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Encapsulation and Enhanced Retention of Fragrance in Polymer Microcapsules

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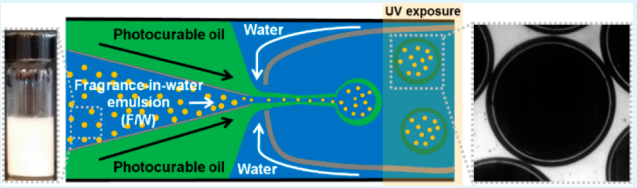
Supporting Information

ABSTRACT: Fragrances are amphiphilic and highly volatile, all of which makes them a challenging cargo to efficiently encapsulate and retain in microcapsules using traditional approaches. We address these limitations by introducing a new strategy that combines bulk and microfluidic emulsification: a stable fragrance-in-water (F/W) emulsion that is primarily prepared from bulk emulsification is incorporated within a polymer microcapsule via microfluidic emulsification. On the basis of the in-depth study of physicochemical properties of the microcapsules on fragrance leakage, we demonstrate that enhanced retention of fragrance can be achieved by using a polar polymeric shell and forming a hydrogel network within the microcapsule. We further extend the utility of these microcapsules by demonstrating the enhanced retention of encapsulated fragrance in powder state.



KEYWORDS: *fragrance, emulsions, encapsulation, microcapsules, microfluidics, retention*

1. INTRODUCTION

Fragrances, small volatile substances with scent, are attractive for applications in toiletries, cosmetics, and home care products.[1,2] These aroma molecules add pleasant scent to human body, animals, objects, and living spaces, providing favorable effect on our emotional perception.[3] While some volatility of fragrance is essential for our sensory response, their highly volatile nature often causes undesired loss during storage; this limits their effective usage as additives in various products.

Several methods have been developed to mitigate the volatility of fragrance.[4−9] One approach, so-called profragrance,[4−6] involves covalent binding of volatile fragrance to substrates to obtain nonvolatile compound, which can be released only upon external stimuli; for instance, some deodorants contain profragrances that are released upon exposure to moisture. However, this approach is limited to fragrances with chemical functionalities such as aldehydes or ketones.[10] A more generic method is the encapsulation approach, which introduces a protective shell around the cargo to form a capsule; this shell can perform as a diffusion barrier and enhance the retention of pristine fragrance.[7−9] Conventional encapsulation techniques, such as interfacial polymerization,[11] complex coacervation,[12] and sol−gel encapsulation,[13] are utilized to encapsulate fragrance in microcapsules, dispersed in aqueous phase; however, these techniques lack highly efficient encapsulation and retention of fragrance in microcapsules. Since fragrances are mostly amphiphilic (hydrophobic while exhibiting partial water solubility), substantial loss can occur during the emulsification of fragrance in aqueous phase.[9] Furthermore, these techniques result in microcapsules with uncontrolled size, shell thickness, and structures; this limits optimal protective shell design that effectively encapsulates and retains cargo. Indeed, for cargo such as fragrance with molecular weight less than 300 Da,[14] high mobility of fragrance[6,11,12] leads to rapid leakage through the shell and, consequently, to significant loss of encapsulated cargo during storage. Therefore, there is an unmet need for an encapsulation strategy that remediates amphiphilicity of volatile cargo as well as enables production of monodisperse microcapsules with precisely controllable shell thickness and shell materials.

In this article, we describe a promising alternative strategy that leverages both microfluidic and bulk emulsification to achieve highly efficient encapsulation and enhanced retention of fragrance. By using microfluidic emulsification,[15−22] microcapsules with precisely tunable size, shell thickness, and shell materials can be produced, providing a firm basis for systematic study. Then, in concert with bulk emulsification, which enables a facile route to prepare emulsion formulation, amphiphilicity of fragrance is resolved by directly incorporating a preformed fragrance-in-water (F/W) emulsion in the microcapsules. A

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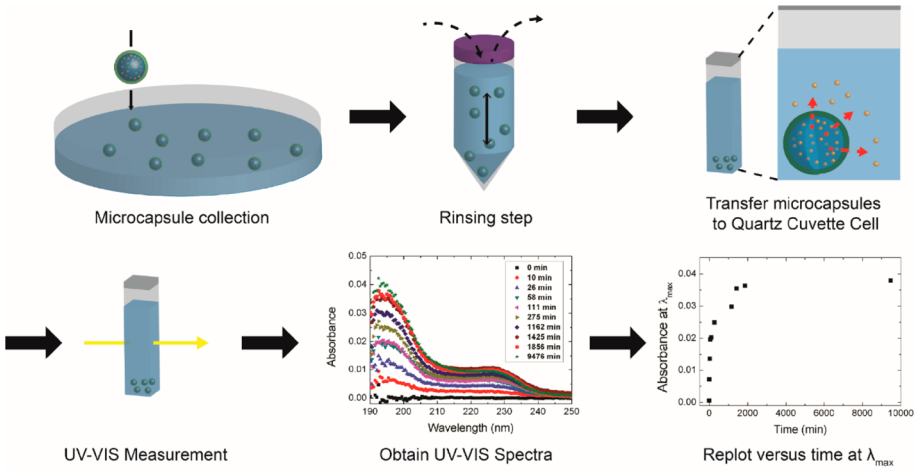
Scheme 1. Schematics Showing the Detailed UV−Vis Spectroscopy Procedures To Acquire the α-Pinene Leakage Profile



preformed F/W emulsion phase co-flows with a photocurable oil phase, which are then flow-focused by the aqueous continuous phase and photopolymerized to produce polymer microcapsules containing model fragrance. On the basis of this strategy, we demonstrate that the low solubility of the capsule shell with the encapsulated fragrance significantly reduces the fragrance leakage rate. Furthermore, we achieve enhanced retention of fragrance in aqueous media as well as in powder state by forming a hydrogel network within the microcapsule.

2. EXPERIMENTAL SECTION

2.1. Materials. All photocurable oil, trimethylolpropane ethoxylate triacrylate (ETPTA, M_w = 428 g/mol), trimethylolpropane triacrylate (TMPTA), dipentaerythritol penta-/hexa-acrylate (DPHA), and photocurable hydrophilic poly(ethylene glycol) diacrylate (PEG-DA, M_w = 700 g/mol) were purchased from Sigma-Aldrich and used as received without further purification. Model fragrance (α-pinene), poly(vinyl alcohol) (PVA, M_w = 13−23 000 g/mol, 87−89% hydrolyzed), tween 80, photoinitiator (2,2-dimethoxy-2-phenylacetophenon), and *n*-octadecyltrimethoxyl silane were purchased from Sigma-Aldrich, and 2-[methoxy(polyethyleneoxy)propyl] trimethoxyl silane was purchased from Gelest. Distilled water (>18.2 MΩ·m, Millipore) (DI water) and ethanol (≥99.5%, Sigma-Aldrich) were used for all experiments.

2.2. Fabrication of Glass Capillary Microfluidic Device. Glass capillary microfluidic device was prepared using previously published protocols.[23,24] Briefly, two cylindrical glass capillaries (World precision Instruments) of inner and outer diameters 0.58 and 1.00 mm, respectively, were tapered to a diameter of 40 μm with a micropipette puller (P-97, Sutter Instrument). These tapered cylindrical capillaries were then sanded to final outer diameters of 60 and 400 μm and inserted in a square capillary (Atlantic International Tech., 1.05 mm i.d.) from the opposite direction; prior to insertion, the cylindrical capillary with smaller orifice was treated with *n*-octadecyltrimethoxyl silane to make the surface hydrophobic, whereas the larger orifice was treated with 2-[methoxy(polyethyleneoxy)propyl] trimethoxyl silane to make the surface hydrophilic. After the assembly, the *xy* plane as well as the *z*-axis configuration of cylindrical capillaries was checked for proper alignment.

2.3. Drop Generation, Polymerization, and Image Analysis. To control the flow rates, we used syringe pumps (Harvard Apparatus) and recorded the production of triple emulsion drops containing multiple internal fragrance drops within the microfluidic devices using an inverted microscope (Leica) equipped with a high-speed camera (Phantom V9). The photocurable oil in the middle phase was then *in situ* polymerized by UV exposure for 1−2 s (Omnicure S1000, 100W) at the exit of the capillary device. We note that all photocurable oil contains 1% (v/v) photoinitiator and that microcapsules with a hydrogel network contain 10% (v/v) photocurable hydrophilic PEG-DA in the aqueous phase of the F/W emulsion unless further specified. To measure the outer radius and shell thickness of the microcapsules generated, we performed image analysis using ImageJ on multiple images that we obtained from optical microscopy. The interface between the F/W emulsion and the capsule shell can be distinguished by the position of the thin white layer within the microcapsule; this enables determination of the outer radius and the shell thickness from the image analysis. In all cases, we analyzed at least 100 microcapsules to determine the average value of the outer diameter and the shell thickness. Provided that the shell is sufficiently well-defined, image analysis provides an accurate measure of both the outer radius and the shell thickness. To ensure that the shell is well-defined, we *in situ* polymerized the photocurable oil in the emulsion drops at the exit of the capillary device to achieve concentric microcapsules with uniform shell thicknesses; otherwise, collection and subsequent UV irradiation (off-chip polymerization) result in generation of off-centered microcapsules with a very thin shell on one side, as shown in the optical images of Supporting Information Figure S1, due to the inherent density mismatch between the F/W emulsion phase and the photocurable oil. These cannot be analyzed as well, and we did not use them. We also note that the error bars shown in Table 1 are not due to the image analysis used for processing the images but mainly originate from the generation of emulsion drops in the jetting regime resulting in some polydispersity in the capsule size and shell thickness.

2.4. Leakage Characterization. The leakage profile is monitored using a UV−vis spectrophotometer (Cary 50, Agilent Technologies) at room temperature (approximately 25 °C). The detailed step-by-step experimental procedures are described in Scheme 1. First, microcapsules encapsulating the F/W emulsion were collected at the exit of the capillary device. The collected microcapsules were rinsed at least three times with an excess volume of DI water to remove the residual PVA as well as α-pinene that may have leaked during the rinsing procedure; however, we observed no significant reduction in the final concentration of fragrance inside the microcapsule after rinsing compared to the variability in each capsule from the same batch. Then, five randomly selected microcapsules were transferred to 3.0 mL of DI water in a quartz cuvette cell (3.5 mL, Agilent) and double-sealed with poly(1,1,2,2-tetrafluoroethylene) (PTFE) lid and parafilm to prevent evaporation and maintain a closed system. Due to the high volatility of α-pinene (~3 mmHg, 20 °C),[25] complete sealing of the cuvette cell is required during the leakage study; otherwise, a noticeable reduction in the absorbance signal is observed during the measurement. Immediately after the microcapsules were transferred, defined as t = 0 min, UV−vis spectra were obtained at different time intervals with agitation before each measurement. Next, UV−vis spectra were replotted versus time at λ_{max} ~ 200 nm.[26] This procedure was repeated three times to obtain error bars in the leakage study.

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Due to volatility and low solubility in DI water (2.49 mg/L, 23.5 °C),[27] we estimated the percentage of α-pinene remaining in each microcapsules by transferring the as-prepared and leakage study performed microcapsules to 3 mL of ethanol, a good solvent for α-pinene. Each quartz cuvette cell containing one microcapsule was vortexed for 1−2 min and stored for at least 1 day prior to UV−vis measurement to ensure complete extraction of α-pinene from each microcapsule.

3. RESULTS AND DISCUSSION

3.1. Preparation of Polymer Microcapsules Encapsulating Fragrance Emulsion. We prepared polymer microcapsules encapsulating a preformed F/W emulsion in a glass capillary microfluidic device. This device consists of a tapered cylindrical injection and a cylindrical collection capillary that are coaxially aligned within a square capillary, as shown in Figure 1. We first prepared a stable F/W emulsion solution by

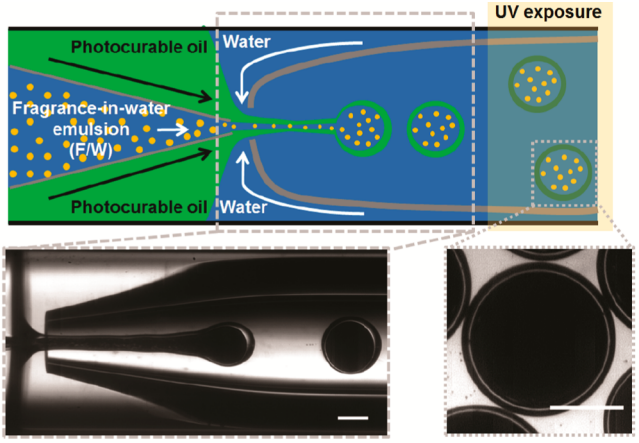

Figure 1. Schematic illustration of the glass capillary microfluidic device for preparing polymer microcapsules encapsulating a preformed fragrance-in-water (F/W) emulsion. Bottom optical microscope image shows the generation of triple emulsion drops containing multiple internal fragrance drops. Upon UV irradiation, the photocurable oil in the middle phase polymerizes to form a polymeric shell. Scale bar represents 200 μm.

mixing the model fragrance, α-pinene, with an aqueous surfactant solution consisting of 5% PVA and 4% Tween 80 in a 50:50 volume ratio for 1 min. This stable F/W emulsion was injected through the cylindrical injection capillary. A photocurable oil was injected as a middle phase through the interstices of the square and injection capillaries from the same side with the injection capillary. An aqueous phase of 5% PVA was injected through the square capillary from the other side as the continuous phase to emulsify the co-flowing biphasic fluids into monodisperse triple emulsion drops containing multiple internal fragrance drops. Then, microcapsules were obtained by cross-linking the photocurable oil phase in the triple emulsion drops at the exit of the collection capillary *via in situ* photopolymerization. The preformed F/W emulsions were effectively encapsulated within a polymer shell and dispersed in an aqueous solution, as evidenced by the dark interior, which is caused by the scattering of the concentrated fragrance drops, as shown in Figure 1.

3.2. Effect of Shell Material on Fragrance Leakage. We monitored the leakage behavior of model fragrance α-pinene with respect to shell material using UV−vis spectroscopy. To investigate the effect of shell material on α-pinene leakage, we tuned the cross-linking density as well as the polarity of the shell by varying the photocurable oil composition in the middle phase; these compositions include TMPTA, ETPTA, and a 50:50 (w/w) mixture of TMPTA and DPHA. We first used triacrylate nonpolar oil, TMPTA, to produce a hydrophobic polymer shell. To increase the concentration of cross-linkable acrylate groups in the middle phase, in another set of experiments, we mixed TMPTA with DPHA that contains a higher number of acrylate groups. We also studied the effect of shell polarity on the leakage of α-pinene by replacing TMPTA with ETPTA, an ethoxylated analogue of TMPTA, in the middle phase. To minimize the effect of microcapsule size and the shell thickness on the leakage of α-pinene, we kept the three liquid flow rates, inner preformed F/W emulsion phase (Q_I), middle photocurable oil phase (Q_M), and outer continuous phase (Q_O), constant at 1000, 1000, 10 000 μL/h, respectively; indeed, the outer radius and the shell thicknesses are the same for all three compositions, as shown in Table 1. For these microcapsules with different middle phase compositions, we observed slower leakage of α-pinene by addition of DPHA in TMPTA and even slower leakage when a polar polymer shell prepared from ETPTA was used, as shown in the leakage profile of Figure 2a. While addition of DPHA in TMPTA can potentially increase the cross-linking density in a polymer shell and reduce the leakage rate, a polymer shell prepared from the ethoxylated analogue of TMPTA (ETPTA) offers low solubility with the encapsulated cargo and therefore can further reduce the leakage rate.[28−30]

3.3. Effect of Shell Thickness on Fragrance Leakage. To investigate the effect of shell thickness on the leakage of α-pinene, we prepared ETPTA microcapsules with the same size but with different shell thicknesses. This is modulated by controlling the flow rates of the inner (Q_I) and middle (Q_M) phases while keeping their sum constant. The resulting microcapsules with different shell thicknesses are shown in the bright-field micrographs of Figure 2b. The outer radius and the shell thickness plotted as a function of Q_M/Q_I ratio confirms that the overall size of the microcapsule remains the same while the shell thickness increases from 11 ± 3 to 24 ± 6 to 37 ± 4 μm. While our results show that increasing the shell thickness reduces the leakage rate of α-pinene, as shown in the leakage profile of Figure 2c, increasing the shell thickness inevitably exacerbates the loading efficiency; for instance, increasing the shell thickness by approximately 3-folds results in an ∼42% reduction in the volume occupied by the fragrance emulsion. In addition, this reduction in leakage rate is negligible compared to the effect of the shell material. The significant effect of the shell material reveals that in the regime where the leakage involves a long diffusion path, on the order of tens of micrometers, the solubility of the shell material with the

Table 1. Outer Radius and Shell Thickness of the Microcapsules Prepared

	TMPTA	TMPTA + DPHA	ETPTA	ETPTA (+ hydrogel network)
outer radius (μm)	202 ± 9 μm	226 ± 8 μm	209 ± 6 μm	211 ± 9 μm
shell thickness (μm)	22 ± 3 μm	23 ± 9 μm	24 ± 6 μm	26 ± 4 μm

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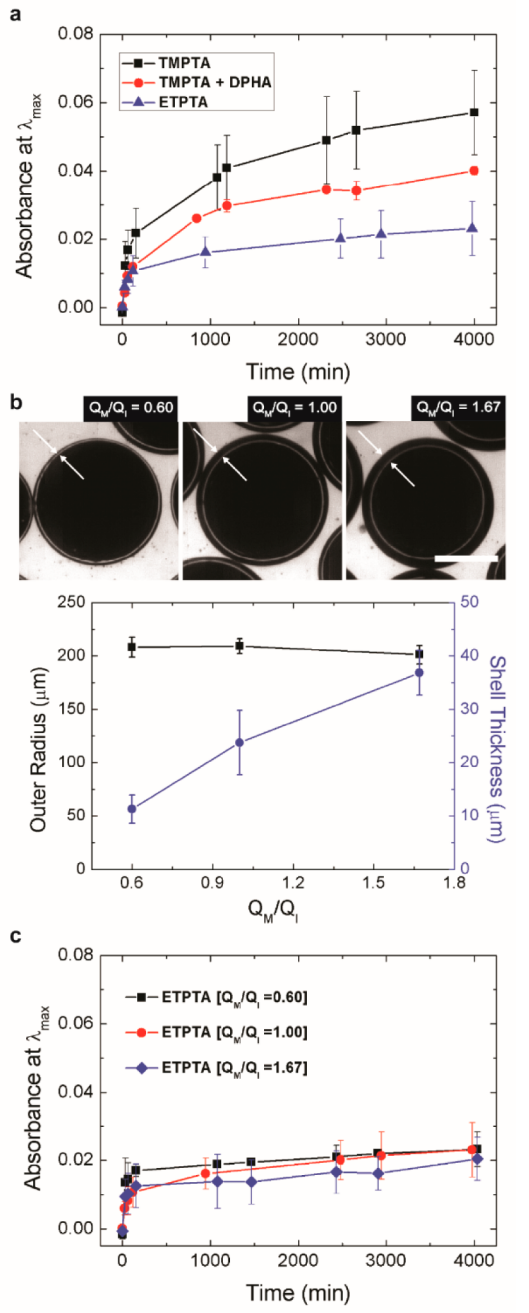

Figure 2. (a) Graph showing absorbance versus time with variation in the photocurable oil composition. All photocurable oil contains 1% (v/v) photoinitiator. (b) Optical microscope images of ETPTA microcapsules prepared at various ratios of Q_M/Q_I denoted on the images. Scale bar represents 200 μm. The sum of the inner and middle phase flow rates ($Q_I + Q_M$) is 2000 μL/h, and the outer continuous phase flow rate (Q_O) is 10 000 μL/h. The graph below shows the outer radius and the shell thickness as a function of Q_M/Q_I. (c) Graph showing absorbance versus time with variation in the shell thicknesses for ETPTA microcapsules.

encapsulated fragrance becomes the dominating factor in reducing the leakage rate.

3.4. Effect of Hydrogel Network on Fragrance Leakage. While shell material and shell thickness can be modulated to achieve a significant reduction in the leakage rate of α-pinene, the density mismatch within the preformed F/W emulsion phase ($\rho_{\alpha\text{-pinene}} \sim 0.86$ and $\rho_{5\%\ PVA} \sim 1.02$) promotes leakage because the α-pinene drops can rise due to buoyancy and directly contact the inner surface of the capsule shell (Supporting Information Figure S2). To prevent this undesirable leakage mechanism and thus achieve a further reduction in the leakage rate, we rigidified the continuous phase of the preformed F/W emulsion within the microcapsule. To accomplish this, we added 10% (v/v) photocurable hydrophilic PEG-DA and 0.1% (v/v) photoinitiator to the aqueous phase of the F/W emulsion; upon exposure to UV, this forms a hydrogel network, as schematically shown in Figure 3a. This hydrogel

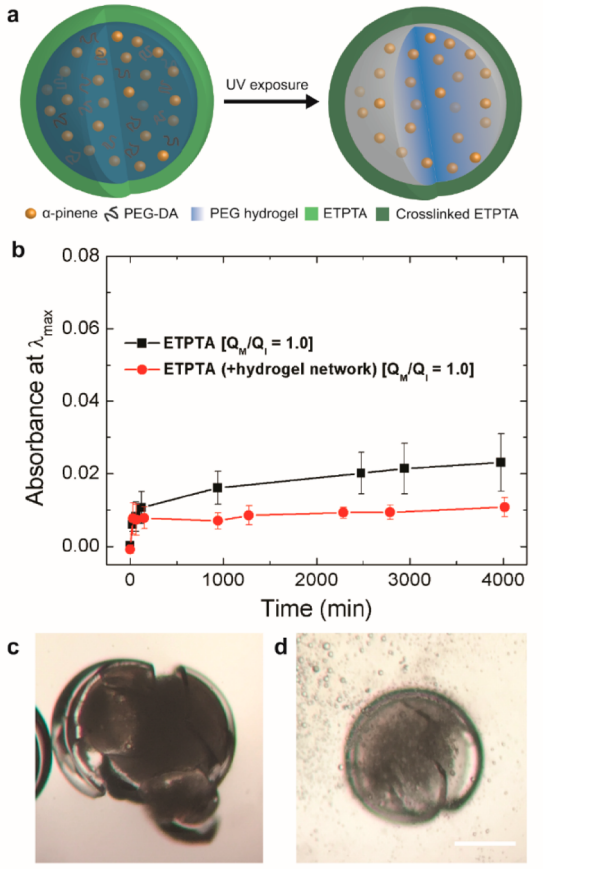

Figure 3. (a) Schematic illustration of preparing microcapsules containing a hydrogel network. ETPTA and PEG-DA are polymerized simultaneously upon UV exposure. (b) Graph showing the absorbance versus time for ETPTA microcapsules (Q_M/Q_I = 1.0) with and without a hydrogel network. (c) Optical microscope image of ETPTA microcapsules with a hydrogel network ruptured between two glass slides. (d) Optical microscope image of ETPTA microcapsules without a hydrogel network ruptured between two glass slides. Scale bar represents 200 μm.

network locks the position of individual α-pinene drops within the microcapsule and performs as a physical barrier. Indeed, the resulting microcapsules significantly reduce the leakage rate of α-pinene compared to that of the control microcapsules without a hydrogel network, as shown in the leakage profile of Figure 3b. We also investigated the effect of concentration of PEG-DA and thus the mesh size of the hydrogel network on the leakage profile by use of 20% (v/v) PEG-DA in the aqueous phase of the F/W emulsion. We observed that increasing the concentration of PEG-DA by 2-fold reduced the leakage rate of α-pinene, as shown in the leakage profile of Supporting

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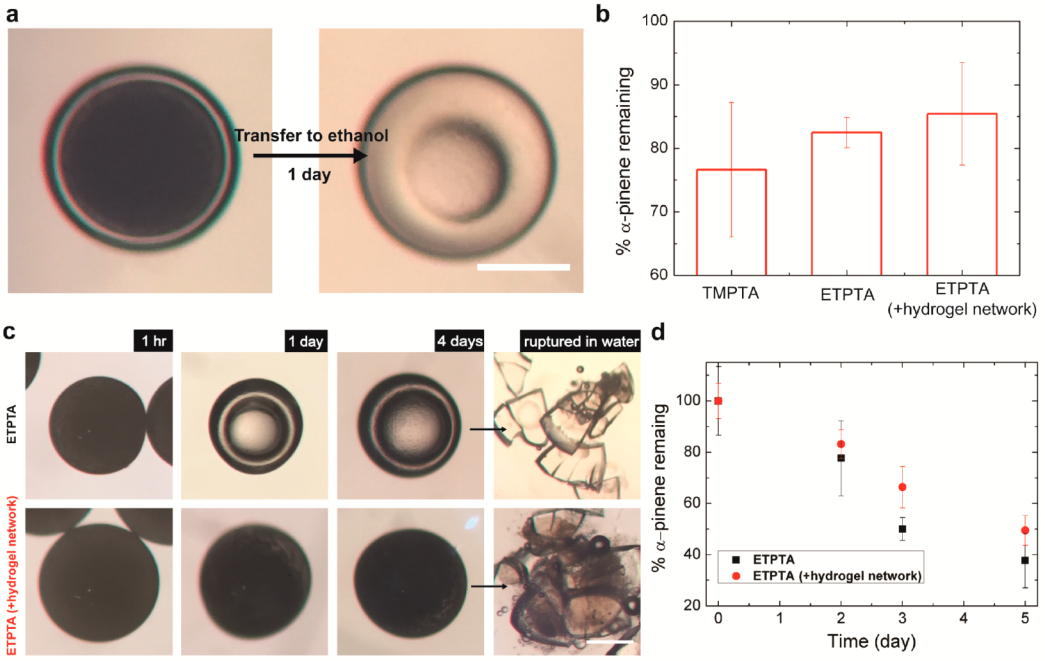

Figure 4. (a) Optical microscope images of ETPTA microcapsules before and after transfer to ethanol. Transfer to ethanol results in complete extraction of α-pinene from the microcapsule. Scale bar represents 200 μm. (b) Graph showing the percentage of α-pinene remaining in microcapsules after approximately ~2.8 days of dispersion in DI water. (c) Sets of optical microscope images of ETPTA microcapsules with and without a hydrogel network upon removal of the capsule dispersion media. Scale bar represents 200 μm. (d) Graph showing the percentage of α-pinene remaining with time upon removal of the capsule dispersion media.

Information Figure S3. However, this reduction in leakage rate is negligible compared to the effect associated with the presence of the hydrogel network itself, shown in the leakage profile of Figure 3b. To verify the presence of the hydrogel network within the microcapsules, we applied mechanical stress to rupture the microcapsules between two glass slides and observed that individual α-pinene drops were held cohesively even upon rupture, as shown in the bright-field images in Figure 3c. By contrast, for microcapsules without a hydrogel network, we observed instantaneous release of α-pinene drops upon rupture, as shown in Figure 3d. Overall, these results indicate that rigidifying the aqueous phase of a preformed F/W emulsion can effectively prevent individual α-pinene drops from directly contacting the capsule shell and thus can further suppress the leakage of α-pinene.

3.5. Quantification of α-Pinene Remaining in Microcapsules. Although monitoring the leakage of α-pinene with respect to shell material, shell thickness, and microcapsule structure revealed the key design parameters for enhanced retention of fragrance in aqueous media, it is often more desirable to quantitatively determine the amount of encapsulated α-pinene remaining in the microcapsule after the leakage study. To quantify the amount of α-pinene, we transferred both the as-prepared and the leakage study performed microcapsules to ethanol, a good solvent for α-pinene, and measured the UV–vis spectra in this media to estimate the amount of α-pinene remaining in the microcapsule. Unlike microcapsules dispersed in water, encapsulated α-pinene was completely extracted from the microcapsules after transferring into ethanol within a day, as evidenced by the clear interior and buckled shell in the bright-field micrographs of Figure 4a. This approach enabled us to estimate the percentage of α-pinene remaining in the microcapsules after the leakage study. We found that 77 ± 11% of α-pinene remained in TMPTA microcapsules with the most leakage, whereas 85 ± 8% of α-pinene remained in ETPTA microcapsules with a hydrogel network with the least leakage after approximately ~2.8 days of dispersion in DI water, as shown in a plot of α-pinene remaining in various systems of Figure 4b.

3.6. Effect of Hydrogel Network on Retention of Fragrance in Microcapsule Powder. To extend the utility of microcapsules containing the F/W emulsion to applications that require fragrance retention in powder state, we removed the capsule dispersion media and monitored the retention of α-pinene. Visual inspection of the microcapsule morphology in the powder state revealed that the aqueous phase of the preformed F/W emulsion was replaced by air[19] as water evaporates, as shown in the bright-field images of Figure 4c; this is partially due to the higher vapor pressure of water (~17.5 mmHg at 20 °C)[31] compared to that of α-pinene (~3 mmHg, 20 °C)[25] and thus faster evaporation of water. By contrast, for the microcapsules containing a hydrogel network, we observed no apparent difference in morphology in the powder state; we attribute this stark visual contrast to the hydrogel network suppressing the evaporation of water. This hydrogel network prevents individual α-pinene drops from directly contacting the capsule shell and thus can enhance the retention of α-pinene. Indeed, quantitative assessment of α-pinene retention showed that 38 ± 11% of the initial amount of α-pinene remained in the microcapsule without the hydrogel network, whereas 49 ± 6% of α-pinene remained in the microcapsule with the hydrogel network after 5 days, as shown in the plot of α-pinene versus time in Figure 4d. These results indicate that rigidifying the aqueous phase of the preformed F/W emulsion phase is also effective for applications that require sustained release of encapsulated fragrance in the powder state such as fabric softeners.

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4. CONCLUSIONS

Here, we introduce the strategy of combining bulk and microfluidic emulsification to encapsulate and retain fragrance in polymeric microcapsules: a stable F/W emulsion that is primarily prepared from bulk emulsification is incorporated within a polymer microcapsule via microfluidic emulsification. These sequential emulsifications enable highly efficient encapsulation of fragrance as well as fabrication of the microcapsules with precisely tunable size and shell properties such as cross-linking density, polarity, and thickness to achieve enhanced retention of fragrance. In addition, a strategy of rigidifying the continuous phase of the preformed F/W emulsion within the microcapsule was also introduced to further enhance the fragrance retention. The approaches outlined in this work are general and can be further extended to encapsulate multiple fragrances in a mixture of F/W emulsions depending on the application requirement. Moreover, these approaches are not limited to fragrances but can be applied for other challenging active molecules such as drugs and therapeutics that are either volatile or have mutual solubility with the capsule shell. This opens up new opportunities for a wide range of encapsulation and delivery applications such as hair products, agricultural products, and liquid laundry detergents, to name a few.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b11351.

Optical microscope images of microcapsules, absorbance versus time data for ETPTA microcapsules with different concentration of PEG-DA (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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