

Polyurea Microcapsules in Microfluidics: Surfactant Control of Soft Membranes

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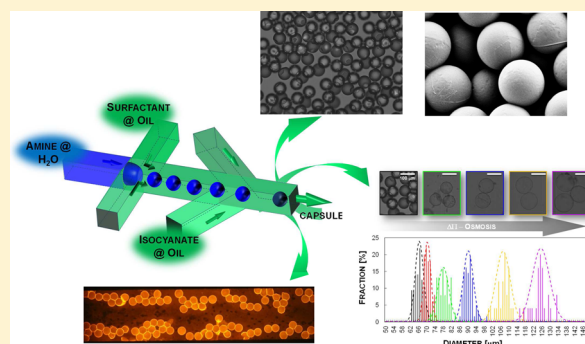
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S Supporting Information

ABSTRACT: Interfacial polymerization techniques offer a versatile route for microcapsule synthesis. We designed a microfluidic process to synthesize monodisperse polyurea microcapsules (PUMCs); the microcapsules are formed by an interfacial polymerization of isocyanate dissolved in the oil and an amine dissolved in water. We measure the mechanical properties of the capsule as well as transport properties through the membrane using two microfluidic methods. We show that the elasticity and the permeability of the shell are controlled by surfactant additives, added during the synthesis. The control of the nanostructure of the shell by surfactants provides new means to design encapsulation systems with tailored mechanical and physicochemical properties.



INTRODUCTION

Compartmentalization is a key process in living and technological systems. From a technology viewpoint, encapsulation is of particular importance in drug delivery, catalysis, and screening, and it may have applications in agriculture, textile, paper manufacturing, and biotechnology, among others.^{1–15} In almost any encapsulation system, the ability to actively control the release of the encapsulated ingredient or to selectively control the transport of molecules in and out of the capsule is critical. The structure of the shell of the capsules is therefore a key to be controlled. Reactive encapsulation techniques provide rapid and versatile methods to prepare microcapsules and to efficiently and reliably entrap active ingredients in a micro-environment.^{16–19} Due to their chemical and mechanical stability, polyurea microcapsules (PUMCs) are very attractive.^{20–29} PUMCs are synthesized by an interfacial poly-addition. This method is a convenient technique for the rapid production of microcapsules under mild conditions of pressure and temperature. As the aqueous droplets containing an amine and the oil phase containing an isocyanate are brought in contact, a solid polyurea shell forms at the interface within a few milliseconds.¹⁹ This fast reaction limits the control over the PUMC shell material properties such as the crystallinity or molecular weight of the polyurea.¹⁹ Such a control is however important as these properties determine the elasticity, toughness, and permeability of the shells. Mechanistic studies have shown that one of the dominating steps at the wall formation is the migration of the water-soluble monomer,^{16–18,38,39} but a detailed understanding of interfacial polymerization mechanisms and kinetics is still lacking.¹⁹ The role of additives used as interface stabilizing agents (surfactants) on the polyurea

morphology is to date poorly understood.^{19,30} The main reason is that batch processes lead to polydisperse capsules in a short time scale, hindering quantitative analysis.^{31,32}

Microfluidics offer the tools to quantitatively study interfacial processes^{33–35} and have been used to generate droplets, multiple emulsions, and microcapsules with well-defined structures at narrow size distribution.^{6,8,36–39} It is therefore a promising technique to study interfacial polymer film formation during the polyurea microencapsulation, at the time scale and length scale relevant to this process.

Here, we use PDMS microfluidic devices to generate monodisperse polyurea microcapsules. We measure both their elastic moduli by the controlled osmotic swelling of PUMCs and their permeability by the release of a fluorescent dye. We show that surfactants added during the synthesis have a notable impact on the microcapsule morphology, mechanical properties, and permeation properties. We focus our investigations on nonionic surfactants. We find that the surfactant has a drastic influence on both the micro and nanometer scale of the polymer film which denotes the template-assisted shell formation of the surfactant at the interfacial polymerization. With increasing hydrophilic–lipophilic balance (HLB) of the surfactant the elastic modulus of the polyurea increases; in parallel, the permeability of the material decreases. Importantly, these changes are not related to a change of the partitioning coefficient between the aqueous phases and the shell, revealing the role of the nanostructure of the polymer shell on the

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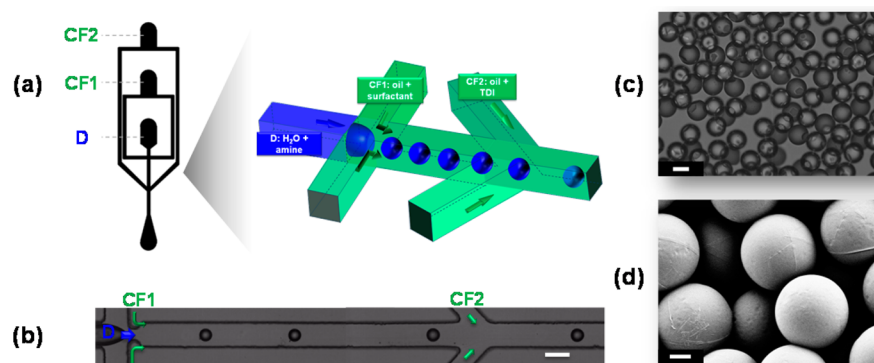


Figure 1. (a) Schematic of the polyurea microencapsulation and microfluidic chip design as well as (b) optical micrographs of the encapsulation process and (c) optical micrograph and SEM image of purified PUMCs (d) (scale bars: c, 100 μm ; d, 20 μm).

permeation. Our approach finally offers a facile route for the generation of PUMCs with well-defined morphological, elastic, and permeation properties.

EXPERIMENTAL SECTION

Materials. Amines polyethylenimine (PEI, branched, $M_N = 600$ g/mol) and tetraethylenepentamine (TEPA), the isocyanate 2,4-toluene diisocyanate (TDI), surfactants Span 20, Span 80, Tween 20, Synperonic F108, Pluronic P-123, Brij L4, Brij 52, and sodium dodecyl sulfate (SDS) are purchased from Sigma-Aldrich and used without prior purification. The KMC oil (diisopropyl naphthalene isomer mixture) is purchased from Fisher Scientific and the surfactant Abil EM 90 from Evonik Industries. The fluorescent dye sulforhodamine B (SRB) is purchased from Life Technologies.

Microfluidics. We use microfluidic devices to generate the polyurea microcapsules. The PUMC synthesis device consists of a cross-junction for emulsification of water droplets in oil, connected to a V-junction with dimensions 100 and 50 μm in width and height (see Figure 1). The device is prepared in poly(dimethylsiloxane) (PDMS) using standard techniques of soft lithography.⁴⁰ To prevent a wetting of the water droplets at the PDMS, the device is functionalized with a hydrophobic treatment (Aqualap).

Synthesis of Monodisperse Polyurea Microcapsules.

The microfluidic device flow structure consists of the dispersed fluid (D, aqueous) and two continuous fluids CF1 and CF2 (Figure 1a,b). We use syringe pumps (Nemesys Instruments) for injection of D, CF1, and CF2. The PUMCs are synthesized using a microfluidic drop maker to form an emulsion consisting of aqueous amine (8×10^{-3} mol %) / NaCl (5 wt %) droplets in continuous fluid 1 consisting of a KMC oil/surfactant (1 wt %) mixture. Consecutively, continuous fluid 2, consisting of KMC oil and TDI (2.5 wt %), is added to initiate the *in situ* polyurea shell formation. The surfactant has two roles here: first it prevents droplet coalescence before the shell is formed, and second, it prevents aggregation of the capsules once they are formed. Capsules are collected by gently flowing the outlet tubing into a glass vial. Capsules are kept at room temperature for 14 h prior to use to guarantee a completion of the shell growth. The reaction of diisocyanates with the surfactants can be neglected for the applied experimental conditions; no altering or shell formation of W/O emulsion droplets after 14 h has been detected in the absence of amine.

Osmotic-Driven Inflation. Inflation experiments are carried out separately in microplate chambers. The suspension

consisting of PUMCs in the oil mixture is transferred to the chambers; due to the higher density, the capsules settle down to the bottom. To remove residual TDI and surfactant, the capsules are decanted and washed with *n*-hexane several times. After removal of the *n*-hexane phase, the capsule surface is gently blown dry with air. The NaCl concentration at the PUMC interior is a fixed parameter. Adjustment of the osmotic difference, for inflation purposes, is realized by treating the PUMCs with aqueous NaCl solutions. The inflation is initiated by adding a NaCl/SDS (1 wt %) solution at NaCl concentrations ranging between 1–5 wt %.

Imaging. Electron micrographs are generated using a FESEM Ultra Plus from Zeiss and a REM from Hitachi S5500 at 5 and 15 keV, respectively. EDS mapping is performed on a FESEM Ultra55 from Zeiss. Transmission electron microscopy is done on a TEM 2100 from JEOL at 100 keV.

Fluorescent Dye Release. Release measurements of polyurea microcapsules are performed using fluorescence microscopy. Capsules are settled in a microfluidic release column; the device design and a micrograph of a common experimental setup are provided in Figure S4 in Supporting Information. Fluorescence images of a capsule array are taken stack-wise; illumination of the sample is programmed solely for the imaging term. We use sulforhodamine B (SRB) as fluorescent probe at a concentration of 30 $\mu\text{mol}\cdot\text{L}^{-1}$. At this SRB concentration, a linear regime of the fluorescence intensity versus concentration dependency is given (see Figure S5 in Supporting Information).

RESULTS AND DISCUSSION

We produce water-in-oil (W/O) polyurea microcapsules in PDMS devices using 2,4-toluene diisocyanate (TDI) as the monomer in the oil phase and polyethylenimine (PEI) in the aqueous phase. To prevent clogging of the channels during the interfacial reaction, we decouple the droplet formation from the reaction (Figure 1a,b). The droplets are formed by injecting the aqueous phase containing the amine and sodium chloride into an oil phase containing the surfactant via a T-junction. The TDI-containing oil phase is added downstream through a V-junction. The polyurea microcapsules generated are monodisperse with highly reproducible production conditions (Figure 1c,d). The shell thickness of PUMCs produced using PEI/TDI typically range between 90–110 nm, as reported earlier.^{38,39}

Another type of capsule is prepared by simply changing one of the reagents. When the PEI is replaced by a shorter chain such as tetraethylenepentamine (TEPA), capsules are also formed in microfluidics with similar monodispersity and dimensions. For similar conditions, we obtained thicknesses of the shell in a range between 680 nm (see Figure 2a) for

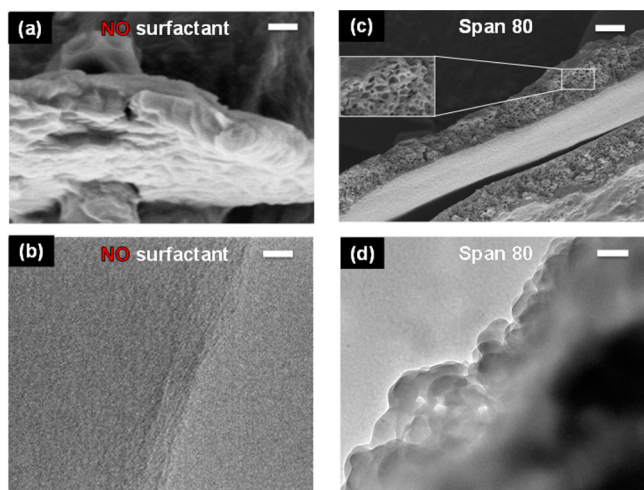


Figure 2. SEM (a,c) and TEM (b,d) images of W/O polyurea microcapsule shells using no surfactant (a,b) and the nonionic surfactant Span 80 (c,d). PUMCs generated without surfactant have no further fine-structure while Span 80-templated PUMCs have a sponge-like secondary structure in the membrane (scale bars: a,c 600 nm; b,d 5 nm).

TEPA concentrations of 5 wt % and 100 nm for 0.1 wt %. In the following, capsules produced by the reaction of TEPA/TDI will be called T, and capsules produced by the reaction of PEI/TDI will be called P.

In the absence of surfactant, the T shells are formed as smooth layers without a well-defined fine-structure at the nanoscale (Figure 2 a,b). The TEM images reveal a

homogeneous distribution of the polymer layer along the shell (Figure 2b). We also investigated T PUMCs fabricated by using the same monomer concentrations and the nonionic surfactant Span 80 (2.5 wt %). Important to mention is that the overall shell thickness (710 nm) is similar to that of the nonsurfactant-templated shells. However, we detect a certain closed lamellar substructure within the wall. The average diameter of the closed polymer-filled vesicles is 80 nm. The TEM images reveal a nanoscopic sponge-like fine-structure in the walls; the average diameter of the spherical compartments is 3.7 nm. Thus, the use of surfactant at the polyurea microencapsulation has a tremendous impact on the resulting shell morphology on both the micro- and nanometer scale caused by the interaction of surfactant molecules at the interfacial polyaddition reaction. To show that the surfactant is directly embedded into the capsule walls, we generated T PUMCs by the use of the ionic surfactant sodium dodecyl sulfate (SDS) that gave a contrast to the surrounding polyurea network in the EDS spectrum. SEM images as well as EDS mapping results are given in the Supporting Information (Figure S1 in Supporting Information).

Most PUMC encapsulations are carried out using common surfactants such as Span 80 or Tween 20 simply due to the advantageous abilities of these components in increasing the kinetic stability at the oil/water interface that prevents a fast coalescence of the aqueous droplets.^{20–29} The impact of the surfactant on the polyurea encapsulation, however, is not understood, because the dynamics of the surfactant adsorption and the kinetics of the reaction are difficult to decouple.

To study the impact of the surfactant on the PUMC-formation, we first focus on one surfactant: Abil EM 90, an organosiloxane-polyoxyalkylene that is preferably used for stabilization of water-in-oil emulsions and applied in care materials.^{41–43} We prepare two types of capsules from our two reagents to obtain P and T capsules with the surfactant. We are here interested in the properties of the shells for encapsulation applications, and we designed two experimental schemes to characterize the elastic and permeation properties of the shells.

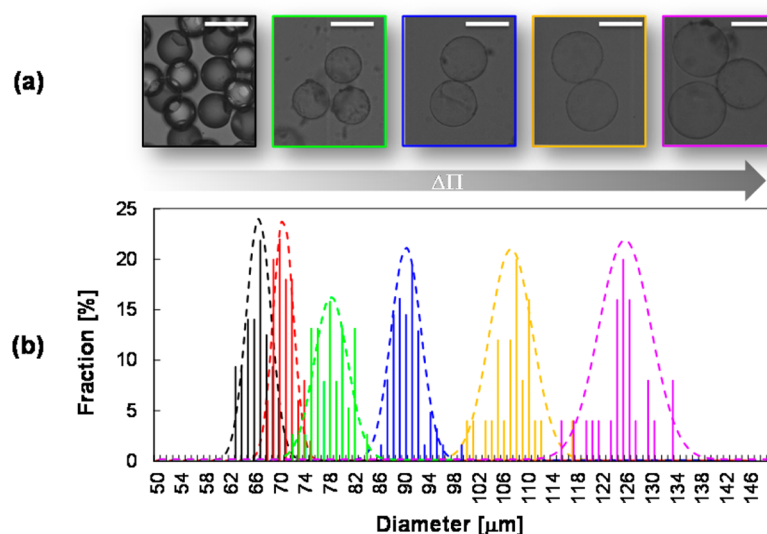


Figure 3. (a) Osmotic-driven inflation of W/O polyurea microcapsules and corresponding diameter distribution (b). Border colors in (a) indicate appropriate data exhibited in (b). $\Delta\Pi$ (black) = 0 kPa, $\Delta\Pi$ (red) = 40 kPa, $\Delta\Pi$ (green) = 460 kPa, $\Delta\Pi$ (blue) = 890 kPa, $\Delta\Pi$ (yellow) = 1.310 kPa, $\Delta\Pi$ (purple) = 1.740 kPa. Microcapsules are prepared using PEI (0.35 wt %) and TDI (2.5 wt %) and Abil EM 90 (2.5 wt %) as surfactant; NaCl (4.3 wt %) is added to the aqueous phase for osmolality increase and aqueous SDS/NaCl solutions are used to adjust $\Delta\Pi$ (scale bar: 100 μm).

We define the mechanical properties of the shells through the Young's modulus E of the elastic capsules. The method to measure E is based on osmotic inflation of the capsule: after fixing the osmolarity difference between the continuous phase and the interior of the capsule, we measure the equilibrium inflation of the capsule acting as a permeable membrane for water. This method, which was originally established for thin-walled polyelectrolyte capsules,⁴⁴ provides a measurement of E according to eq 1:

$$E = \left(\left(\frac{2r}{r_0} - 1 \right)^2 - 1 \right) \frac{h}{2\pi \cdot r_0 \cdot \Delta\Pi \cdot (1 - \nu)} \quad (1)$$

where h is the capsule shell thickness, r_0 is the initial capsule radius, and ν is Poisson's ratio ($\nu \approx 0.5$, an established value for glassy polymeric materials). Equation 1 is valid solely for small deformations, continuously to a radius strain ϵ below 0.5. Practically, the Young's modulus E of the shell is obtained as the initial slope according to eq 2:

$$\frac{\Delta\Pi \cdot 2\pi \cdot (1 - \nu)}{h} = \left(\left(\frac{2r}{r_0} - 1 \right)^2 \cdot r_0^{-1} - r_0^{-1} \right) \cdot E \quad (2)$$

After production of W/O-PUMCs, we decant the continuous-phase-containing residues of unreacted TDI and the surfactant and wash the capsules with *n*-hexane for several times by decanting. The capsules are placed in a microplate chamber and gently blown dry with air. The inflation process is initiated by adding an aqueous SDS/NaCl solution (Figure 3a), and we measure the average size of the capsule as a function of osmolarity differences (Figure 3b). With increasing values of $\Delta\Pi$, r increases; radii are in a range between 66 and 125 μm which correspond to strains ϵ ranging between 0 and 3. The inflation is reversible for strains below 1.5, which was proven by consecutive addition of an aqueous 5 wt % solution of NaCl right after the inflation. Inserting r into eq 2 using a shell thickness h of 80 ± 10 nm measured by SEM (see Figure S2 in Supporting Information) yields a Young's modulus of 0.9 ± 0.1 $\text{kN} \cdot \text{mm}^{-2}$ for a P capsule with Abil EM 90 as the surfactant. Repeating the experiment with the T capsules, we obtain 0.2 ± 0.1 $\text{kN} \cdot \text{mm}^{-2}$ ($h = 120 \pm 12$ nm), corresponding to a significantly softer capsule. According to the experimentally determined E-moduli, the thin polyurea membranes can be understood as glassy polymer materials; further stabilization by intra- and intermolecular hydrogen bonding is suggested. As a note, another mechanical parameter of interest, the toughness of the shells, namely, their maximum strain before rupture, is also a function of the reaction: the toughness of the P capsules is much higher than that of the T capsule for which the rupture is observed at $\epsilon < 1.8$. Therefore, the T capsules are both softer and more susceptible to break.

The second parameter we measure is the shell permeation. To measure the permeation properties, we measure the release time of a model dye sulforhodamine B (SRB) from the capsule using fluorescence microscopy. We encapsulate water-soluble SRB (30 μM) in W/O-PUMCs and place the suspension in a specifically designed microfluidic flushing column (Figure S3 in Supporting Information). To remove the continuous oily phase, we flush the device with an aqueous 30 μM SRB solution ($150 \mu\text{L} \cdot \text{h}^{-1}$) for 18 h. We initiate the release by flushing the capsules with Millipore water ($150 \mu\text{L} \cdot \text{h}^{-1}$). For quantification of the SRB diffusivity, we measure the relative fluorescence

intensity of the polyurea microcapsules over time.^{45,46} We expect an exponential decay as the result of the diffusive transport through the shell

$$\frac{I}{I_0} = e^{-t/\tau} \quad (3)$$

where I_0 and I_t are the fluorescence intensities at times 0 and t and τ equals a time constant. Neglecting the SRB diffusion in the aqueous media ($\sim 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$) and establishing the membrane diffusion as the rate-determining step in the whole diffusion, the diffusion coefficient of the SRB in the membrane, D_m , is calculated from the decay time scale τ as

$$D_m = \frac{R \cdot h}{3 \cdot \tau \cdot K} \quad (4)$$

⁴⁵where R is the capsule radius, and K is the membrane/solution partitioning coefficient of the dye.⁴⁷ The partitioning coefficient K for SRB in the polyurea/water system are determined independently, as described in the Supporting Information, and are marginally affected by the presence of surfactant during the synthesis. The measurements of the fluorescent intensity of the capsules as a function of the time are shown in Figure 4. First, we obtained leakage rates of less

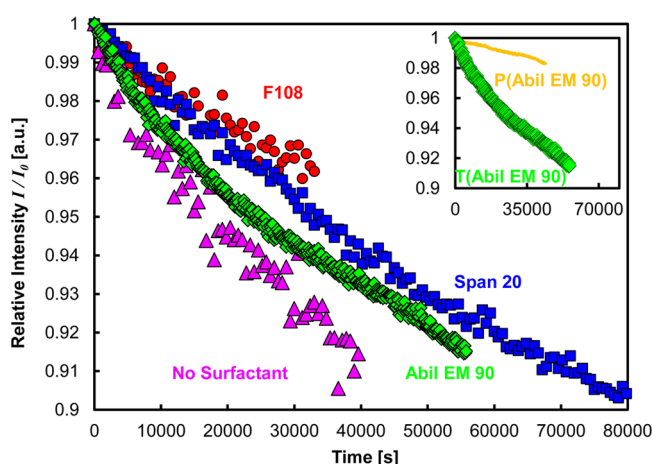


Figure 4. Release plots of PUMCs prepared using TEPA/TDI without surfactant (purple $\blacktriangle$) and with surfactants Abil EM 90 (HLB = 5, green $\blacksquare$), Span 20 (HLB = 8.6, blue $\blacksquare$), Syneronic F108 (HLB = 27, red $\bullet$). The calculated diffusion coefficient after the Zvolinski⁴⁶ model using the experimentally determined partitioning coefficients are $3.06 \pm 0.22 \times 10^{-18} \text{ cm}^2 \cdot \text{s}^{-1}$ (no surfactant, $\tau = 2.08 \times 10^{-6} \text{ s}$), $2.27 \pm 0.13 \times 10^{-18} \text{ cm}^2 \cdot \text{s}^{-1}$ (Abil Em 90, $\tau = 1.44 \times 10^{-6} \text{ s}$), $2.02 \pm 0.20 \times 10^{-18} \text{ cm}^2 \cdot \text{s}^{-1}$ (Span 20, $\tau = 1.27 \times 10^{-6} \text{ s}$), $1.85 \pm 0.08 \times 10^{-16} \text{ cm}^2 \cdot \text{s}^{-1}$ (Syneronic F108, $\tau = 1.05 \times 10^{-6} \text{ s}$). The variance is determined over 2–3 measurements. Inset: comparison of the permeation properties of P (yellow —, $0.61 \times 10^{-19} \text{ cm}^2 \cdot \text{s}^{-1}$; $\tau = 3.42 \times 10^{-6} \text{ s}$) and T (green $\blacksquare$) shells using Abil EM 90.

than 10% over more than 10 h for all systems tested, indicating the good stability of the encapsulation. Second, the time scale is dependent on the reaction, and we obtained $0.61 \times 10^{-19} \text{ cm}^2 \cdot \text{s}^{-1}$ ($\tau = 3.42 \times 10^{-6} \text{ s}$) for the P capsules and $2.27 \times 10^{-18} \text{ cm}^2 \cdot \text{s}^{-1}$ ($\tau = 1.44 \times 10^{-6} \text{ s}$) for the T capsules.

We obtain here a correlation between the mechanical properties and the permeation properties, which shows that softer capsules are also more permeable, keeping all other parameters—partitioning coefficient, thickness of the shell—constant. This result is reminiscent of the transport through

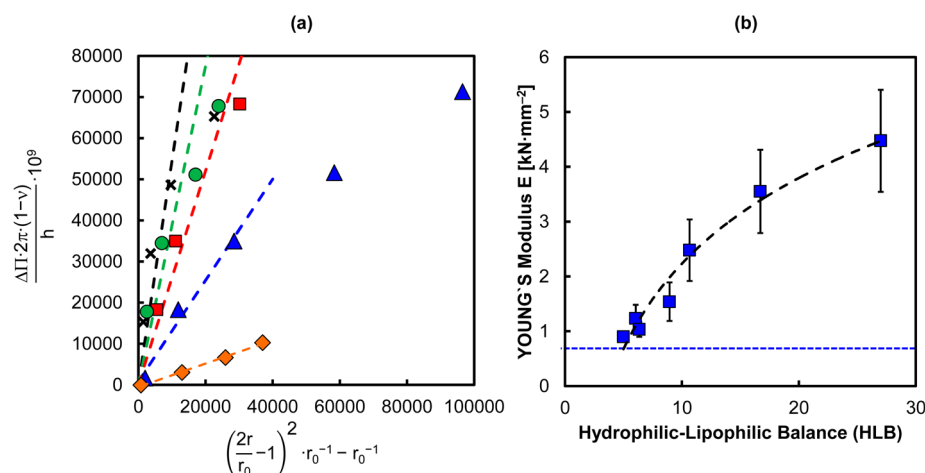


Figure 5. (a) Reduced stress–strain relation (eq 2) for osmotic-driven inflation of PEI/TDI polyurea microcapsules using the surfactants Synperonic F108 (x), Tween 20 (green ●), Span 20 (red ■) and Abil EM 90 (blue ▲), as well as TEPA/TDI-PUMCs using Abil EM 90 (orange ■). The slopes of the linear fits at small strains yield the Young's moduli in $\text{kN}\cdot\text{mm}^{-2}$. We measure PEI/TDI-PUMC elastic moduli $4.5 \pm 0.9 \text{ kN}\cdot\text{mm}^{-2}$ (Synperonic F108), $3.6 \pm 0.7 \text{ kN}\cdot\text{mm}^{-2}$ (Tween 20), $1.5 \pm 0.5 \text{ kN}\cdot\text{mm}^{-2}$ (Span 20), and $0.9 \pm 0.1 \text{ kN}\cdot\text{mm}^{-2}$ (Abil EM 90) and for TEPA/PEI (Abil EM 90) $0.2 \pm 0.1 \text{ kN}\cdot\text{mm}^{-2}$. (b) Young's moduli E of the PEI/TDI microcapsule polyurea as a function of the HLB of the surfactant used for the emulsification. The dotted blue line indicates the E value for the non-surfactant PUMCs ($E = 0.67 \text{ kN}\cdot\text{mm}^{-2}$). The HLB values are determined by the Griffin method.⁴⁹

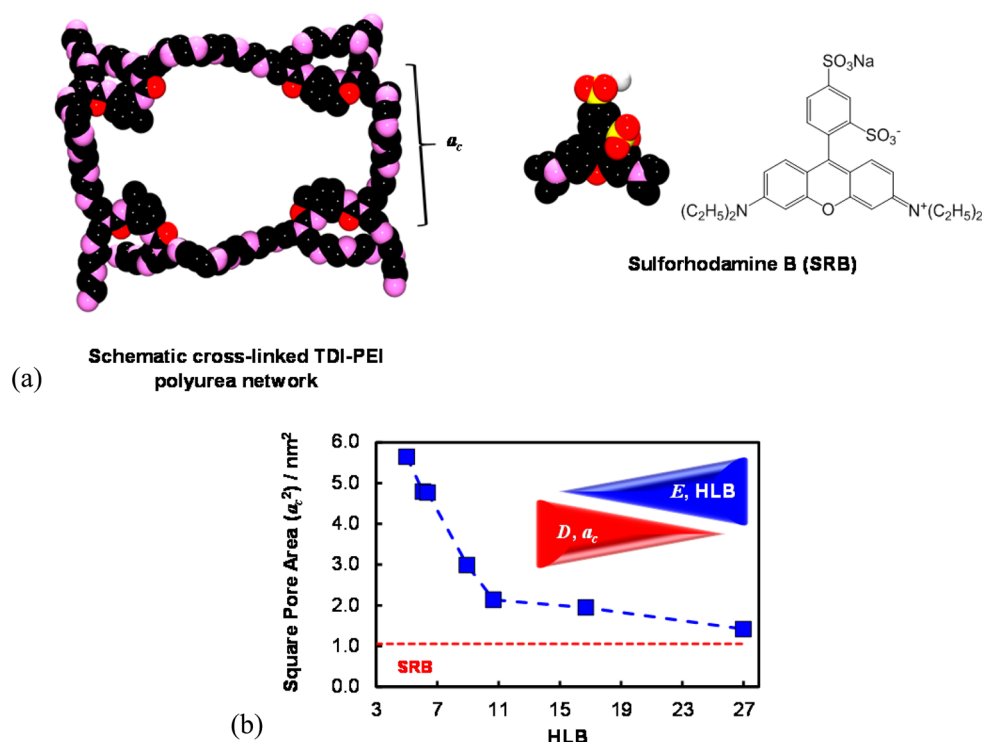


Figure 6. (a) Schematic of a square-shaped pore in the cross-linked TDI-PEI polyurea network with side length a_c as well as calotte model of the fluorescent dye Sulforhodamine B (SRB) used in the release studies. (b) Estimated square-shaped pore areas in nm^2 from cross-linking density data is given in the Supporting Information (Figure S3) as a function of the HLB. Length scales are determined from energy minimized molecular modellings using MMFF94.

bilayers, which was shown to depend on the rigidity of the membrane.⁴⁸ These results show, in addition, how surfactant can be used to tune the properties of capsules formed in microfluidics and might provide guidelines to optimize batch processes.

Interestingly, despite the apparent increase of the shell porosity visible in the SEM and TEM image (Figure 2), the permeability of the capsule is lower for the shell synthesized

with the surfactant (see Figure 4 for “Span 20” and no “surfactant”). This result indicates that the nanostructure of the shell is controlling the permeability. To further address this point, in a final set of experiments, we produced libraries of particles using other surfactants in order to show that the surfactant systematically affects the properties of the capsules. We used Brij L4, Brij 52, Tween 20, Synperonic F108, and Span 20 (see Supporting Information) to produce T capsules

and P capsules. An established quantity to classify surfactants in terms of its chemical structures and the emulsion stabilization characteristics is the HLB.^{49–51} The HLB value is a measure of the ratio between the hydrophilic and the lipophilic part of the molecule. Young's moduli are measured using the more stable capsules (P). Using the osmotic-driven inflation, we measure the Young's moduli of all particles and show a correlation between the HLB of the surfactant and the elasticity of the shell (Figure 5a,b) using the P capsules. With increasing HLB value (increasing hydrophilicity) of the surfactant, the elastic modulus of the polyurea shell increases (shell thickness 80 ± 10 nm); E values range almost by a factor of 10 (0.67 ± 0.1 – 4.47 ± 0.9 kN·mm^{−2}). The increase of the polyurea elastic modulus E is equivalent to an increase in the cross-linking density, which is commonly expressed by the average molecular weight M_c [g/mol] between two knots in the network. An estimation applying the modified Mooney–Rivlin model^{52–56} is shown in the Supporting Information section (Figure S6, S7). We calculate cross-linking densities M_c ranging between 135–272 g/mol. Thus, the bigger the hydrophilic part of the surfactant is at the interfacial polymerization, the denser and stiffer is the polyurea. The behavior can be explained by a stronger association of the surfactant onto the hydrophilic PEI/TDI network.

Using the dye release experiment, we measure the diffusion through the shell for the T capsules. We again find a correlation between the HLB and the time scale of release (Figure 4): We find that the membrane diffusion coefficients D_m (eq 4) for the surfactant-templated PUMCs follow the trend Synperonic F108 (1.85×10^{-18} cm²·s^{−1}) > Span 20 (2.02×10^{-18} cm²·s^{−1}) > Abil Em 90 (2.27×10^{-18} cm²·s^{−1}) > no surfactant (3.06×10^{-18} cm²·s^{−1}), which reflects the fact that with increasing HLB values, denser PUMCs are generated. The transport through the shell is decreasing when the typical pore size of the cross-linked network reaches the size of the molecule to be transported.

In summary, we studied the effect of surfactant on the on-chip preparation of microcapsules based on polyurea. We show that both the mechanical and permeation properties are affected by surfactant additives. The encapsulation process on the molecular scale proceeds in a template manner, and our results show that a variation of the HLB of the surfactant used during the polyurea microencapsulation can be used to fine-tune the physical properties of the capsules. Figure 6 summarizes the results described in this work: the morphology and the mechanical properties of polyurea microcapsules at the surfactant-templated generation in microfluidic devices are highly dependent from the surfactant type used for the emulsification. We find that with increasing HLB, the elastic modulus of the polymer film increases, whereas in the same order, the mesh size decreases; denser materials result with decreased permeability properties. Our results provide an easy path for the fabrication of microcapsules with controllable shell properties.

CONCLUSION

We describe the impact of the surfactant on the polyurea microcapsule shell morphology, elastic and permeability properties. PUMCs are generated using microfluidic PDMS devices to ensure constant particle parameters at narrow size distribution of the particles in a reproducible and reliable manner. The formation of a certain sponge-like fine-structures on the PUMC shell morphology is caused by the surfactant; we

evidently show the surfactant to be embedded into the polymer film. The elastic modulus E of the polyurea varies in a range between 0.6 and 4.5 kN·mm^{−2}; stiffer shells result with increasing HLB of the surfactant that is used for the PUMC generation. In a comparable order, the membrane permeability, elucidated by the diffusivity of the fluorescent dye sulforhodamine B, decreases, which confirms the fact that denser shells are created with increasing HLB. The results reveal a facile route for the generation of polyurea microcapsules with controlled stiffness and release properties.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in the text, including SEM micrographs, design schematics, logarithmic plots of fluorescence intensity, and additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS:

PUMC polyurea microcapsule; W/O water-in-oil; TDI 2,4-toluene diisocyanate; PEI polyethylenimine; TEPA tetraethylenepentamine; HLB hydrophilic–lipophilic balance; P PUMCs prepared using the combination PEI/TDI; T PUMCs prepared using TEPA/TDI; SRB sulforhodamine B; SDS sodium dodecyl sulfate; PDMS poly(dimethylsiloxane); D dispersed fluid; CF1 continuous fluid for emulsification; CF2 continuous fluid for encapsulation

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