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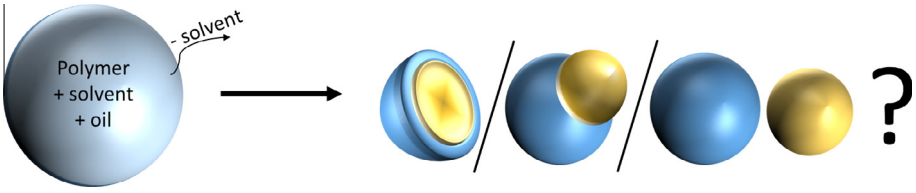
Regular Article

The effect of surfactant chain length on the morphology of poly(methyl methacrylate) microcapsules for fragrance oil encapsulation

Alison Louise Tasker [a,b,*], James Paul Hitchcock [b], Ling He [b], Elaine Alice Baxter [c], Simon Biggs [a], Olivier Jean Cayre [b]

[a] Faculty of Engineering, Architecture and Information Technology, University of Queensland, St Lucia, Queensland 4072, Australia
[b] School of Chemical and Process Engineering, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, United Kingdom
[c] Procter & Gamble, London Innovation Centre, Rusham Park, Whitehall Ln, Egham TW20 9NW, United Kingdom

GRAPHICAL ABSTRACT



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ABSTRACT

The solvent evaporation method for producing microcapsules relies upon the correct wetting conditions between the three phases involved in the synthesis to allow core-shell morphologies to form. By measuring the interfacial tensions between the oil, polymer and aqueous phases, spreading coefficients can be calculated, allowing the capsule morphology to be predicted. In this work we explore the effect of surfactant chain length on capsule morphology using poly(methyl methacrylate) as the polymer and hexadecane as the core. We compared the predicted morphologies obtained using the polymer as a solid, and the polymer dissolved in dichloromethane to represent the point at which capsule formation begins. We found that using the polymer in its final, solid form gave predictions which were more consistent with our observations. The method was applied to successfully predict the capsule morphologies obtained when commercial fragrance oils were encapsulated.

1. Introduction

The manufacture of liquid core microcapsules is of considerable practical interest across a range of industries for the encapsulation of active ingredients including drugs [1], pesticides [2], flavours [3,4], enzymes [5] and fragrances [6]. In most cases, such microcapsules are designed to protect the actives from unfavourable external conditions and to control their subsequent release. There are various methods which can be used to create liquid core microcapsules [7]. For example interfacial polymerization can be used to create a polymer shell around an oil droplet dispersed in water (or the reverse system), by reacting monomers in the oil

Abbreviations: C_{12}TAB, dodecyltrimethylammonium bromide; C_{14}TAB, tetradecyltrimethylammonium bromide; C_{16}TAB, hexadecyltrimethylammonium bromide; C_{18}TAB, octadecyltrimethylammonium bromide; C_{10}DAB, didecyldimethylammonium bromide; C_{12}DAB, didodecyldimethylammonium bromide; CMC, critical micelle concentration; DCM, dichloromethane; PMAA, poly(methacrylic acid); PMMA, poly(methyl methacrylate); PVA, poly(vinyl alcohol); γ_{ow}, oil-water interfacial tension; γ_{pw}, polymer-water interfacial tension; γ_{op}, oil-polymer interfacial tension; S_x, spreading coefficient.

* Corresponding author at: Faculty of Engineering, Architecture and Information Technology, University of Queensland, St Lucia, Queensland 4072, Australia.
E-mail address: a.tasker@uq.edu.au (A.L. Tasker).

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phase with monomers in the aqueous phase [8]. Other methods lead to the production of colloidosomes [9–11], liposomes [12] and dendrimers [13], which have been used to encapsulate various active materials, such as pharmaceuticals [13–15], enzymes [12,16–19] and dyes [20–24].

Another method, which we will use in this work, involves the preparation of liquid core/polymer shell structures via a solvent extraction method, which induces a polymer to precipitate as a film (the shell) at the oil/water interface. In this method the core to be encapsulated (the encapsulate) and the polymer are initially dissolved in a highly volatile solvent and emulsified into a stabilizer solution. The volatile solvent is subsequently extracted from the emulsion droplets, resulting in the core material being encapsulated by the precipitated polymer shell [25–28]. Here, it is crucial that the solvent contained in the emulsion dispersed phase is a good, but highly volatile solvent for the polymer and that the encapsulate is a non-solvent for the polymer, so that precipitation is induced upon extraction of the solvent [26].

In this work, we initially use poly(methyl methacrylate) (PMMA) as the polymer forming the capsule shell, dichloromethane (DCM) as the good solvent, and hexadecane as the encapsulate. Subsequently, we exchange the hexadecane for various oils commonly used as fragrance oils in cosmetic and personal care products. The solution of polymer and encapsulate oil in DCM forms the core phase. The core phase is emulsified in an aqueous solution of a stabilizer, in our case a surfactant [26,29,30], but polymers [25,26,31–33] and particles [34] have also been successfully used. The resulting emulsion is diluted, allowing the DCM to evaporate slowly, creating polymer-rich droplets of DCM within the oil phase. It is believed that at this stage, the droplets are mobile and migrate to the oil-water interface, whereupon the remaining solvent leaves the core phase thus forcing the polymer to precipitate and to form a shell around the non-solvent core [25,29,35].

As depicted in Fig. 1, this process can lead to several possible morphologies in addition to the desired core-shell morphology where the polymer forms a complete shell around a single core. Alternative morphologies include acorns, where the polymer precipitates separately to the oil, occluded capsules, where the polymer precipitates around multiple cores or complete dissociation between the core and the shell.

The resulting capsule morphology is controlled by the balance of interfacial tensions for the three phases involved in the capsule formation and relates to the wetting conditions within the system. Torza and Mason studied the behaviour of systems where two immiscible liquid droplets were brought together in a third, mutually immiscible liquid [36]. By measuring the interfacial tensions between the three phases, they predicted the equilibrium morphology of the droplets from the resulting spreading coefficients. Eq. (1) shows, as an example, how the spreading coefficient is calculated.

$$S_3 = \gamma_{12} - (\gamma_{23} + \gamma_{13}) \quad (1)$$

where γ_{12} is the interfacial tension between phases 1 and 2. When phase 2 is the aqueous phase, as is usually the case [37], and phase 1 is taken to be that of highest interfacial tension with water (as compared to phase 3), it follows that there are only three possible combinations of spreading coefficients, as shown by Eqs. (2)–(4).

$$S_1 < 0,\ S_2 < 0,\ S_3 > 0 \quad (2)$$

$$S_1 < 0,\ S_2 < 0,\ S_3 < 0 \quad (3)$$

$$S_1 < 0,\ S_2 > 0,\ S_3 < 0 \quad (4)$$

For a core-shell morphology to successfully form, the polymer must be able to wet the oil in the aqueous phase preferentially (see Fig. 1). Several studies have considered the effect of these spreading coefficient combinations on capsule morphology [26,29,38–40]. Loxley and Vincent measured the interfacial tension between the oil phase and various aqueous phases using the DuNuoy ring method, and calculated the polymer-oil and polymer-aqueous phase interfacial tensions from contact angle measurements of oil and water droplets on dry films of the polymer forming the capsule shell [26]. Using this method they found that, for the range of stabilizers they tested, only the polymeric stabilizers were suitable to form core-shell morphologies. Feczkó et al. also used contact angle measurements to calculate the interfacial tension between the shell material and the other two phases and used pendant drop tensiometry to measure interfacial tensions between the liquid phases [38]. They found that this method accurately predicted the final capsule morphology obtained when using poly(methacrylic acid) (PMAA) as a stabilizer, but that the predictions failed for the other two stabilizers used, poly(vinyl alcohol) (PVA) and Tween 80. Pisani et al. also used pendant drop tensiometry to measure the interfacial tensions between the various phases [29]. However, they assumed the polymer phase would still be dissolved in the co-solvent at the time of migration to the oil-water interface, and that this was the critical point at which spreading occurs. Consequently, they measured the interfacial tension of polymer-DCM solutions rather than using a dry polymer film to perform contact angle measurements [26,38–40]. Using a selection of polymers and surfactants to stabilize their capsules, they found that Torza and Mason's spreading coefficient method did not accurately predict the final capsule morphology in two out of the three cases they investigated.

Initially in this work, we aim to ascertain whether it is possible to predict the morphology of capsules synthesized using a common cationic surfactant family, studying both the effect of the hydrocarbon chain length and the number of chains attached to the head group. We compare the ability of the prediction methods reviewed above by measuring the polymer–surfactant interfacial tension using either a dry polymer film or a polymer solution in DCM. The model systems investigated in this part of the work are based on a hexadecane core. The final objective of this work is to use the chosen prediction methodology to verify its ability to predict the morphology of structures obtained for a range of fragrance oils to

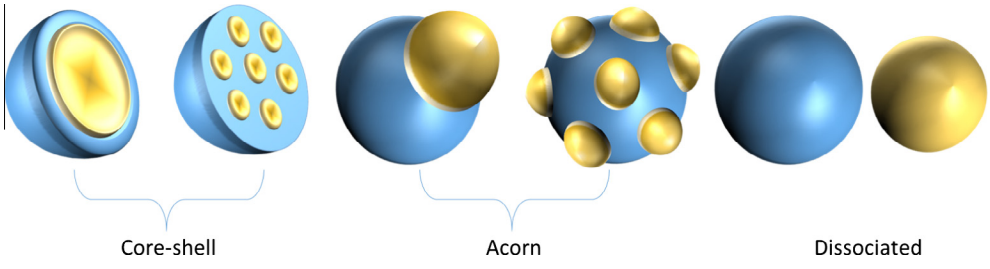

Fig. 1. Possible final microcapsule morphologies (post solvent-evaporation) dependent on spreading coefficients of the different phases. From left to right, core-shell morphologies result when Eq. (2) is satisfied, multi core-shell morphologies result when Eq. (2) is satisfied and $S_3 \gg 0$ and acorn morphologies result when Eq. (3) is satisfied, and dissociation results when Eq. (4) is satisfied.