Desirable Properties of Microcapsules for Consumer Products and Their Characterisation

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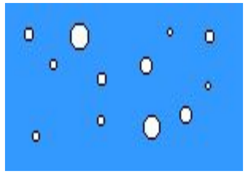
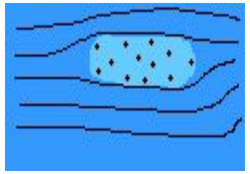
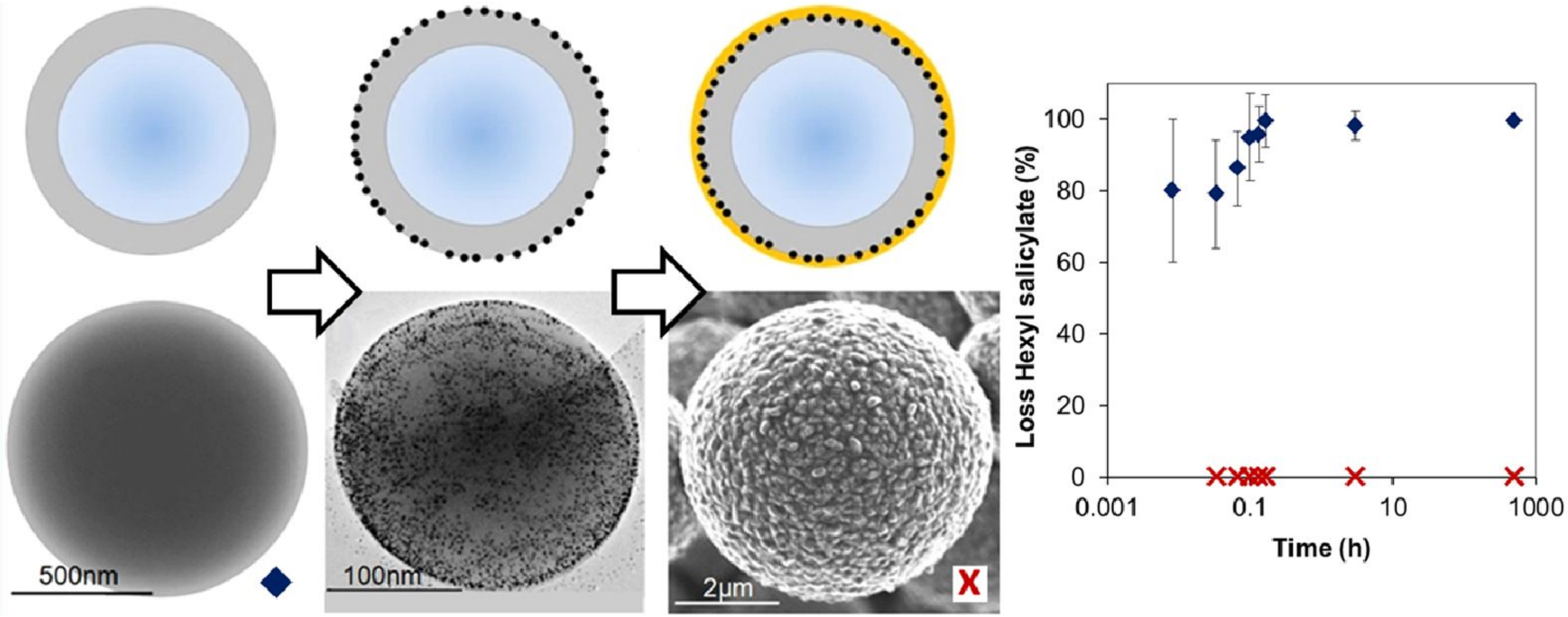
Outline

- Importance to characterise the various properties of microcapsules
- Measuring the mechanical properties of microcapsules based on micromanipulation and numerical modelling
- Characterising the release rate of active ingredient from the microcapsules using an accelerated release test methodology
- Measuring adhesion of microcapsules to substrate

Desirable Properties

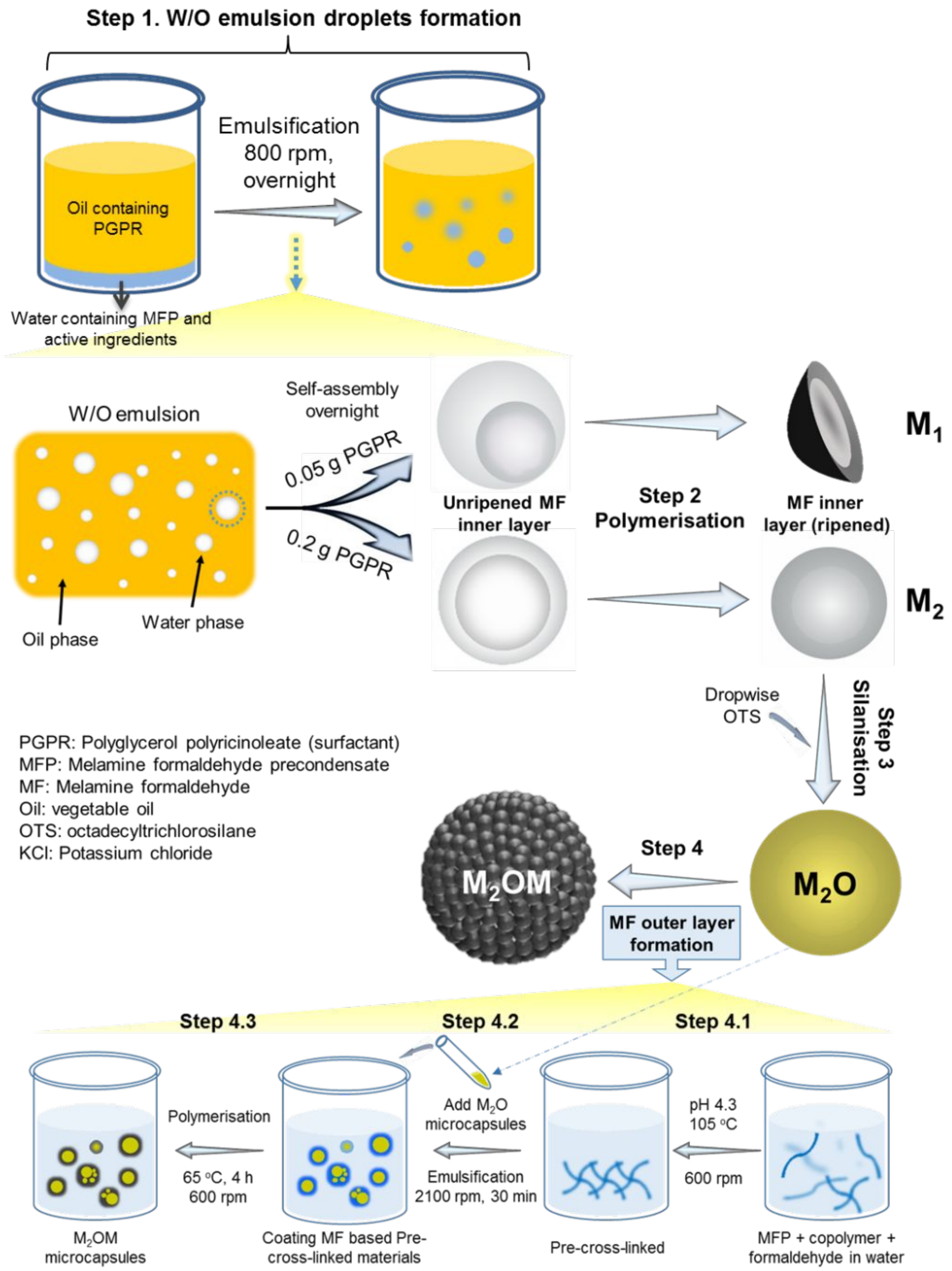
- Microcapsules should be non-permeable during their shelf life.
- Microcapsules should have sufficient and/or optimum mechanical strength.
- Microcapsules should be adhesive to certain substrates for some applications.
- The shell of microcapsules should ideally be microplastic-free.

Defect Type		Size	Materials
Atomic Vacancies		0.1 nm	Metals
Dislocations		1 nm - 10 µm	Metals
Voids		0.1 nm - 1 µm	Metals
Holes		0.1 nm - 10 µm	Polymers

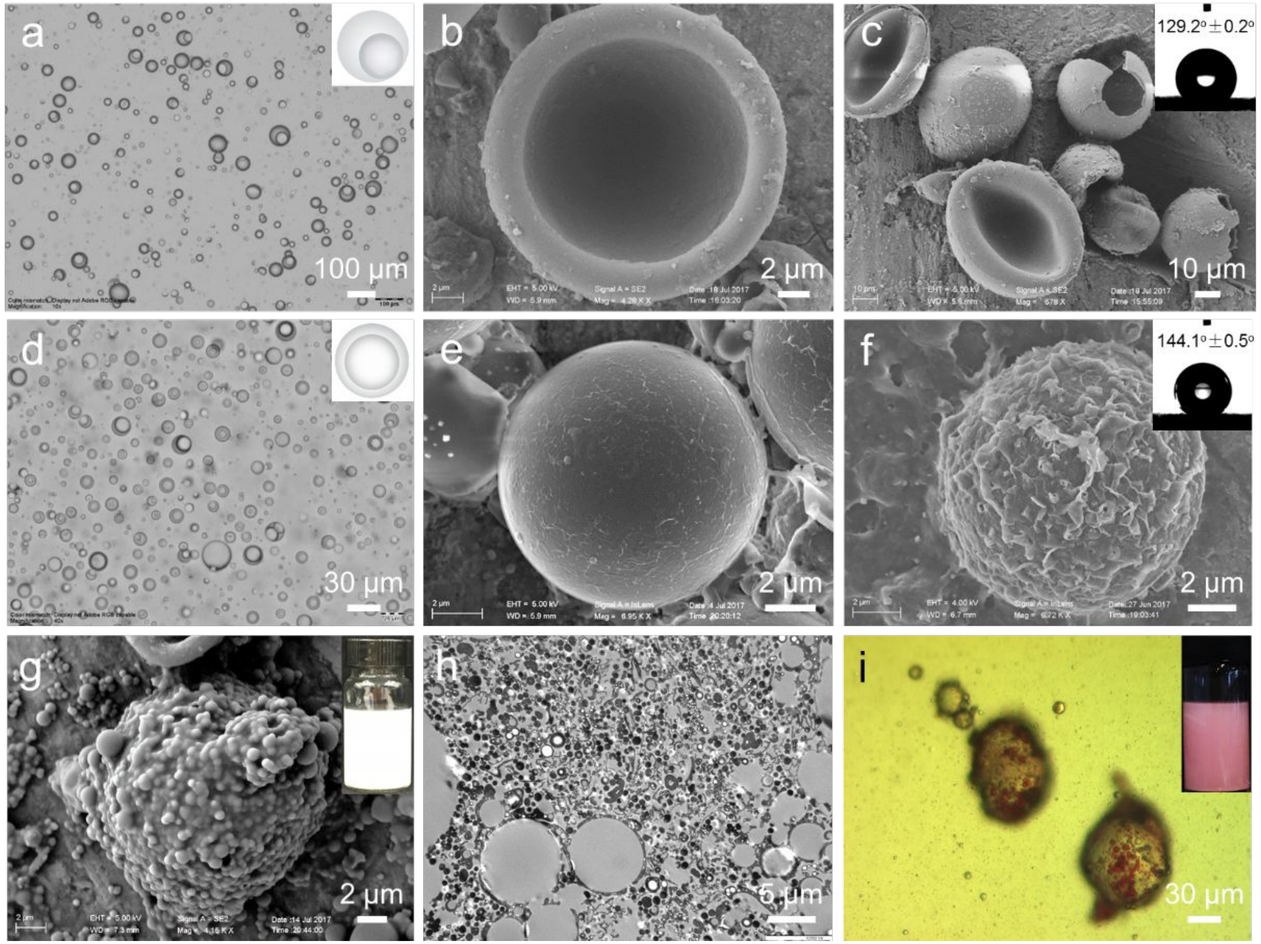


Hexyl salicylate release profile from PMMA capsules and (×) gold coated PMMA capsules, placed in 4:1 ethanol–water at 40°C.

Hitchcock, Tasker, Baxter, Biggs & Cayre, *ACS Appl. Mater. Interfaces,* 2015



Zhang, Z., Sui, C. and Preece, J. A. (2019) *Microcapsules*, WO 2019/145731.



Optical micrographs of (a) unripened M1-KCl, (d) unripened M2-KCl and (i) M2OM-dye microcapsules; SEM images of (b) M1-KCl, (c) M1O-KCl, (e) M2-KCl, (f) M2O-KCl and (g) M2OM-KCl microcapsules; (h) transmission electron microscopy (TEM) image of the ultra-thin cross-section of M2OM-KCl microcapsules embedded in epon/araldite rosin

Why do we need to measure the mechanical properties of microcapsules?

- To prevent the damage to microcapsules in processing equipment (e.g. stirred vessel, pump, extruder)
- To maintain their long-term mechanical stability
- To realise triggered release of active ingredients from microcapsules by mechanical forces

Techniques for Characterizing the Mechanical Properties of Microcapsules

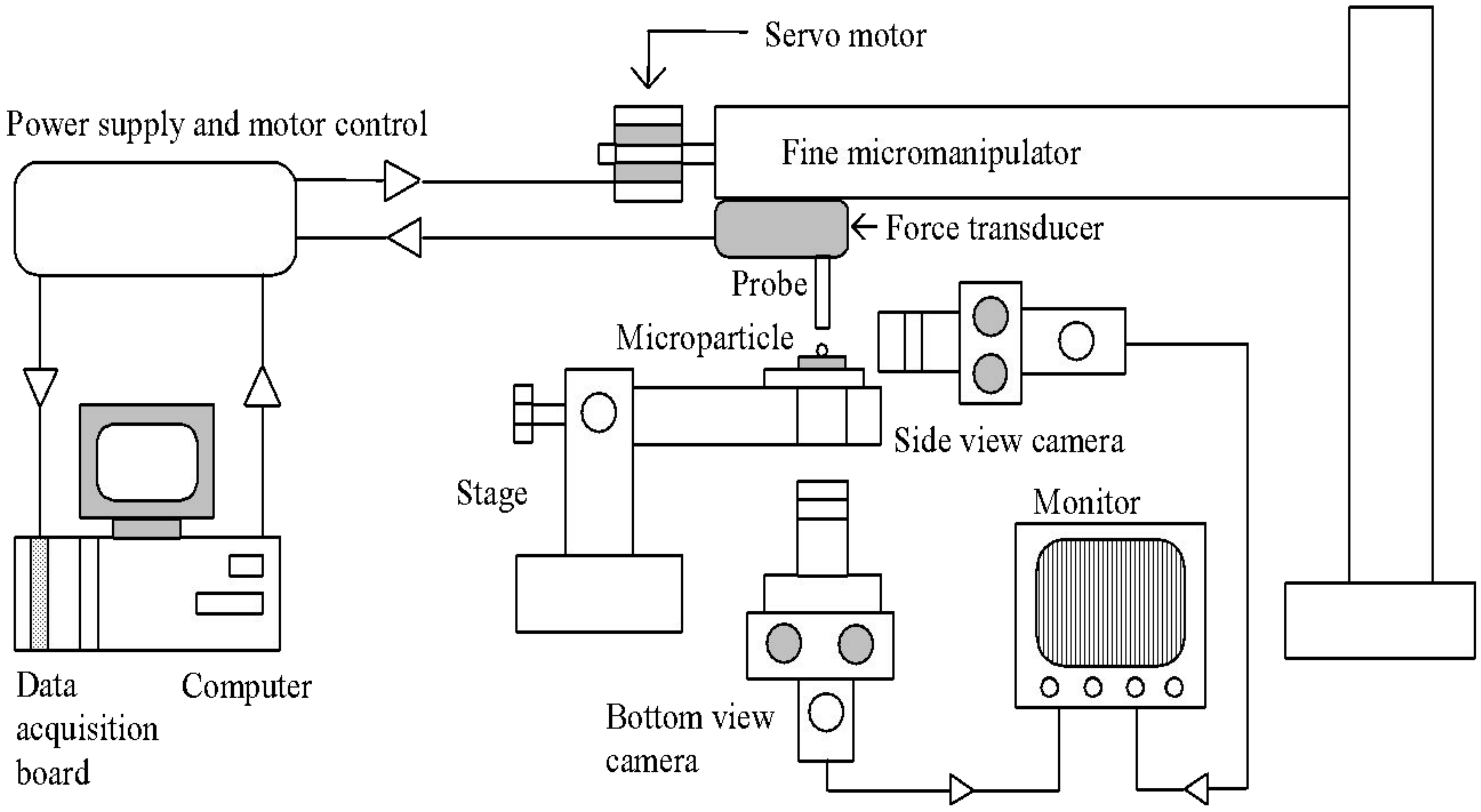
Microcapsule Population

- Compression between two plates
- Osmotic pressure (only for semi-permeable microcapsules)
- “Shear” device (e.g. sparging, agitation and shaking)

Single Microcapsules

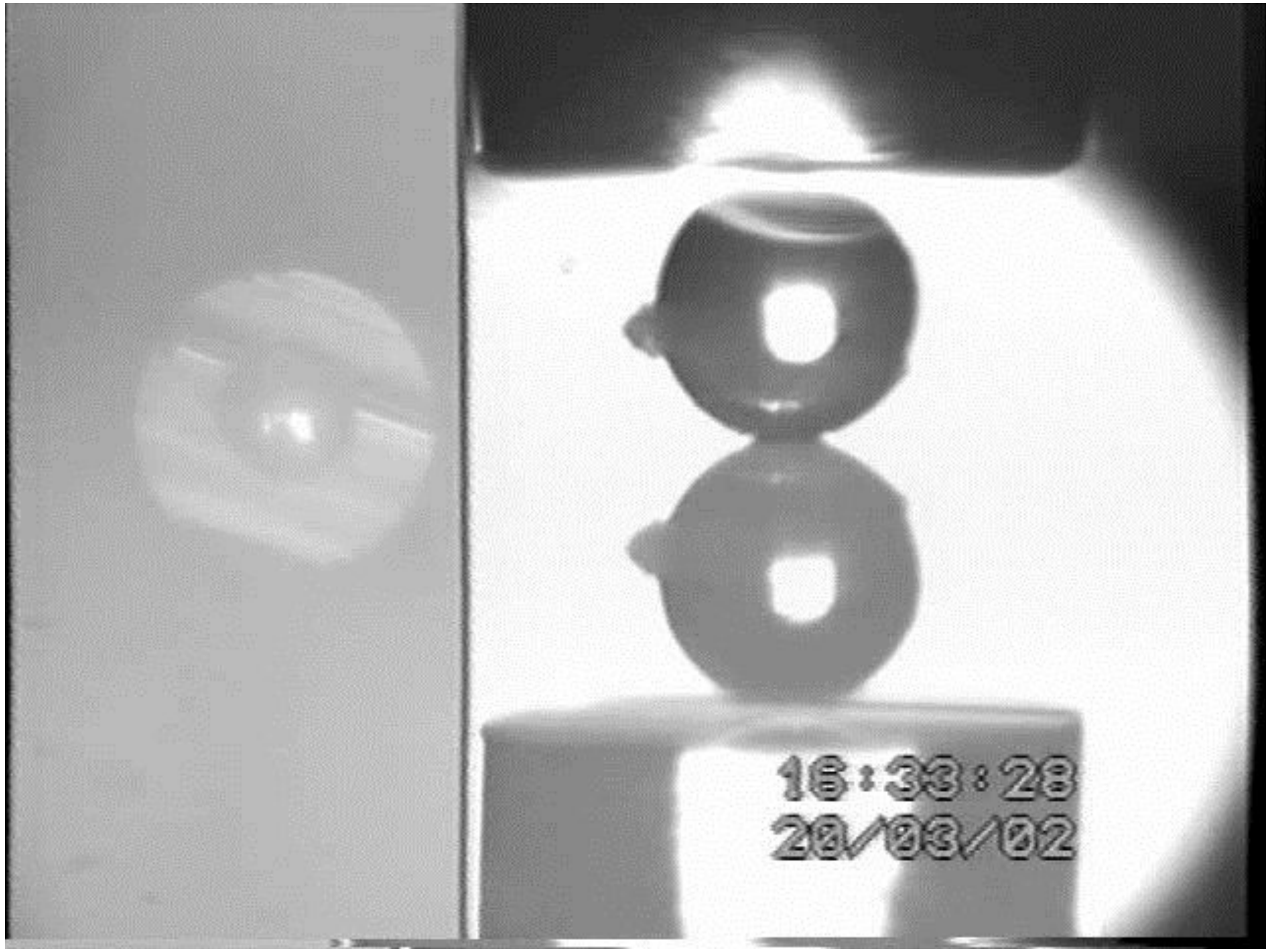
- Optical tweezers (~pN)
- Shear flow (pN-µN)
- Micropipette aspiration (pN-nN)
- Atomic force microscopy (pN- µN)
- Micromanipulation (µN-N)

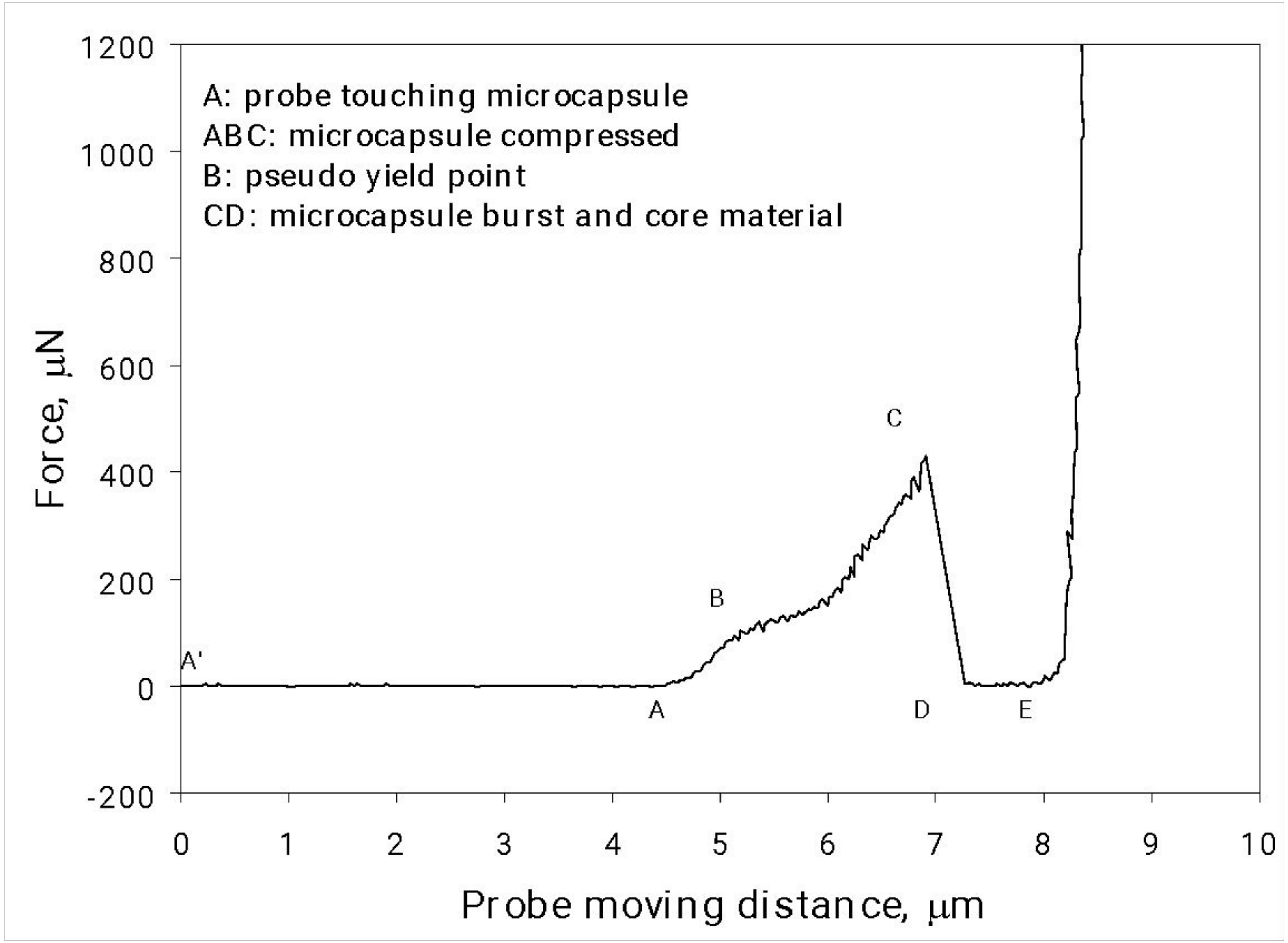
Neubauer, Poehlmann and Fery (2014) *Adv Colloid Interface Sci* 207:65-80.

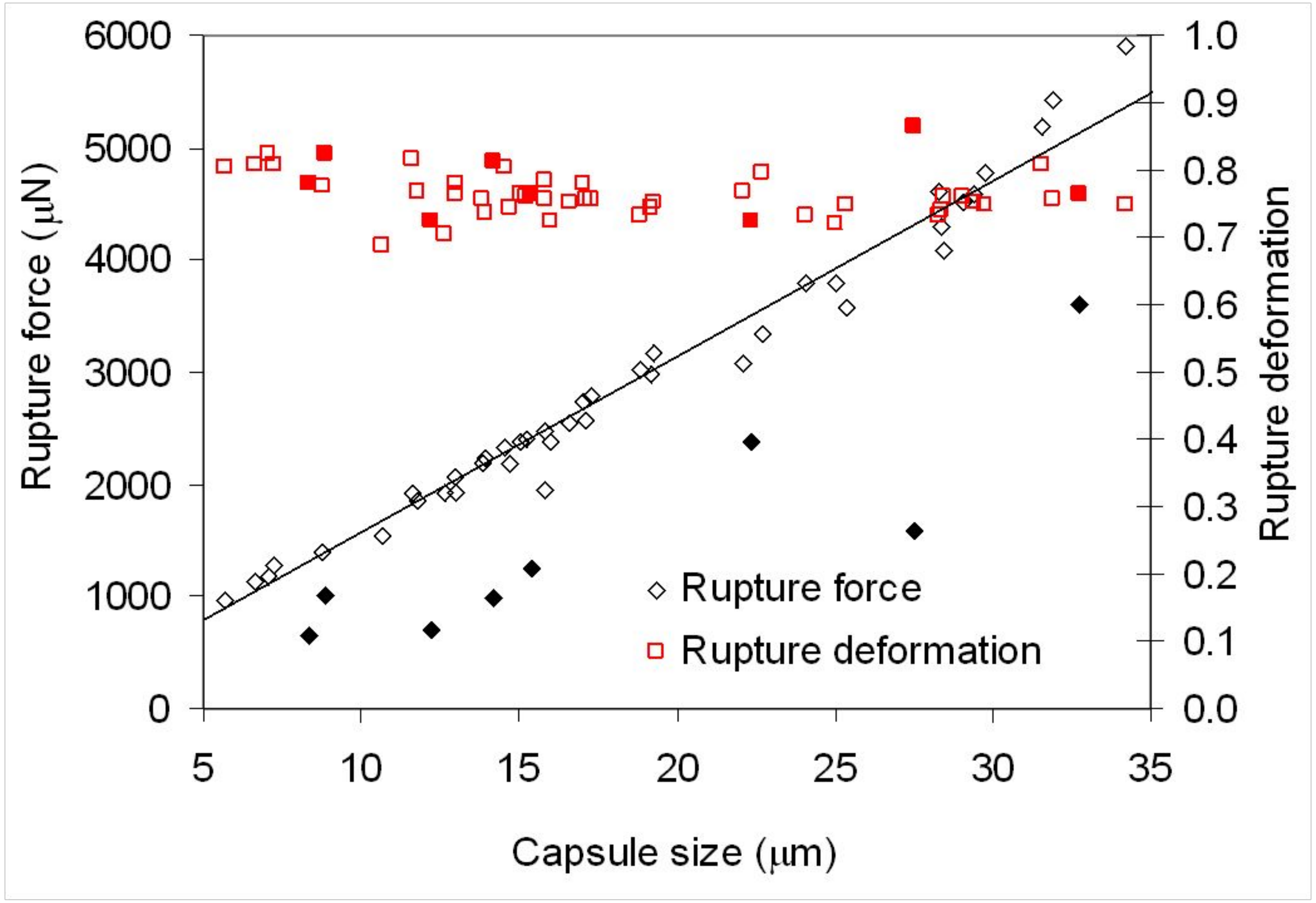


Schematic diagram of a micromanipulation rig

Sun and Zhang (2001) *J. Microencapsulation* 18: 593-602.


16:33:28
20/03/02

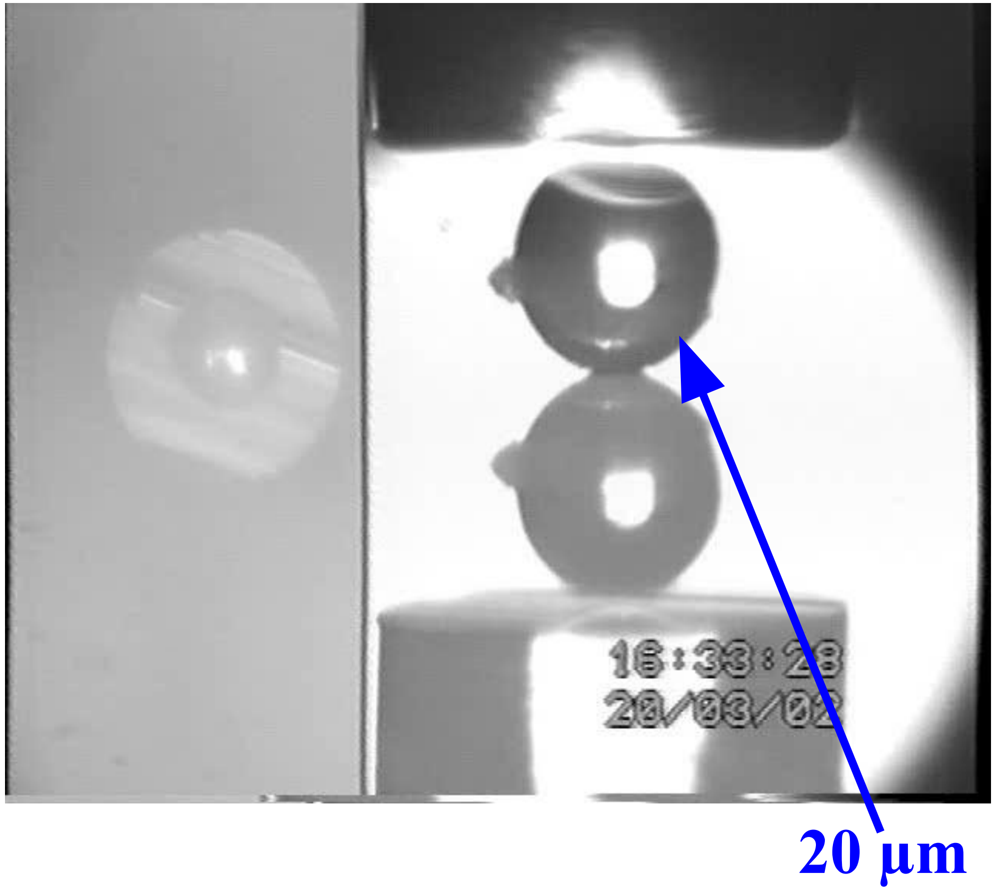

A: probe touching microcapsule
ABC: microcapsule compressed
B: pseudo yield point
CD: microcapsule burst and core material
Force, µN
1200
1000
800
600
400
200
0
-200
A'
A
B
C
D
E
0
1
2
3
4
5
6
7
8
9
10
Probe moving distance, µm

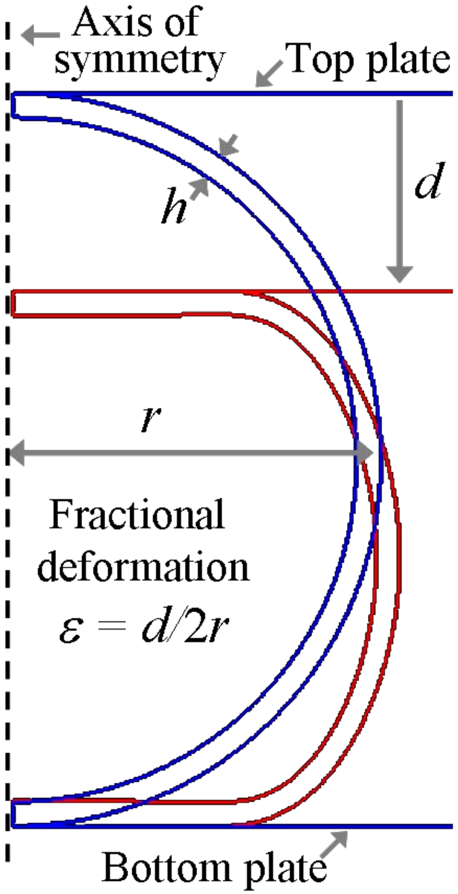


Rupture force (diamonds) and fractional deformation at rupture (squares) of microcapsules of different sizes

Mercade-Prieto et al. (2011) Chem. Eng. Sci. 66: 2042-2049.

Micromanipulation to measure the rupture force of single microcapsules and finite element analysis (FEA) to determine their intrinsic mechanical property parameters

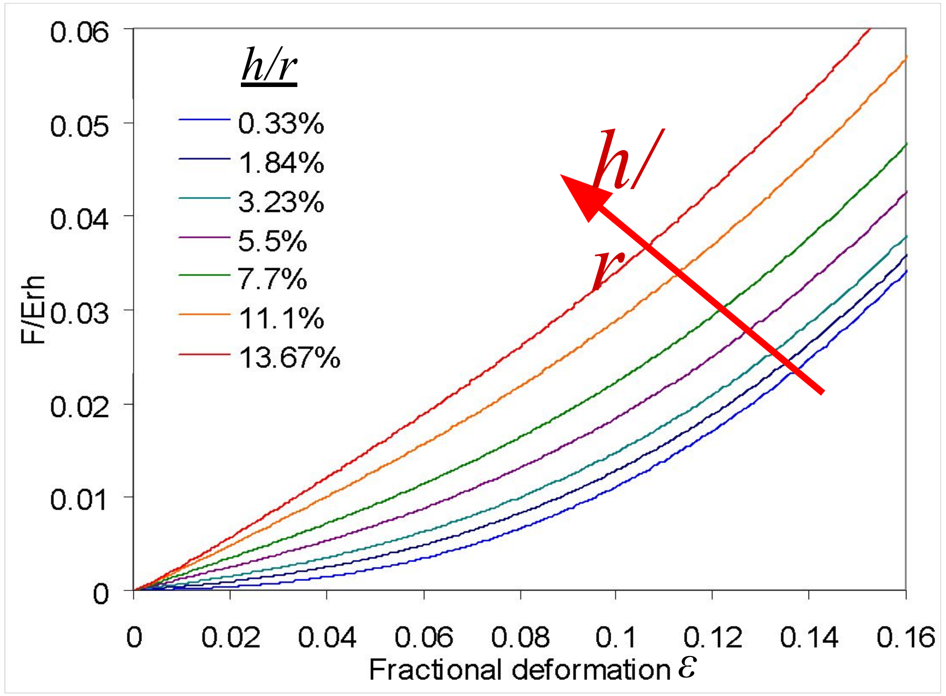




FEA – Elastic shell

Determination of the Elastic Modulus (E):

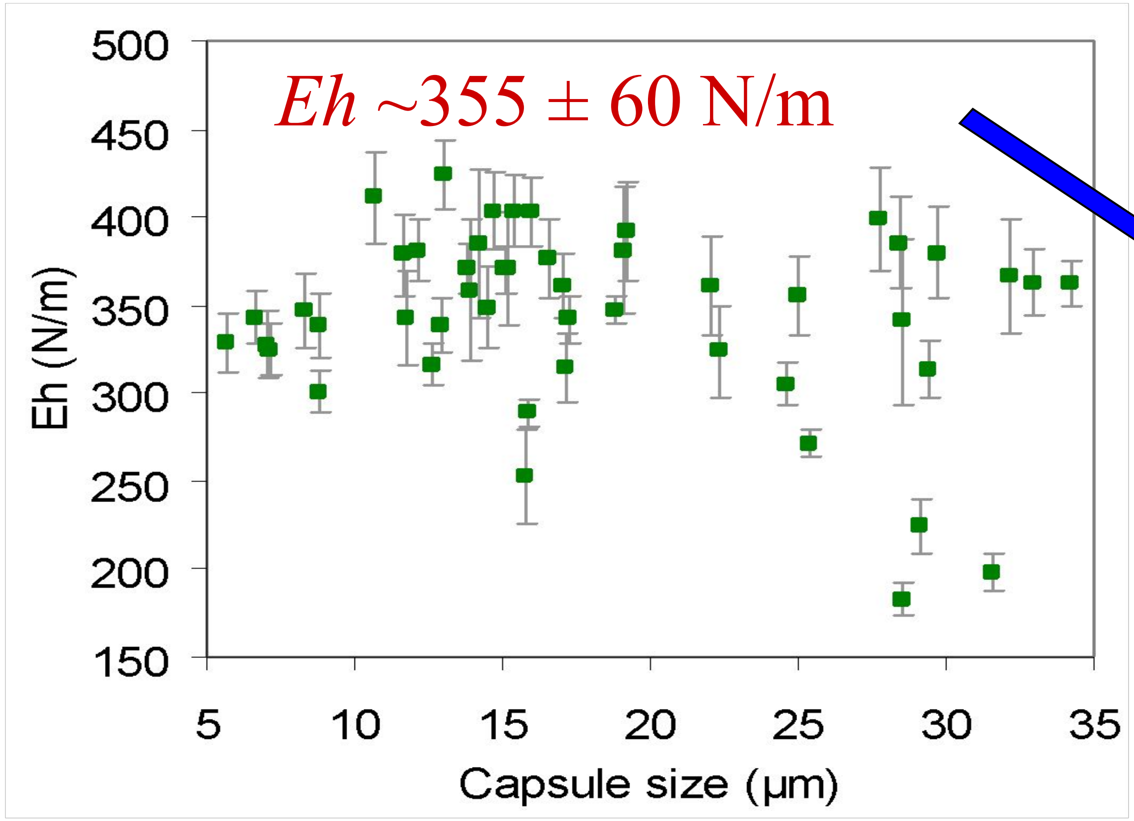
- MF microcapsules are known to be elastic at small fractional deformations $\varepsilon < 0.15$



- The force profile depends on *h/r* at small fractional deformations
- We can estimate *h/r* using the shape of the force profile

Mercade-Prieto et al. (2011) *Chem. Eng. Sci.* 66: 2042-2049.

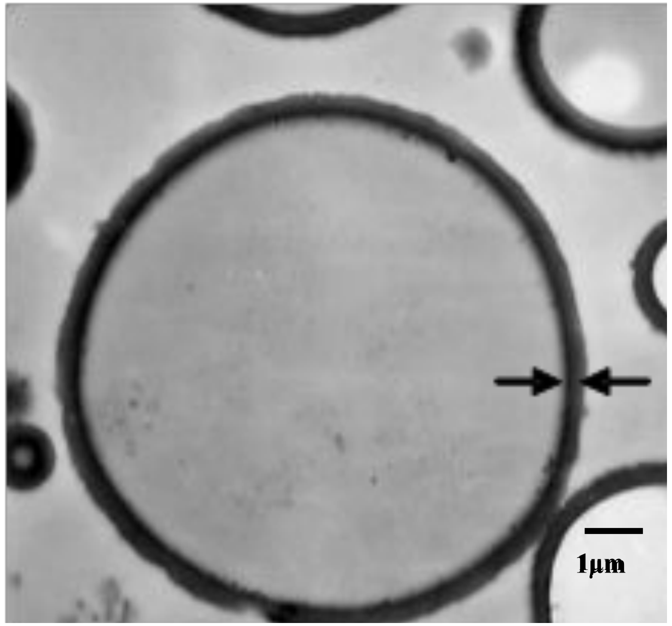
MF capsules – Elastic shell – Estimate *Eh*



Eh is independent of the capsule size.

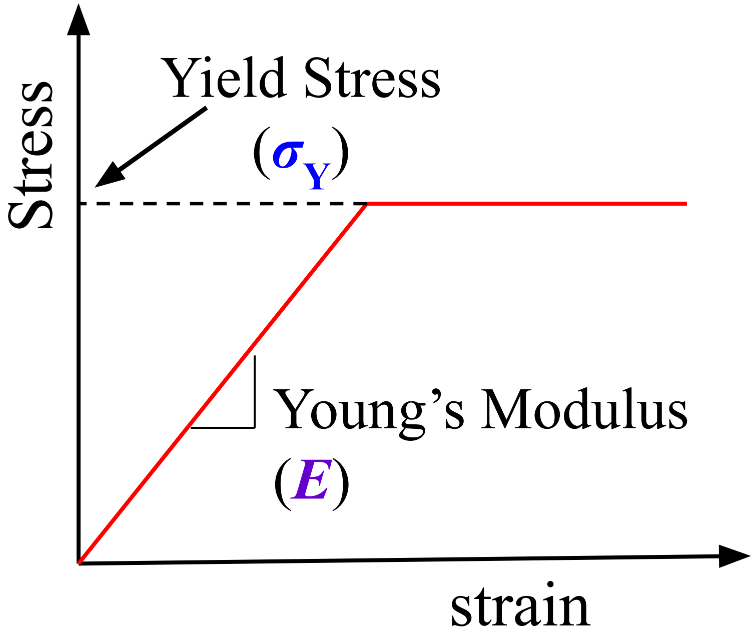
h ~0.2 µm

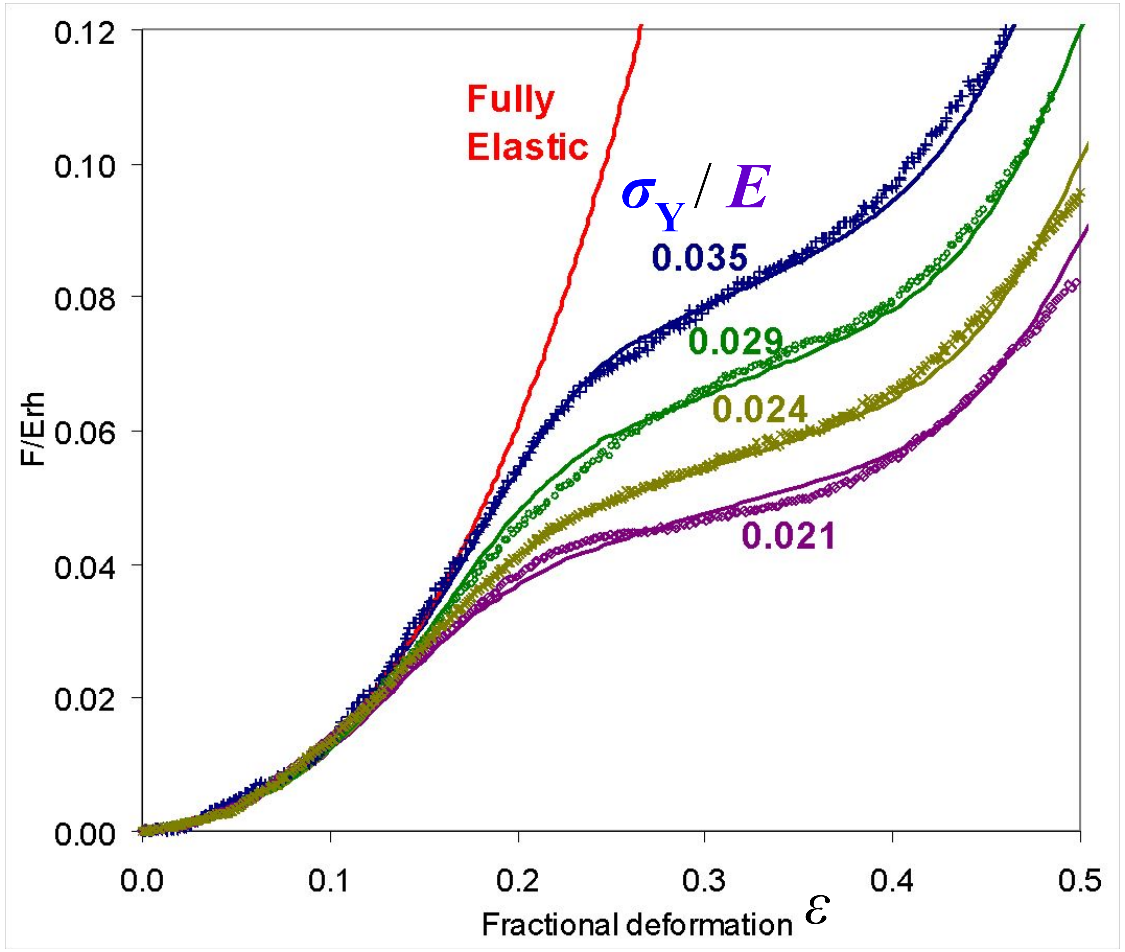
E ~1.8 ± 0.3 GPa



MF capsules – Elastic perfectly-plastic shell

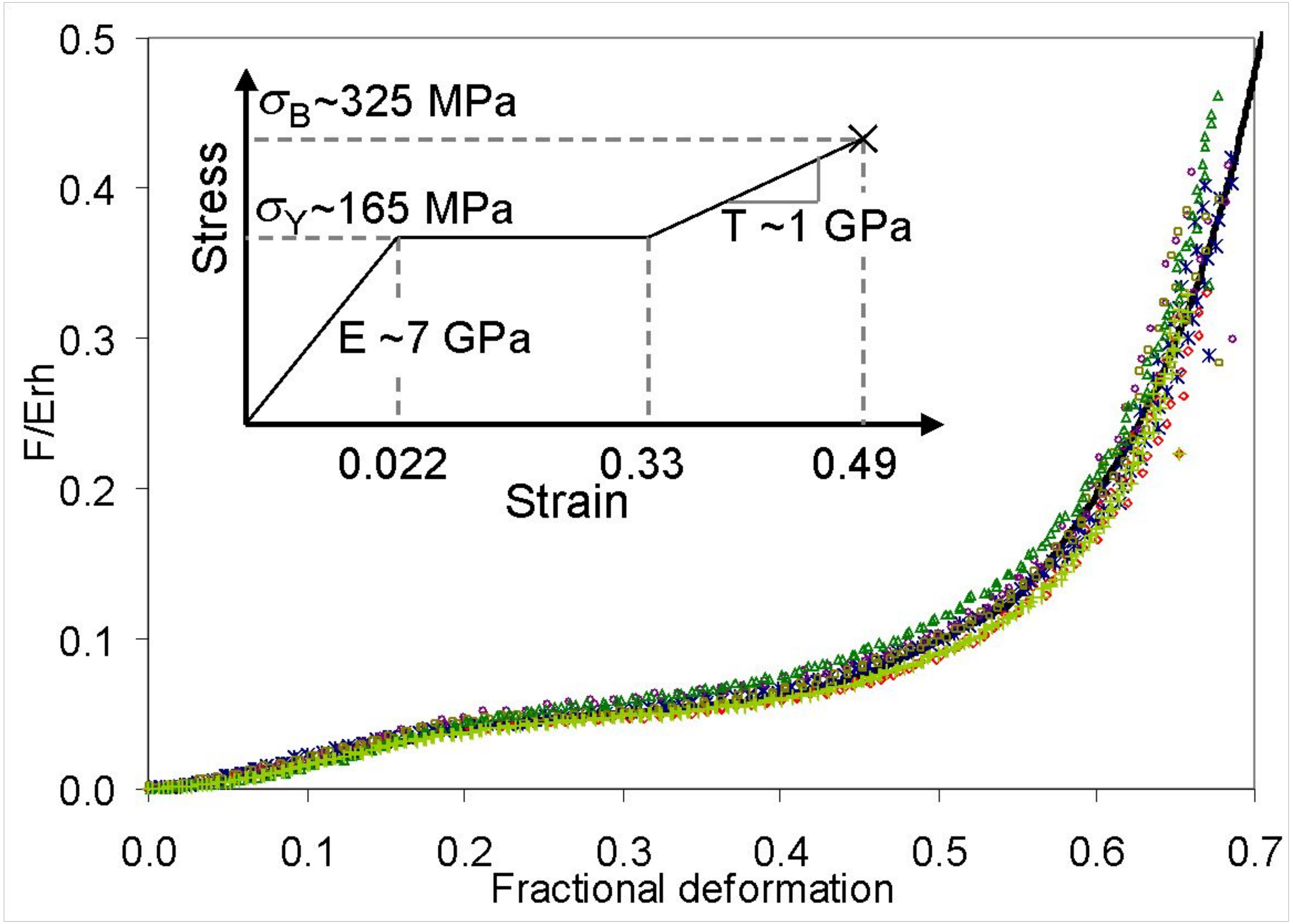
- At high deformations (*e.g.* $\varepsilon > 0.1$), MF microcapsules deform plastically
- Consider the simplest plasticity scenario: Perfect plasticity





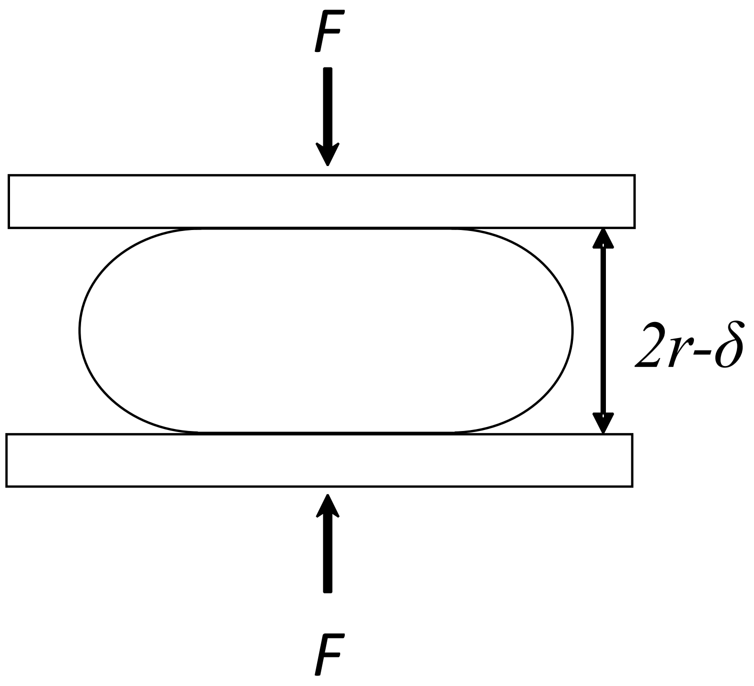
Mercadé-Prieto et al., *Chem. Eng. Sci*. (2011) 66:1836-1843.

FEM – Determination of rupture parameters



Mercadé-Prieto et al. (2012) *AIChEJ* 58 : 2674–2681.

Hertz model



$$F = \frac{4E\sqrt{r}}{3\left(1 - \nu^2\right)}\left(\frac{\delta}{2}\right)^{\frac{3}{2}}$$

where r, *E*, ν and δ are the radius, Young's modulus, Poisson's ratio and displacement of the sphere respectively.

Relationship between the Young's moduli of whole microcapsules and their shell material established by micromanipulation measurements

FEA:

$$\frac{\square}{\square_{\square\square\square\square\square}\square} = \square_1 \square^2 + \square_2 \square + \square_3, \quad \square 0.03 < \square < 0.1 \square$$

$$\square = \square_{\square\square\square\square\square}\square\square_1 \left(\frac{\square}{\square}\right)^3 + \square_2 \left(\frac{\square}{\square}\right)^2 + \square_3 \left(\frac{\square}{\square}\right) \square \left(\frac{\square}{2}\right)^{3/2} \square^{1/2}$$

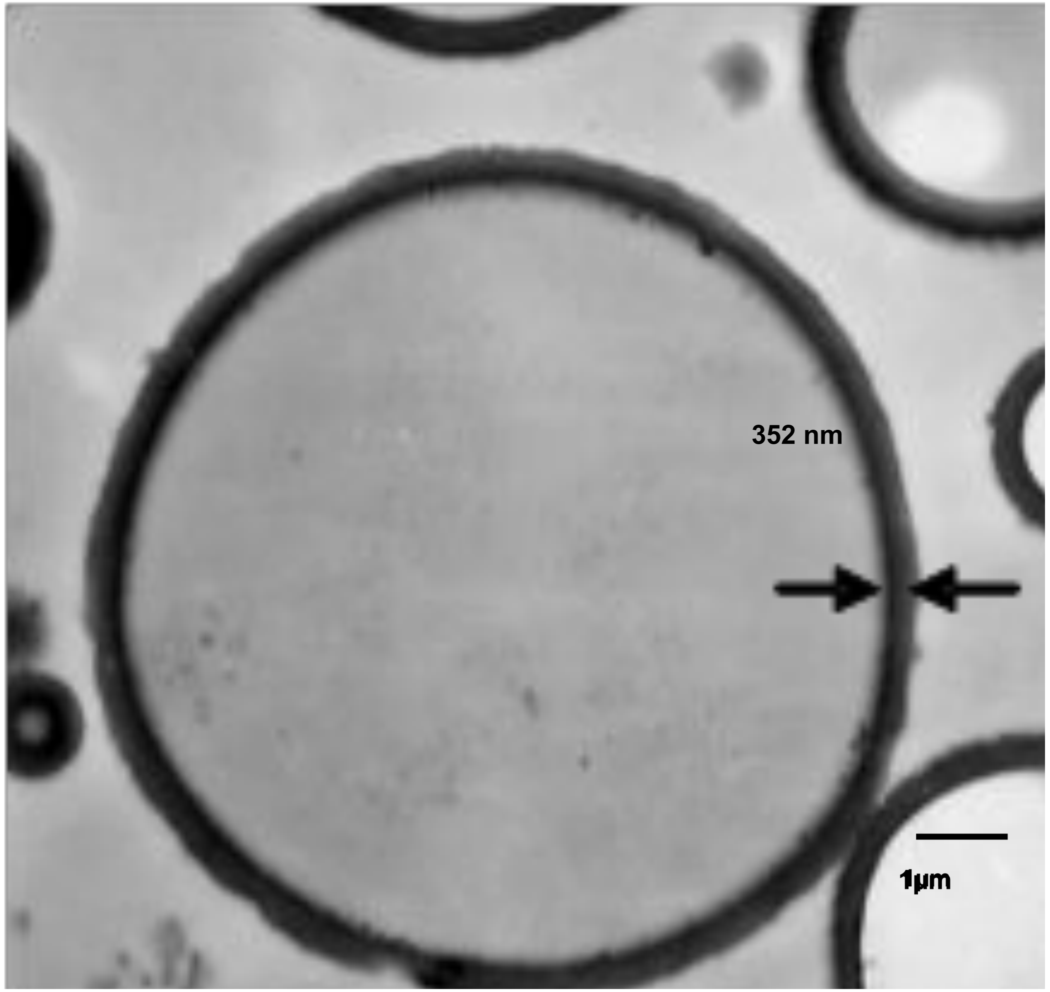
Hertz model:

$$\square = \frac{\square}{1 - \square^2} \square_{\square} \square^2 \left(\frac{\square}{2\square}\right)^{3/2}$$

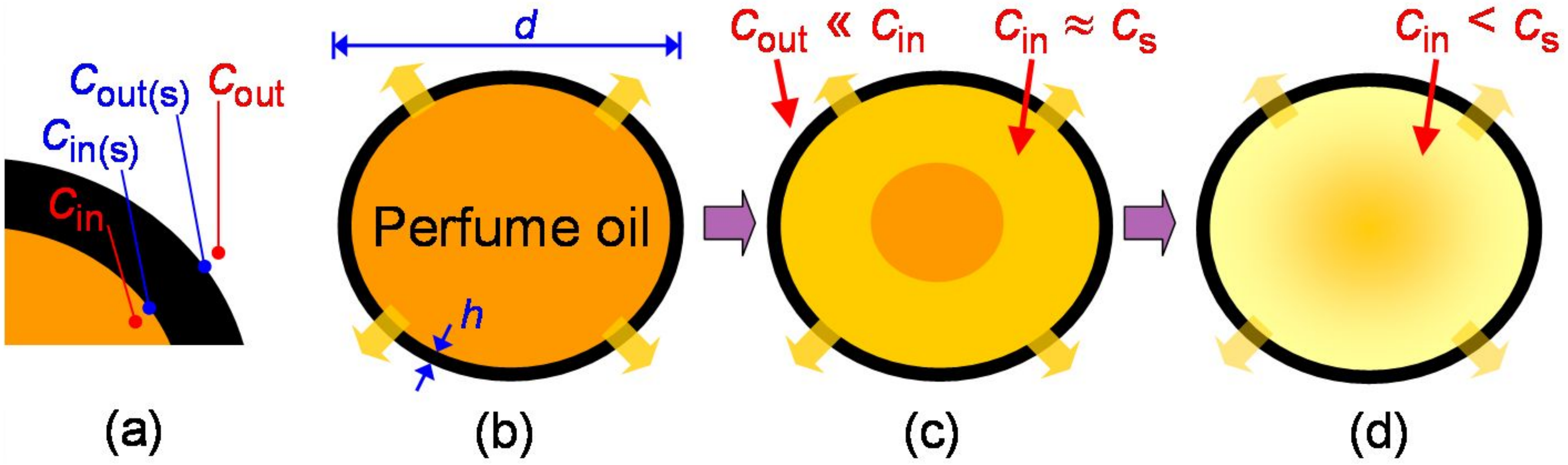
$$\frac{\square_{\square}}{\square_{\square\square\square\square\square}} = \square_1 \left(\frac{\square}{\square}\right)^3 + \square_2 \left(\frac{\square}{\square}\right)^2 + \square_3 \left(\frac{\square}{\square}\right)$$

where $k_1 = 8.4673$, $k_2 = 2.5728$, and $k_3 = 0.1597$

Baiocco, D., Zhang, Z.H., He, Y. P. and Zhang, Z. (2023) *Micromachines* 14(1): 123



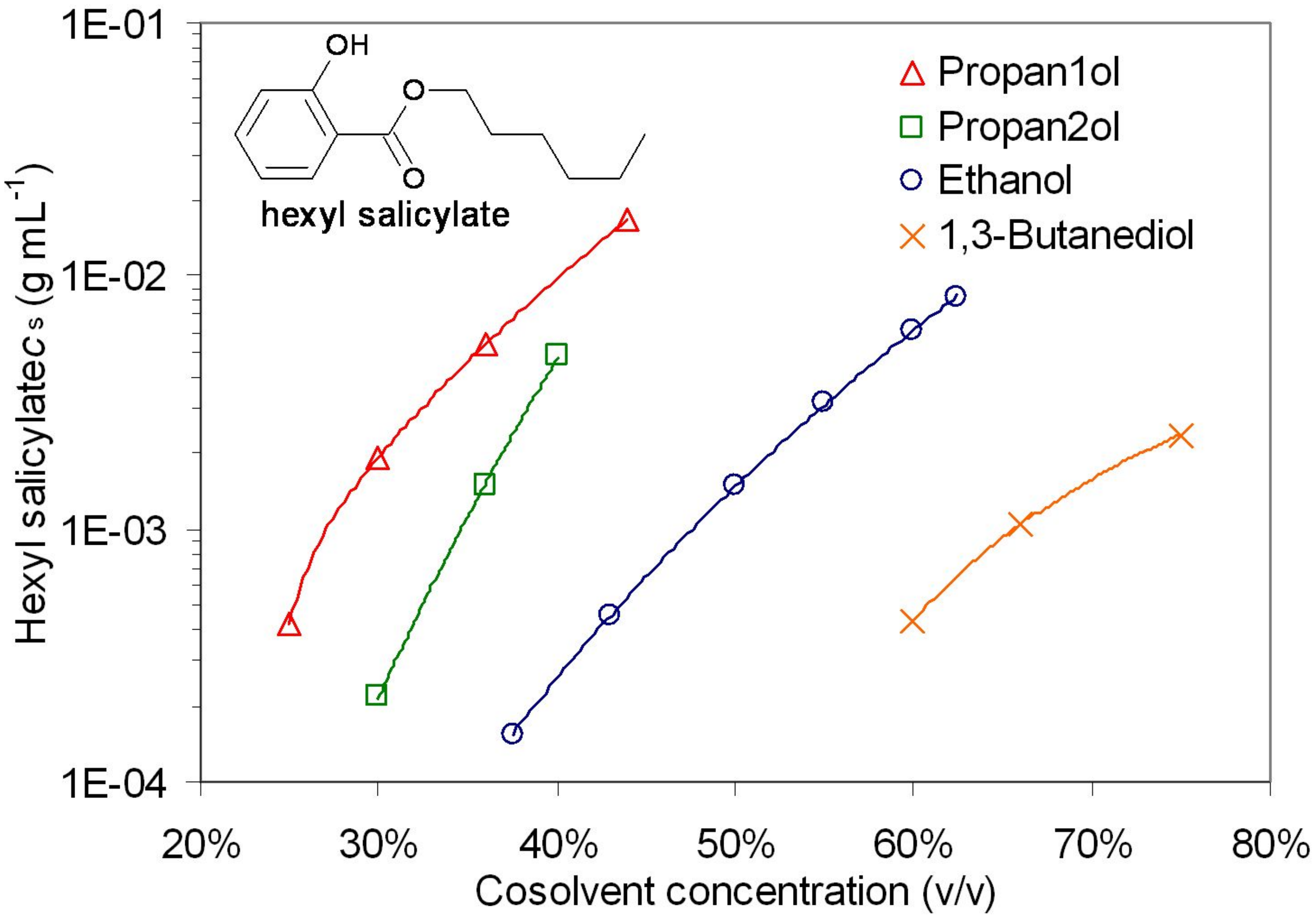
Long, Preece, York and Zhang (2009) *J. Mat. Chem.* 19: 6882–6887.



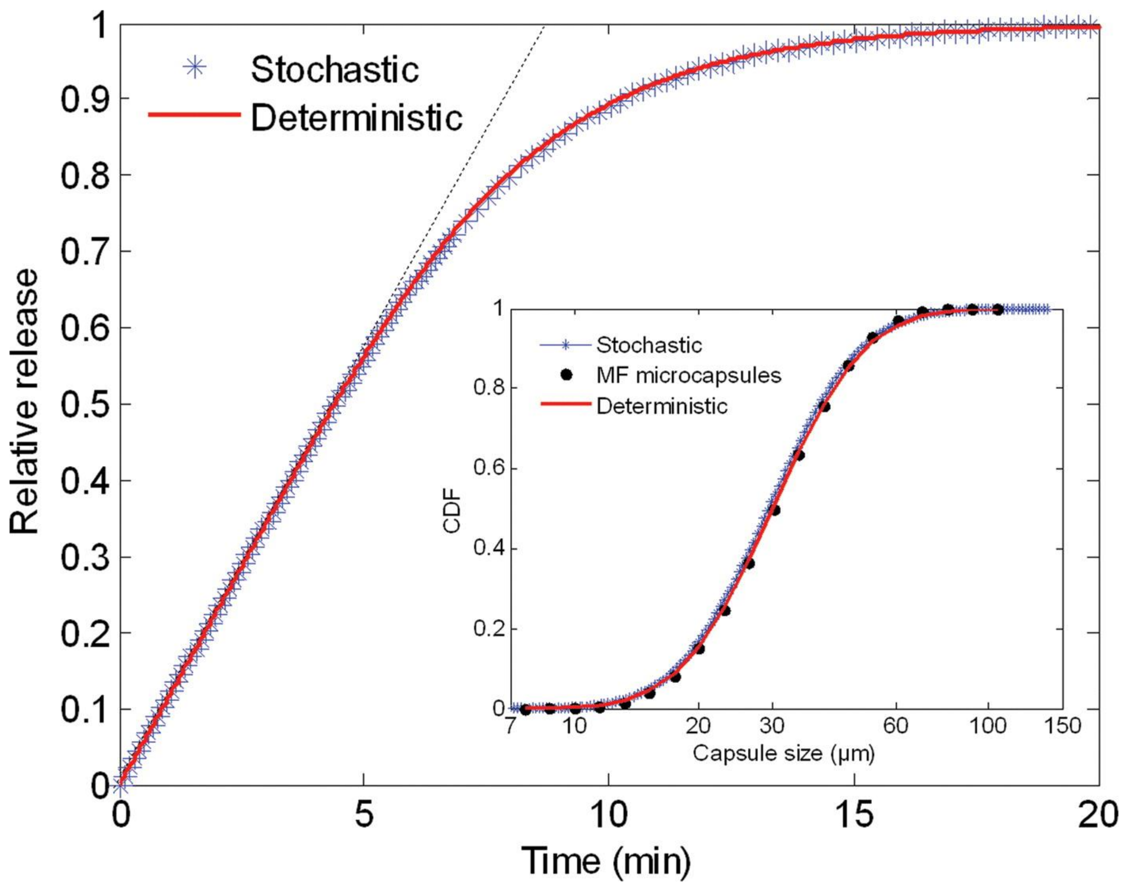
$$J = \frac{D}{h}\left(c_{in(s)} - c_{out(s)}\right) = \frac{P}{h}\left(c_{in} - c_{out}\right)$$

Schematic diagram of the release of the inner perfume oil through the microcapsule shell.

Mercadé-Prieto et al. (2012) *J. Microencapsulation* 29: 463-474.



Saturation concentration (c_s) of hexyl salicylate in different water-solvent solutions at 22^0C



Verification of the release profiles using the stochastic and the deterministic models for a population of microcapsules with the same lognormal size distribution shown in the inset

$$C_{out}(t) = \frac{\pi d^2}{V_{Solvent}} \frac{P}{h} C_s t$$

$$R(t) = \frac{V_{Solvent} C_{out}(t)}{\frac{1}{6}\pi(d-2h)^3 \rho_{oil}}$$

Is there any relationship between the fracture strength and oil release rate ?

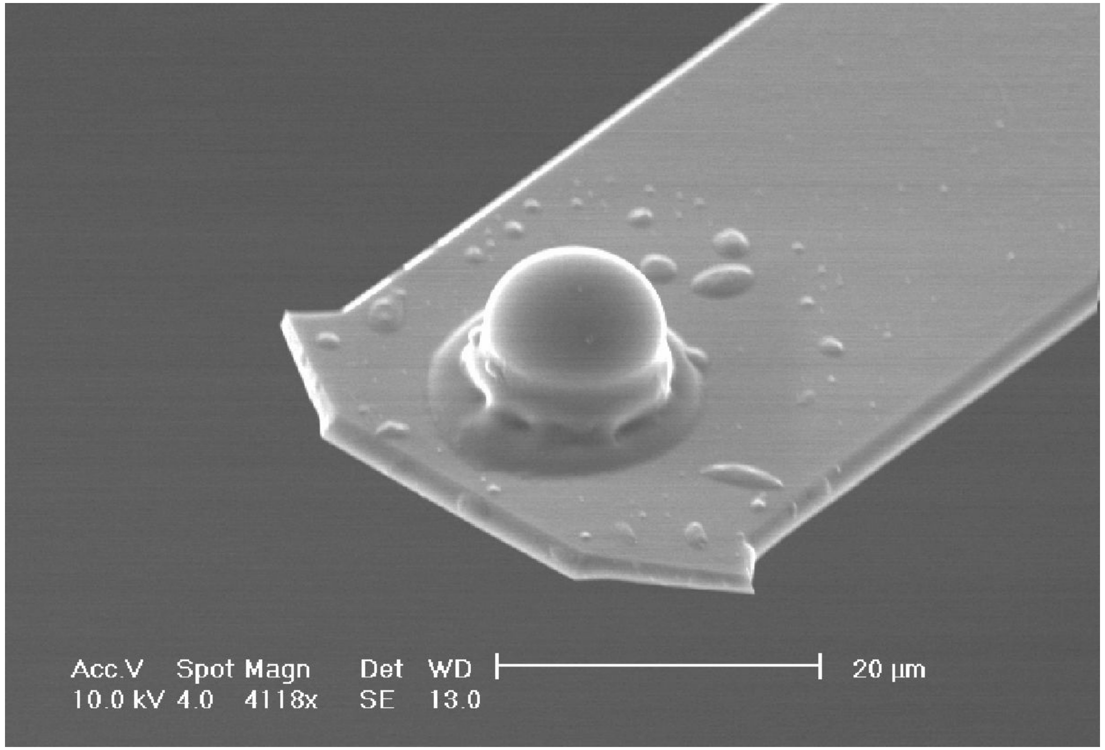
The fracture strength is mainly determined by the macro-structure.

$$\frac{F}{Erh} = a\varepsilon^2 + b\varepsilon + c \qquad 0.03 < \varepsilon < 0.1$$

The oil release rate is dominated by the fine structure, particularly for small molecules.

$$J = \frac{D}{h}\left(c_{in(s)} - c_{out(s)}\right) = \frac{P}{h}\left(c_{in} - c_{out}\right)$$

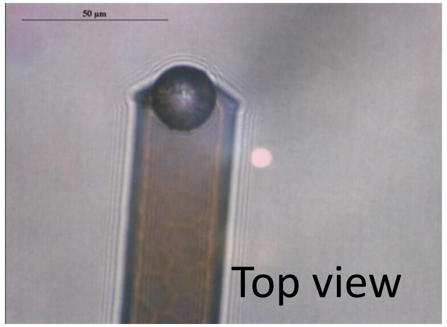
Shell thickness h affects both the fracture strength and oil leakage rate!

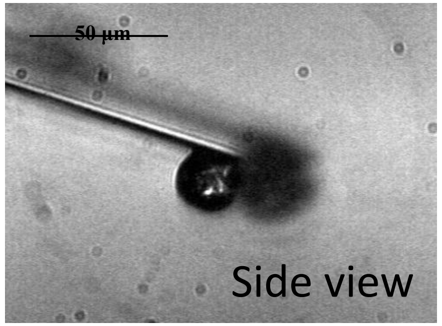


SEM image showing an encapsulate (11.9 µm) was attached to a tipless cantilever

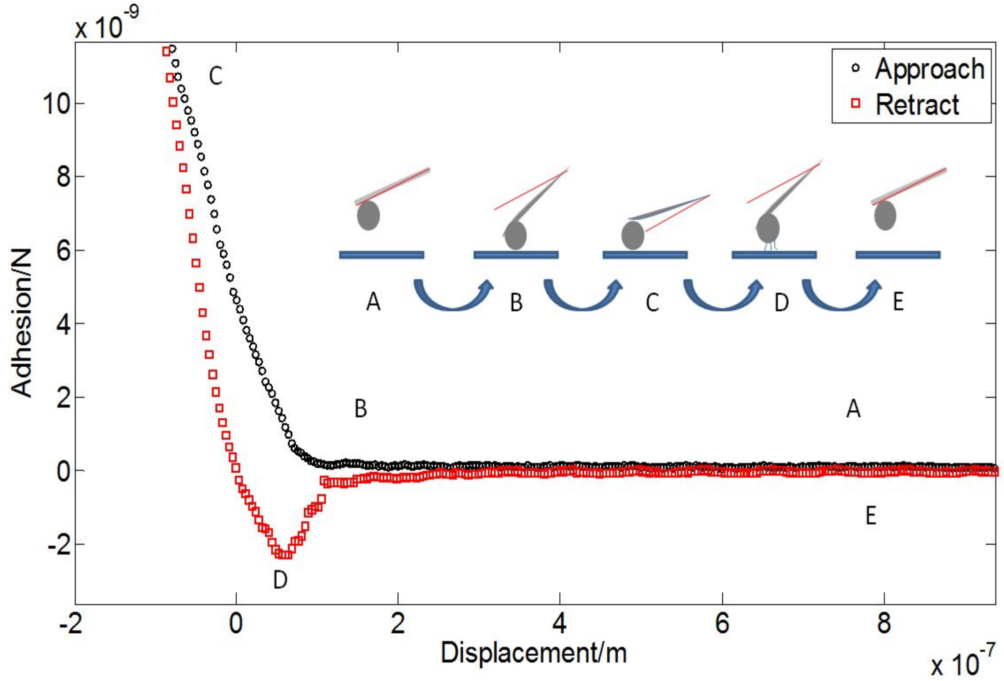
Liu et al., *J. Adhesion Sci. Technol*. 2013

Adhesion Investigation by AFM





Capsule colloidal probe



Schematic representations of steps during a typical force interaction between a capsule and a cellulose film.

He et al. (2014) *J Microencapsulation* 31: 430-439.

Fabric care R&D in Procter & Gamble

Laundry Liquid Detergents (HDL)

Fabric Enhancers

Laundry UnitDose

Conclusions

- Characterising the structural, barrier, mechanical and surface properties of microcapsules is essential to ensure their functionalities.
- The micromanipulation technique has been demonstrated to be very powerful to measure the mechanical strength of single microcapsules. A new instrument "Microparticle Strength Tester" has been commercialised by Microforce Measurement Ltd UK (http://microforce-measurement-ltd.co.uk/)
- Accurate characterisation of their shell permeability via accelerated tests can help to predict their long-term storage stability.
- AFM is a useful tool to directly measure adhesion of single microcapsules to substrate.
- Future work will focus on developing microplastic-free microcapsules assisted by using various state-of-art characterisation techniques.

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- Arjo Wiggins Research and Development Ltd., UK;
- Bayer, Germany;
- Bavarian Nordic, Germany;
- Merck Sharp & Dohme, UK;
- Procter & Gamble, UK, Belgium & USA, China, Japan and Germany;
- Unilever, UK and The Netherlands;
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- Tithebarn Ltd., UK;
- IAMS, USA;
- Roche, Switzerland;
- Phoqus Ltd., UK;
- Rhodia, France
- National Starch, USA;
- Firmenich, Switzerland;
- Givaudan Schweiz AG, Switzerland and UK;
- Appleton Paper Inc. (Encapsys), USA
- Philips UK
- Lesaffre France
- International Favours and Fragrances, USA
- DSM, Switzerland
- Cytec, UK
- Symrise AG, Germany
- Lexon, UK
- Syngenta, UK
- Mondelez, USA
- Coty, Switzerland
- Microcaps AG, Switzerland
- GEM INNOV S.A.S, France
- Xampla, UK