Expansion and rupture of pH-responsive microcapsules†

Sujit S. Datta,a‡ Alireza Abbaspourrad,a‡ and David A. Weitz*a

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 20XX
DOI: 10.1039/b000000x

We study the deformations of pH-responsive spherical microcapsules – micrometer-scale liquid drops surrounded by thin, solid shells – under the influence of electrostatic forces. When exposed to a large concentration of NaOH, the microcapsules become highly charged, and expand isotropically. We find that the extent of this expansion can be understood by coupling electrostatics with shell theory; moreover, the expansion dynamics is well described by Darcy’s law for fluid flow through the microcapsule shell. Unexpectedly, however, below a threshold NaOH concentration, the microcapsules begin to disintegrate, and eventually rupture; they then expand non-uniformly, ultimately forming large, jellyfish-like structures. Our results highlight the fascinating range of behaviors exhibited by pH-responsive microcapsules, driven by the interplay between electrostatic and mechanical forces.

Microcapsules – micrometer-scale liquid drops, each surrounded by a thin, solid shell – are promising candidates for the encapsulation and controlled release of many technologically important active materials. These applications often require microcapsules to have unique mechanical properties, such as the ability to withstand large deformations. One common way of characterizing this behavior is to monitor how a microcapsule responds to forces exerted on its shell. These can be mechanical forces, externally imposed by poking, squeezing, or uniformly pressurizing the microcapsule. Alternatively, these forces can be generated by physico-chemical modifications to the shell itself, such as changing it; under certain conditions, the repulsion between the charges on the shell can cause it to deform. Electrostatic forces arise in many applications of soft matter, and consequently, this approach is frequently used to induce deformations in a variety of bulk materials. Nevertheless, systematic investigations of how electrostatic forces deform microcapsules are scarce. Thus, despite their prevalence in many real-world situations, a full understanding of how these forces affect microcapsules is lacking.

In this Communication, we study the deformations of spherical microcapsules exposed to a pH stimulus. We choose NaOH as the stimulus; when exposed to this base, the microcapsule shells become highly charged. For large NaOH concentrations, the microcapsules expand isotropically. We find that the extent of the microcapsule expansion can be understood by coupling electrostatics with shell theory; moreover, the dynamics of this expansion is well described by Darcy’s law for flow through the porous microcapsule shell. Surprisingly, below a threshold NaOH concentration, the microcapsules begin to disintegrate, and eventually rupture; they then expand non-uniformly, ultimately forming large, jellyfish-like structures. Our results thus highlight the rich behavior exhibited by microcapsules, driven by the interplay between electrostatic and mechanical forces.

We fabricate monodisperse thin-shelled microcapsules using water-in-oil-in-water (W/O/W) double emulsion templates prepared by microfluidics. The inner and outer phases are 6 wt % and 10 wt % solutions of polyvinyl alcohol (PVA), respectively, while the middle oil phase is a mixture of a pH-responsive polymer, suspended in tetrahydrofuran (THF), and another photo-polymerizable pH-unresponsive monomer. We use UV light to polymerize the pH-unresponsive monomer in situ, immediately as the double emulsions are generated, forming a highly cross-linked network around the inner core. This network is a solid characterized by a Young’s modulus of approximately 600 MPa; it is impermeable to hydrated Na+ and OH− ions, but is permeable to water. We then collect the microcapsules in water adjusted to have pH = 6, and let the THF evaporate; this forces the pH-responsive polymer to precipitate, completing the formation of a solid, hybrid shell, schematized in Figure 1(a). We then remove the supernatant, and repeatedly wash the microcapsules with pure water, to remove any surfactant from the continuous phase.

When exposed to NaOH, the pH-responsive polymer chains at the microcapsule exteriors become highly charged and repel each other; this repulsion is screened by any residual Na+ or OH− ions. To probe the microcapsule deformations under these conditions, we immerse them in an aqueous solution with cNaOH = 500 mM, and monitor them using optical
microscopy. Strikingly, the hybrid microcapsules quickly become opaque, reflecting the development of heterogeneities in the shell, and abruptly expand in irregular shapes; representative optical micrographs of this process are shown in Figure 1(b) and Movie S1. The microcapsules ultimately expand into spheres, as shown by the last frame of Figure 1(b); this entire process occurs over a timescale of ~10 s.

We quantify this behavior by measuring the maximal expansion, \( \gamma \equiv (R_f - R_0)/R_0 \), where \( R_0 \) and \( R_f \) are the average initial and final microcapsule radii, respectively. We also measure the average time taken for the microcapsules to expand into their final spherical shapes, \( \tau \). To elucidate the expansion behavior, we explore even lower values of \( c_{NaOH} \). Intriguingly, \( \gamma \) increases strongly with decreasing \( c_{NaOH} \), as shown in the upper panel of Figure 2, reaching a value exceeding 1 at \( c_{NaOH} = 25 \text{ mM} \); the expansion time \( \tau \) concomitantly increases, but only weakly, as shown by the grey squares in the lower panel of Figure 2. Unexpectedly, at \( c_{NaOH} = 25 \text{ mM} \), the microcapsules also begin to disintegrate, forming fragments of size ~1 \( \mu \text{m} \), as indicated by the arrows in Figure 1(c). At even smaller \( c_{NaOH} \), the microcapsules first disintegrate, as shown by the first frame of Figure 1(d); this ultimately results in the formation of a hole in each shell after a time delay \( \tau_1 \sim 10 - 100 \text{ s} \). The microcapsules then begin to intermittently expand outward, starting at the hole perimeters, as exemplified by the last three frames of Figure 1(d) and Movie S2; the region of the shell that expands is indicated by the arrow in each frame. This process occurs over a time period \( \tau_2 \sim 10 - 100 \text{ s} \); the expansion then stops, leaving wrinkled jellyfish-like structures, approximately 300 \( \mu \text{m} \) in size, as shown in Movie S2.

The isotropic expansion at high \( c_{NaOH} \geq 25 \text{ mM} \) is due to the charging of the microcapsule shells; when exposed to NaOH, the pH-responsive polymers at the microcapsule exteriors become highly charged, leading to a surface charge density \( \sigma \). We thus expect that the repulsion between the charges on each spherically-symmetric shell leads to a force, directed radially outward, on the shell. We estimate the magnitude of the resultant electrostatic pressure as \( p_e \approx \sigma^2 \kappa^{-1} \varepsilon \varepsilon_0 R \), where \( \varepsilon \approx 80 \) is the dielectric constant of water, \( \varepsilon_0 \) is the permittivity of free space, \( R \) is the time-dependent radius of the spherical microcapsule, \( \kappa^{-1} \) is the length over which the repulsive interactions are screened. The quantity of NaOH required to fully charge the shell is small, consequently, the excess Na\(^+\) and OH\(^-\) ions, which screen the surface charges on the shell, have a concentration \( \approx c_{NaOH} \), and thus \( \kappa^{-1} = A/\sqrt{c_{NaOH}} \), with \( A \approx 0.304 \text{ nm} \cdot \text{M}^{1/2} \). As the microcapsule expands isotropically, a tensile stress builds up within its shell; this resists the expansion. We use shell theory to estimate this stress, \( p_m = Eh(1/R_0 - 1/R) \), where
results suggest that the microcapsule expansion can be understood using Darcy’s law. We estimate this inflow rate using Darcy’s law, $p_e - p_m = \mu R/3k$, where $\mu \approx 1$ mPa·s is the viscosity of water and $k$ is the shell permeability; this yields a characteristic expansion time $\tau = \mu R^2/(1 + 1/E)$. We use our measurements of $\tau$, as well as the fit to the measurements of $\gamma$ shown in the top panel of Figure 2, to directly test this prediction. We find excellent agreement between the data and the theoretical prediction, as shown by the solid line in the bottom panel of Figure 2; fitting the experimental data yields a shell permeability $k \approx 10^{-21}$ m$^2$. The agreement between the data and the theoretical prediction thus suggests that the dynamics of the microcapsule expansion can be understood using Darcy’s law.

As $c_{NaOH}$ decreases, the screening length $\kappa^{-1}$ increases; consequently, the stress in the microcapsule shell increases, ultimately reaching $p_m = p_e \approx 10$ MPa at $c_{NaOH} = 25$ mM. For even smaller $c_{NaOH}$, the microcapsules begin to disintegrate into $\sim 1$ μm fragments, and eventually rupture. We hypothesize that, under these conditions, the stress that builds up in the shell exceeds the stress required to fracture it. To test this hypothesis, we estimate the fracture stress using the Griffith criterion, $\sqrt{2EGc/\pi a} \approx 6 - 20$ MPa, where $G_c \sim 0.1 - 1$ J/m$^2$ is the surface energy per unit area of the shell material and $a \approx 1$ μm is the characteristic size of a shell fragment, measured using optical microscopy. Interestingly, this value is in good agreement with our estimate of the maximal stress that develops in the shell, $p_m \approx 10$ MPa, suggesting that the observed disintegration at $c_{NaOH} \leq 25$ mM reflects the fracturing of the microcapsule shell.

Finally, we monitor the dynamics of the disintegration, rupture, and subsequent expansion of the microcapsule shell that occurs at $c_{NaOH} < 25$ mM. Intriguingly, both the time period over which the shell fractures before a hole forms in it, $\tau_1$, and the time period over which the shell subsequently expands into a jellyfish-like structure, $\tau_2$, both increase with decreasing $c_{NaOH}$, as shown by the blue triangles and red circles in Figure 2, respectively. A complete understanding of these dynamics remains a puzzle requiring further inquiry.

Our work highlights the fascinating range of structures exhibited by pH-responsive microcapsules, driven by the interplay between electrostatic and mechanical forces. Intriguingly, many of the morphologies we observe are reminiscent of structures, also induced by electrostatic effects, that often
occur in other soft matter systems, such as viruses\textsuperscript{16,20,21} and red blood cells\textsuperscript{22}.

It is a pleasure to acknowledge Esther Amstad, Michael Brenner, Alberto Fernandez-Nieves, Rodrigo Guerra, and Zhigang Suo for stimulating discussions. This work was supported by the NSF (DMR-1006546) and the Harvard MRSEC (DMR-0820484). SSD acknowledges funding from ConocoPhillips. AA acknowledges Evonik Industries for generously donating the Eudragit S-100 polymer used.

References

1 S. S. Datta, A. Abbaspourrad, E. Amstad, J. Fang, S. H. Kim, M. Romanowsky, H. C. Shum, B. J. Sun, A. S. Utada, M. Windbergs, S. Zhu and D. A. Weitz, \textit{in preparation}, 2013.
2 V. D. Gordon, X. Chen, J. W. Hutchinson, A. R. Bausch, M. Marquez and D. A. Weitz, \textit{J. Am. Chem. Soc.}, 2004, \textbf{126}, 14117.
3 H. M. Wyss, T. Franke, E. Mele and D. A. Weitz, \textit{Soft Matter}, 2010, \textbf{6}, 4550.
4 A. Fery, F. Dubreuil and H. Mohwald, \textit{New J. Phys.}, 2004, \textbf{6}, 18.
5 S. S. Datta, S. H. Kim, J. Paulose, A. Abbaspourrad, D. R. Nelson and D. A. Weitz, \textit{Phys. Rev. Lett.}, 2012, \textbf{109}, 134302.
6 W. T. S. Huck, \textit{Materials Today}, 2008, \textbf{11}, 24.
7 Z. Suo, \textit{MRS Bull.}, 2012, \textbf{37}, 218.
8 B. G. D. Geest, S. D. Koker, J. Demeester, S. C. D. Smedt and W. E. Hennink, \textit{Polym. Chem.}, 2010, \textbf{1}, 137.
9 B.-S. Kim and O. I. Vinogradova, \textit{J. Phys. Chem. B}, 2004, \textbf{108}, 8161.
10 K. Kohler, P. M. Biesheuvel, R. Weinikamer, H. Mohwald and G. B. Sukhorukov, \textit{Phys. Rev. Lett.}, 2006, \textbf{97}, 188301.
11 A. S. Utada, E. Lorenceau, D. R. Link, P. D. Kaplan, H. A. Stone and D. A. Weitz, \textit{Science}, 2005, \textbf{308}, 537.
12 Further details are available in the Electronic Supplementary Information online.
13 T. H. Lin, W. H. Huang, I. K. Jun and P. Jiang, \textit{Chem. Mater.}, 2009, \textbf{21}, 2039.
14 S. H. Kim, S. J. Jeon and S. M. Yang, \textit{J. Am. Chem. Soc.}, 2008, \textbf{130}, 6040.
15 A. Abbaspourrad, S. S. Datta and D. A. Weitz, \textit{submitted}, 2013.
16 A. Siber and R. Podgornik, \textit{Phys. Rev. E}, 2007, \textbf{76}, 061906.
17 J. N. Israelachvili, \textit{Intermolecular and surface forces}, Academic Press, 2011.
18 L. D. Landau and E. M. Lifshitz, \textit{Theory of Elasticity}, Elsevier, 3rd edn, 1986.
19 T. L. Anderson, \textit{Fracture Mechanics: Fundamentals and Applications}, CRC Press, 3rd edn, 2004.
20 W. K. Kegel and P. van der Schoot, \textit{Biophys. J.}, 2004, \textbf{86}, 3905.
21 A. L. Bozic, A. Siber and R. Podgornik, \textit{Phys. Rev. E}, 2011, \textbf{83}, 041916.
22 M. D. Betterton and M. P. Brenner, \textit{Phys. Rev. Lett.}, 1999, \textbf{82}, 1598.