# Core-shell microcapsules from clay-stabilised Pickering emulsions

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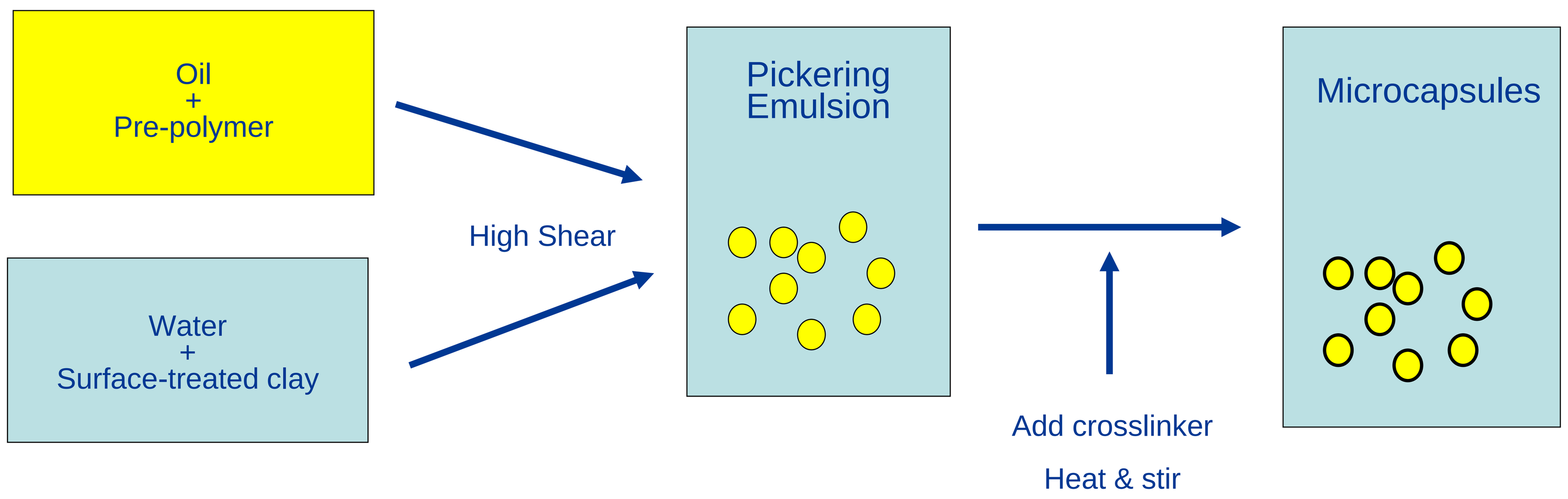
***Abstract***

Core-shell microcapsules are typically made by first preparing an emulsion and then forming a wall around the droplets by, for example, interfacial polymerisation, precipitation or coacervation. Conventionally, the emulsion is stabilised by surfactants or polymers. Alternatively, emulsions can be stabilised by fine particles – in this poster we discuss capsules made from ultrafine kaolin stabilised Pickering emulsions via interfacial polymerisation.
Using mineral particles as the emulsion stabiliser for encapsulation has a number of potential benefits. The droplet/capsule size can be controlled and varied simply by the dose of particles used, and Ostwald ripening is prevented. Particles become incorporated into the polymer shell of the capsule, potentially offering different mechanical properties and reduced permeability compared with pure polymers. The surface of such capsules is rough, allowing a powdered product to be made easily without adhesion of capsules to each other, and potentially giving improved entrapment in fabrics etc. The presence of mineral particles scatters light and offers some protection from photodegradation.



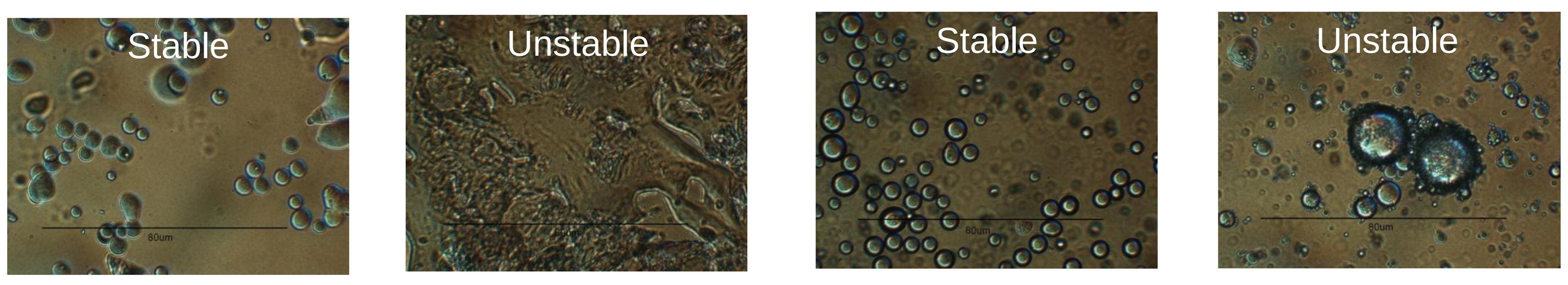

**Simple Pickering Emulsion Microencapsulation process**

The energy of attachment of a particle to an oil/water interface is maximised when the contact angle is 90° For a flat, disc-shaped particle it can be approximated by assuming that the effects of the edges are negligible

$$\Delta G = \pi r^2 \gamma_{ow}(1-\cos\Theta)$$ Energy to move flat particle from interface to oil phase

For a 0.1µm radius disc, $\Delta G_{max} \approx 4 \times 10^5$ *kT,* or ~ 2J/g. Particles lie flat, and do not spontaneously desorb through thermal motion. The emulsion is very stable. *For a surfactant, attachment energy ~ kT or ~ 10J/g.*

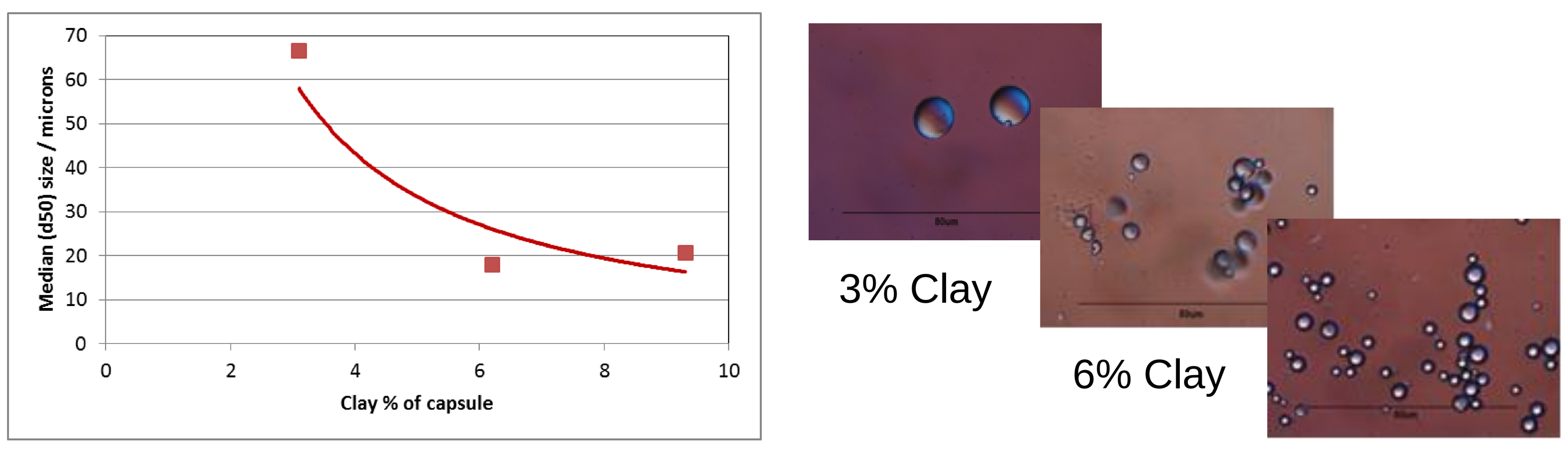
The contact angle of clay particles at the oil/water interface can be optimised by the surface treatment of the clay.



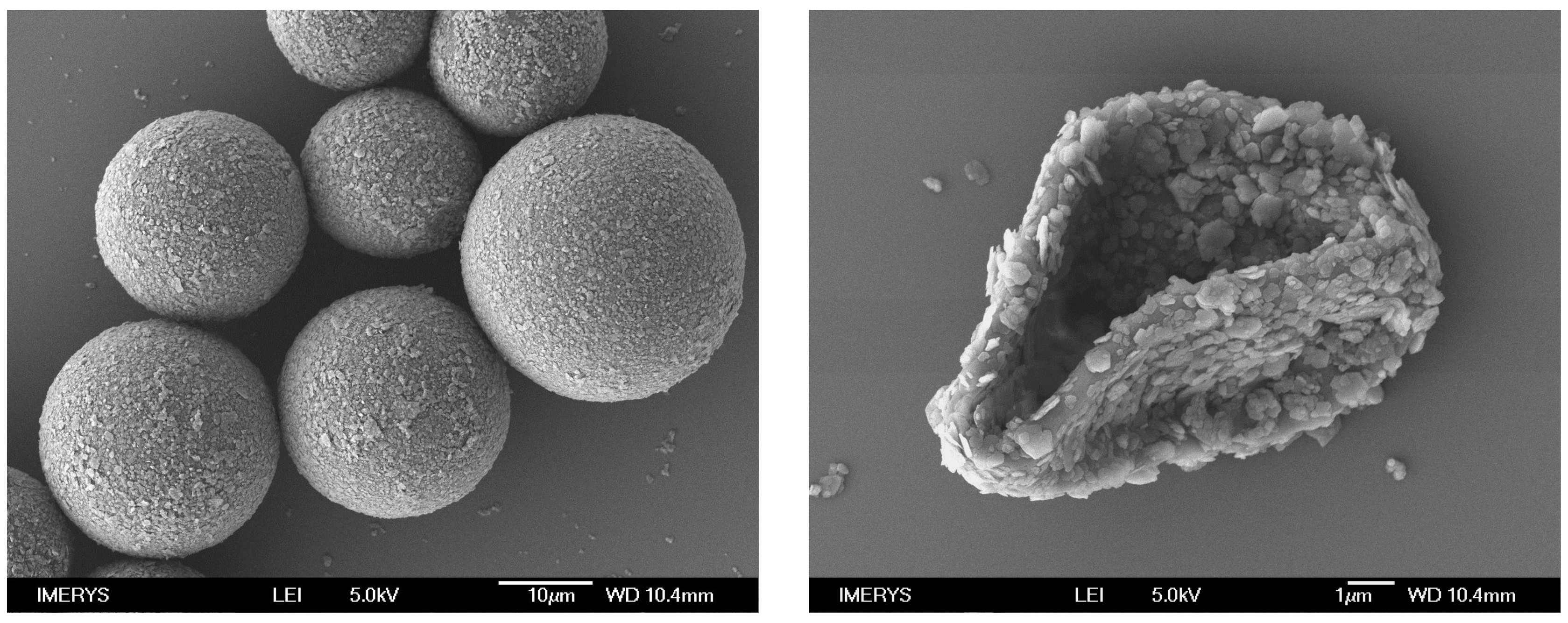

Low polarity oil / Low polarity surface — High polarity oil / Low polarity surface — High polarity oil / High polarity surface — Low polarity oil / High polarity surface

**Surface treatment of clay is tuned for maximum emulsion stability**

Because the attachment energy of the particles to the interface is so high, particles will occupy any free interface created. Emulsion droplet size can thus be controlled by the amount of particles added, provided enough initial shear is applied to create sufficient interface for them to occupy. The ratio of the droplet to the particle diameter must remain large in order to populate the interface with particles. For 0.5µm micron kaolin particles the limiting droplet size is around 15µm.




**Capsule size can be controlled by clay dosage**



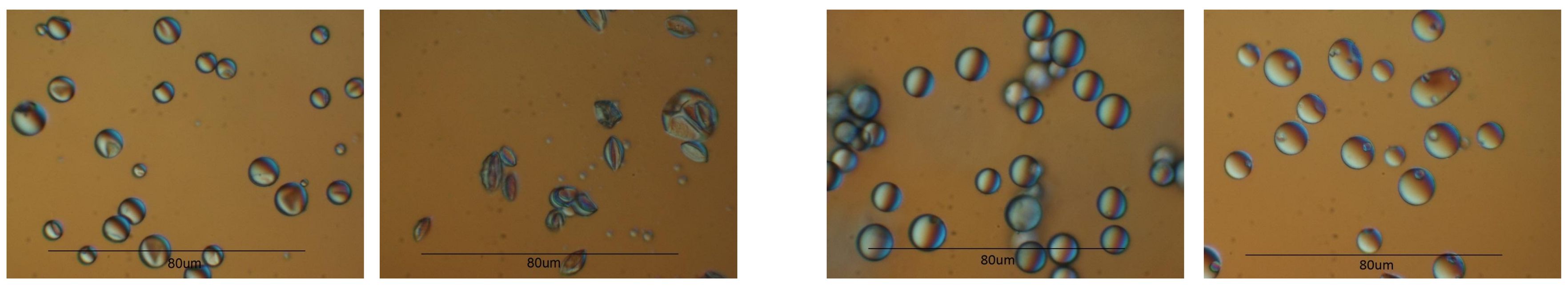
**Clay particles are embedded in the capsule walls**

The Pickering emulsion method enables the formation of capsules around oils covering a wide range of polarities and chemical types, which we have made with a variety of different coupling reactions.

| Polymer Type | Oil-soluble reactant | Water-soluble reactant |
|---|---|---|
| Polyurethane | Polyisocyanate | Polyol |
| Polyurea | Polyisocyanate | Polyamine or water |
| Epoxy | Low $M_w$ di- or tri-functional epoxide | Polyamine |
| Polyamide | Styrene-maleic anhydride copolymer | Polyamine |

**Reactant combinations that have been used to form Pickering microcapsules**

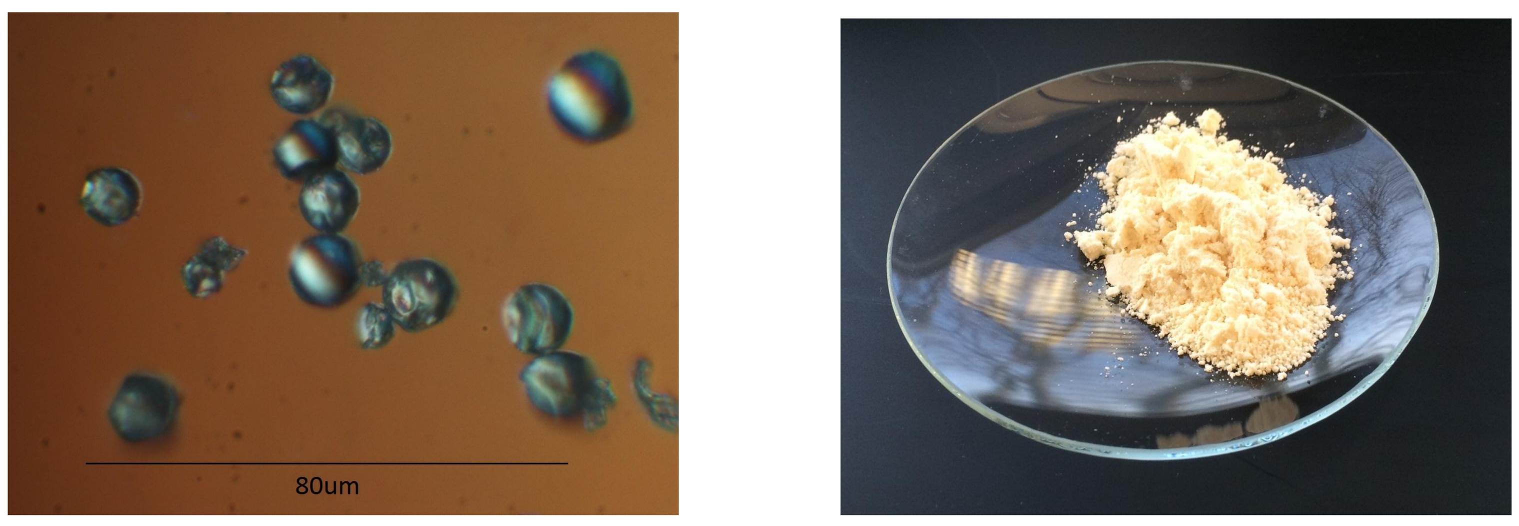
The choice of reactants strongly influences the barrier properties of the capsule wall; whilst most combinations will form core-shell capsules, in some cases the polymer is quite permeable to the encapsulated oil. With the right choice of polymer the capsules can be stable in solvents or surfactant solutions in which the oil is easily soluble. Alternatively, diffusive capsules can be made which will release their contents slowly according to the permeability of the shell



Permeable capsule in water — Permeable capsule in water/IPA — Impermeable capsule in water — Impermeable capsule in water/IPA

**Shell polymer chemistry controls capsule permeability**

The presence of clay particles at the surface of the droplets makes them rough, and resistant to coalescence or film-forming when dried. The capsules can thus be made into a free-flowing powder by thermal drying and gentle disaggregation on a vibrating screen.




Dried capsules in air — Powdered Capsules

**Capsules can be made into a free-flowing powder**

***Conclusions***

A range of industrially-relevant active ingredients of different polarity and composition can be encapsulated via interfacial polymerisation of a Pickering emulsion stabilised by surface-modified kaolin. The capsules are easy to form and may be impermeable or partially permeable to their contents depending upon the chemistry chosen for the capsule wall. The use of clay particles gives the capsules a range of novel and potentially useful attributes.

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