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TOPOLOGICAL REVIEW

Polymer carriers for controlled fragrance release

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Abstract

Fragrance is a class of material commonly used in many consumer products such as food and tobacco. Since most of the fragrance is highly volatile, the successful use of fragrance in practical application requires effective preservation of fragrance with appropriate substrate material. As a low cost and versatile material, polymer holds great promise as a fragrance carrier. In this review, we summarize representative polymer carriers developed recently for sustained and controlled release of fragrance, which include natural polymers and novel synthetic polymers. The results summarized in this mini-review would shed light on the future design of advanced fragrance carrier for various applications.

1. Introduction

The use of fragrance in consumer products not only helps to build pleasant sensory experience for consumers but also benefits the establishment of brand recognition for the products. Nowadays, fragrance has been widely used in a range of consumer products such as food, cosmetics and tobacco [1–3]. For example, essential oil is a mixture of multiple substances that show specific fragrancy. Due to its potential biological function, essential oil is used for skin care, anti-microbial agent, anti-inflammatory agents and cleaning products [4]. A common feature of typical fragrance is its high volatility [5]. The volatility is the key to realize the function of fragrance in practical applications. However, sustained release of the fragrance is normally required to prolong the life time of relating products. For instance, the flavor of food should be preserved in its whole shelf life. Rapid loss of the flavor due to unwanted release of fragrance substances inevitably deteriorate the quality of food. Thus, proper control on the release behavior of the fragrance is particularly important.

Encapsulation or loading of fragrance with a substrate material is an effective approach to regulate the release of the fragrance [6, 7]. A library of natural and synthetic fragrance, ranging from esters, terpenes, aldehydes to alcohols, have been successfully integrated into substrate material for the control of the fragrance release behavior [8, 9]. Generally, the use of the substrate material poses additional physical or chemical resistance for the release of fragrance, thereby leading to a sustained release performance. Furthermore, responsive fragrance release system can be designed on demand by using substrate material with specific stimuli responsiveness [10, 11]. So far, mechanical responsive, chemical responsive, thermal responsive, light responsive fragrance release system were developed by the introduction of functional substrate material.

From the perspective of practical application, an ideal fragrance carrier system should meet the following requirements: (1) the carrier should enable sustained release for the desired application and the duration of the release period should be designed according to specific application; (2) the fragrance release from the carrier should be controllable; (3) the carrier material should not affect the flavor of the fragrance; (4) the carrier material should be chemically inert against the material component in the application; (5) the carrier material should be bio-compatible; (6) the cost of the carrier should be as low as possible. Fragrance carrier system can be classified in many ways. According to the interaction mechanism between the fragrance and carrier, it can be categorized into physically mediated carrier system and chemically mediated carrier system. From the point of the release pattern, the fragrance carrier system can be sorted into stimuli-responsive release system and free

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release system. The fragrance carrier system can be also classified by the material of the carrier. Polymer is a class of material with structure diversity. The composition and the function of polymer can be readily designed according to targeted applications such as fragrance carrier. Besides, since most of the fragrance is organic substance, polymers usually have good compatibility with typical fragrance. Owing to these advantages, polymer is a favorable choice for fragrance carrier. Traditionally, polymers such as poly(ethylene glycol), polymethacrylates, and polyolefins were commonly used as fragrance carriers [12]. With the rapid development of fragrance related products, many novel polymer systems are emerging. The reported polymer carriers for fragrance release can be roughly categorized into natural polymers and synthetic polymers. In the following, the characteristics and performance of these two types of polymer carriers will be summarized.

2. Fragrance carrier based on natural polymers

Natural polymers normally have high affinity with many fragrances, which is beneficial for the stabilization of fragrance molecules within the polymer. In addition, there are a library of natural polymers with different molecule weight and viscosity for the use of targeted applications. More importantly, natural polymers show excellent biocompatibility, which is demanded for almost all consumer products. Furthermore, natural polymers are normally low-cost and environmental friendly. These unique characters make them an ideal polymer carrier for typical fragrance [13].

2.1. Cellulose based fragrance carrier

Cellulose nanocystal (CNC) normally have large surface area and rich hydroxyl groups for post-functionalization. Therefore, CNC is a promising carrier for fragrance. Kunt et al modified CNC with a model enone fragrance (β-Damascone) using a thioester linker [14]. The fragrance can be stabilized on the CNC carrier under acidic conditions. Under basic condition, the CNC carrier system released fragrance though a 1,4-Michael type reaction. Cellulose/silica composite microcapsules loaded with lavender fragrance was prepared through a single-step emulsion process (figure 1(a)) [15]. The composite microcapsule were subsequently coated onto fabrics with water-resistant polysiloxane resin. The use of the composite carrier significantly prolonged the release duration of the fragrance. The modified fabrics could preserve over 30% fragrance after 90 days of keeping (figure 1(b)). In addition, over 30% fragrance was retained after 10 cycles of laundering. Furthermore, this coating provided UV protection to the fabrics. Lignosulfonate is a low-cost polymer derived from wood biomass. Lignosulfonate normally has abundant phenolic hydroxyl groups and sulfonate groups, which makes lignosulfonate water soluble. Piombino et al developed a sonication process to encapsulate thymol derivatives in lignosulfonate microcapsule with a diameter of ∼3.2 μm [16]. The lignosulfonate carrier system showed a first-order-kinetics for the fragrance release and a high release percentage was shown for most of the thymol derivatives investigated. Cork is a natural abundant material with cellular microstructure close to honeycomb. This unique structure makes it impermeable toward gas or liquid. Therefore, cork can be an ideal substrate material for fragrance. Sousa showed that cork granule was able to adsorb and release linalool [17]. The repeated release performance of cork was demonstrated to be superior to activated carbon.
2.2. Chitosan based fragrance carrier

Chitosan nanoparticles encapsulated with tuberose (a mixture fragrance composed of 32 main components) were prepared with an ionic gelation process [18]. A tuberose loading capacity of 29.5% was reached in the nanoparticle and 90% of the tuberose components was encapsulated within the nanoparticle. Due to effective encapsulation of these active components, the composite nanoparticle showed strong antibacterial performance. Amine modified chitosan nanoparticle was prepared by grafting of succinic anhydride on chitosan (figure 2(a)) [19]. Aldehyde containing fragrance was chemically attached to the chitosan nanoparticle. In this polymer carrier system, the fragrance was confined by both physical entrapment and chemical linkage. The strong entrapment of fragrance led to a slow and highly controlled release of fragrance (figure 2(b)). The use of chitosan nanoparticle significantly improves the preservation of the fragrance, which is directly demonstrated with the release experiment. Compared to the fragrance in molecular form, the fragrance retention was 79.9, 85.4, 20.1 and 29.1 times higher with the confinement of chitosan nanoparticle under identical experimental condition for vanillin, cinnamaldehyde, citronellal and citral, respectively. Chitosan-cellulose particle (size: 1–2 mm) with limonene encapsulated was formed by a formation/maturation process [20]. The encapsulation efficiency of limonene in chitosan–cellulose nanoparticle reached ~51%. A two-stage fragrance release behavior was demonstrated for the particle carrier. In the first 24 h, the carrier system showed a high limonene release rate because the fragrance released in this stage was from the physically adsorbed on the outer surface of the particle. In the subsequent 138 h, the particle had a much slower release rate because the released limonene was mainly from the interior of the particle.

2.3. Shellac based fragrance carrier

Shellac is an ester based natural product, which is approved by FDA. Sun et al reported a general microfluidic approach for the preparation of shellac microcapsule and its use for controlled release of a series fragrance such as rosemary oil and lavender oil [21]. A high encapsulation efficiency of 89% was achieved for the microcapsule with a shell thickness of ~2.4 μm. The protection of the fragrance with the shell prevented undesired release of fragrance under storage conditions. The fragrance can be released by breaking the microcapsule through shaking (figure 3(a)). To improve the intrinsically low mechanical stability of the microcapsule resulted from the low shell thickness, chitosan was decorated onto the shell of the shellac microcapsule through electrostatic interaction (figure 3(b)). The novel shellac–chitosan based microcapsule could realize both sustained release and accelerated release upon pH changes. The combination of these features makes the carrier system favorable for applications where extended release and stimuli-responsive release are required. Formation of a compact and rigid protective layer for fragrance helps to extend the life-time of the carrier system. To achieve this goal, shellac coated melamine formaldehyde polymer carrier was developed [22]. As a natural polyester, shellac is highly stable with excellent anti-permeability against water and acid. The composite polymer carrier had a high rupture stress of 21.0 MPa and showed 37 times lower fragrance leaking compared with the pristine melamine formaldehyde polymer carrier. Therefore, this composite polymer carrier could successfully realize highly controllable release behavior. Later, another melamine formaldehyde polymer carrier system was reported [23]. A covalent linkage was built between the shell of melamine formaldehyde polymer and the encapsulated fragrance. Such a linkage helped to construct a stable microcapsule system with prolonged release.
2.4. Cyclodextrin based fragrance carrier
Cyclodextrin, derived from starch, is a biocompatible host material with tunable cavity size. Due to its excellent biocompatibility and host performance, cyclodextrin is considered to be a promising fragrance carrier [24]. Direct inclusion of apple fragrance in \(\beta\)-cyclodextrin through hydrophobic-hydrophobic interaction was demonstrated to extend the duration of the fragrance release [25]. The cotton fabrics coated with the \(\beta\)-cyclodextrin/apple fragrance complex could stably deliver scent for at least 80 days. Furthermore, the effect of functional groups in \(\beta\)-cyclodextrin on the fragrance release behavior was also studied [26]. Another cyclodextrin based fragrance delivery system was prepared by interfacial polymerization of \(\beta\)-cyclodextrin with 4,4\('\)-methylene(bisphenyl isocyanate) in emulsion containing nerolin fragrance [27]. The resultant capsule was coated onto polyamide fabrics by crosslinking. The fragrance carrier system was highly robust, with 32% nerolin remained after 30 repeated washing cycles. To further improve the fragrance release behavior of cyclodextrin carrier, \(\beta\)-cyclodextrin was tethered to a solid surface pre-deposited with poly(4-vinylbenzyl chloride) [28]. Stable chemical linkage could be formed between the surface and \(\beta\)-cyclodextrin through a nucleophilic substitution reaction. This \(\beta\)-cyclodextrin based fragrance release system was applied on cotton fabrics. The fragrance release system containing fragrance such as lavender and jasmine could deliver strong scent even after several months. Nanoparticle composed of 2-hydroxypropyl-\(\beta\)-cyclodextrin complexes and silk fibroin was also proposed for the loading and release of fragrance [29]. 2-hydroxypropyl-\(\beta\)-cyclodextrin was a favorable host for fragrance molecules. The use of silk fibroin in the composite carrier was demonstrated to improve the preservation of fragrance in the carrier and regulate the kinetics of release. For example, 2-hydroxypropyl-\(\beta\)-cyclodextrin/silk fibroin nanoparticle showed over 90% encapsulation efficiency for fragrance such as rose oxide and limonene. In addition, an ideal zero-order release kinetic was achieved in this carrier system.

2.5. Other natural polymer-based fragrance carrier
Pectin is a natural anionic polysaccharide obtained from plant cell walls. Due to its environmental friendliness, pectin has been widely used in food and cosmetic products. Liu et al proposed the loading of citronella with pectin gel [30]. It was found that interaction of the pectin chain with citronella played a decisive role on the release performance of citronella. Such an interaction can be adjusted with esterification degree of pectin and proper crosslinking of the gel. A sustained citronella release was achieved with pectin gel carrier with high esterification degree and \(\mathrm{CaCl}_2\) crosslinking. Corn zein, an amphiphilic protein, was used to stabilize eugenol, which is major constituent of essential oil [31]. It was revealed that the evaporation of eugenol was significantly suppressed once a zein film was formed. In addition, the use of zein helps to prevent the penetration of eugenol into epidermis, which is important for the safe use of eugenol.

In some specific application, thermal triggered fragrance release is required. To this end, Wei et al screened a series of natural polymer for stabilization of fragrance and accelerated release of fragrance at elevated temperature [32]. Sorbitan monostearate (SM) was identified as an ideal polymer carrier due to its high affinity to the fragrance.
with the fragrance (menthol) and its optimal thermal property. At room temperature, menthol was highly stable in SM and little loss of menthol was observed after incubation in open condition at 40 °C. When the temperature was raised to 80 °C, menthol quickly released from sorbitan monostearate carrier. The key to the fast release of menthol at elevated temperature is the good compatibility between SM and menthol and uniform melting behavior of the fragrance carrier system (figure 4(A)). Composite fragrance carrier based on mixture of SM and guar gum could also deliver menthol stably at 80 °C (figure 4(B)). Such a designed release behavior can help to realize the long-term storage of relating product and timely release of the fragrance under desired heating condition.

3. Fragrance carrier based on synthetic polymers

Synthetic polymers can integrate different functional segments desired for specific fragrance release process. Therefore, tailor-designed synthetic polymers is a versatile carrier material for fragrance release. In the following, we will focus on the use of traditional organic polymer and coordination polymer carriers for fragrance release.

3.1. Synthetic organic polymer based fragrance release system

A prominent advantage of organic polymer carrier is its tunability of release behavior by molecule design. Therefore, smart fragrance behavior can be introduced. One of such examples is stimuli-responsive release of fragrance enabled by organic polymer. With the advances in the development of stimuli-responsive polymers [33], more and more smart polymer carriers were reported. In addition, the synthetic organic polymer can be engineered into carrier of different morphology, which helps to regulate the release behavior of the carrier system.

3.1.1. Polymer carrier system based on nanostructures

For the thermal-triggered release of the fragrance, thermal responsive poly(stearyl acrylate) nanoparticles with a diameter of ~180 nm was developed [34]. The pendant side chain of the polymer underwent order-disorder transitions at 45 °C. Such a change led to release of fragrance initially immobilized between the side chain of the poly(stearyl acrylate) (figure 5(a)). Acid responsive smart fragrance release system was also reported. For example, the fragrance molecule can be covalently tethered on the polymer chains and such a tethering can be degraded with acid stimuli to release the fragrance. An acid responsive copolymer carrier was prepared by radical polymerization of methacrylate monomer bearing acetal moiety and PEG dimethacrylate [35]. Upon acid treating, the acetal moiety on the polymer was degraded, leading to the generation and release of octanal. In addition, the release of octanal from the copolymer could also be controlled by the hydrophobicity of the...
polymer. Controlled octanal release could be extended to a period of 600 h with this copolymer. Photo-triggered fragrance release from polymer carrier has a unique advantage of fast ‘turn on/off’ capability. Wang et al.

developed a dual-component photo-responsive fragrance release system [36]. This composite system contains a polymer bearing liable anisaldehyde group and a photo-responsive acid. Once the composite system was subjected to 470 nm light, the photo-responsive acid would change the acidity of the composite, which in turn lead to the release of anisaldehyde from the polymer component (figure 5(b)). These results offer a useful strategy for the design of responsive fragrance release system. Polyethylene glycol methyl ether modified chitosan (PEO–chitosan) was also investigated for the loading and responsive release of fragrance [37]. In aqueous condition, PEO–chitosan was self-assembled to form a microsphere with PEO layers surrounding the sphere. The interaction of PEO component with water was temperature sensitive. At a low temperature (below the lower critical solution temperature, LCST), strong interaction between PEO and water occurred, leading to the de-aggregation of the microsphere and subsequent fragrance release. At temperature above LCST, release of fragrance was suppressed. The LCST of this polymer carrier system can be readily controlled by the ZnSO₄ concentration in the aqueous system.

A nanoprecipitation process was used to fabricate poly-L-lactic acid (PLA) carrier for chlorobenzene [38]. A prolonged release of 48 h was shown with the PLA carrier. The reported PLA carrier was highly biocompatible. The PLA carrier didn’t show any side effect on skin microbiome. In addition, the carrier could adsorb the fatty acid produced on the skin, which helps to cover the skin odor. A core–shell fragrance delivery system, with hydrophobic poly(lactic acid) as the core and soya lecithin/poly(ethylene glycol) as the shell was developed [39]. Lily fragrance was loaded into the polymer carrier by solvent displacement with an encapsulation efficiency of 21.9%. After 24 h, 6% of the encapsulated lily fragrance was released from the carrier system, much lower than the release amount of the free lily fragrance (42.47%). A phase inversion procedure was proposed to prepare polysulfone/vanillin microcapsule for the long-lasting release of vanillin [40]. The microcapsule with an average diameter of 17.8 μm. A maximum encapsulation efficiency of 45% was obtained with this microcapsule. The fragrance release period was extended to 144 h with the polysulfone/vanillin microcapsule.

Polymer carrier with designed nanoporosity was used to tune the fragrance release behavior. Chen et al. prepared polyurethane acrylate of different swollen states and investigated the release of a common top note (benzyl acetate) [41]. Their theoretical prediction suggested that nanoporous polymer with pore diameter below 16 nm was essential for the longevity of the fragrance release. Guided by this prediction, nanoporous polyurethane acrylate that could extend fragrance release period to up to 3 months was developed. The diffusion of fragrance from polymer carrier can also be controlled by the aggregated architecture of polymer. Utilizing the micelle formation capability of poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide) copolymer (EO₁₀₅PO₂₇EO₁₀₅), sustained release of model fragrance (e.g. benzyl acetate and linalool) was achieved [42]. The key to the long-lasting fragrance release is the suppressed diffusion of fragrance in the gelated copolymer micelle.

Dendritic polymer nanoparticle has unique backbone structure, abundant branches/cavities and rich functional groups. These characters allow for the host of guest molecules through interactions such as hydrophobic–hydrophobic interactions. Therefore, a high uptake of fragrance on dendrite polymer could be expected. Polymidoamine dendritic polymer was synthesized and used for encapsulation of thyme oil, which was a natural fragrance with antimicrobial activity [43]. The fiber mats doped with 10 wt% polymidoamine dendritic polymer achieved a long term thyme oil release for up to 12 days. Additionally, the doped fiber mats

Figure 5. Scheme showing the fragrance release from a typical (a) thermo-responsive polymer [34] John Wiley & Sons. © 2015 Society of Cosmetic Scientists and the Société Française de Cosmétologie. and (b) photo-responsive polymer carrier [36] John Wiley & Sons. [Controlled Release of Fragrant Molecules with Visible Light]
was able to resist the bacterial growth of *Escherichia coli* and *Staphylococcus aureus* within 2 weeks due to the prolonged release of thyme oil. Polypropylene-imine dendrimer was also applied to carry fragrance for fabric applications [44]. Successful prolongation of the fragrance release was demonstrated with the use of dendrimer.

### 3.1.2. Polymer carrier system based on microcapsule

Traditional polymerization technique is commonly used to generate polymer fragrance carriers. Simultaneous formation of the microcapsule and encapsulation is a commonly used method to prepare a polymer carrier based fragrance release system. Zhao *et al* polymerized ethylene glycol dimethacrylate in an emulsion containing dementholized peppermint oil [45]. By carefully control over the composition of the emulsion, dementholized peppermint oil loaded microcapsule with an average diameter of 261 nm was formed. The encapsulation efficiency of this polymer carrier was as high as 86.3%. Encapsulation of tuberose in polybutylcyanoacrylate was achieved through emulsion polymerization [46]. The resultant microcapsule had an average diameter of ~200 nm and 50.9% of tuberose was loaded inside the microcapsule. Application of the microcapsule onto fabrics endowed the fabric long lasting and robust fragrance release performance. A large proportion of tuberose was still preserved within the microcapsule after 60 days of incubation or 50 washing cycles. Poly(methyl methacrylate-co-butyl methacrylate)/paraffin microcapsule with fragrance encapsulated was prepared by suspension polymerization (Figure 6(a)) [47]. The use of the composite polymer carrier dramatically improved the longevity of the fragrance release. A high fragrance retention of 63.9% after 3 months of storage in open air was achieved (Figure 6(b)). In addition, the microcapsule is also highly thermal stable, which is favorable for the practical use of this polymer carrier.

Poly(urea-formaldehyde) microcapsule was prepared with jasmine essence encapsulated [48]. A high encapsulation efficiency of 92% and a long release period of 22 days was demonstrated with this polymer carrier system. Sustained release of tea tree oil was also shown with the poly(urea-formaldehyde) carrier [49]. The use of melamine formaldehyde carrier based fragrance was shown by Elesini *et al* [50]. In their application, commercial male and female fragrance were encapsulated into the melamine formaldehyde capsule. Subsequently, the capsule with fragrance was printed onto bow tie through screen printing. The shell of the capsule prevented the leakage of fragrance. During wear, facilitated fragrance release could be realized simply by rubbing the bow-tie, which causes the rupture of the capsule. Using melamine resin microcapsule as a mode material, the fragrance release performance from polymer carrier was investigated with essential oil containing different notes over a time period of 2400 h with solid phase microextraction-gas chromatography-mass spectrometer [51]. It was shown that in the sustained release mode, the middle note and base note was the dominant odor species. While in the ‘broken release’ state (the microcapsule for uptaking the fragrance was broken), the released odor was mainly the top note. This result emphasized that the control over the odor of the carrier system was equally important with the control of release duration.

Poly(urea-urethane) core–shell microcapsule was prepared with interfacial polymerization [52]. The microcapsule was degraded with UV stimuli to generate fragrance as well as gas molecules (CO and CO₂). The generation of gas molecules increased the internal pressure of the microcapsule and caused the rupture of the shell. The rupture of the shell then allowed for the diffusion and release of the generated fragrance molecules from the microcapsule. By engineering the composition of the microcapsule, different modes of light responsive fragrance release was also designed. Poly(1,4-butanediol dimethacrylate) microcapsule with dementholized peppermint oil was synthesized by interfacial polymerization in an oil-in-water emulsion [53]. The
 encapsulation significantly slowed down the evaporation of fragrance. At a temperature of 50 °C, dementholized peppermint oil placed in an open environment completely evaporated. In contrast, dementholized peppermint oil encapsulated in the microcapsule retained 70% of its original content under identical conditions.

A stable microcapsule prepared by alternant layer by layer assembly of tannic acid and bovine serum albumin on the fragrance droplet [54]. Impressively, the fragrance used contains 10 ingredients to mimic the complexity of the practical perfume system. The composite microcapsule resulted from the layer-by-layer assembly was intact and thus could well preserve the fragrance. The fragrance remained stable in the microcapsule after 2 months of keeping at 4 °C. Due to different solubility of the fragrance components, the encapsulation efficiency of these components into the microcapsule differed. In addition, the composition of the released fragrance changed with the incubation time. A polyelectrolyte complex was formed with positively charged casein and negatively charged sodium alginate (figures 7(a) and (b)) [55]. Vanillin loaded into the polyelectrolyte complex showed a time dependent release behavior, with a rapid release period in the first 7.5 h and a subsequent slow release period (figure 7(c)). The suppressed vanillin release was explained by the physical barriers and intermolecular interactions provided by the polyelectrolyte complex carrier.

3.1.3. Other polymer carrier system
A composite polymer carrier based on ethylcellulose, hydroxypropyl methylcellulose and poly(vinyl alcohol) was prepared by a simple solvent displacement process. The constitute of this polymer carrier is highly biocompatible, thus making it particularly favorable for practical applications. To demonstrate the versatility of this composite polymer carrier, 6 representative fragrance with different chemical composition was loaded into the carrier and long-lasting release of these fragrance was demonstrated. As an example, citronellal could be loaded into the carrier with a high encapsulation efficiency of 92.3% and effective prolongation of the release period of citronellal was shown.

Functionalized biomolecules can be used for the controlled release of fragrance. β-citronellol was loaded onto an odorant binding protein functionalized with carbohydrate binding molecule and spacer molecule [56]. The loaded β-citronellol was then applied onto fabrics for the sweat triggered fragrance release. The fragrance release profiles of the modified fabrics showed that the fabric rapidly released fragrance upon acidic sweat treatment. A polypeptide analog was developed to improve the biocompatibility of the fragrance carrier system [57]. This novel polymer carrier was composed of hydrophilic poly(2-ethyl-2-oxazoline) block (mimicking polypeptide) and hydrophobic acid labile Schiff-base block (for linking and release of fragrance). The fragrance molecule tethered onto the polymer can be released under acid conditions for up to 120 h.

Apart from the search of novel polymer carrier materials, the optimization of synthetic methods for the polymer carrier is also investigated. Polymer microcapsule constructed with ‘thiol–ene’ chemistry was reported for the controlled release of fragrance [51]. Due to the high efficiency of the reaction, the whole fabrication process can be finished within 40 min. The fabricated microcapsule showed a high oil encapsulation efficiency over 90%. Such a carrier system could realize a sustained fragrance release for 1 month at room temperature.

3.2. Coordination polymer-based fragrance release
Metal organic framework (MOF) is a type of coordination polymer, which is featured by its high surface area and highly ordered microporosity. These unique porous properties make MOF particularly suitable for the uptake of guest molecules. MOF is normally constructed by metal node and organic linker. Both the metal node and organic linker can be tailored to introduce specific function, such as stimuli responsive property. Therefore, MOF is highly promising for the stimuli triggered release of fragrance.

Figure 7. TEM image of the polyelectrolyte complex (a) before and (b) after loading vanillin. (c) Vanillin release behavior of the polyelectrolyte complex. Reprinted from [55]. Copyright (2019), with permission from Elsevier.
UiO-66 was selected as the carrier for a series fragrance such as eugenol due to its excellent chemical and thermal stability (figure 8(a)) [58]. The fragrance was loaded into the micropores of UiO-66 through solution impregnation. It was suggested that the solvent had a great impact on the uptake of fragrance by UiO-66 because the hydrogen bond formed between the solvent and fragrance would hinder the fragrance uptake. Cyclohexane was identified as an appropriate solution for a high fragrance uptake in UiO-66. The UiO-66 carrier could realize efficient and long-term release of the studied fragrance (figure 8(b)). In addition, functionalization of UiO-66 with hydroxyl groups could improve the uptake and release performance for ester-based fragrance. Liu et al. showed that the hydroxyl groups in the functionalized UiO-66 facilitated the formation of H bond between the ester and fragrance and UiO-66, which improved the uptake and release performance of the functionalized UiO-66 [59].

Moisture sensitive fragrance release system is also important in some specific field (e.g. underarm products). Zn based MOFs (Zn₃(bpdc)₃(bpy)·4DMF·H₂O and Zn₂(bpdc)₂(bpee)·2DMF) were synthesized for moisture triggered release of fragrance [60]. These MOFs have one dimensional open pores and their structure would rupture when exposed to moisture. As a result of these properties, these MOFs were able to show a prolonged release of fragrance. In contrast to most of the reported fragrance release system, the reported MOFs could host and release both hydrophobic (e.g. D-limonene) and hydrophilic (e.g. ethyl butyrate) fragrance. The high compatibility of the carrier with different types of fragrance is important because practically used fragrance is usually a mixture of different fragrances.

4. Conclusion and perspective

Recent development in the use of natural polymer and synthetic polymer carriers for controlled fragrance release is summarized. Natural polymers are by far the most commonly used carrier material for fragrance release due to their excellent safety performance, good affinity with typical fragrance and low cost. Effective immobilization and regulated fragrance release can be realized by both physical interaction or chemical linkage between natural polymer and fragrance. To date, there are a number of commercially available products based on the natural polymer fragrance carrier. However, natural polymer may not be suitable for some specific applications where sophisticated fragrance release patterns are required. In this regard, synthetic polymer may be more favorable because the structure of the synthetic polymer carrier can be tailored designed to meet the requirement for specific application. A good example of this is that many stimuli responsive synthetic polymer carrier has been developed to realize complex fragrance release behavior. Despite its multi-functionality, the biocompatibility and cost of the synthetic polymer should be carefully optimized for practical applications.

There are many important considerations for the successful use of fragrance carrier system in practical applications. For example, typical fragrance containing consumer products such as perfume is a mixture of odorants [61]. In addition, many products require programmable release of fragrance. For example, top note, middle note and base note of perfume should be released in sequence. So far, most of the investigated polymer carrier for fragrance release is still on the 'proof of principle' stage. Although sustained release of single fragrance has been demonstrated for many polymers, controlled uptake and release of multiple fragrances on a polymer substrate remains a challenge. Furthermore, an ideal fragrance release system should deliver constant fragrance performance without interfering by the changing environment. To meet the challenges above, theoretical and experimental investigation on the interaction mechanism between the polymer carrier and fragrance/solvent should be conducted. The results from these studies can provide useful guidelines for the design of polymer carrier for targeted applications. Development of composite polymer carrier or polymer carrier with multiple uptake/release units is a promising solution to meet above challenge. Furthermore, the odor quality of the
fragrance is sensitive to a number of factors. Studies on the effect of polymer carrier and their working condition on the odor quality of the loaded fragrance should be also performed in the future. We believe that, with the advancement in the understanding of the working mechanism of the fragrance carrier system, more and more delicate polymer carrier material will be reported in the near future.

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