Core-Shell Particles

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This talk is dedicated to my former “2-i-c” (1995-2000) and good mate:

Dr Peter Dowding

Many congratulations on

Being Awarded the McBain Medal

and

Burnley’s promotion to the Premiership!!

Pete in “serious” mode ?

PROFESSOR BRIAN VINCENT'S

RESEARCH LABORATORIES

OPENED ON 21ST NOVEMBER 2002

BY

DR. PETER DOWDING

&

DR. ALEXANDER ROUTH

Pete in “relaxed” mode ?

BV Group shark-fishing trip, Cornwall, Summer 2000

Pete's "Shark"

And so to the science ….

Pete worked on 3 projects with me between 1995 & 2000:

1)Oil-water microemulsions (EPSRC + the Hull Group).

2) Porous polymer beads for drug delivery (EU + Jim Goodwin + Pharmacia & several other industrial partners).

3)Oil Core – Polymer Shell Particles (Zeneca)

CORE – SHELL PARTICLES

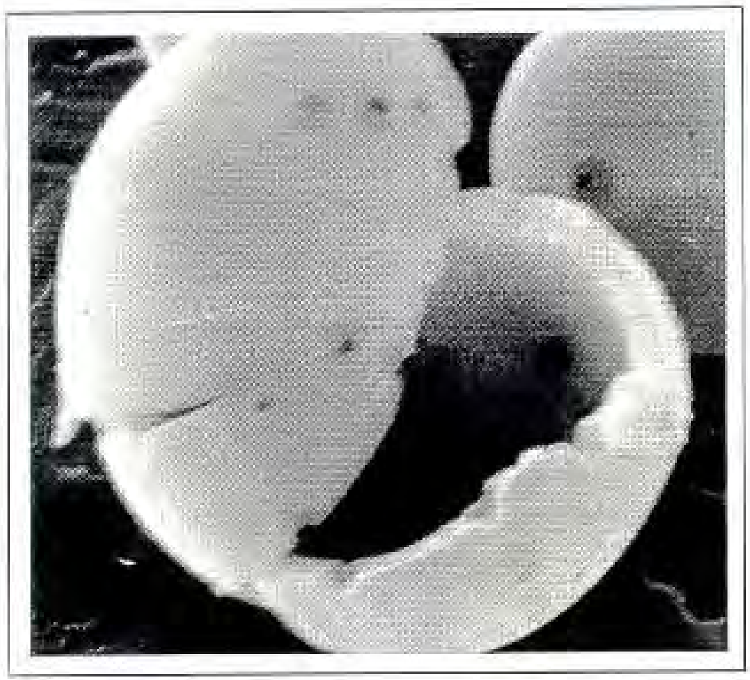
(An overview of some of the BV Group work in this area)

Firstly, many thanks to my co-workers and our sponsors:

Dr Andrew Loxley	EPSRC
Dr Mike Goller	EPSRC
Dr Peter Dowding	Zeneca
Dr Philippe Bouillot	Zeneca
Dr Rob Atkin	P&G + EPSRC
Dr Mike O'Sullivan	Schlumberger

An early example of what we were aiming for:

(Broken) Liquid Core / Solid Shell Particle *



*** Hexadecane core / PMMA shell:**

Loxley & Vincent, J. Colloid Interface Sci, 1998 208 49-62

CORE / SHELL PARTICLES

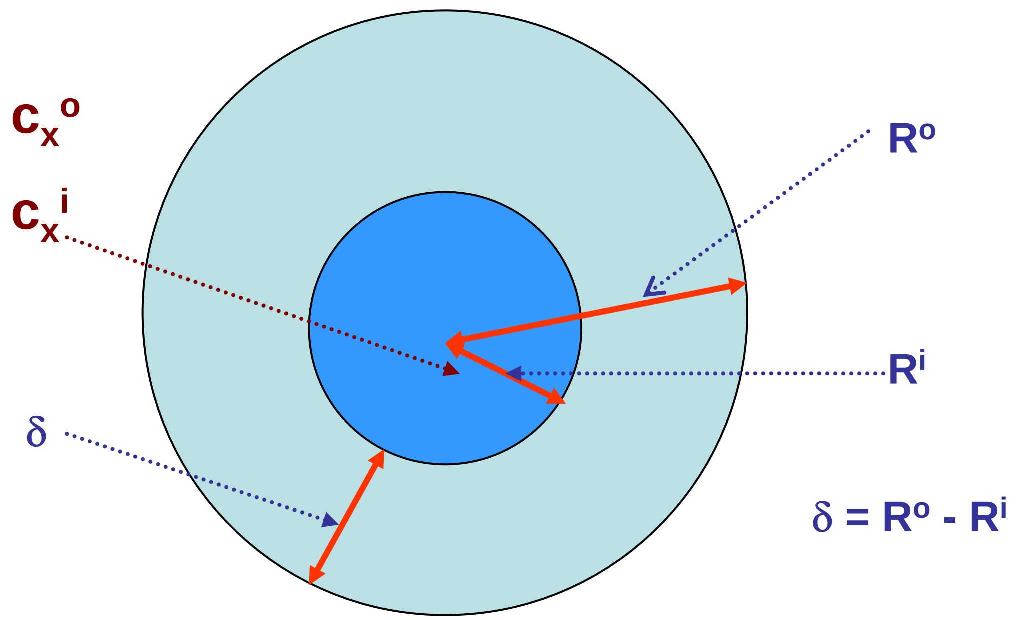
give:

(1) ***protection*** **and/or**

(2) ***controlled release*** **of some active ingredient (A.I.), e.g.**

- **agrochemical (pesticides, herbicides, fungicides, fertilizers, plant growth promoters, insect pheromones).**
- **pharmaceutical (targeted drugs)**
- **food additives (e.g. flavourings)**
- **laundry products (perfumes, sequesterants, bleaches, enzymes, buffers)**
- **dyes and pigments**
- **flocculating / gelling agents**

CORE / SHELL PARTICLES



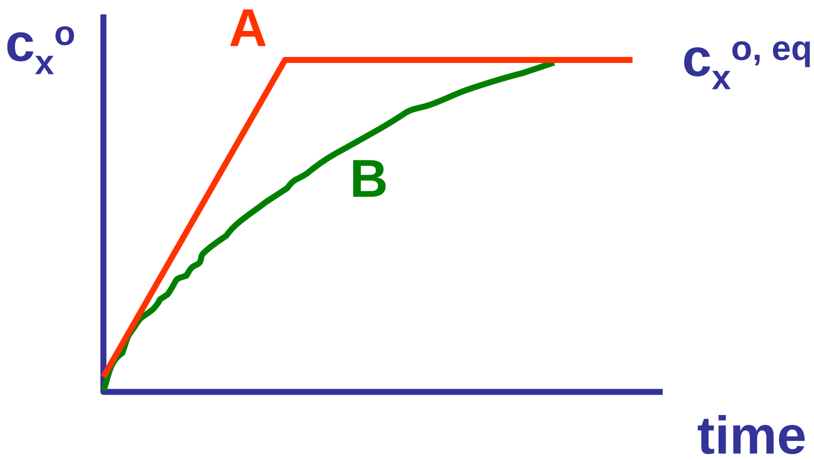
Permeability [P] of the shell depends on:

(1) porosity of the shell

(2) solubility of X in the shell

(3) diffusion coefficient of X in the shell

STANDARD RELEASE PROFILES

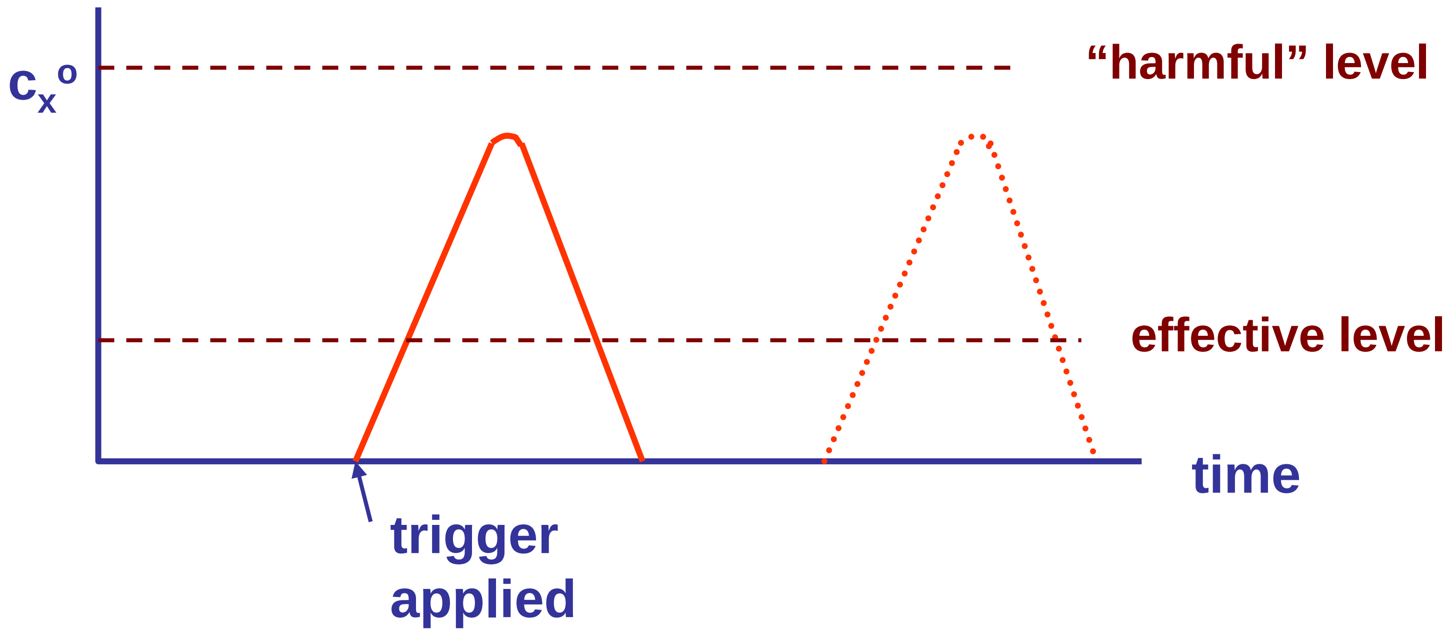


A = ***zeroth*** **order :** ***constant*** **release rate (X is solid or in saturated solution)**

B = ***first*** **order:**

$$\frac{dc_x^0}{dt} = \frac{4\pi R^o R^i P\left(c_x^0 - c_x^i\right)}{\delta}$$

TRIGGERED RELEASE PROFILE



note **: now *consumption* of X is occurring, as well as release.**

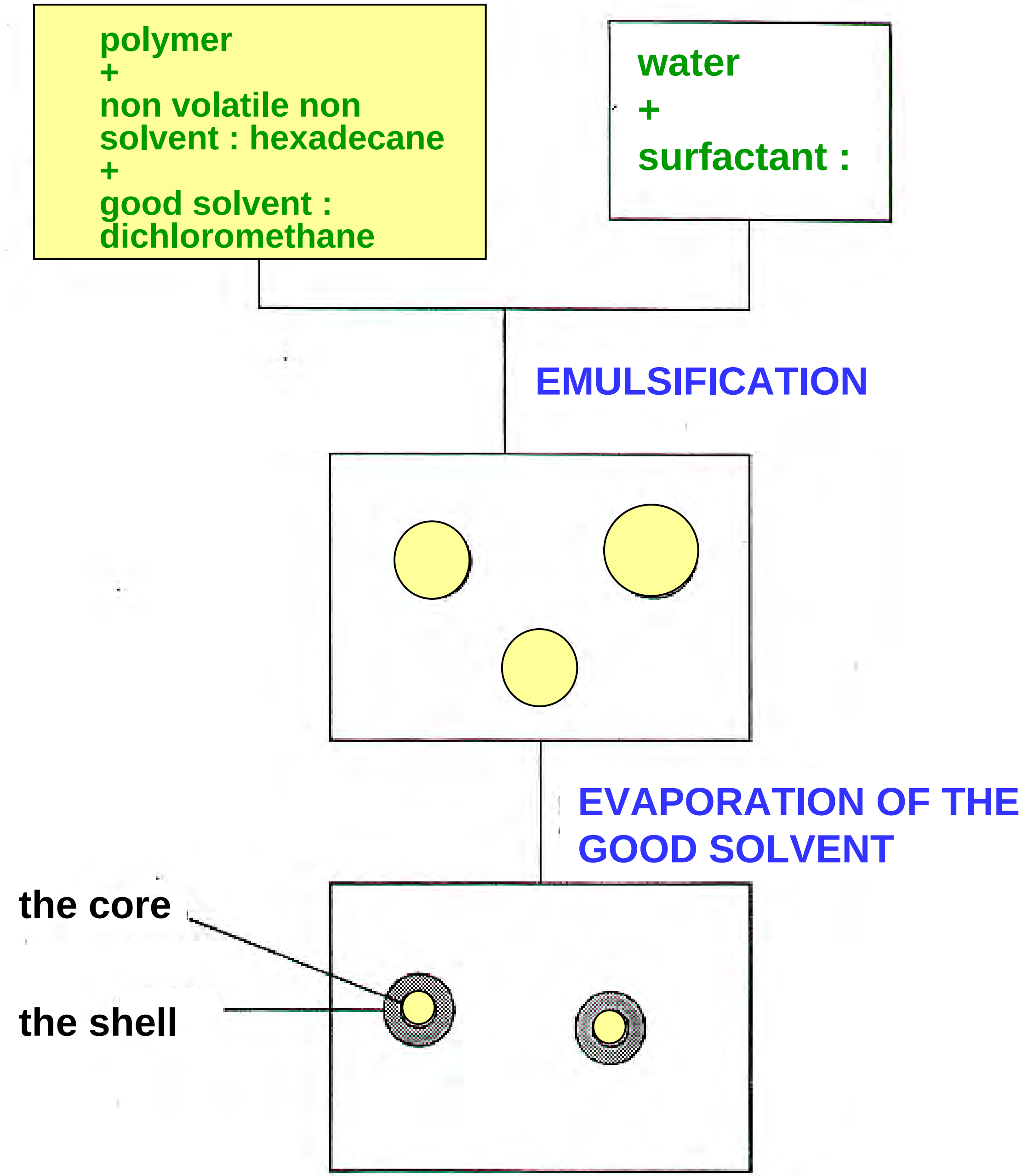
triggers:

- **dissolution of the shell (e.g. polylactides)**
- **swelling of the shell (e.g. ΔT, ΔpH, ΔI)**
- **osmotic swelling of core (e.g. ΔI)**
- **mechanical (e.g. applied pressure, vigorous agitation)**
- **light**

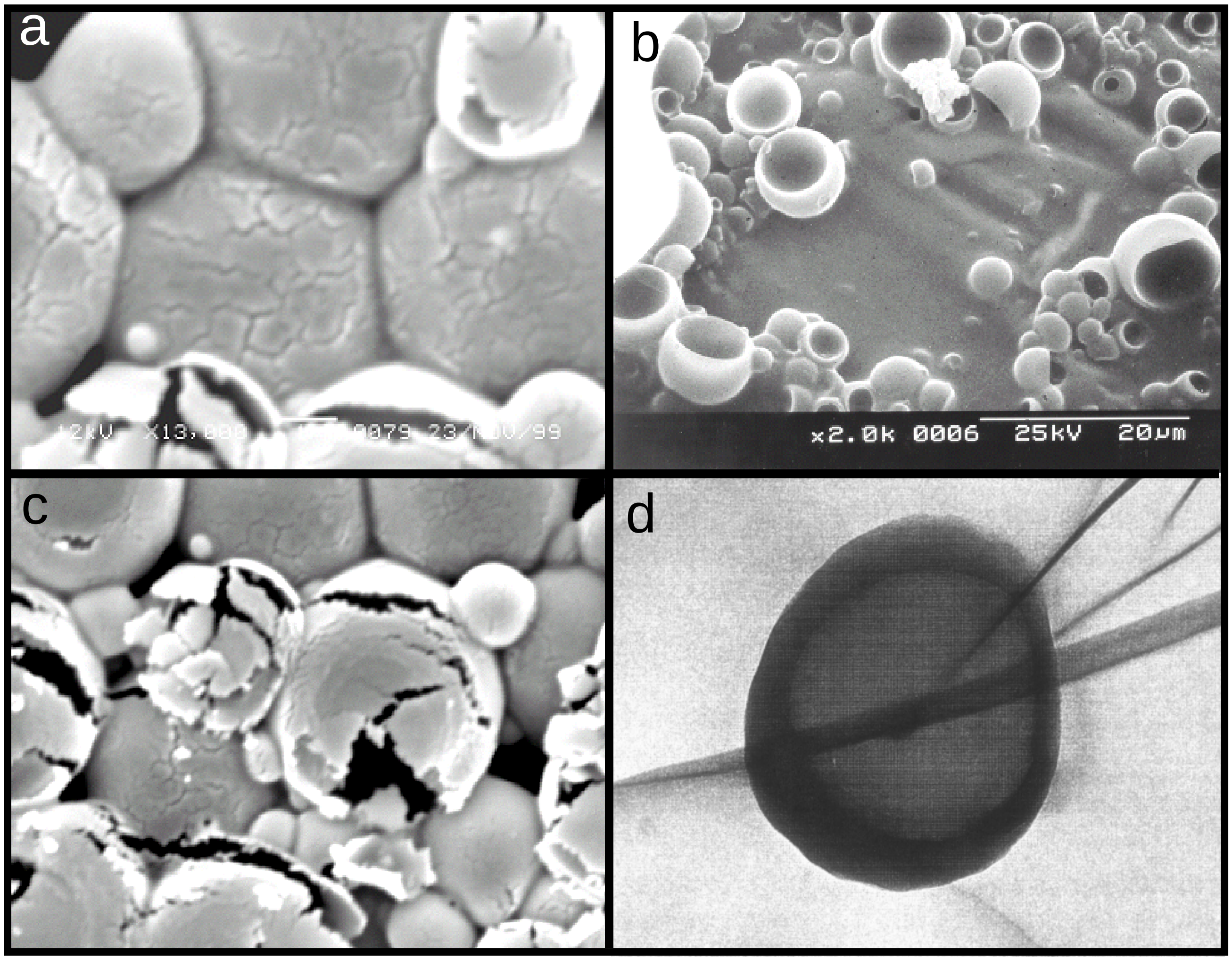
OIL CORE / POLYMER SHELL PARTICLES

Loxley & Vincent, J. Colloid Interface Sci, 1998 208 49-62

Process

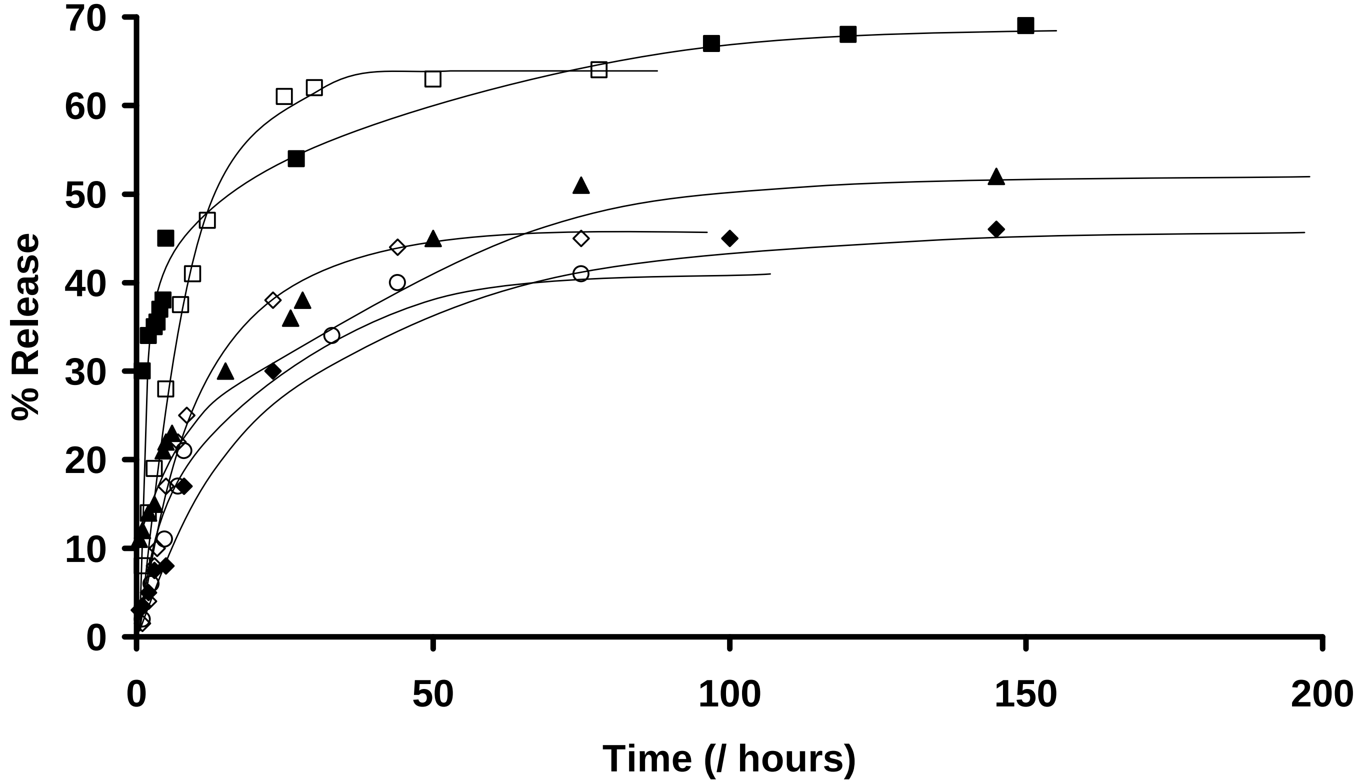

polymer
+
non volatile non solvent : hexadecane
+
good solvent : dichloromethane
water
+
surfactant :
EMULSIFICATION
EVAPORATION OF THE GOOD SOLVENT
the core
the shell

Polystyrene Capsules



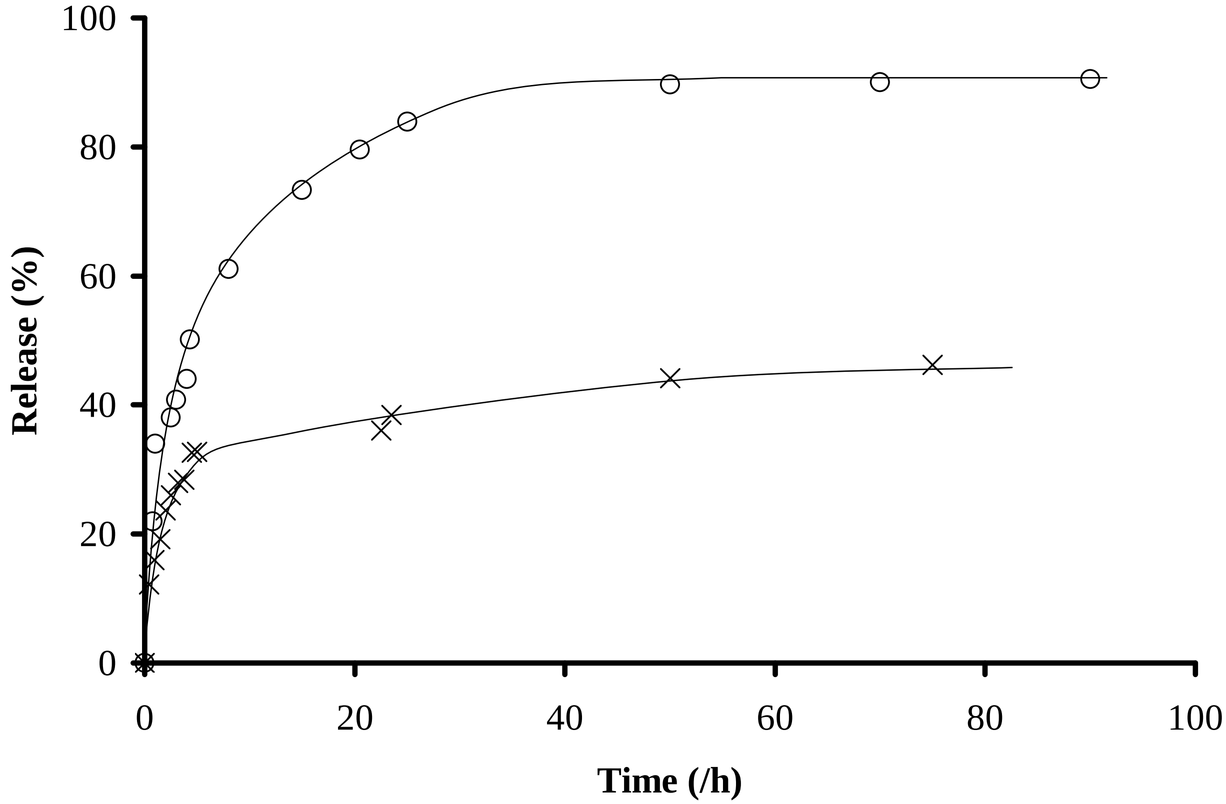
Dowding, Atkin, Vincent & Bouillot, Langmuir, 2004 <u>20</u> 11374 & 2005 <u>21</u> 5278

Effect of variation the thickness (polymer mass) of the shell



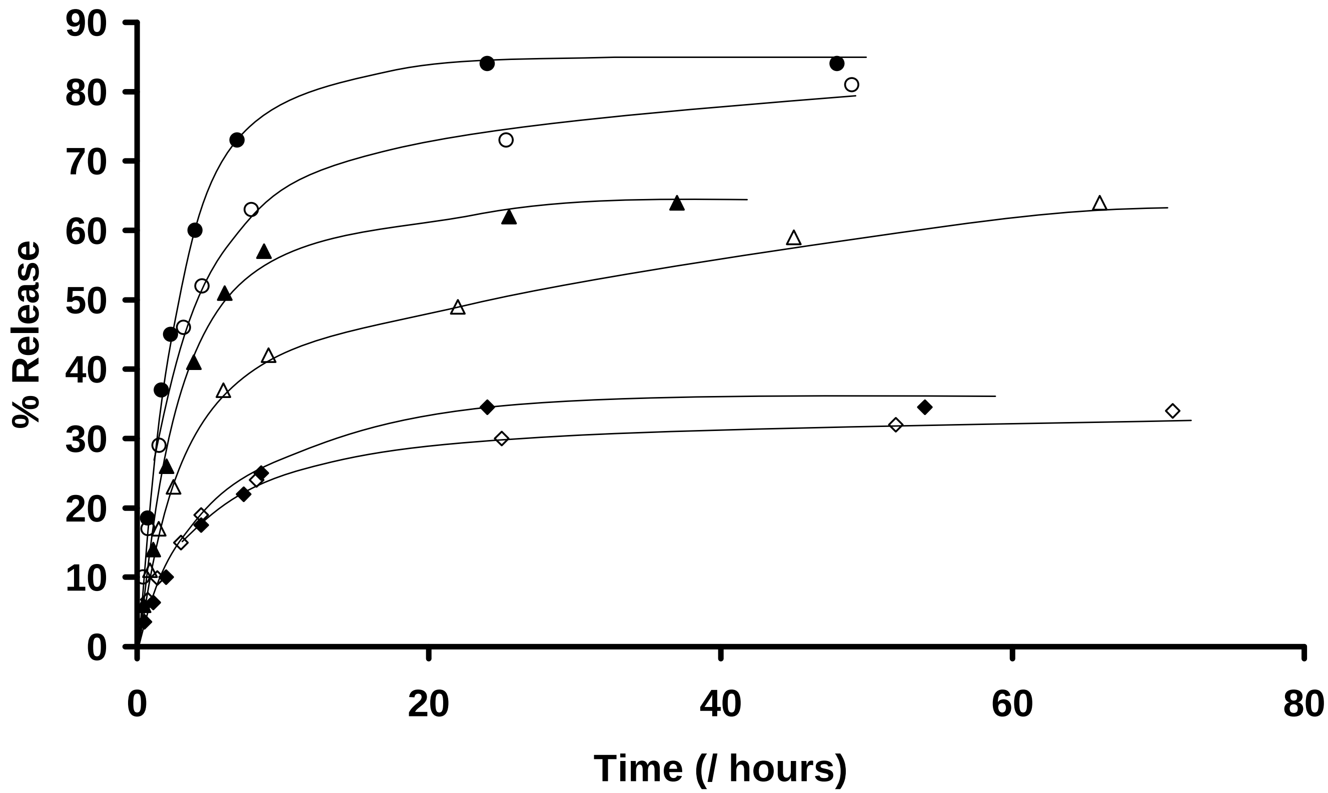
the release profile of 4-nitroanisole: for PVPK (■) 3.8 g, (▲) 5 g, (♦) 8 g; for PMMA (□) 2.5 g, (◊) 3.0 g, (○) 3.8 g.

Release Profile: Effect of Post Cross-Linking the Shell



release profile of 4-nitroanisole: (○) un-cross-linked polystyrene, (x) cross-linked polystyrene (10 wt % DVB)

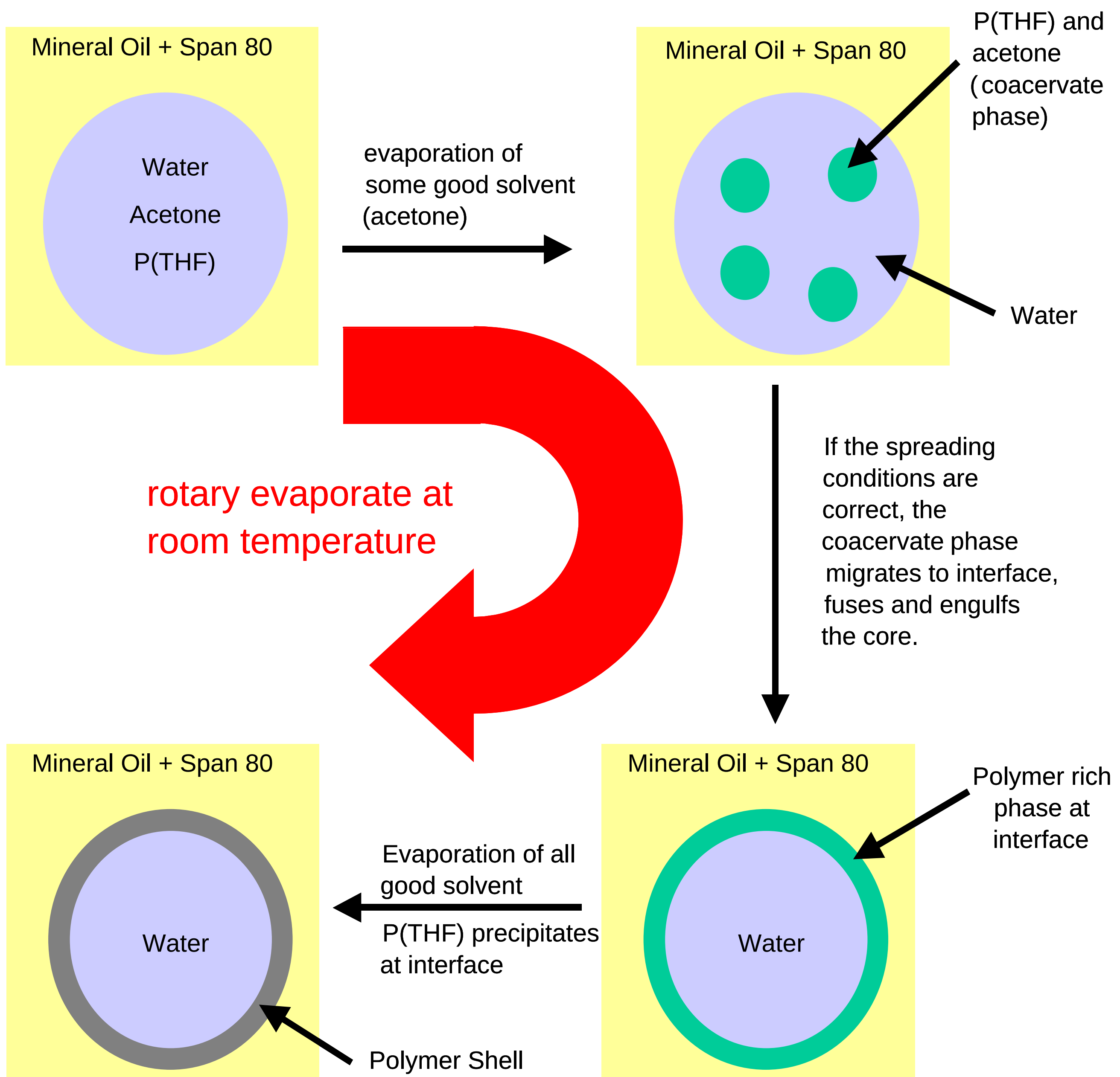
Effect of heating the shell polymer above its Tg value



release profiles (at room temp) of 4-nitroanisole from microcapsules with various polymer shells: PVPK (Tg = 58°C) (◊,♦); PIBMA (Tg = 55°C) (○, ●); PEMA-co-MA (Tg = 48°C) (Δ,▲). Closed symbols: system not heated; open symbols: system heated to 10°C above the Tg

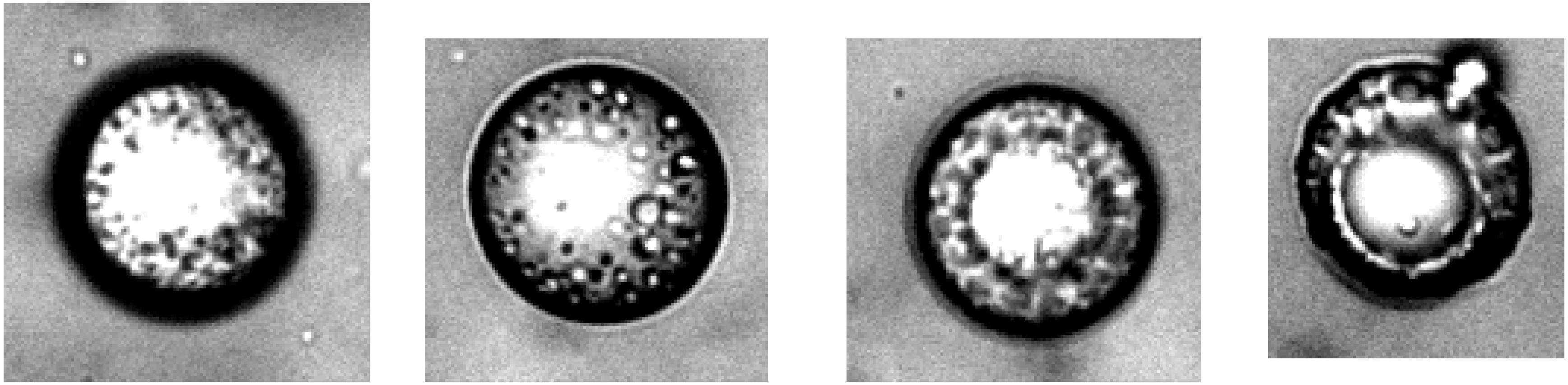
WATER CORE / POLYMER SHELL PARTICLES

Atkin, Davies, Hardy & Vincent, Macromolecules, 2004 37 7979



Schematic representation of the preparation of core/shell particles with aqueous cores.

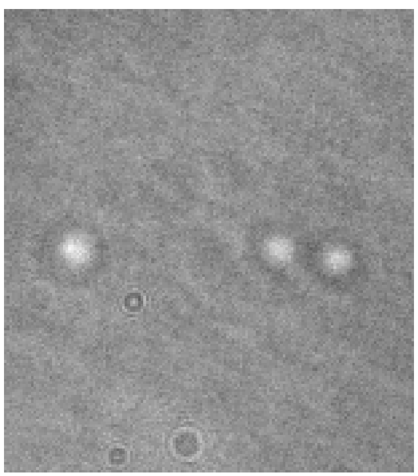
Phase Separation



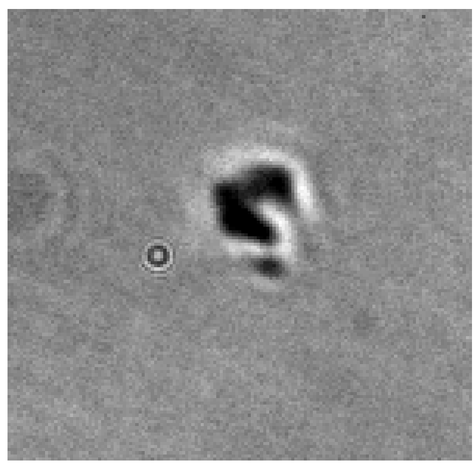
OM

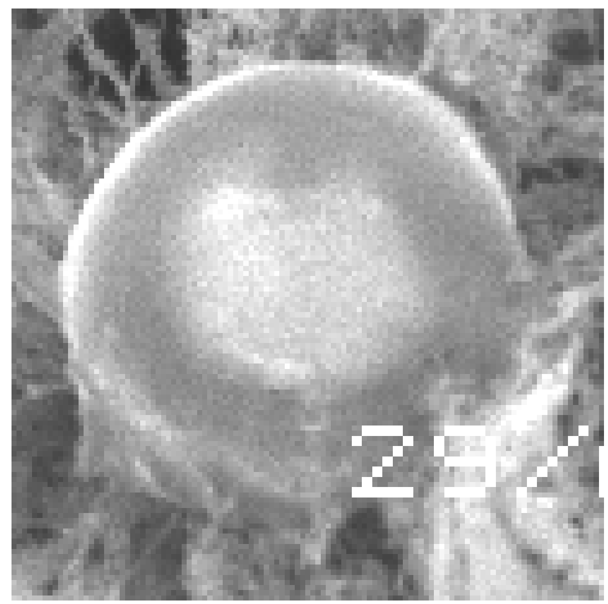
SEM ↓

final form

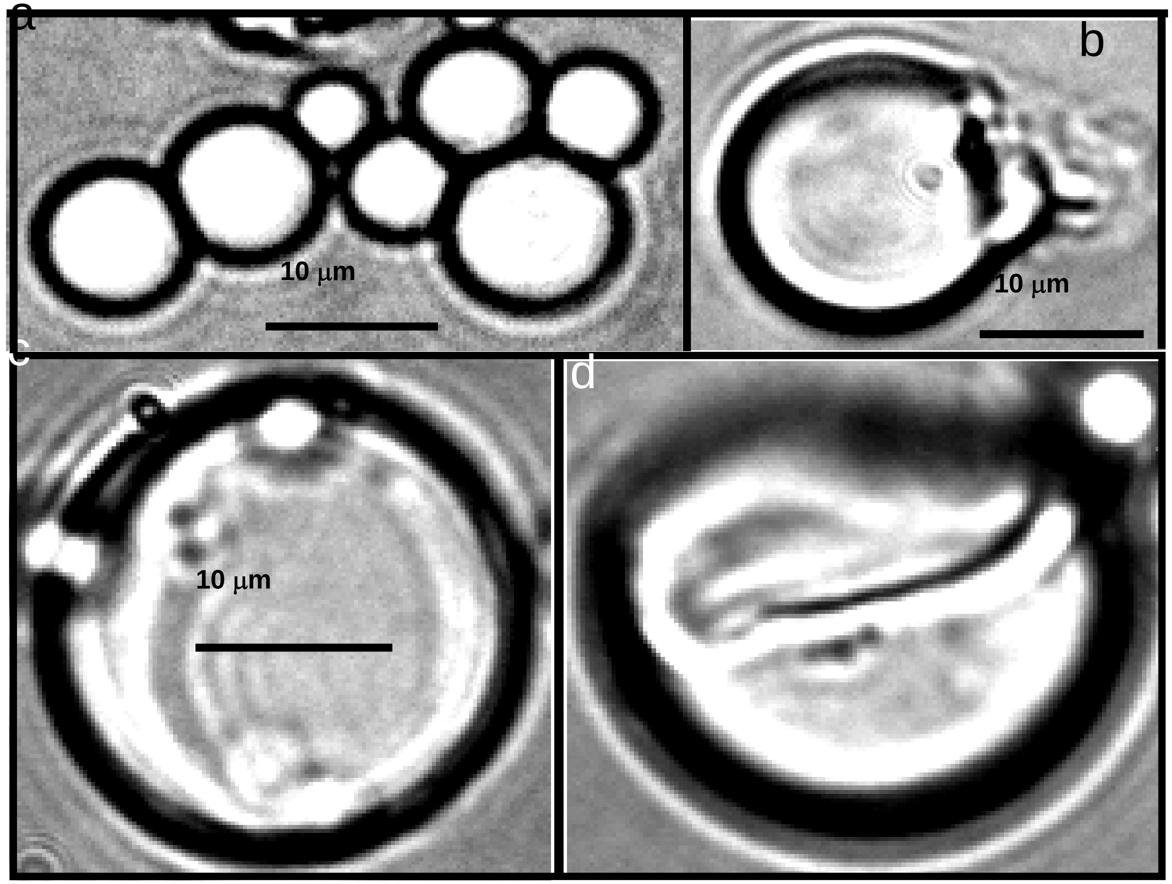


applied pressure





Poly(methylmethcrylate) Capsules



OIL CORE /

SILICA SHELL

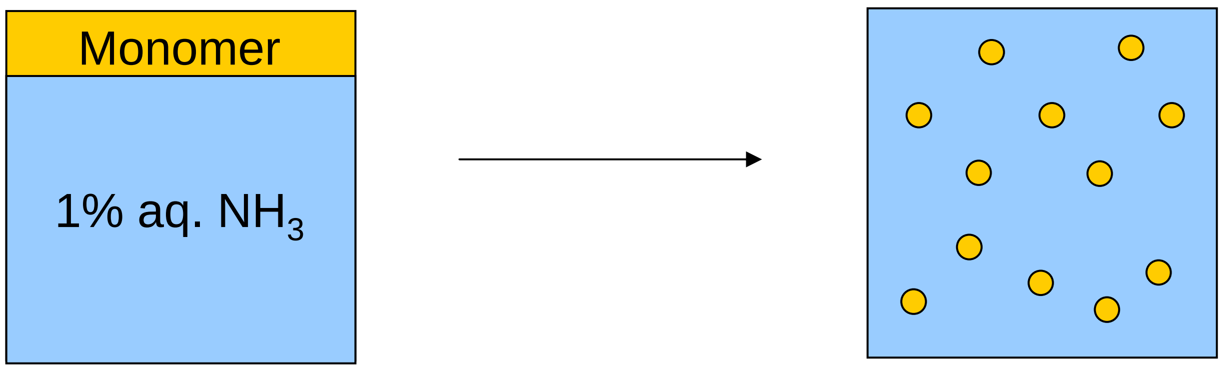
PARTICLES

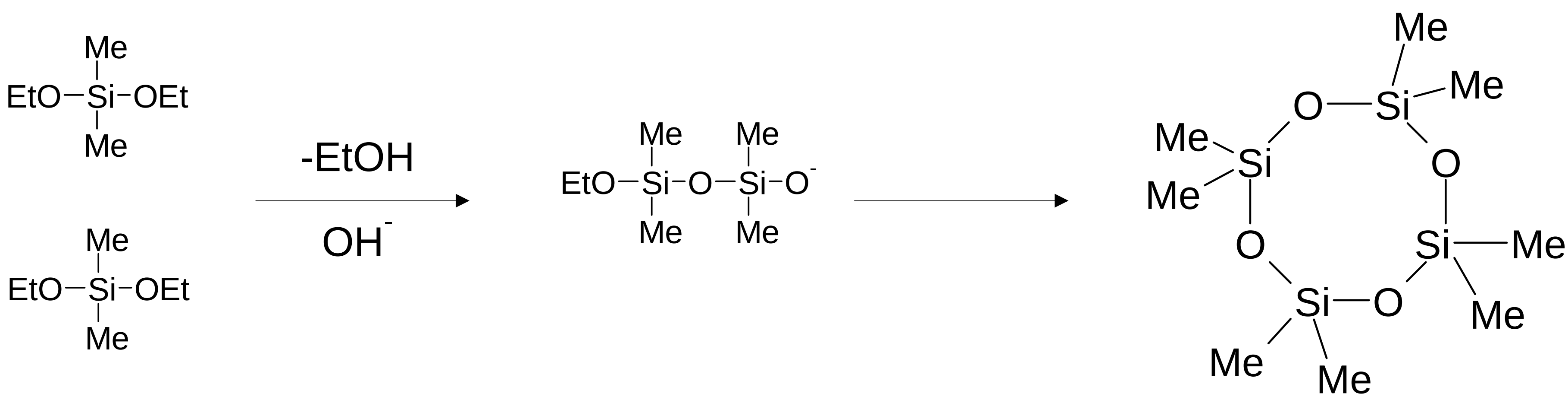
PDMS ("silicone oil") cores + silica-like shells

O'Sullivan, Zhang &Vincent, Langmuir, 2009 25 7962

Silicone Oil Droplet Synthesis

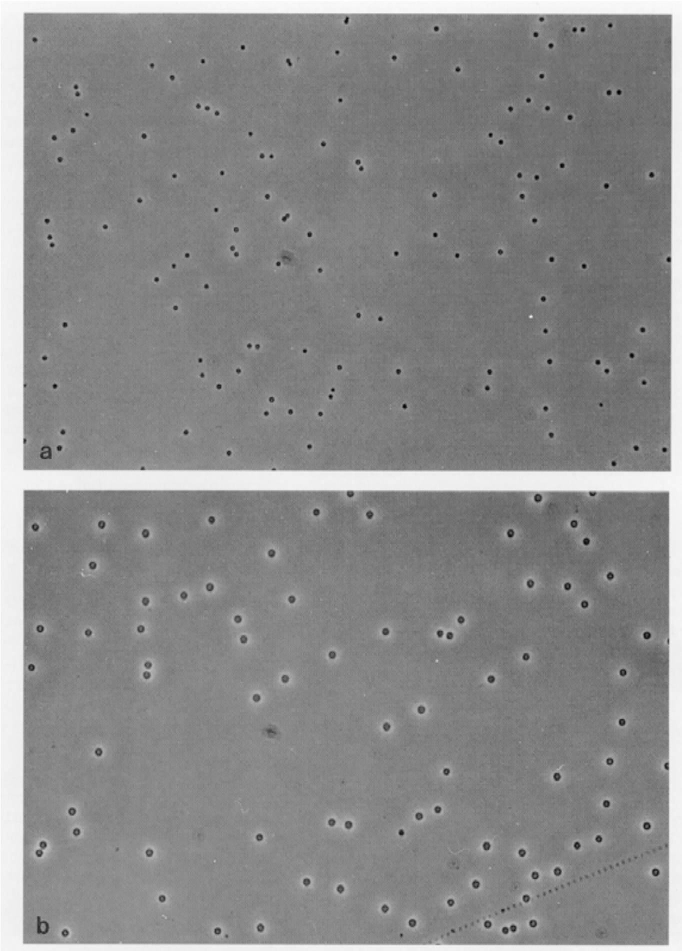
c.f. the Stöber synthesis of hard silica particles





Obey and Vincent J. Colloid and Interface Science, 1994 163 454

optical micrographs of silicone oil droplets



monodisperse and

charge-stabilised

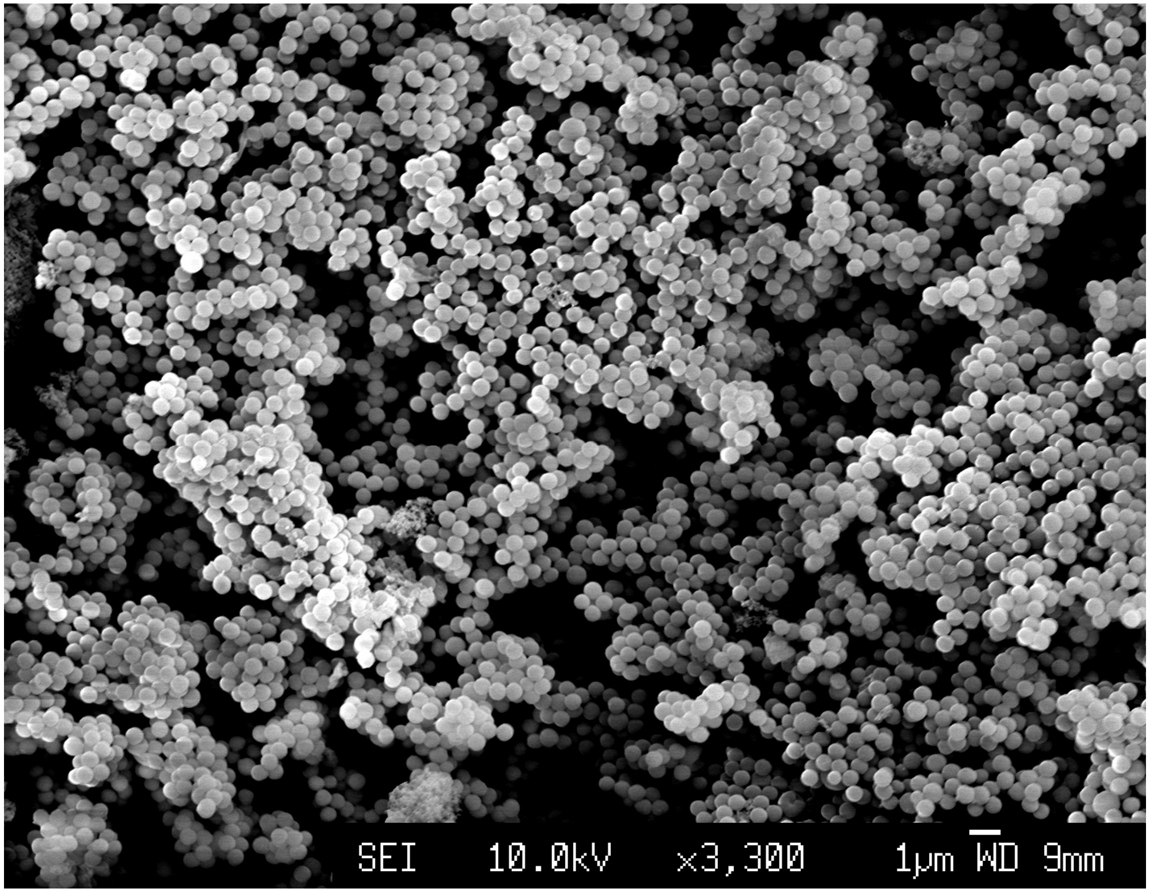
(no surfactant added)

average diameter 1.5 μm

average diameter 2.5 μm

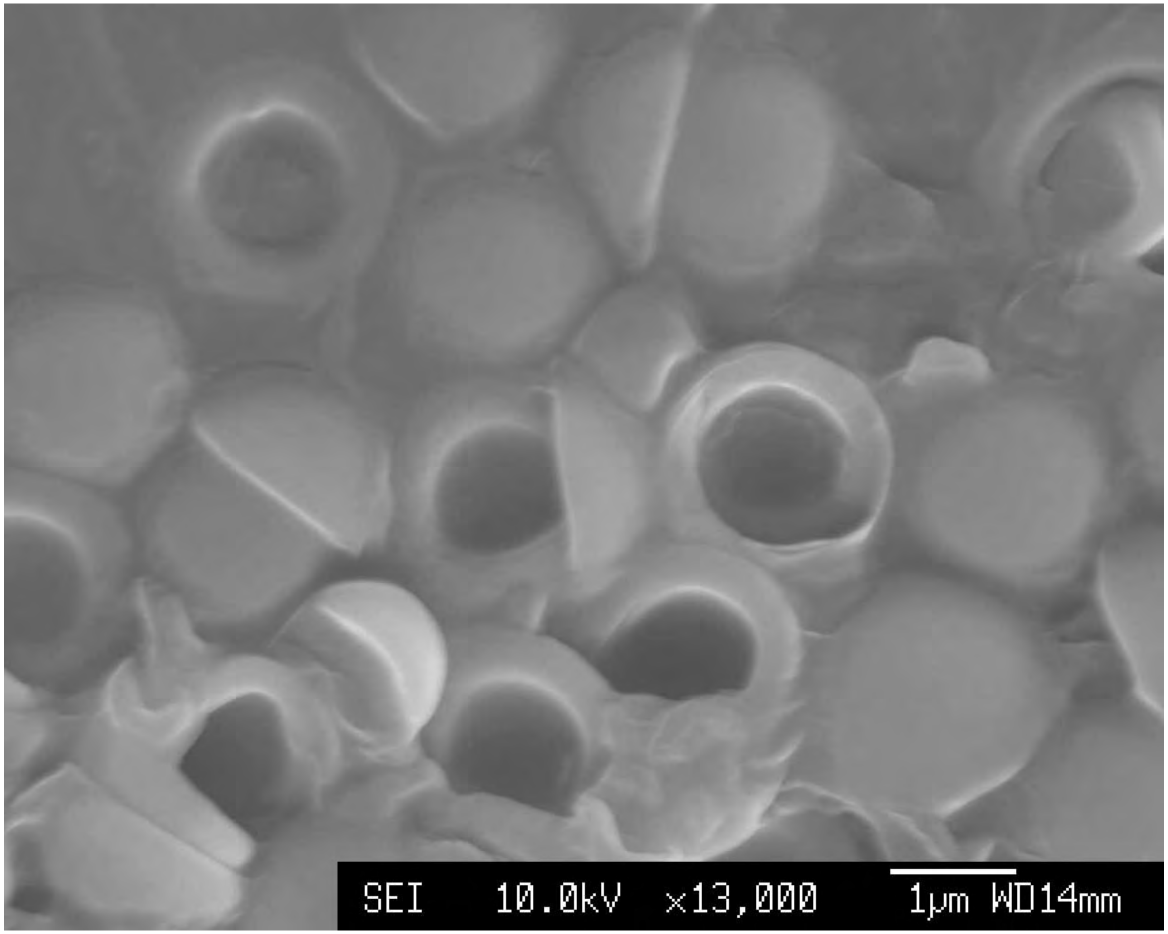
Formation of Silica Shells around Silicone Oil Droplets

Add TEOS + DEODMS to aqueous phase (+ base)

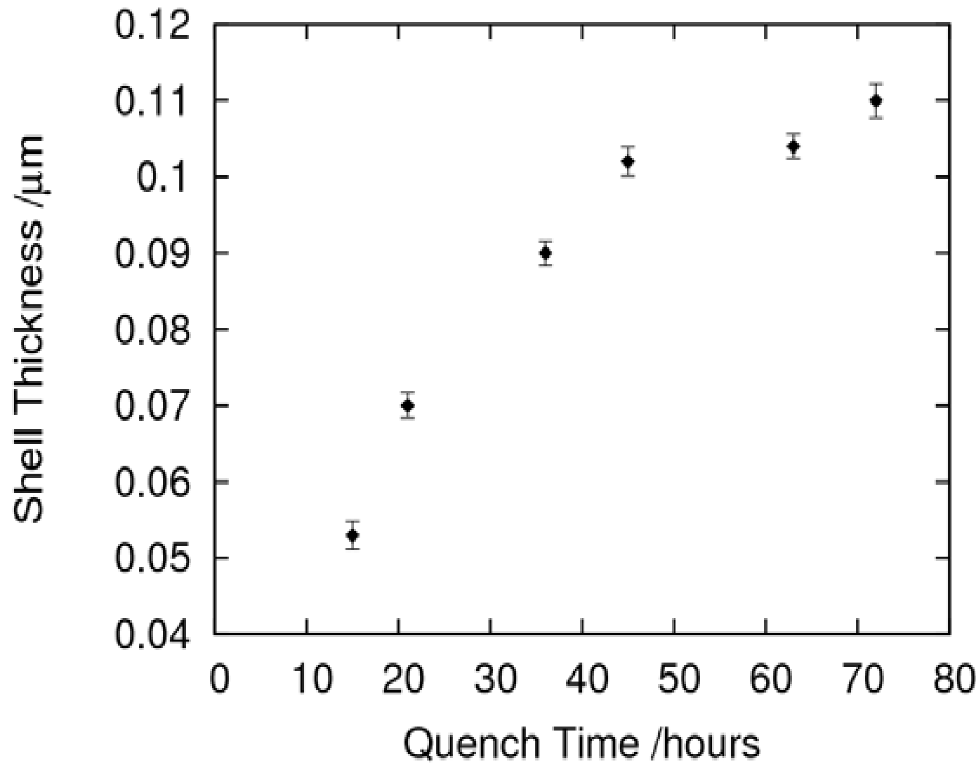


DEODMS conc. = 0.023 mol dm^{-3}

TEOS conc. = 0.018 mol dm^{-3}



Shell thickness as a function of reaction quench time

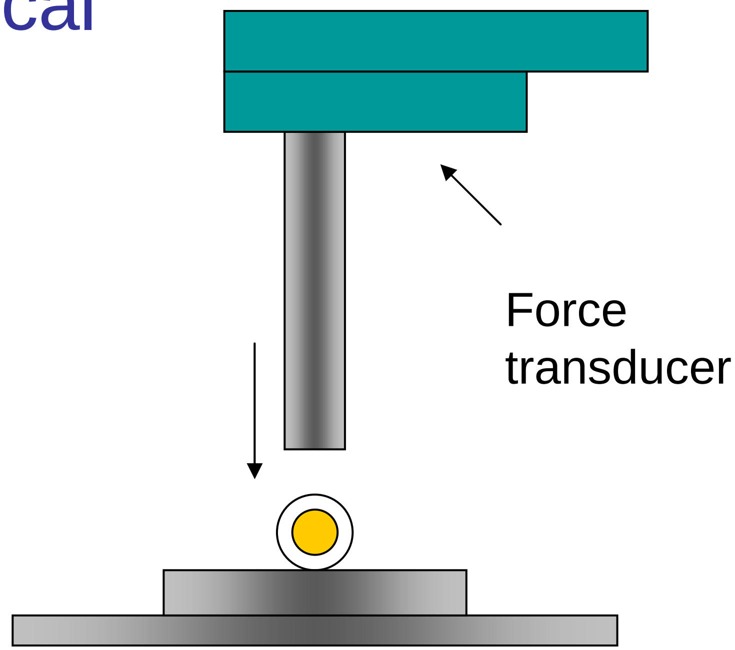


DEODMS conc. = 0.023 mol dm^{-3}; TEOS conc. = 0.018 mol dm^{-3}

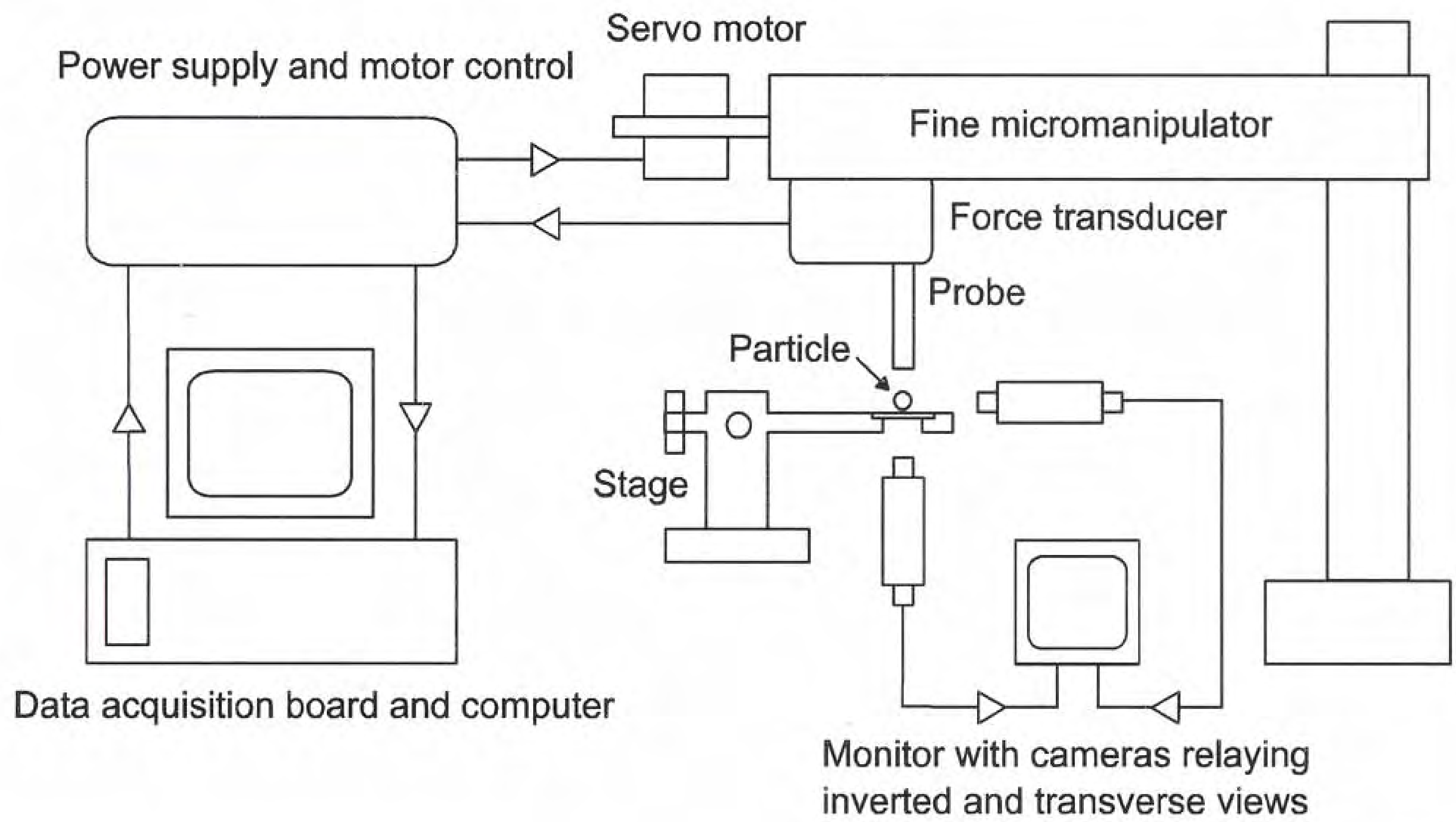
Mechanical Strength Studies

- Micromanipulator
- Need particles large enough to be viewed under an optical microscope

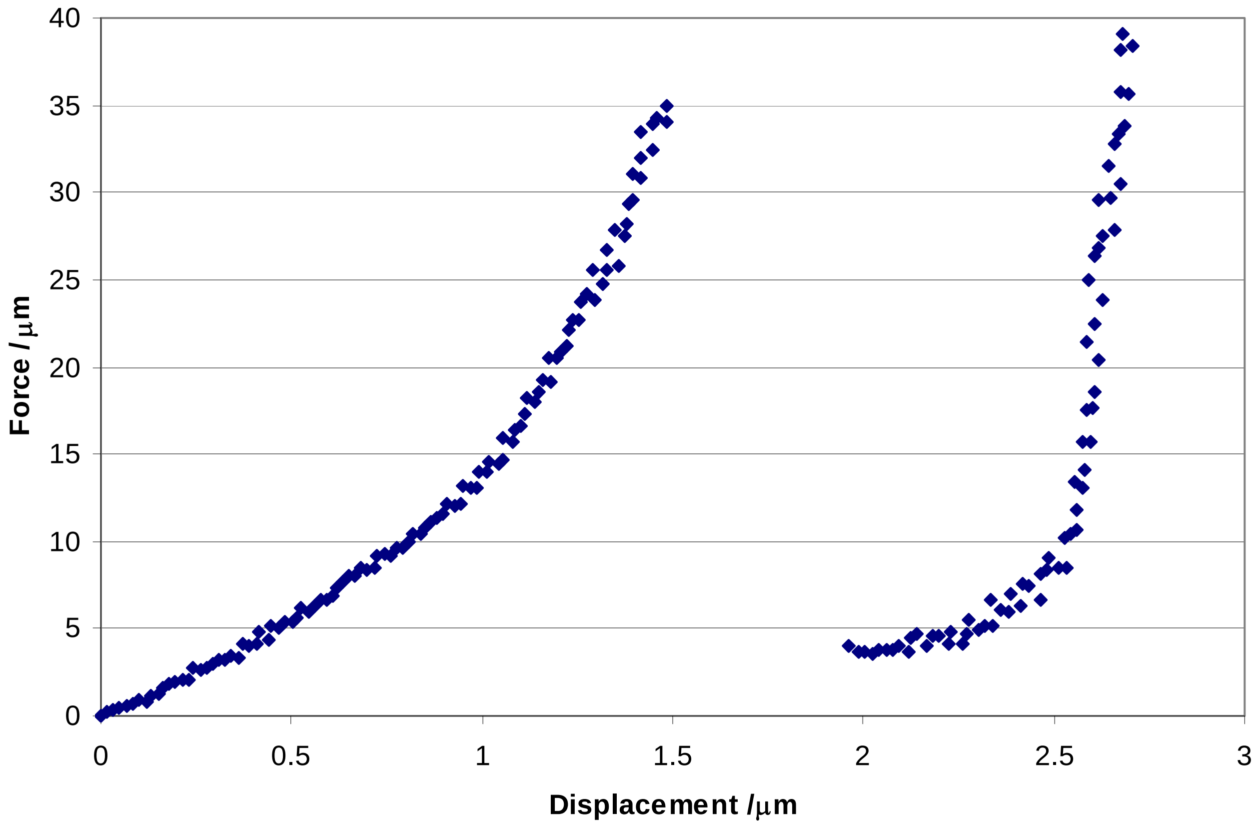
Mechanical Strength of Microcapsules Made of Different Wall Materials, Sun and Zhang, *International Journal of Pharmaceutics*, **242**, 307-311, 2002



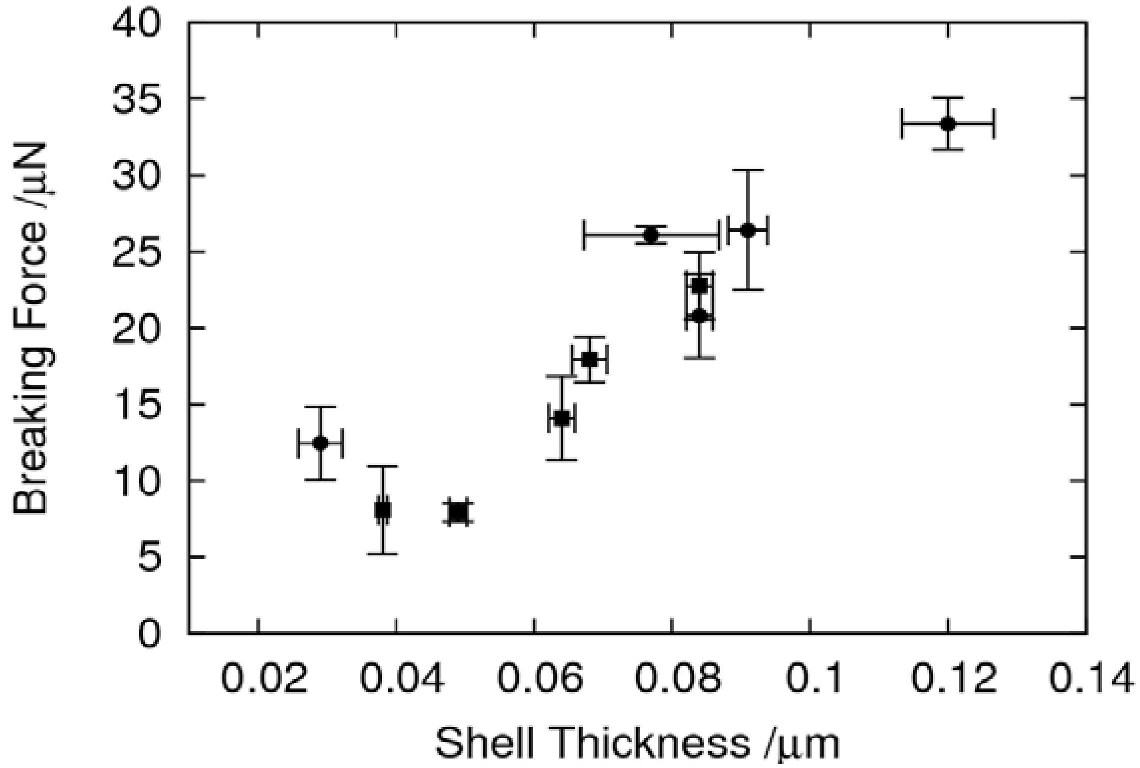
The Equipment



Breaking Force/Displacement



Breaking force as a function of shell thickness



NB TEOS conc. fixed, and increasing amounts of DEODMS used to vary the thickness

CONCLUSIONS

- core/shell particles for the protection and / or controlled release of active materials may be prepared by a variety of methods.
- the cores may be oil or water (or solid).
- the shells may be inorganic or polymeric.
- the release rate profile may be varied by careful control of the nature of the shell and the form / concentration of the active ingredient.

And finally…!!

A personal tribute to a worthy and well-deserving winner of the McBain Medal

From an old mate

(and a long-standing cricket and rugby supporter to a truly dedicated soccer supporter … !!)

Here’s to Pete’s Pride and Joy!

The “Clarets” and Turf Moor