Peripherally decorated binary microcapsules containing two liquids†

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In this work, ~1.4 μm dibutylphthalate (DBP) filled urea–formaldehyde (UF) microcapsules were used as Pickering stabilizers to create larger ~140 μm microcapsules containing a second liquid phase, dicyclopentadiene (DCPD). The binary microcapsules were made by encapsulating the dispersed DCPD liquid (stabilized with the UF(DBP) microcapsules in water) *via* an isocyanate–alcohol interfacial polymerization reaction. Fluorescent optical microscopy and scanning electron microscopy (SEM) showed that the resulting microcapsules have a central liquid core decorated at its periphery with a layer of microcapsules containing the second liquid. The presence of both the encapsulated liquids within a single capsule structure was demonstrated by differential scanning calorimetry (DSC). DSC data analysis indicated a DBP volume fraction of 8.8%. This value was validated by the calculated theoretical fraction on the basis of the observed architecture and capsule dimensions.

Introduction

Microencapsulation provides the capability to store and protect functional liquids from the external environment and to handle them as solids. Many review articles and books have been published on the subject,[1–3] addressing numerous techniques to create a wide variety of liquid filled microarchitectures. These methods include for example the use of polymers,[4] liposomes[5] and silica[6] to encapsulate various organic and non-organic liquids in core–shell particles. Microcapsules having a liquid core can be found in a wide variety of products ranging from carbon copy paper to drug delivery systems and food additives.

Recently, the use of microcapsules as liquid storage containers inside structural materials has received great interest with the development of self-healing polymer systems.[7] In these systems, microcapsules act as a storage medium for liquid monomers inside a polymer matrix and release their reactive contents upon fracture of the surrounding material. In order to design new microcapsules containing reactive liquid media for self-healing materials, we investigated the possibility of creating capsules releasing two reactive liquids upon capsule failure. Different designs of microcapsules in which multiple liquids are stored separately, made by double emulsion methods, have been reported before.[8–11] The approach reported here is not based on such a strategy, but employs a surface stabilization technique to encapsulate two liquids in a single microcapsule.

Solid particles can create stable liquid dispersions by a phenomenon known as Pickering stabilization[12] and offer interesting design tools for liquid encapsulation. Pickering[12] and Ramsden[13] were the first to report that particles can adhere to liquid–liquid interfaces and stabilize emulsions. Later Finkle *et al.*[14] and Pieranski[15] found that the explanation for such strong adherence of particles at liquid–liquid interfaces lies in the fact that the particles are partly wettable by the two phases and that the depth of the surface energy well is a function of temperature, particle size and surface tension. In addition, Leunissen *et al.*[16] recently reported the influences of electrostatic interactions. Different types of polymer particles have previously been shown to be suitable Pickering stabilizers. The most common examples of polymeric particles used as Pickering stabilizers are solid poly(methyl methacrylate) (PMMA) and polystyrene (PS) microspheres.[17,18] In this work, we demonstrate that urea–formaldehyde (UF) microcapsules containing a liquid core also stabilize oil/water emulsions and can create a new microcapsule and colloidosome architecture[17] that has a central liquid core decorated at its periphery with microcapsules containing the secondary liquid. We present the synthesis method and characterization of these binary microcapsules. The novel binary microcapsule architecture is schematically shown in Fig. 1.

Experimental methods

Materials

All materials were used as received without further purification. Urea, resorcinol, ammonium chloride (NH_4Cl), dibutylphthalate (DBP), trimethylol propane (TMP) and perylene fluorescent dye were all purchased from Sigma-Aldrich (USA). Dicyclopentadiene monomer (DCPD, 95% *endo*) was ordered through Acros Organics (Belgium). Formaldehyde 37% in water solution was

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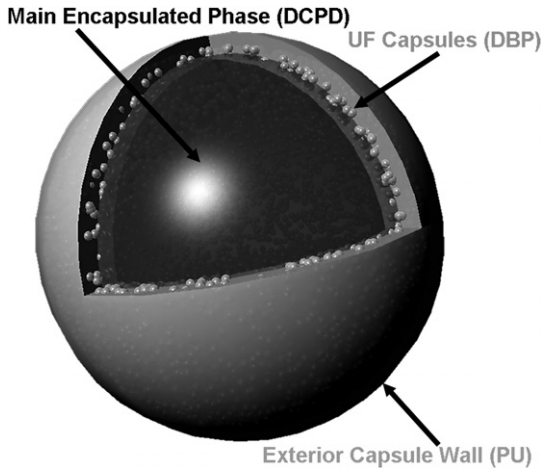

Fig. 1 Schematic representation of the binary microcapsule architecture.

obtained from Fischer Scientific (USA). Ethylene–maleic anhydride copolymer (EMA) was purchased from Zeeland Chemicals (Zeeland MI, USA). Airthane PHP-80D polyurethane pre-polymer (NCO content 11 wt%) was kindly provided by Air Products (USA). Epon 828 and diethyltriamine (DETA) were purchased from Miller-Stephenson (USA).

Synthesis of liquid filled Pickering stabilizers

Dibutylphthalate (DBP) filled urea–formaldehyde (UF) microcapsules used as Pickering stabilizers were synthesized according to the method described by Blaiszik *et al.*[19] To encapsulate DBP, the liquid was emulsified in water at room temperature using a polymeric surfactant, ethylene–maleic anhydride copolymer, and a sonication treatment (Cole-Palmer ultrasonic homogenizer 750 W at 40% intensity). For spectroscopic reasons, a small quantity of perylene fluorescent dye was pre-dissolved in the oil phase. Subsequently, an *in situ* polymerization reaction between urea and formaldehyde at 55 °C for 4 h was used to encapsulate the DBP within a polymeric (UF) shell wall.[20] The resulting urea–formaldehyde capsules were centrifuged, decanted and redispersed in de-ionized H_2O five times to remove the free EMA polymeric surfactant.

Synthesis of binary microcapsules

The binary capsule structures with dicyclopentadiene (DCPD) as the core material were made by preparing a water–DCPD (50 ml : 10 ml) emulsion using 0.5 g of NaCl and 0.28 g of the earlier synthesized ~1.4 μm DBP filled UF microcapsules as Pickering stabilizer without addition of surfactant. Using a mechanical impeller at 400 rpm the water/DCPD dispersion was agitated until the dispersed DCPD was homogenized and non-coalescing at elevated temperature within the time of capsule preparation. Prior to the emulsification, 1.5 g Airthane PHP-80D polyurethane (PU) prepolymer was dissolved in the DCPD. The emulsion was then heated to 60 °C and the PU microcapsule shell wall was created by the addition of 10 ml [1.3 M] trimethylol propane (TMP)–water solution to the stirring emulsion. The addition of TMP started the interfacial polymerization[21] with the

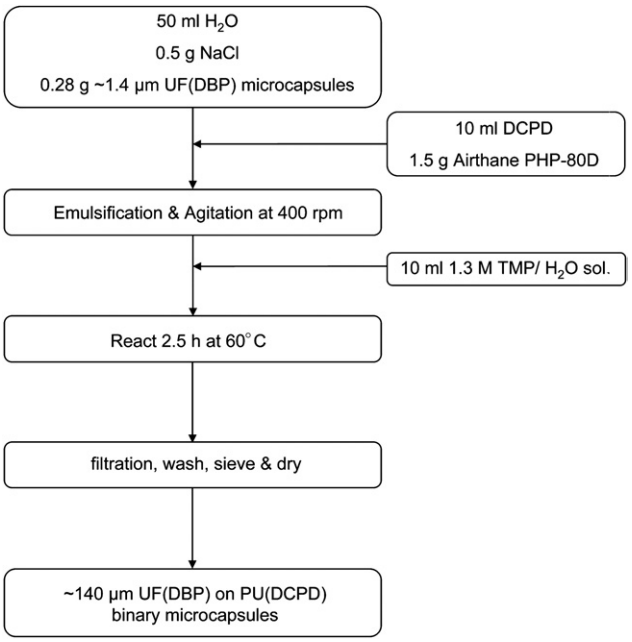

Fig. 2 Production procedure for UF(DBP) on PU(DCPD) binary microcapsules.

PU prepolymer in the oil phase. After 2.5 h reaction time, the microcapsules were filtrated, washed, sieved and dried. The product yield was approximately 7.7 g on 9.82 g DCPD, 0.28 g DBP filled microcapsules and 1.68 g wall material (PU prepolymer + TMP).

The terminology UF(DBP) on PU(DCPD) designates a polyurethane encapsulated DCPD core with UF(DBP) capsules in the shell wall. The binary capsule production procedure is outlined in Fig. 2.

Preparation of binary capsule embedded epoxy resin

The resin was prepared by dispersing 10% of binary capsules by weight in 6.0 g of Epon 828 (bisphenol-A diglycidyl ether). Subsequently, 0.72 g of curing agent (DETA) was added and mixed with the resin. The entrapped air was removed under reduced pressure and the resin was poured into cylindrical molds. The resin was cured over 24 h at room temperature and an additional 24 h at 35 °C. The binary capsule containing epoxy samples were fractured using a razor blade.

Focused extinction analysis

The DBP filled UF microcapsule size distribution was determined by an AccuSizer FX focused extinction particle sizer (0.7–20 μm). The UF(DBP) microcapsule–water dispersion was diluted to create a stable semi-transparent microcapsule dispersion. Of this dispersion, 10 ml was analyzed and sizing was performed for ~10^6 particles.

Optical-fluorescent and electron microscopy studies

The binary microcapsules were characterized using a Leica optical microscope (fluorescent mode). The DBP filled UF microcapsules were made visible by excitation of perylene dye

(excitation ~350–450, emission ~450–550 nm). Using this technique, the location of the UF microcapsules in the binary capsule could be determined.

Scanning electron microscopy (SEM) studies were performed on a Hitachi S-3000N and a Philips XL30 ESEM-FEG. Samples of both DBP filled UF microcapsules and binary microcapsules were deposited on carbon-coated tape and sputter-coated with Au/Pd.

Thermal analyses

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) experiments were carried out to characterize the binary capsules and determine the presence of the two liquid components. DSC was performed using a Mettler-Toledo DSC821e and TGA was carried out using a TGA/SDTA 851e. All experiments were conducted from 40 °C to 390 °C at a heating rate of 10 °C min^{-1} under flowing N_2 gas.

Results and discussion

DBP filled UF microcapsules were stable after drying and homogeneous in size as shown in Fig. 3a. An average diameter of 1.4 μm, with a standard deviation of 0.4 μm, was measured by focused extinction. A plot of the capsule size distribution can be found in Fig. 4a.

A stable DCPD–water Pickering emulsion was produced using the UF(DBP) microcapsules as an emulsion stabilizer. An isocyanate–alcohol interfacial step-growth polymerization[21–23] was selected to fixate the assembled UF(DBP) capsules on the DCPD droplet and encapsulate the contents. The PU prepolymer (isocyanate end-capped) was dissolved in the DCPD prior to emulsification, and the TMP was added to the water phase. The insolubility of each component in the other liquid phase leads to an interfacial polymerization reaction only occurring at the liquid–liquid interface.[24,25] The polymerization between the –NCO end-groups of the PU prepolymer and the –OH end-groups of the TMP leads to the formation of a polymeric (PU) shell wall that encloses the UF(DBP) microcapsules at the oil/water interface into the shell wall of the larger microcapsule, creating the binary microcapsule architecture.

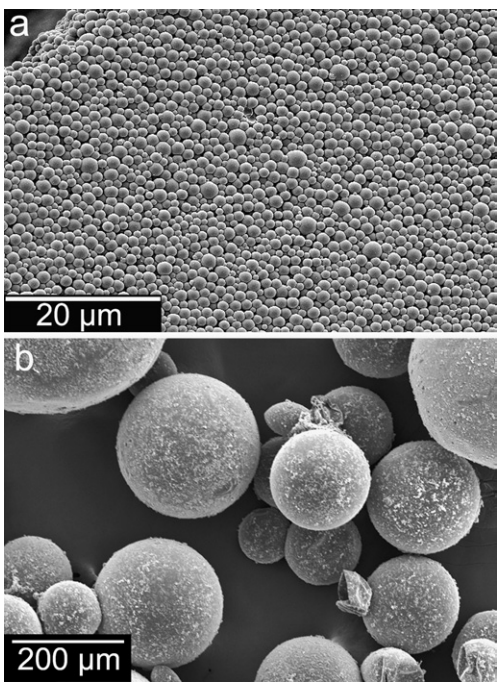

Fig. 3 Electron microscopy images of a) UF(DBP) microcapsules prepared according to the method of Blaiszik *et al.*[19] after drying, b) binary UF(DBP) on PU(DCPD) microcapsules.

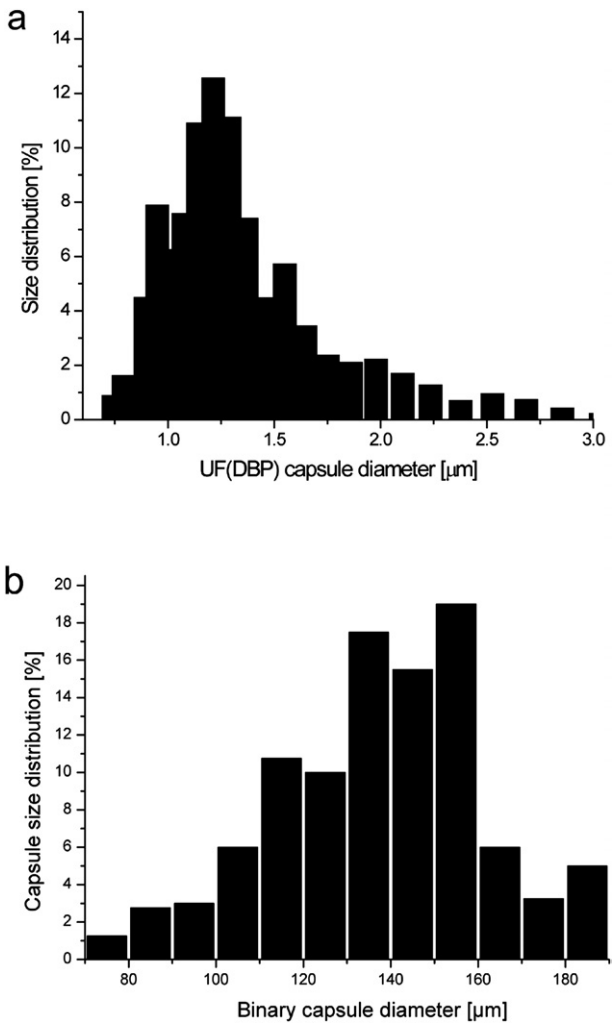

Fig. 4 Capsule size distribution: a) UF(DBP) capsules, b) binary UF(DBP) on PU(DCPD).

Fig. 3b shows an SEM image of filtered and dried binary capsules synthesized with DBP filled UF microcapsules as Pickering stabilizers. The outer capsule morphology is characterized by a slightly rough texture which is a result of residual UF polymer particle adherence. The few observed buckled structures are caused by liquid depletion/evaporation in the SEM vacuum environment. These binary capsules had a mean diameter of 140 μm, with a standard deviation of 24 μm, which was determined from sizing 200 individual capsules *via* optical microscopy (OM). The size distribution is shown in Fig. 4b. After filtration, the binary capsules were air dried to produce a free flowing powder. The combined physical characteristics of the UF(DBP) and PU(DCPD) microcapsules are provided in Table 1.

Table 1 Microcapsule physical characteristics

Core	Shell	Shell wall thickness	Mean capsule diameter	Notation
DBP	Urea–formaldehyde	~75 nm[a]	1.4 μm	UF(DBP)
DCPD	Polyurethane	~ 3–9 μm[b]	140 μm	PU(DCPD)

[a] Blaiszik *et al.*[19] for similarly prepared DCPD capsules of ~1.5 μm (determined from TEM images). [b] Experiments indicate a strong dependence of the polyurethane capsule shell wall on the capsule diameter (determined from SEM images).

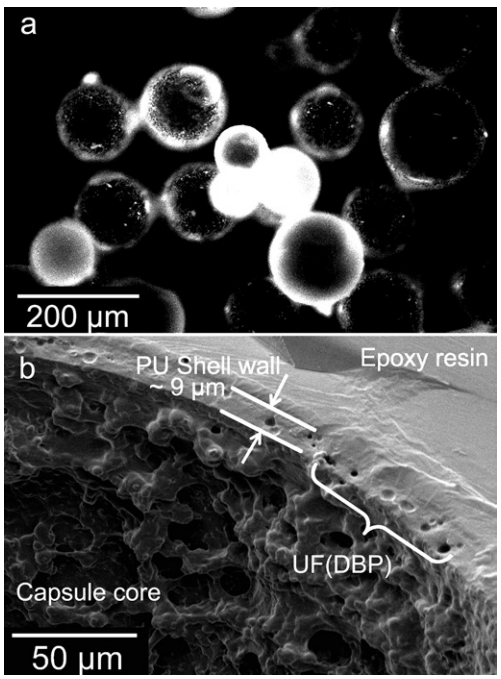

Fig. 5 a) Fluorescent mode micrograph of the UF(DBP) on PU(DCPD) microcapsules. b) SEM image of a fractured UF(DBP) on PU(DCPD) capsule embedded in epoxy resin.

Upon excitation of the binary microcapsules in optical microscopy experiments, the UF(DBP) microcapsules fluoresce strongly. The microscope fluorescent image (Fig. 5a) clearly indicates that light is emitted from the rim of the binary capsules. Hence, the UF(DBP) microcapsules are located on the periphery of the binary capsule surface. SEM of fractured microcapsules embedded in epoxy resin (Fig. 5b) confirmed the capsular architecture. The image shows the fractured shell wall and the rough exposed interior wall of a fractured binary microcapsule. The rough morphology on the shell wall indicates the presence of the UF(DBP) capsules in the shell wall, which is supported by the observation of ruptured UF(DBP) capsules visible on the shell wall fracture surface. The capsule architecture (depicted in Fig. 1) is a direct result of the Pickering stabilization, the subsequent interfacial polymerization and the entrapment of the UF(DBP) microcapsules in the capsule wall. Due to the hydrophilic nature of the polyurethane polymer, the shell wall is created on the water side of the oil/water interface. Since the UF(DBP) Pickering stabilizers firmly adhere to the interface,

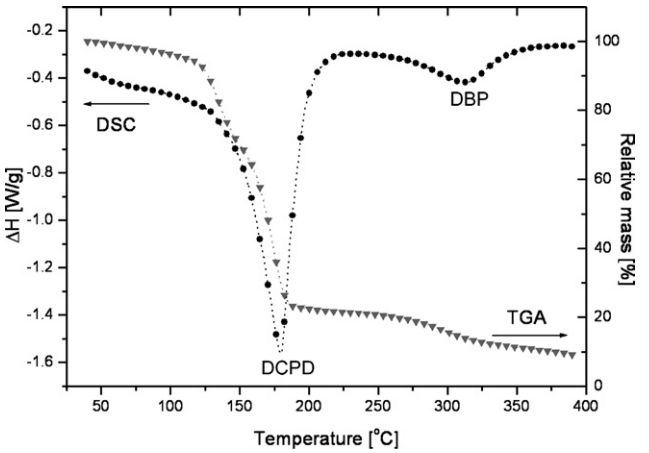

Fig. 6 DSC (●-●) and TGA (▼-▼) measurements of a UF(DBP) on PU(DCPD) binary capsule system.

they are fully incorporated into the shell wall. A similar morphology of peripherally organized colloidosomes was also reported by Bon and Chen[26] who demonstrated the construction of binary hollow silica vessels *via* Pickering stabilization.

The presence of both liquid components (DCPD and DBP) within the same structure was demonstrated by performing DSC and TGA analysis on the binary capsules. The data of both thermal analyses are shown in Fig. 6. In both experiments, we observed two separate transition processes corresponding to the two encapsulated materials. The DSC plot showed two endothermic peaks representing the evaporation of DCPD and DBP with minima at 179 °C and 313 °C, respectively. By integrating the transition peaks, the heats of evaporation for both liquids were determined. Using the measured specific heats of evaporation for the DCPD and DBP grades used, it was possible to calculate the volume ratio between the two components in the binary capsule structures. The volume ratio $f_{\mathrm{Vol}}^{\mathrm{Exp}}$ is defined as follows:

$$f_{\mathrm{Vol}}^{\mathrm{Exp}} = \frac{V_{\mathrm{DBP}}}{V_{\mathrm{DCPD}}} = \frac{\Delta H_{\mathrm{DBP}}^{\mathrm{Trans}}}{\Delta H_{\mathrm{DCPD}}^{\mathrm{Trans}}} \frac{\Delta H_{\mathrm{DCPD}}^{\mathrm{Vap}}}{\Delta H_{\mathrm{DBP}}^{\mathrm{Vap}}} \frac{\rho_{\mathrm{DCPD}}}{\rho_{\mathrm{DBP}}} \quad (1)$$

In eqn (1), properties of each phase are expressed using V for the volume, $\Delta H^{\mathrm{Trans}}$ to represent the measured heat of evaporation, and ΔH^{Vap} and ρ as the specific heat of evaporation and the density of two encapsulated phases respectively.

Using the data listed in Table 2 along with eqn (1), the DBP concentration was 8.8% by volume. TGA measurements of the binary capsules yielded a similar DBP concentration of 8.3% by weight.

Based on the average dimensions of the capsules shown previously in Table 1, the theoretical volume fraction of DBP was calculated assuming uniform spherical geometries and perfect hexagonal packing of the microcapsules (see ESI† for the derivation) as

$$f_{\mathrm{Vol}}^{\mathrm{Theory}} = \frac{V_{\mathrm{DBP}}^{\mathrm{caps}} \cdot n_{\mathrm{DBP}}}{V_{\mathrm{DCPD}}^{\mathrm{caps}}} = \frac{\frac{1}{6}\pi d^3}{\frac{1}{6}\pi D_{\mathrm{eff}}^3} \cdot \frac{\pi D_{\mathrm{eff}}^2 \varphi}{\frac{1}{2}\sqrt{3} d^2} = \frac{\pi d \varphi}{\frac{1}{2}\sqrt{3} D_{\mathrm{eff}}} \quad (2)$$

In eqn (2), V^{caps} is the calculated volume for the DBP and DCPD content of a single capsule and n_{DBP} is the number of UF(DBP)

Table 2 Component analysis of binary capsules by DSC

Component	T_{peak}/°C	ΔH^{Trans}/J	ΔH^{Vap}/J g^{-1}	ρ/g cm^{-3}	V/cm^3
DBP	313	−0.22	−345.2	1.043	6.1×10^{-4}
DCPD	179	−2.01	−296.3	0.982	6.9×10^{-3}

capsules on a binary capsule surface. Furthermore, d is the average UF(DBP) capsule diameter, $D_{eff} = D - 2h$ (where h is the PU shell wall thickness) is the inner polyurethane capsule diameter, and the parameter φ denotes the coverage fraction of the UF(DBP) microcapsules enclosed into the PU shell wall. Assuming a full monolayer droplet coverage, $\varphi = 1$, and using the average geometric values in Table 1 the theoretical volume fraction of DBP is 3.6% with an absolute error of 1.6%, based on the polydispersity of the microcapsule size. The calculated volume fraction is only an estimate, taking into account its error, but indicates that more than a single monolayer of UF(DBP) microcapsules ($\varphi > 1$) was enclosed into the binary capsule shell wall.

By combining eqn (1) and (2), we derive an estimate for the experimental coverage fraction, φ_{Exp}:

$$\varphi_{Exp} = f_{Vol}^{Exp} \frac{\frac{1}{2}\sqrt{3}D_{eff}}{\pi d} \quad (3)$$

Using the experimental data, a coverage fraction of 2.5 ± 1.1 is obtained. This value suggest that on average the total number of enclosed UF(DBP) particles exceeds the amount for a monolayer of hexagonal packed UF(DBP) colloidal capsules by a factor of 2.

Conclusions

A unique fabrication method to create binary microcapsules containing two distinct liquid components *via* small scale liquid filled microcapsules as Pickering stabilizers in combination with interfacial polymerization was demonstrated. The capsule morphology, confirmed by fluorescent optical microscopy and SEM, showed that the small DBP filled UF microcapsules form a layer around the main liquid core and are polymerized into the shell wall during encapsulation. The presence of both of the encapsulated phases within a single capsule structure was confirmed by DSC experiments, and analysis indicated a DBP volume fraction of 8.8%. This value is in good agreement with a calculated theoretical fraction on the basis of the observed architecture and dimensions.

Having demonstrated the ability to construct binary capsules containing two isolated liquid phases, we note that the resulting ratio of the liquid phases is a function of the synthesis conditions and depends on both microcapsule dimensions. The liquid stoichiometry can be tailored by adjusting the Pickering particle concentration and/or the applied shear stress during emulsification. Binary capsule structures not only provide a novel storage and delivery platform for self-healing materials, but their unique architecture may find use in diverse applications such as therapeutic pharmaceuticals or security devices where a chemical reaction is desired after microcapsule rupture or degradation.

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