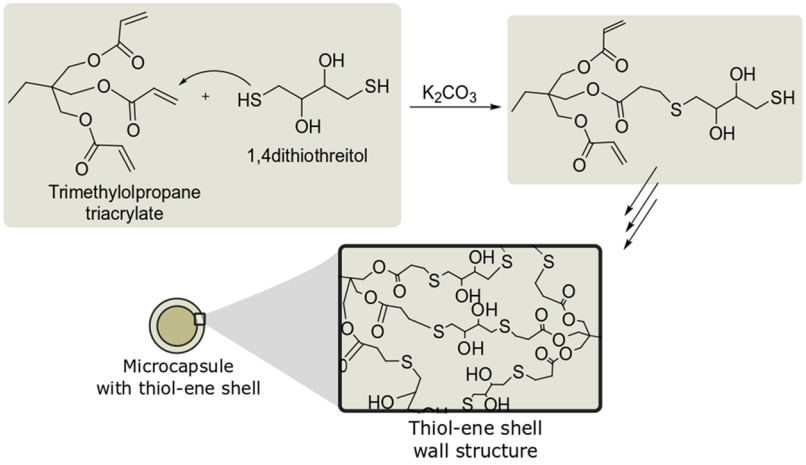

Figure 8. Interfacial thiol−ene reaction of a triacrylate and dithiol in a thiol−ene cross-link reaction, as described by Liao et al. (2016). Thiol−ene reaction is here catalyzed by the addition of potassium carbonate.

resulting in quite promising microcapsules.[60,91] But the requirements for the reagents used in this technique remain the same (most notably high reactivity), which unfortunately also increases potential toxicity in these microcapsules.

INSIGHTS

As mentioned above, aminoplast-type shell walls such as the MF-type provide excellent shell material for specific high demanding cosmetic and household products such as laundry detergents. Although MF capsules potentially present benefits in terms of resource use and their processing often manages to eliminate formaldehyde exposure, the search for environmentally benign microcapsules, specifically of biobased origins and with a clear biodegradable profile, is ongoing. It is obvious that searching for these types of capsules is a puzzling task with no clear solution presented yet. Still, as is clear from this overview, efforts toward a more sustainable generation of microcapsules are made on many fronts. In terms of sustainability, using naturally available biopolymers as the building blocks for microcapsules is an obvious choice. Most efforts to encapsulate fragrances with natural polymers were done via some variation of a simple or complex coacervation technique which has seen increased interest from all microencapsulation fields due to its simplicity and high %ee.[66] The hardening or cross-linking phase of the coacervation step also gives a certain flexibility on the cross-link density of the final shell wall. Still, it remains questionable if the natural polymer-based shell walls will ever be up to the high standards of commercial laundry-type microcapsules, of which prolonged stability in detergent-type solutions and subsequent controlled release over an extended period are crucial requirements.

When microcapsules are produced specifically for use in laundry-type microcapsules, it is probably most helpful to determine their release rate in application-specific conditions. For laundry-type applications, this constitutes the rather unforgiving release test in media with high concentrations of detergent at increased temperatures for prolonged amounts of time. The results of these experiments give great insights in the viability of alternative shell wall material. The limited results[75−77] in this regard make it obvious that significant steps forward are still necessary for natural polymer-based capsules if they ever are to be considered viable high-performant microcapsule alternatives. One of the shortcomings of these natural polymer shells is their high permeability for smaller molecules because of their porous hydrogel-type microstructure.[93] Although cross-linking can alter the permeability of the shell, common cross-linkers (e.g., GA, STP) only target specific functional groups in the natural polymer structure. This puts questions on the potential cross-link density of biopolymer-based capsules which might limit its performance in high-demanding applications. It is reasonable to assume that advances in this area will involve modification of natural polymers with functional groups to alter the cross-link density and blending of different (modified) natural polymers. Although from reports on synthetic methods it is clear that thiol−ene reactions are interesting to stabilize or even form rigid capsule shells, reports of thiol−ene reactions used to harden (modified) natural polymer shells are far less common. In this regard, natural proteins containing a significant amount of free thiol groups are an obvious candidate in combination with acrylate-type additives. Wheat gluten, which is already successfully used as shell material in food applications,[94,95] has shown improved mechanical properties in other applications when involved in thiol−ene cross-link reactions via the use of a modified acrylate-based cross-linker.[96]

The use of synthetic polymers provides more flexibility in terms of the desired shell wall material properties. However, the use of any synthetic polymer also puts doubt on the sustainability aspect of the produced capsules, as the origin of the starting material, its synthetic route and the biodegradability of the resulting capsules (i.e., an LCA) should be considered. Extensive biodegradability tests on the synthetic capsules produced are needed to assess their proneness to biodegradation in common environments (aqueous, marine, sludge, ...). Biodegradable aliphatic polyesters (e.g., polylactide) were used successfully to encapsulate some volatile compounds. Still, although encapsulation was successful, mild release studies in water showed a significant release of encapsulated material after 1 and 5 days of measuring.[13] It is obvious from these kinds of results that PLA-based shell walls are not ready to be subjected to detergent-type media. Variations in the used technique and the introduction of reactive functional groups in the PLA backbone to create a more thorough hardening/cross-linking phase could create a more resistant shell wall. Although it is possible to put reactive cross-linkable groups on aliphatic polyesters,[97] examples of its

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use in microencapsulation applications are rare. A vinyl-functionalized lactide monomer was used for ring opening polymerization with L-lactide to obtain functionalized PLLA, which was used for cross-linking a PLLA nanoemulsion shell.[98] The efficient thiol−ene cross-linking reaction was initiated via UV and a radical initiator. Many other strategies to incorporate unsaturated moieties in the PLA backbone are possible. One example is the use of a renewable unsaturated C6-dicarboxylic acid molecule which was successfully used as a monomer in the polycondensation with lactic acid, resulting in an interesting functionalizable branched PLA network.[99] It is clear that functionalization of known biodegradable polymers with reactive (e.g., cross-linkable) groups can benefit high demanding microcapsule applications. Apart from giving the shell more stability and better mechanical properties, incorporation of functionalizable groups in a biodegradable polymers can also offer the incorporation of a variety of triggers in the shell wall, as the functionalization of monomers in the biodegradable chain can include ones that are chemically (or by other means) triggered ("programmed") to decompose in certain environments. Ultimately, this could lead to biodegradable cross-linked polymer shells with specific trigger groups present resulting in completely tailored release profiles of sustainable and functional microcapsules.

Interfacial and *in situ* polymerization for microcapsule production can arguably provide one of the most closely packed microcapsule shells, ideal for high demanding applications. Where techniques such as solvent displacement or complex coacervation are using (mostly) linear polymers to fit around an oily core, *in situ* and interfacial polymerization techniques are more tailor-made approaches in which the shell is constructed around the inner core. The tightly packed 3-dimensional cross-linked MF-type shell wall is the prime example of the potential of *in situ* polymerization. Hence, it is only reasonable to try and adapt this technique toward the production of more sustainable, nontoxic and biodegradable shell walls. However, interfacial and *in situ* polymerization encapsulation requires a certain type of fast and high-yielding reaction type which limits the possibilities. Approaches such as the one described by Pascu et al. (2008) are interesting, as they use epoxy-type resins in combination with poly acid compounds to produce microcapsules with the preferred hydrolyzable ester bonds via interfacial polymerization.[100] But these types of mechanisms (such as the epoxy-acid reaction described) are still borderline too slow to encapsulate volatile compounds efficiently. When we analyze successful *in situ* encapsulation procedures, reaction mechanisms are mostly radical or thiol/aldehyde-based. Liao et al. (2016) enforces this statement with the successful production of microcapsules carrying fragrance via interfacial thiol−ene reaction.[60] While omitting formaldehyde as a cross-linking unit, the thiol−ene click reaction with a dithiol and triacrylate shows quite a similar 3-dimensional network. While the resulting microcapsules had promising properties, used starting reagents were mostly fossil-based and the biodegradability of the thio−ether linkages is unknown. Sustainable acrylate-containing monomers such as sugar-derived dilactone diacrylate compounds perhaps offer solutions to improve the sustainability of these types of microcapsule.[101]

Although the discussion on the viability of various shell wall properties and polymerization mechanisms for these laundry-type microcapsules is present in literature, any mention of biodegradation is solely based on knowledge of bulk polymer materials. The field of microcapsule biodegradation is truly in its infancy. It is clear that potentially sustainable microcapsule alternatives should ultimately be tested for their biodegradability and assessed via LCA. The biggest challenge in this area is to find the balance between cross-link density and shell wall biodegradability, two parameters which are inversely proportional.

CONCLUDING REMARKS

Commercially used fragrance-containing microcapsules are rigid, stable structures and display excellent release properties for all kinds of volatile compounds, which make them the mainstay encapsulation material for the fabric care market. This paper has reviewed the possible alternatives for these petroleum-based microcapsules with a focus on environmental sustainability in terms of biobased origins and/or degradability. Although many fragrances are encapsulated via natural polymers, the resulting shell walls are usually too permeable to be considered in laundry-type detergents. Increased cross-link density, via modification of the technique, the type of cross-linking or functionalization of the natural polymer could still improve natural polymer shells to bring them up to the criteria of current cross-link (petroleum-based) standards. Synthetic shell walls have more flexibility, with *in situ* and interfacial polymerization techniques enabling almost tailored-like capsules which greatly improves the overall quality of the shell wall. Still, efforts toward biobased and biodegradable monomers for these types of polymerization techniques have to result in more competitive sustainable microcapsules. Finally, when functional and biodegradable capsules are presented or discovered, a full LCA should eventually be undertaken, to allow a comparison in full fairness to the current MF-type capsules.

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Notes

The authors declare no competing financial interest.

Biographies

Kevin Bruyninckx has a M.Sc. in Chemistry (KU Leuven, 2011). He obtained his Ph.D. in Chemistry in 2016 being part of a multidisciplinary team working on improving gluten-based Bioplastic. His skillset ranges from organic and polymer synthesis to analysis of

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biomacromolecules and the evaluation of material properties. In our team, he has been involved in the synthesis of PLA-based polymers for the production of tailored biodegradable packaging and the search toward new sustainable polymer shells for the microencapsulation of volatile compounds.

Michiel Dusselier obtained his Ph.D. degree in Bioscience Engineering (Catalytic Technology, 2013) at KU Leuven under the guidance of Prof. Bert Sels and Prof. Pierre Jacobs, inventing new catalytic routes for bioplastics synthesis. In 2014−15, he did postdoctoral work with Prof. Mark Davis at Caltech, studying the synthesis of zeolites and methanol-to-olefins. He is now a tenure-track research professor at the Center for Sustainable Catalysis and Engineering of KU Leuven focusing on zeolite synthesis methods, heterogeneous catalysis—generally in the context of sustainable chemistry—and functional bio(degradable) plastics. He has (co)authored ca. 50 peer-reviewed papers and 6 patents, of which one transferred to industry.

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■ ABBREVIATIONS

%ee, encapsulation efficiency; BSA, bovine serum albumine; CO, citronella oil; DMF, dimethylformamide; EC, ethyl-cellulose; EO, essential oil; GA, glutaraldehyde; HPMC, hydroxypropyl methyl-cellulose; LbL, layer-by-layer; MF, melamine−formaldehyde; OCMTS, octamethyl sodium triphosphate; PGPR, polyglycerol polyricinoleate; PLLA, poly L-lactide; PVA, poly(vinyl alcohol); STP, sodium triphosphate; ZLO, *Zanthoxylum limonella* oil

■ REFERENCES

(1) Lidert, Z. *Microencapsulation: An Overview of the Technology Landscape*; William Andrew Inc., 2005; DOI: 10.1016/B978-081551504-3.50013-4.

(2) Kaur, R.; Kukkar, D.; Bhardwaj, S. K.; Kim, K. H.; Deep, A. Potential Use of Polymers and Their Complexes as Media for Storage and Delivery of Fragrances. *J. Controlled Release* **2018**, *285* (July), 81−95.

(3) He, L.; Hu, J.; Deng, W. Preparation and Application of Flavor and Fragrance Capsules. *Polym. Chem.* **2018**, *9* (40), 4926−4946.

(4) Majeed, H.; Bian, Y.-Y.; Ali, B.; Jamil, A.; Majeed, U.; Khan, Q. F.; Iqbal, K. J.; Shoemaker, C. F.; Fang, Z. Essential Oil Encapsulations: Uses, Procedures, and Trends. *RSC Adv.* **2015**, *5* (72), 58449−58463.

(5) Vishwakarma, G. S.; Gautam, N.; Babu, J. N.; Mittal, S.; Jaitak, V. Polymeric Encapsulates of Essential Oils and Their Constituents: A Review of Preparation Techniques, Characterization, and Sustainable Release Mechanisms. *Polym. Rev.* **2016**, *56* (4), 668−701.

(6) McCoy, M. Delivering Value in the Laundry Room. *Chem. Eng. News* **2018**, *96* (5), 18−21.

(7) Martins, I. M.; Barreiro, M. F.; Coelho, M.; Rodrigues, A. E. Microencapsulation of Essential Oils with Biodegradable Polymeric Carriers for Cosmetic Applications. *Chem. Eng. J.* **2014**, *245*, 191−200.

(8) Salvador Cesa, F.; Turra, A.; Baruque-Ramos, J. Synthetic Fibers as Microplastics in the Marine Environment: A Review from Textile Perspective with a Focus on Domestic Washings. *Sci. Total Environ.* **2017**, *598*, 1116−1129.

(9) Merline, D. J.; Vukusic, S.; Abdala, A. A. Melamine Formaldehyde: Curing Studies and Reaction Mechanism. *Polym. J.* **2013**, *45* (4), 413−419.

(10) Pretzl, M.; Neubauer, M.; Tekaat, M.; Kunert, C.; Kuttner, C.; Leon, G. G.; Berthier, D.; Erni, P.; Ouali, L.; Fery, A.; et al. Formation and Mechanical Characterization of Aminoplast Core/ Shell Microcapsules. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2940−2948.

(11) León, G.; Paret, N.; Fankhauser, P.; Grenno, D.; Erni, P.; Ouali, L.; Berthier, D. L. Formaldehyde-Free Melamine Microcapsules as Core/Shell Delivery Systems for Encapsulation of Volatile Active Ingredients. *RSC Adv.* **2017**, *7* (31), 18962−18975.

(12) Tavera, E. M.; Kadali, S. B.; Bagaria, H. G.; Liu, A. W.; Wong, M. S. Experimental and Modeling Analysis of Diffusive Release from Single-Shell Microcapsules. *AIChE J.* **2009**, *55* (11), 2950−2965.

(13) Martins, I. M.; Rodrigues, S. N.; Barreiro, M. F.; Rodrigues, A. E. Release of Thyme Oil from Polylactide Microcapsules. *Ind. Eng. Chem. Res.* **2011**, *50* (24), 13752−13761.

(14) Fomina, N.; McFearin, C.; Sermsakdi, M.; Edigin, O.; Almutairi, A. UV and Near-IR Triggered Release from Polymeric Nanoparticles. *J. Am. Chem. Soc.* **2010**, *132* (28), 9540−9542.

(15) Paret, N.; Trachsel, A.; Berthier, D. L.; Herrmann, A. Controlled Release of Encapsulated Bioactive Volatiles by Rupture of the Capsule Wall through the Light-Induced Generation of a Gas. *Angew. Chem., Int. Ed.* **2015**, *54* (7), 2275−2279.

(16) Esser-Kahn, A. P.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Triggered Release from Polymer Capsules. *Macromolecules* **2011**, *44* (14), 5539−5553.

(17) Microplastics Flushed by Floods. *C&EN Glob. Enterp.* **2018**, *96* (12), 5−5,.

(18) Browne, M. A.; Crump, P.; Niven, S. J.; Teuten, E.; Tonkin, A.; Galloway, T.; Thompson, R. Accumulation of Microplastic on Shorelines Woldwide: Sources and Sinks. *Environ. Sci. Technol.* **2011**, *45* (21), 9175−9179.

(19) Azizi, N.; Chevalier, Y.; Majdoub, M. Isosorbide-Based Microcapsules for Cosmeto-Textiles. *Ind. Crops Prod.* **2014**, *52*, 150−157.

(20) Hu, J.; Xiao, Z.; Ma, S.; Zhou, R.; Wang, M.; Li, Z. Properties of Osmanthus Fragrance-Loaded Chitosan-Sodium Tripolyphosphate Nanoparticles Delivered through Cotton Fabrics. *J. Appl. Polym. Sci.* **2012**, *123* (6), 3748−3754.

(21) Sedlak, D. Three Lessons for the Microplastics Voyage. *Environ. Sci. Technol.* **2017**, *51* (14), 7747−7748.

(22) Nelms, S. E.; Galloway, T. S.; Godley, B. J.; Jarvis, D. S.; Lindeque, P. K. Investigating Microplastic Trophic Transfer in Marine Top Predators. *Environ. Pollut.* **2018**, *238*, 999−1007.

(23) Qin, Y.; Lv, X.; Li, J.; Qi, G.; Diao, Q.; Liu, G.; Xue, M.; Wang, J.; Tong, J.; Zhang, L.; et al. Assessment of Melamine Contamination in Crop, Soil and Water in China and Risks of Melamine Accumulation in Animal Tissues and Products. *Environ. Int.* **2010**, *36* (5), 446−452.

(24) Jemec, A.; Horvat, P.; Kunej, U.; Bele, M.; Kržan, A. Uptake and Effects of Microplastic Textile Fibers on Freshwater Crustacean Daphnia Magna. *Environ. Pollut.* **2016**, *219*, 201−209.

(25) Bône, S.; Vautrin, C.; Barbesant, V.; Truchon, S.; Harrison, I.; Geffroy, C. Microencapsulated Fragrances in Melamine Formaldehyde Resins. *Chimia* **2011**, *65* (3), 177−181.

DOI: 10.1021/acssuschemeng.9b00677
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

(26) Silva, M.; Martins, I.; Barreiro, F.; Dias, M.; Rodrigues, A. E. Preparation and Characterization of Poly(Urethane−urea) Microcapsules Containing Limonene. Kinetic Analysis. *Int. J. Polym. Anal. Charact.* **2017**, *22* (8), 709−724.
(27) Zhang, Y.; Song, J.; Chen, H. Preparation of Polyacrylate/Paraffin Microcapsules and Its Application in Prolonged Release of Fragrance. *J. Appl. Polym. Sci.* **2016**, *133* (42), 1−7.
(28) Emadian, S. M.; Onay, T. T.; Demirel, B. Biodegradation of Bioplastics in Natural Environments. *Waste Manage.* **2017**, *59*, 526−536.
(29) Nova-Institute GmbH. *Biodegradable, bio-based polymers in various environments*. http://bio-based.eu/graphics/#biodegradablebiobasedpolymers (accessed February 14, 2019).
(30) Hermann, B. G.; Debeer, L.; De Wilde, B.; Blok, K.; Patel, M. K. To Compost or Not to Compost: Carbon and Energy Footprints of Biodegradable Materials' Waste Treatment. *Polym. Degrad. Stab.* **2011**, *96* (6), 1159−1171.
(31) Yates, M. R.; Barlow, C. Y. Life Cycle Assessments of Biodegradable, Commercial Biopolymers - A Critical Review. *Resour. Conserv. Recycl.* **2013**, *78*, 54−66.
(32) Denutte, G.; Bianchetti, O.; Boutique, J.-P.; Hugo Robert, G. Patent US9416339B2, 2013.
(33) Hitchcock, J. P.; Elaine Alice Marie, B.; Simon Richard, B. Patent US9944886B2, 2015.
(34) Laubender, M.; Benlahmar, O.; Klein, R.; Stracke, J.; Leibach, P.; Ness, J. Patent US9422505B2, 2013.
(35) Dihora, J. O.; Nijakowski, T. R.; Cetti, J. R. Patent US9732303B2, 2016.
(36) Burakowska-Meise, E.; Denuell, W.; Soltys, T.; Aussant, E. J. L. C.; Fade, A.; Harrison, Li. Patent US10201795B2, 2015.
(37) Smets, J.; Nair, R. J.; Pintens, A.; Yasuhara, T.; Iwasaki, T. Patent US7901772B2, 2011.
(38) Rodrigues, S. N.; Martins, I. M.; Fernandes, I. P.; Gomes, P. B.; Mata, V. G.; Barreiro, M. F.; Rodrigues, A. E. Scentfashion®: Microencapsulated Perfumes for Textile Application. *Chem. Eng. J.* **2009**, *149* (1), 463−472.
(39) Carvalho, I. T.; Estevinho, B. N.; Santos, L. Application of Microencapsulated Essential Oils in Cosmetic and Personal Healthcare Products - A Review. *Int. J. Cosmet. Sci.* **2016**, *38* (2), 109−119.
(40) Nelson, G. Application of Microencapsulation in Textiles. *Int. J. Pharm.* **2002**, *242* (1−2), 55−62.
(41) De Kruif, C. G.; Weinbreck, F.; De Vries, R. Complex Coacervation of Proteins and Anionic Polysaccharides. *Curr. Opin. Colloid Interface Sci.* **2004**, *9* (5), 340−349.
(42) Sagiri, S. S.; Anis, A.; Pal, K. Review on Encapsulation of Vegetable Oils: Strategies, Preparation Methods, and Applications. *Polym.-Plast. Technol. Eng.* **2016**, *55* (3), 291−311.
(43) Turgeon, S. L.; Schmitt, C.; Sanchez, C. Protein−polysaccharide Complexes and Coacervates. *Curr. Opin. Colloid Interface Sci.* **2007**, *12* (4−5), 166−178.
(44) Rojas-Moreno, S.; Osorio-Revilla, G.; Gallardo-Velázquez, T.; Cárdenas-Bailón, F.; Meza-Márquez, G. Effect of the Cross-Linking Agent and Drying Method on Encapsulation Efficiency of Orange Essential Oil by Complex Coacervation Using Whey Protein Isolate with Different Polysaccharides. *J. Microencapsulation* **2018**, *35*, 165−180.
(45) Leclercq, S.; Harlander, K. R.; Reineccius, G. A. Formation and Characterization of Microcapsules by Complex Coacervation with Liquid or Solid Aroma Cores. *Flavour Fragrance J.* **2009**, *24* (1), 17−24.
(46) Sharkawy, A.; Fernandes, I. P.; Barreiro, M. F.; Rodrigues, A. E.; Shoeib, T. Aroma-Loaded Microcapsules with Antibacterial Activity for Eco-Friendly Textile Application: Synthesis, Characterization, Release, and Green Grafting. *Ind. Eng. Chem. Res.* **2017**, *56* (19), 5516−5526.
(47) Gharsallaoui, A.; Roudaut, G.; Chambin, O.; Voilley, A.; Saurel, R. Applications of Spray-Drying in Microencapsulation of Food Ingredients: An Overview. *Food Res. Int.* **2007**, *40* (9), 1107−1121.
(48) Rodríguez, J.; Martín, M. J.; Ruiz, M. A.; Clares, B. Current Encapsulation Strategies for Bioactive Oils: From Alimentary to Pharmaceutical Perspectives. *Food Res. Int.* **2016**, *83*, 41−59.
(49) Soottitantawat, A.; Takayama, K.; Okamura, K.; Muranaka, D.; Yoshii, H.; Furuta, T.; Ohkawara, M.; Linko, P. Microencapsulation of L-Menthol by Spray Drying and Its Release Characteristics. *Innovative Food Sci. Emerging Technol.* **2005**, *6* (2), 163−170.
(50) Rojas-Moreno, S.; Cárdenas-Bailón, F.; Osorio-Revilla, G.; Gallardo-Velázquez, T.; Proal-Nájera, J. Effects of Complex Coacervation-Spray Drying and Conventional Spray Drying on the Quality of Microencapsulated Orange Essential Oil. *J. Food Meas. Charact.* **2018**, *12* (1), 650−660.
(51) Martins, I. M.; Barreiro, M. F.; Coelho, M.; Rodrigues, A. E. Microencapsulation of Essential Oils with Biodegradable Polymeric Carriers for Cosmetic Applications. *Chem. Eng. J.* **2014**, *245*, 191−200.
(52) Gouin, S. Microencapsulation. *Trends Food Sci. Technol.* **2004**, *15* (7−8), 330−347.
(53) Feczkó, T.; Kokol, V.; Voncina, B. Preparation and Characterization of Ethylcellulose-Based Microcapsules for Sustaining Release of a Model Fragrance. *Macromol. Res.* **2010**, *18* (7), 636−640.
(54) Wischke, C.; Schwendeman, S. P. Principles of Encapsulating Hydrophobic Drugs in PLA/PLGA Microparticles. *Int. J. Pharm.* **2008**, *364* (2), 298−327.
(55) Jain, R. A. The Manufacturing Techniques of Various Drug Loaded Biodegradable Poly(Lactide-Co-Glycolide) (PLGA) Devices. *Biomaterials* **2000**, *21* (23), 2475−2490.
(56) Sinha, V. R.; Bansal, K.; Kaushik, R.; Kumria, R.; Trehan, A. Poly-ϵ-Caprolactone Microspheres and Nanospheres: An Overview. *Int. J. Pharm.* **2004**, *278* (1), 1−23.
(57) Tong, W.; Song, X.; Gao, C. Layer-by-Layer Assembly of Microcapsules and Their Biomedical Applications. *Chem. Soc. Rev.* **2012**, *41* (18), 6103−6124.
(58) Sadovoy, A. V.; Lomova, M. V.; Antipina, M. N.; Braun, N. A.; Sukhorukov, G. B.; Kiryukhin, M. V. Layer-by-Layer Assembled Multilayer Shells for Encapsulation and Release of Fragrance. *ACS Appl. Mater. Interfaces* **2013**, *5* (18), 8948−8954.
(59) Wang, C.; Ye, S.; Sun, Q.; He, C.; Ye, W.; Liu, X.; Tong, Z. Microcapsules for Controlled Release Fabricated via Layer-by-Layer Self-Assembly of Polyelectrolytes. *J. Exp. Nanosci.* **2008**, *3* (2), 133−145.
(60) Liao, Z.; Xue, D.; Li, H.; Shi, L. Fragrance-Containing Microcapsules Based on Interfacial Thiol-Ene Polymerization. *J. Appl. Polym. Sci.* **2016**, *133* (36), 1−7.
(61) Yang, X.; Liu, Y.; Payne, G. F. Crosslinking Lessons From Biology: Enlisting Enzymes for Macromolecular Assembly. *J. Adhes.* **2009**, *85* (9), 576−589.
(62) Sinha, V. R.; Singla, A. K.; Wadhawan, S.; Kaushik, R.; Kumria, R.; Bansal, K.; Dhawan, S. Chitosan Microspheres as a Potential Carrier for Drugs. *Int. J. Pharm.* **2004**, *274*, 1−33.
(63) Luo, Y.; Wang, Q. Recent Advances of Chitosan and Its Derivatives for Novel Applications in Food Science. *J. Food Process. Beverages* **2013**, *1* (1), 13.
(64) Hsieh, W. C.; Chang, C. P.; Gao, Y. L. Controlled Release Properties of Chitosan Encapsulated Volatile Citronella Oil Microcapsules by Thermal Treatments. *Colloids Surf., B* **2006**, *53* (2), 209−214.
(65) Jiang, P.; Li, D.; Xiao, Y.; Yang, X.; Liu, Y. Preparation and Characterization of Chitosan-Based Core−Shell Microcapsules Containing Clove Oil. *J. Nanosci. Nanotechnol.* **2015**, *15* (1), 600−605.
(66) Xiao, Z.; Liu, W.; Zhu, G.; Zhou, R.; Niu, Y. A Review of the Preparation and Application of Flavour and Essential Oils Microcapsules Based on Complex Coacervation Technology. *J. Sci. Food Agric.* **2014**, *94* (8), 1482−1494.
(67) Santoro, M.; Tatara, A. M.; Mikos, A. G. Gelatin Carriers for Drug and Cell Delivery in Tissue Engineering. *J. Controlled Release* **2014**, *190*, 210−218.

DOI: 10.1021/acssuschemeng.9b00677
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

(68) Foox, M.; Zilberman, M. Drug Delivery from Gelatin-Based Systems. *Expert Opin. Drug Delivery* **2015**, *12* (9), 1547−1563.
(69) Maji, T.; Baruah, I.; Dube, S.; Hussain, M. Microencapsulation of Zanthoxylum Limonella Oil (ZLO) in Glutaraldehyde Crosslinked Gelatin for Mosquito Repellent Application. *Bioresour. Technol.* **2007**, *98* (4), 840−844.
(70) Solomon, B.; Sahle, F. F.; Gebre-Mariam, T.; Asres, K.; Neubert, R. H. H. Microencapsulation of Citronella Oil for Mosquito-Repellent Application: Formulation and in Vitro Permeation Studies. *Eur. J. Pharm. Biopharm.* **2012**, *80* (1), 61−66.
(71) Bringas-Lantigua, M.; Valdés, D.; Pino, J. A. Influence of Spray-Dryer Air Temperatures on Encapsulated Lime Essential Oil. *Int. J. Food Sci. Technol.* **2012**, *47* (7), 1511−1517.
(72) Yang, Z.; Peng, Z.; Li, J.; Li, S.; Kong, L.; Li, P.; Wang, Q. Development and Evaluation of Novel Flavour Microcapsules Containing Vanilla Oil Using Complex Coacervation Approach. *Food Chem.* **2014**, *145*, 272−277.
(73) Butstraen, C.; Salaün, F. Preparation of Microcapsules by Complex Coacervation of Gum Arabic and Chitosan. *Carbohydr. Polym.* **2014**, *99*, 608−616.
(74) Dong, Z.; Ma, Y.; Hayat, K.; Jia, C.; Xia, S.; Zhang, X. Morphology and Release Profile of Microcapsules Encapsulating Peppermint Oil by Complex Coacervation. *J. Food Eng.* **2011**, *104* (3), 455−460.
(75) Hussain, M. R.; Maji, T. K. Preparation of Genipin Cross-Linked Chitosan-Gelatin Microcapsules for Encapsulation of Zanthoxylum Limonella Oil (ZLO) Using Salting-out Method. *J. Microencapsulation* **2008**, *25* (6), 414−420.
(76) Ocak, B. Film-Forming Ability of Collagen Hydrolysate Extracted from Leather Solid Wastes with Chitosan. *Environ. Sci. Pollut. Res.* **2018**, *25* (5), 4643−4655.
(77) Li, Y.; Ai, L.; Yokoyama, W.; Shoemaker, C. F.; Wei, D.; Ma, J.; Zhong, F. Properties of Chitosan-Microencapsulated Orange Oil Prepared by Spray-Drying and Its Stability to Detergents. *J. Agric. Food Chem.* **2013**, *61* (13), 3311−3319.
(78) Li, Y.; Huang, Y. Q.; Fan, H. F.; Xia, Q. Heat-Resistant Sustained-Release Fragrance Microcapsules. *J. Appl. Polym. Sci.* **2014**, *131* (7), 1−7.
(79) Prata, A. S.; Grosso, C. R. F. Production of Microparticles with Gelatin and Chitosan. *Carbohydr. Polym.* **2015**, *116*, 292−299.
(80) Li, M.; Rouaud, O.; Poncelet, D. Microencapsulation by Solvent Evaporation: State of the Art for Process Engineering Approaches. *Int. J. Pharm.* **2008**, *363* (1−2), 26−39.
(81) Xiao, Z.; Tian, T.; Hu, J.; Wang, M.; Zhou, R. Preparation and Characterization of Chitosan Nanoparticles as the Delivery System for Tuberose Fragrance. *Flavour Fragrance J.* **2014**, *29* (1), 22−34.
(82) Sansukcharearnpon, A.; Wanichwecharungruang, S.; Leepipatpaiboon, N.; Kerdcharoen, T.; Arayachukeat, S. High Loading Fragrance Encapsulation Based on a Polymer-Blend: Preparation and Release Behavior. *Int. J. Pharm.* **2010**, *391* (1), 267−273.
(83) Tzhayik, O.; Cavaco-Paulo, A.; Gedanken, A. Fragrance Release Profile from Sonochemically Prepared Protein Microsphere Containers. *Ultrason. Sonochem.* **2012**, *19* (4), 858−863.
(84) Martins, I. M.; Rodrigues, S. N.; Barreiro, F.; Rodrigues, A. E. Microencapsulation of Thyme Oil by Coacervation. *J. Microencapsulation* **2009**, *26* (8), 667−675.
(85) Martins, I. M.; Rodrigues, S. N.; Barreiro, M. F.; Rodrigues, A. E. Release Studies of Thymol and p -Cymene from Polylactide Microcapsules. *Ind. Eng. Chem. Res.* **2012**, *51* (35), 11565−11571.
(86) 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. *Can. J. Chem. Eng.* **2016**, *94* (3), 469−475.
(87) Cortial, A.; Vocanson, M.; Bourdon, M.; Agusti, G.; Briançon, S. Encapsulation of Fragrance Mixture I into Poly-ε-Caprolactone Nanoparticles by Nanoprecipitation Process. *J. Colloid* **2015**, *4* (2), 160−169.
(88) Mossotti, R.; Ferri, A.; Innocenti, R.; Zelenková, T.; Dotti, F.; Marchisio, D. L.; Barresi, A. A. Cotton Fabric Functionalisation with Menthol/PCL Micro- and Nano-Capsules for Comfort Improvement. *J. Microencapsulation* **2015**, *32* (7), 650−660.
(89) Hedaoo, R. K.; Gite, V. V. Renewable Resource-Based Polymeric Microencapsulation of Natural Pesticide and Its Release Study: An Alternative Green Approach. *RSC Adv.* **2014**, *4* (36), 18637.
(90) Jacquemond, M.; Jeckelmann, N.; Ouali, L.; Haefliger, O. P. Perfume-Containing Polyurea Microcapsules with Undetectable Levels of Free Isocyanates. *J. Appl. Polym. Sci.* **2009**, *114* (5), 3074−3080.
(91) Soares-Latour, E. M.; Bernard, J.; Chambert, S.; Fleury, E.; Sintes-Zydowicz, N. Environmentally Benign 100% Bio-Based Oligoamide Microcapsules. *Colloids Surf., A* **2017**, *524* (April), 193−203.
(92) Tokiwa, Y.; Calabia, B. P.; Ugwu, C. U.; Aiba, S. Biodegradability of Plastics. *Int. J. Mol. Sci.* **2009**, *10* (9), 3722−3742.
(93) Dardelle, G.; Jacquemond, M.; Erni, P. Delivery Systems for Low Molecular Weight Payloads: Core/Shell Capsules with Composite Coacervate/Polyurea Membranes. *Adv. Mater.* **2017**, *29* (23), 1−6.
(94) Fustier, P.; Achouri, A.; Taherian, A. R.; Britten, M.; Pelletier, M.; Sabik, H.; Villeneuve, S.; Mondor, M. Protein−Protein Multilayer Oil-in-Water Emulsions for the Microencapsulation of Flaxseed Oil: Effect of Whey and Fish Gelatin Concentration. *J. Agric. Food Chem.* **2015**, *63* (42), 9239−9250.
(95) Jiang, Z.-M.; Bai, L.-N.; Yang, N.; Feng, Z.-B.; Tian, B. Stability of β-Carotene Microcapsules with Maillard Reaction Products Derived from Whey Protein Isolate and Galactose as Coating Materials. *J. Zhejiang Univ., Sci., B* **2017**, *18* (10), 867−877.
(96) Bruyninckx, K.; Jansens, K. J. A.; Delcour, J. A.; Smet, M. The Effect of Cross-Linking Additives on the Structure and Properties of Glassy Wheat Gluten Material. *Ind. Crops Prod.* **2016**, *81*, 38−48.
(97) Dusselier, M.; Van Wouwe, P.; De Smet, S.; De Clercq, R.; Verbelen, L.; Van Puyvelde, P.; Du Prez, F. E.; Sels, B. F. Toward Functional Polyester Building Blocks from Renewable Glycolaldehyde with Sn Cascade Catalysis. *ACS Catal.* **2013**, *3* (8), 1786−1800.
(98) Zou, J.; Hew, C. C.; Themistou, E.; Li, Y.; Chen, C. K.; Alexandridis, P.; Cheng, C. Clicking Well-Defined Biodegradable Nanoparticles and Nanocapsules by UV-Induced Thiol-Ene Cross-Linking in Transparent Miniemulsions. *Adv. Mater.* **2011**, *23* (37), 4274−4277.
(99) Dewaele, A.; Meerten, L.; Verbelen, L.; Eyley, S.; Thielemans, W.; Van Puyvelde, P.; Dusselier, M.; Sels, B. Synthesis of Novel Renewable Polyesters and Polyamides with Olefin Metathesis. *ACS Sustainable Chem. Eng.* **2016**, *4* (11), 5943−5952.
(100) Pascu, O.; Garcia-Valls, R.; Giamberini, M. Interfacial Polymerization of an Epoxy Resin and Carboxylic Acids for the Synthesis of Microcapsules. *Polym. Int.* **2008**, *57* (8), 995−1006.
(101) Gallagher, J. J.; Hillmyer, M. A.; Reineke, T. M. Degradable Thermosets from Sugar-Derived Dilactones. *Macromolecules* **2014**, *47* (2), 498−505.
(102) Chang, C. P.; Dobashi, T. Preparation of Alginate Complex Capsules Containing Eucalyptus Essential Oil and Its Controlled Release. *Colloids Surf., B* **2003**, *32* (3), 257−262.
(103) Jiamrungraksa, T.; Charuchinda, S. Preparation and Characteristics of Galangal Essential Oil/Alginate Microcapsules. *J. Met. Mater. Miner.* **2010**, *20* (2), 89−92.
(104) Yang, Z. M.; Liang, G. Q.; Li, L.; Au, W. M.; Zhong, H. Y.; Wong, T. K. S.; Yang, Z. H. Preparation of Antibacterial Cotton Fabric Containing Patchouli Oil Microcapsules by Chemical Cross-linking Method. *Adv. Mater. Res.* **2011**, *221*, 308−315.
(105) Yang, Z.; Zeng, Z.; Xiao, Z.; Ji, H. Preparation and Controllable Release of Chitosan/Vanillin Microcapsules and Their Application to Cotton Fabric. *Flavour Fragrance J.* **2014**, *29* (2), 114−120.

DOI: 10.1021/acssuschemeng.9b00677
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX