Understanding Microcapsule Properties for Developing Consumer Products

Professor Zhibing Zhang
School of Chemical Engineering
University of Birmingham, UK
Tel: 0121 414 5334
Email: Z.Zhang@bham.ac.uk

Biological and Non-biological Materials (1μm - 1mm)

- animal cells
- yeasts
- Bacteria
- fungal hyphae
- plant cells
- cell and debris flocs
- skin cells and chondrocytes
- starch granules
- pollen grains
- biofilms and food fouling deposits
- microcapsules (encapsulates)
- microspheres
- agglomerates
- granules
- textile fibres
- ice crystals
- bubbles
- structured liquids

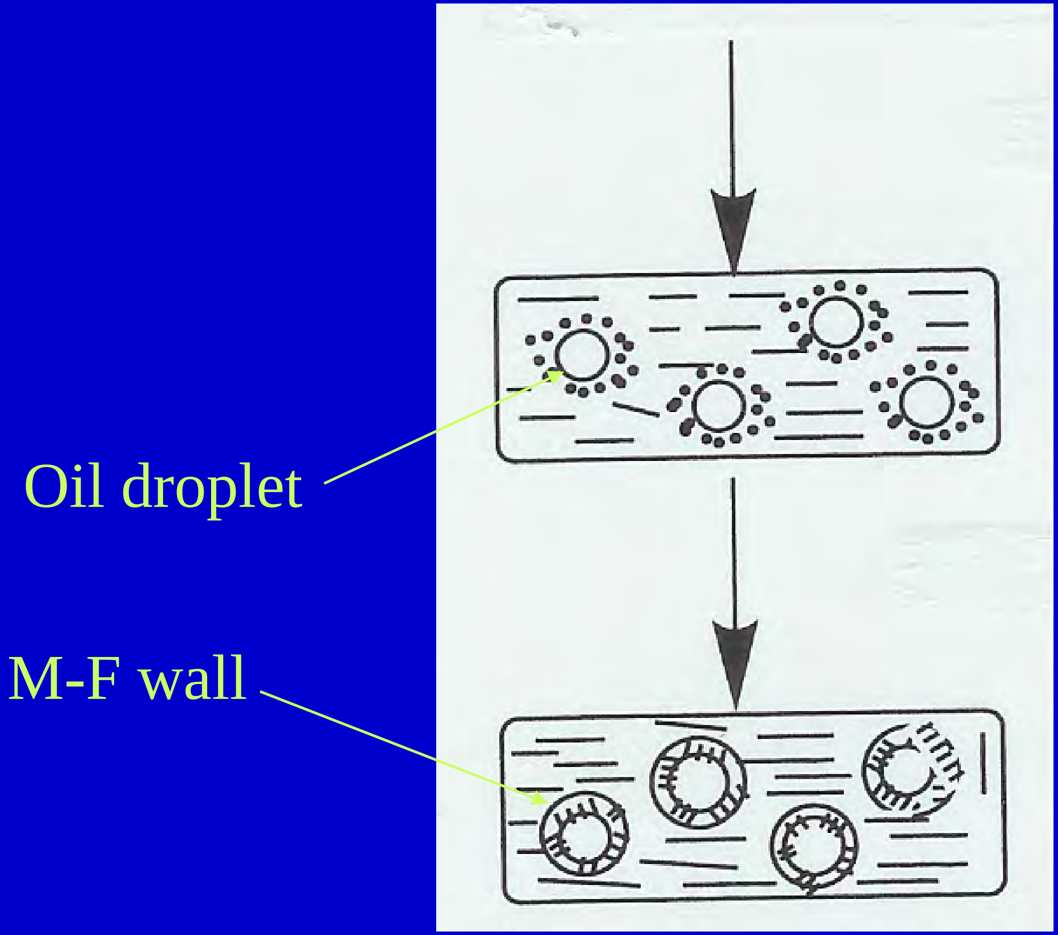
Formulation and Characterisation of functional microcapsules

- Pressure-sensitive materials (e.g melamine formaldehyde perfume capsules; capsules for self healing materials)
- Carriers of speciality chemicals (e.g. peroxide, antimicrobial agents, herbicide)
- Drugs (water soluble, non-soluble, protein)
- Probiotic cells (bacteria and yeast)
- Nutraceutical enzyme (Nattokinase)

http://www.scienceinthebox.com/laundry-perfumes-provide-fresh-scents

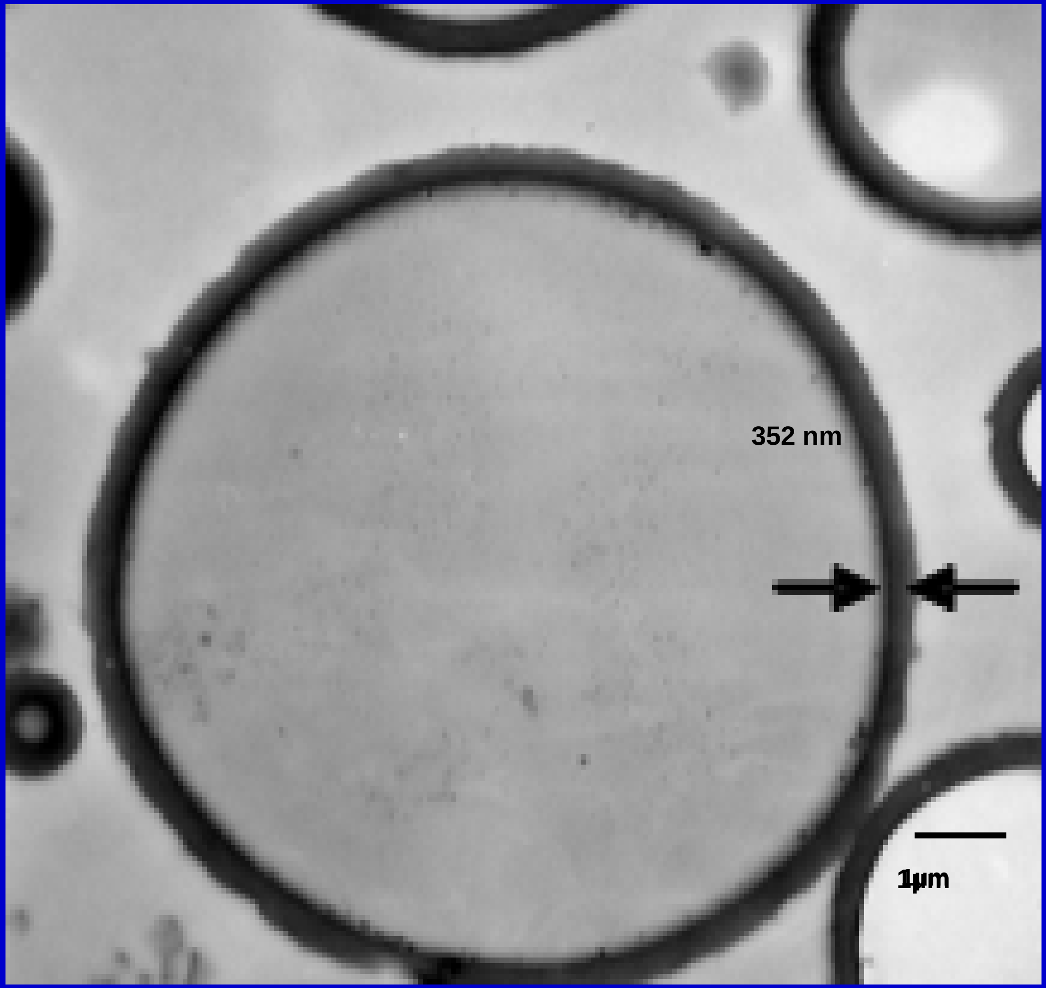
Properties of Capsules

- Core and wall chemical compositions
- Morphology, size and wall thickness
- **Mechanical strength**
- Pore size, structure of wall materials and **release rate**
- Surface charge
- **Adhesion on surface**
- Functionality of active ingredient



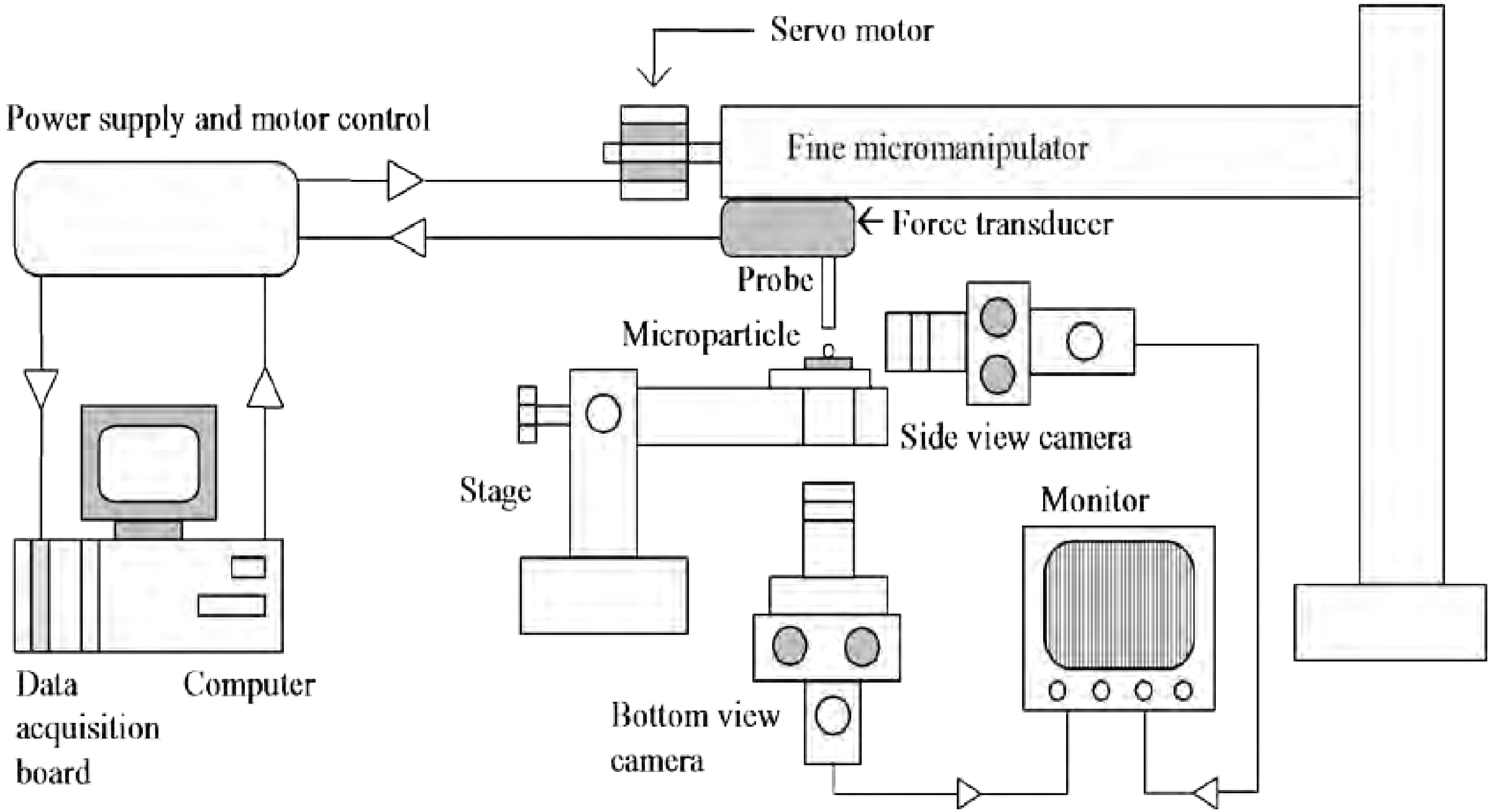
Formation of a melamine formaldehyde (M-F) wall on the surfaces of oil droplets .

Sun and Zhang (2001) *J Microencapsulation*



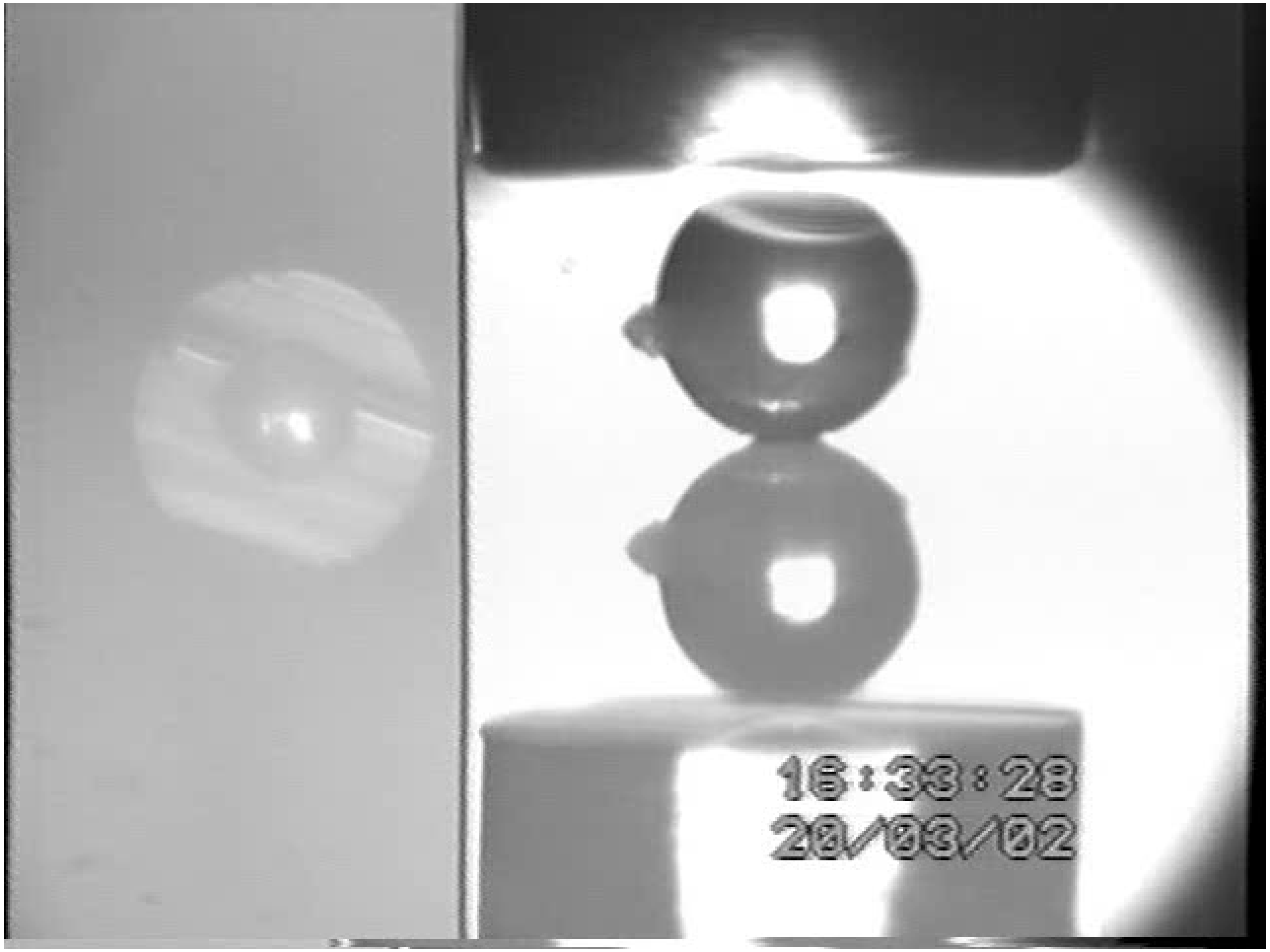
Transmission electron microscopy (TEM) image of melamine formaldehyde microcapsules.

Long, Preece, York and Zhang (2009) *J. Mat. Chem.*



Schematic diagram of the micromanipulation rig

Zhang, Saunders & Thomas (1999) ***J Microencapsulation***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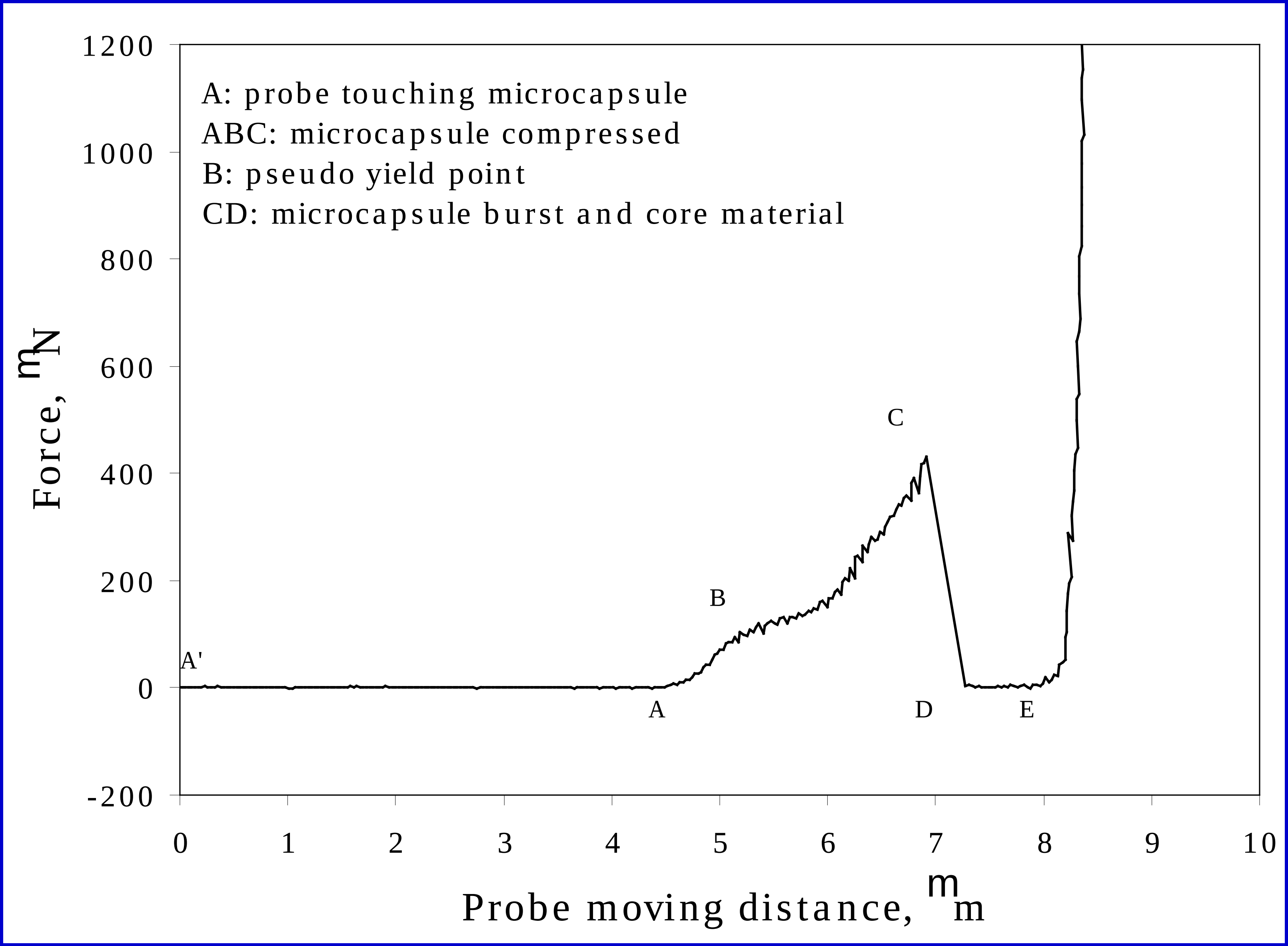
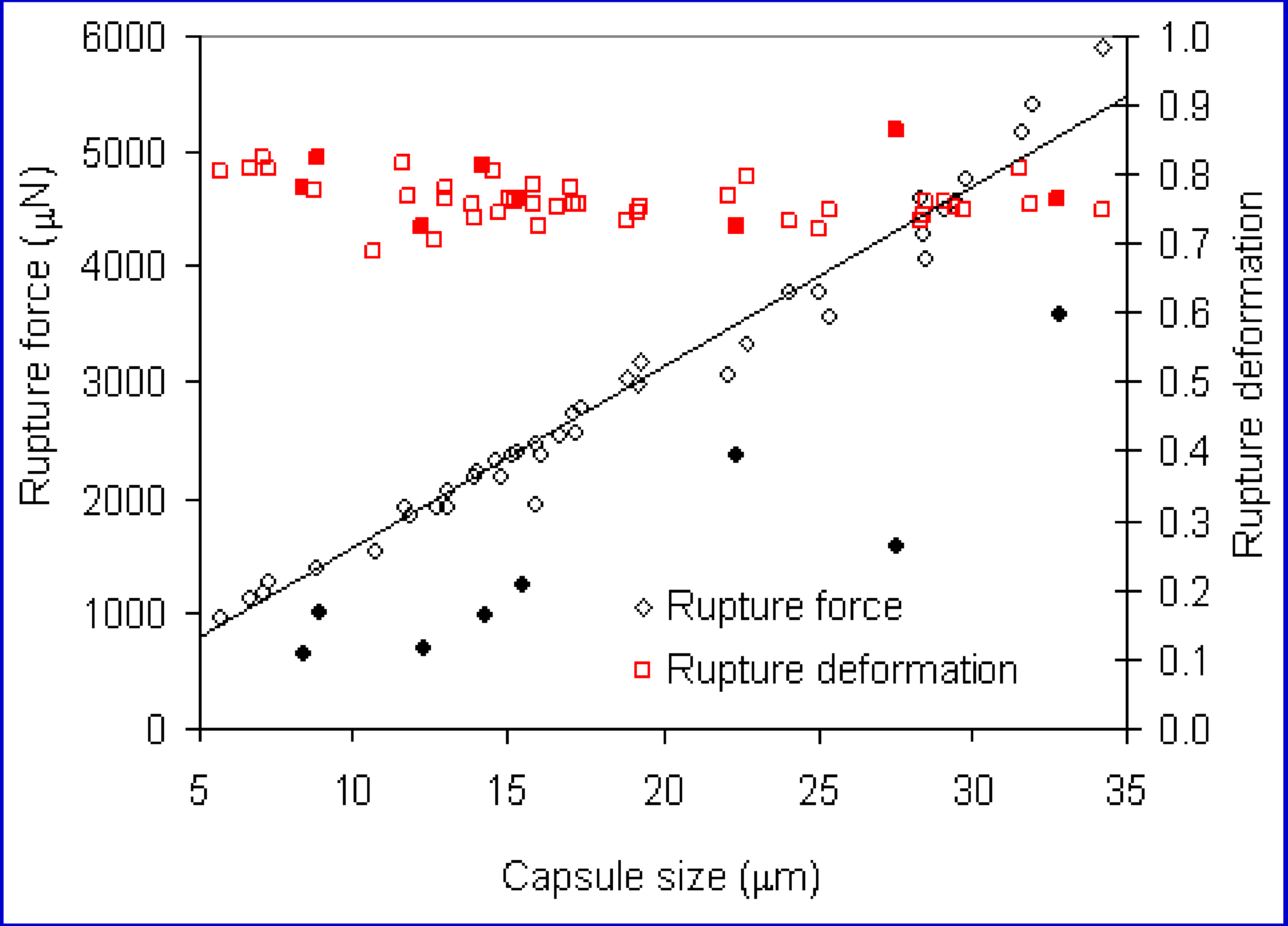


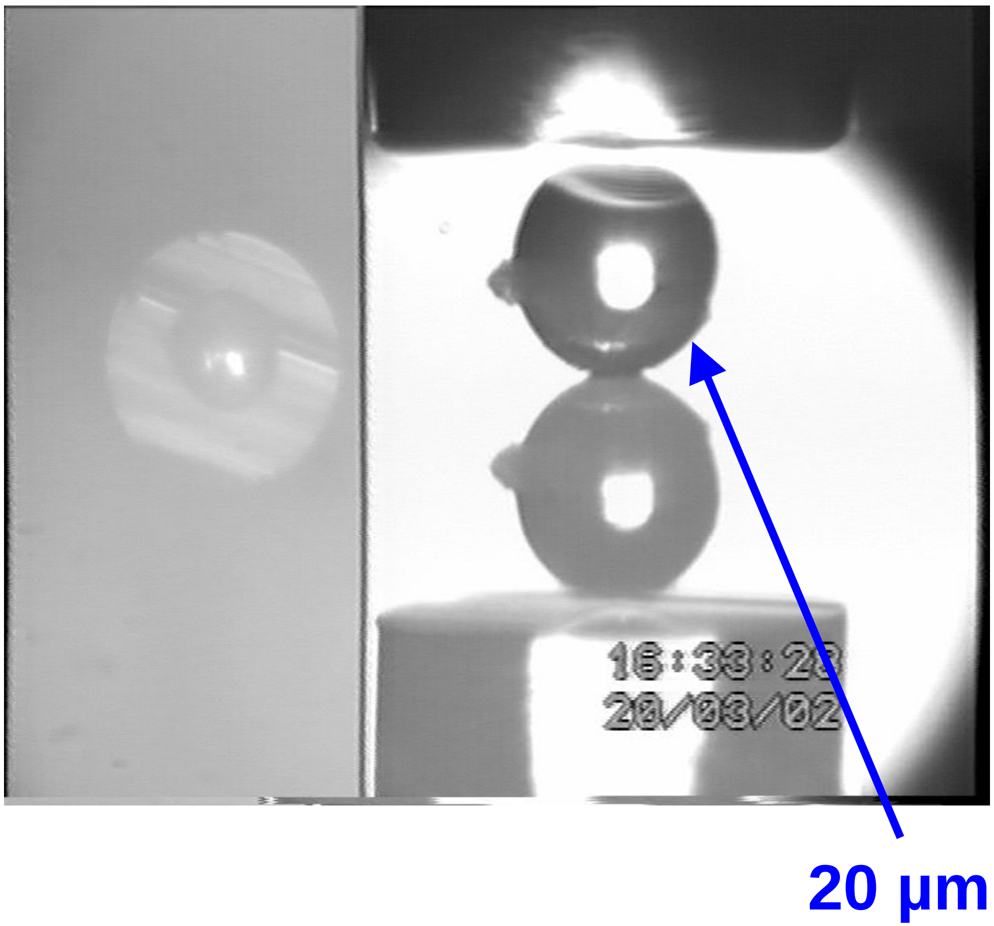
Force versus displacement for compression of a microcapsule to rupture.

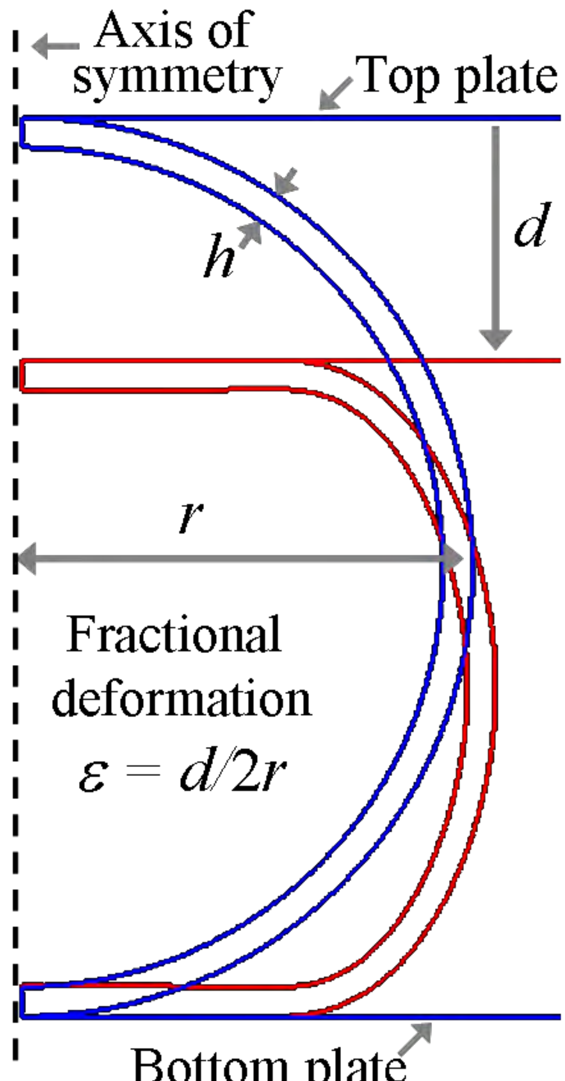
Sun and Zhang (2001) ***J Microencapsulation***



Mercadé-Prieto et al (2011a) *Chem. Eng. Sci.*

Micromanipulation to measure the rupture force of single encapsulates and finite element modelling (FEM) to determine their intrinsic mechanical property parameters

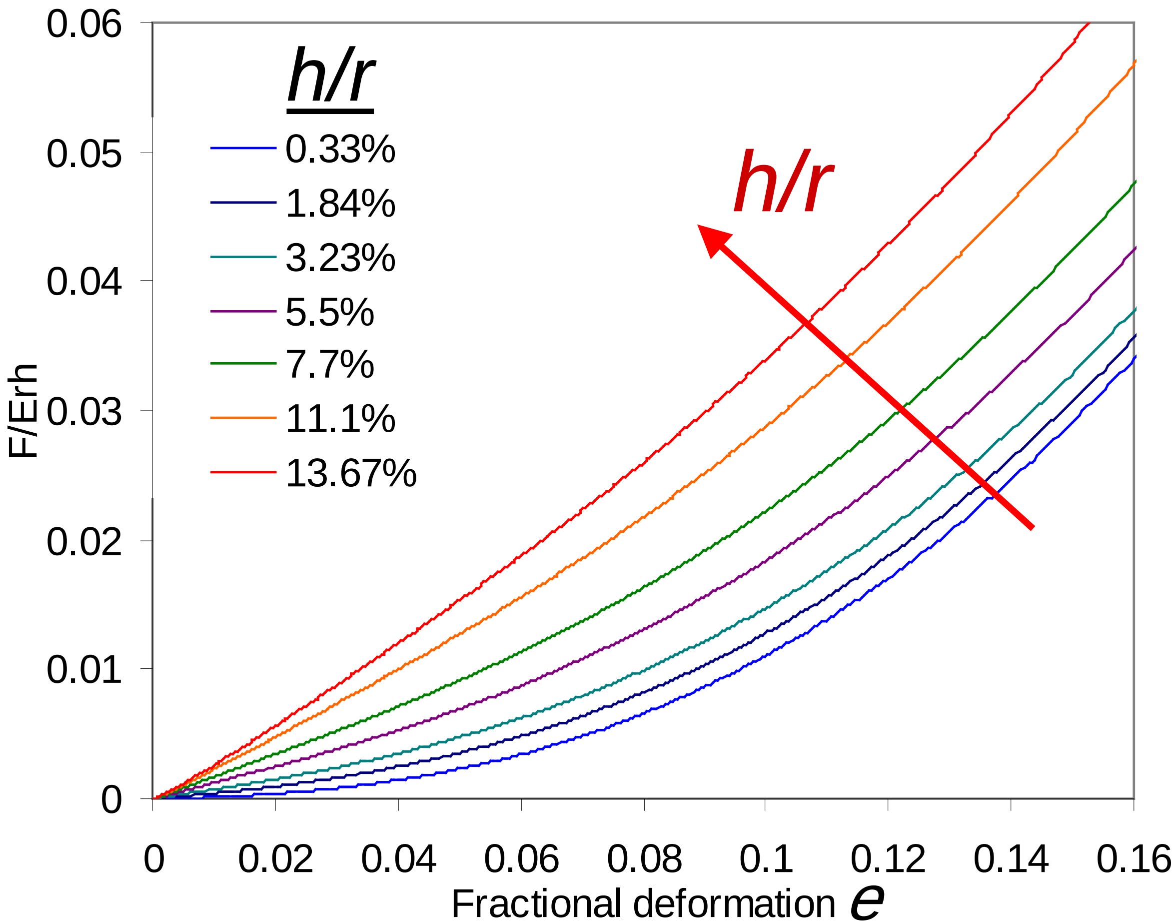




FEM – Elastic shell

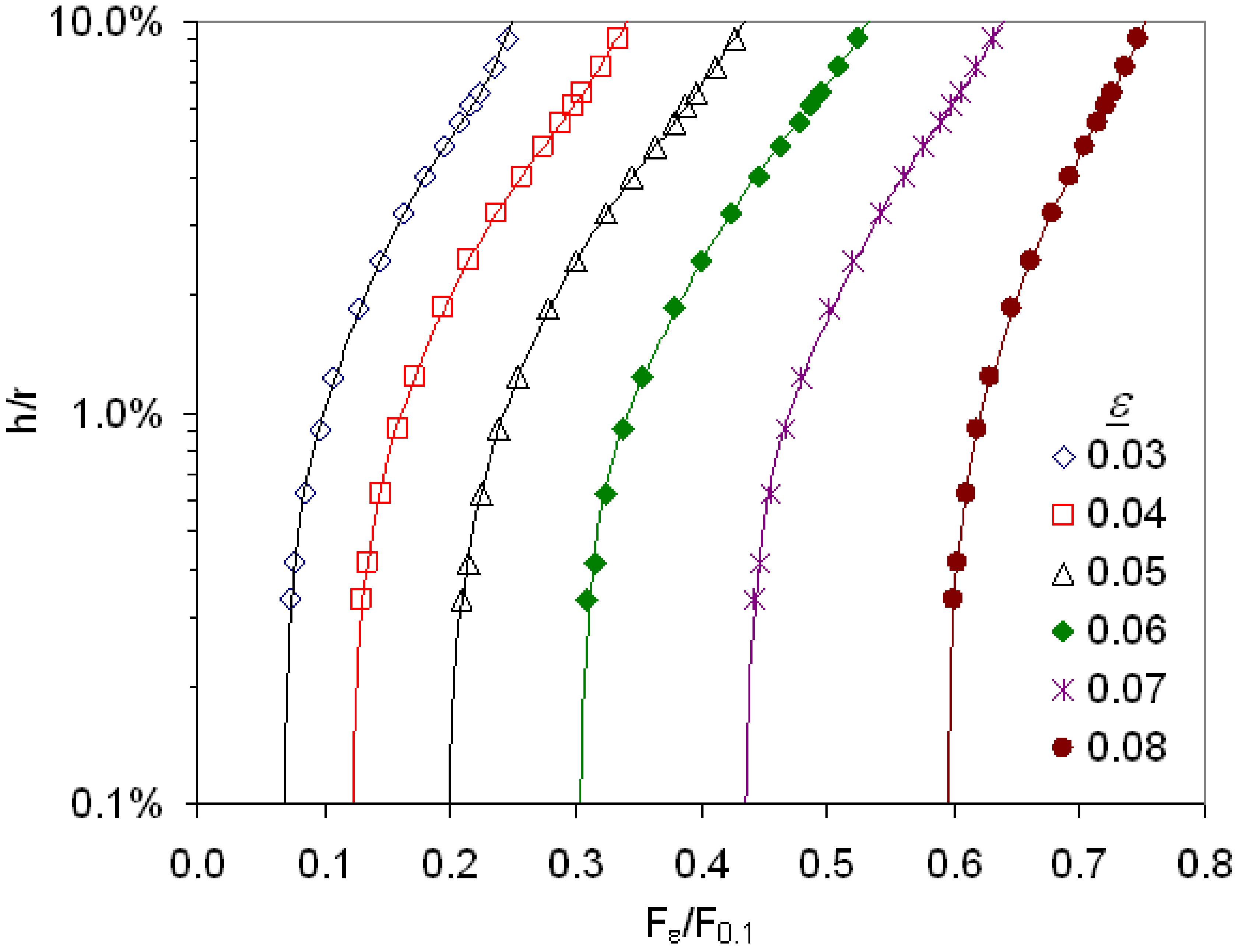
Determination of the Elastic Modulus (E):

- MF encapsulates are known to be elastic at small fractional deformations $e < 0.15$



- 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. (2011a) *Chem. Eng. Sci.*


10.0%
1.0%
0.1%
h/r
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
$F_\varepsilon/F_{0.1}$
ε
0.03
0.04
0.05
0.06
0.07
0.08

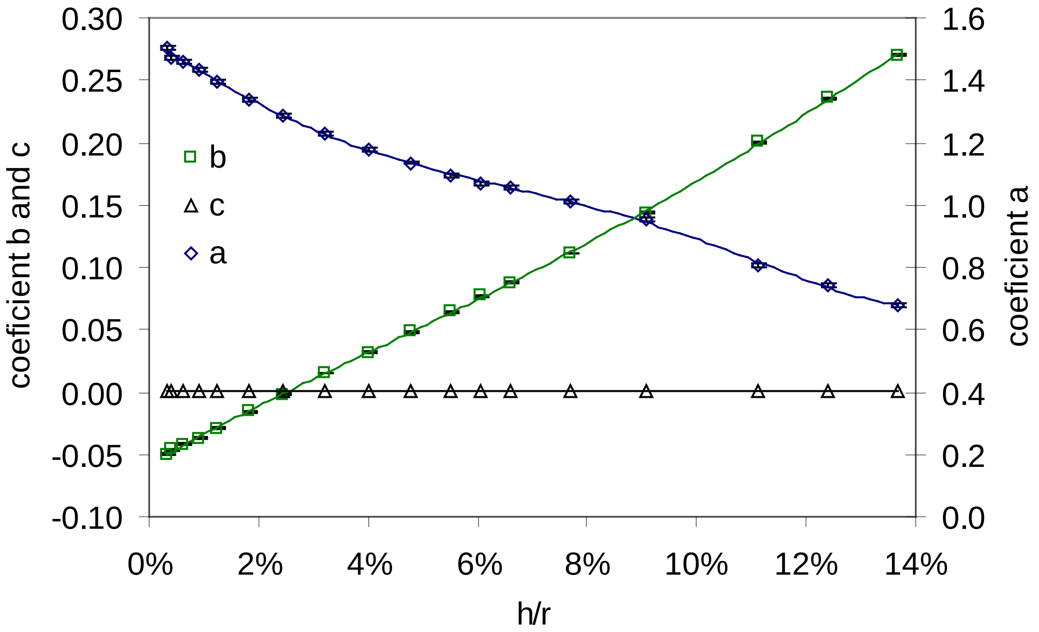
FEM – Elastic shell – Estimate *Eh*

- Once *h* is known we can estimate *Eh*
- Compare experimental force curve with FEM results at the appropriate *h/r*

FEA results:

$$\frac{F}{Erh} = ae^2 + be + c$$

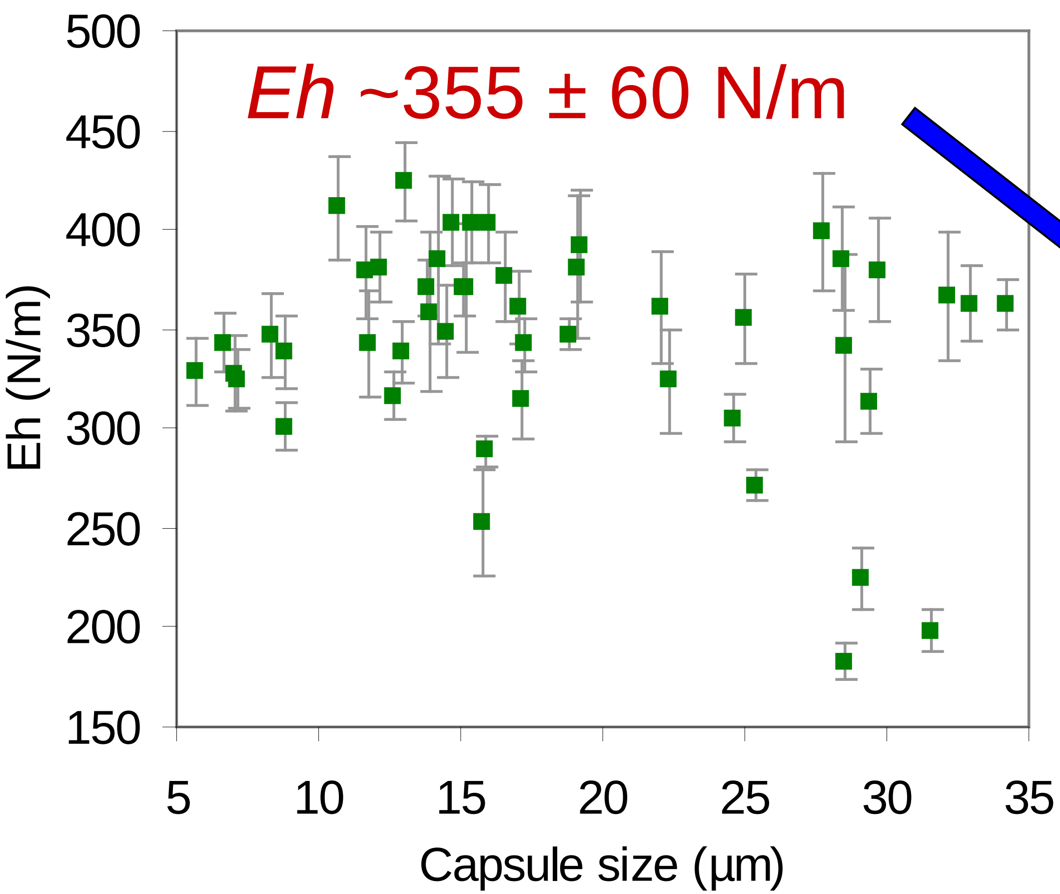
$$0.03 < e < 0.1$$



The experimental *Eh* is calculated at different fractional deformations

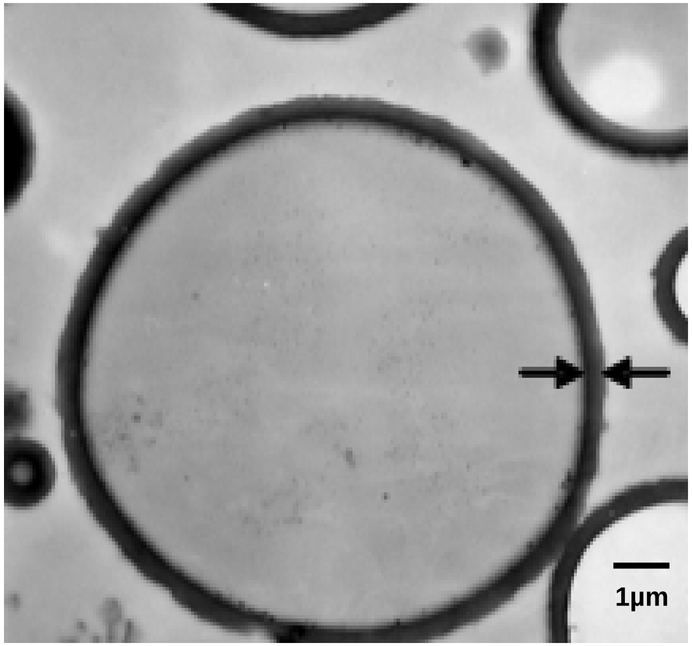
$$Eh_e = \frac{F_e / r}{ae^2 + be + c}$$

MF Encapsulates – Elastic shell – Estimate *Eh*



h ~0.2 µm

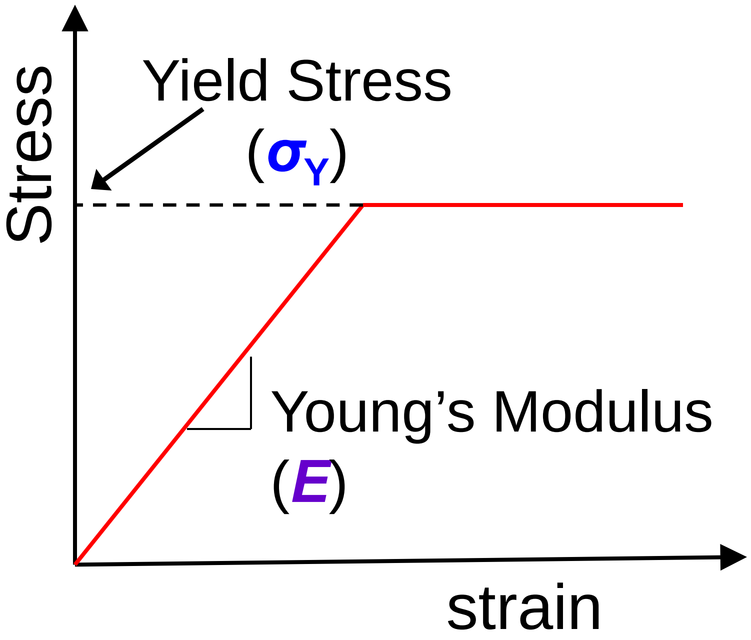
E ~1.8 ± 0.3 GPa

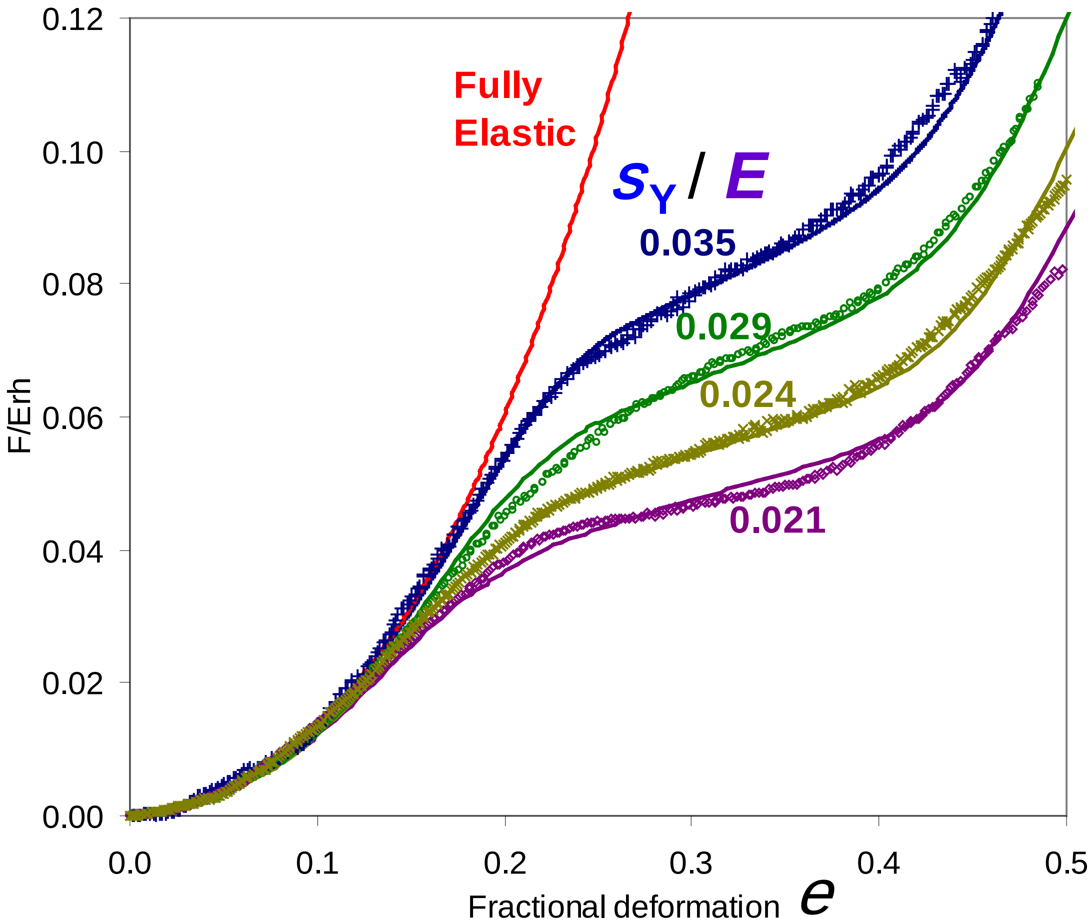


Eh is independent of the encapsulate size.

MF microcapsules – Elastic perfectly-plastic shell

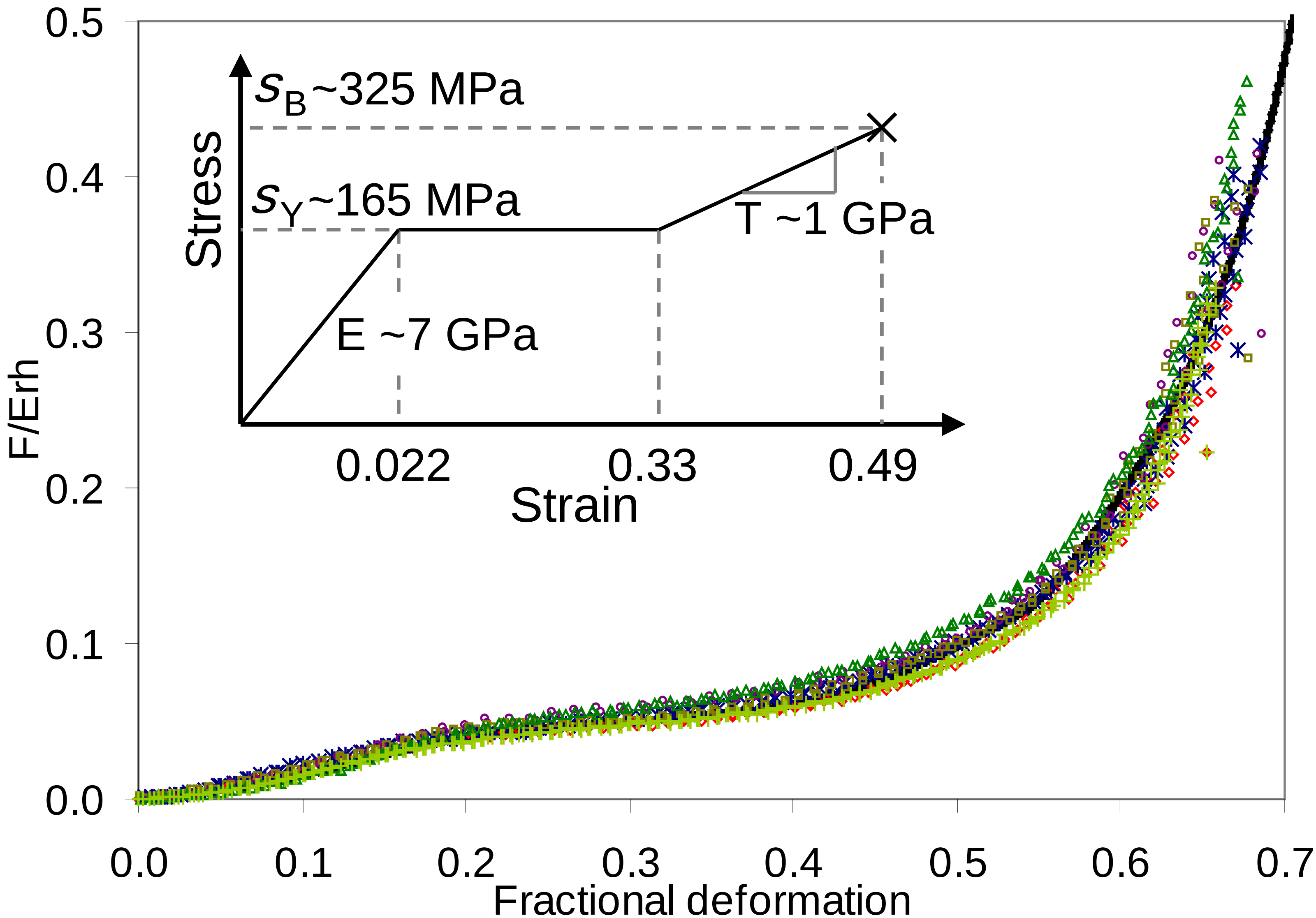
- At high deformations (*e.g. e*> 0.1), MF microcapsules deform plastically
- Consider the simplest plasticity scenario: Perfect plasticity



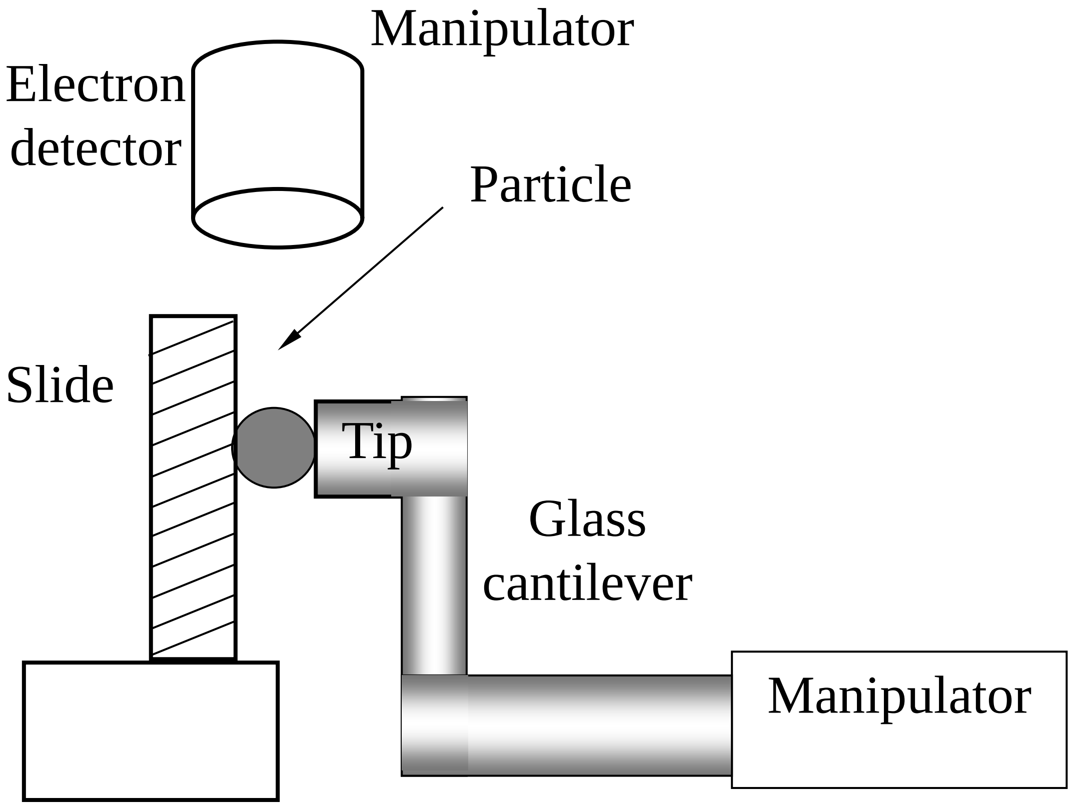


Mercadé-Prieto et al. (2011b)
Chem. Eng. Sci.

FEM – Determination of rupture parameters

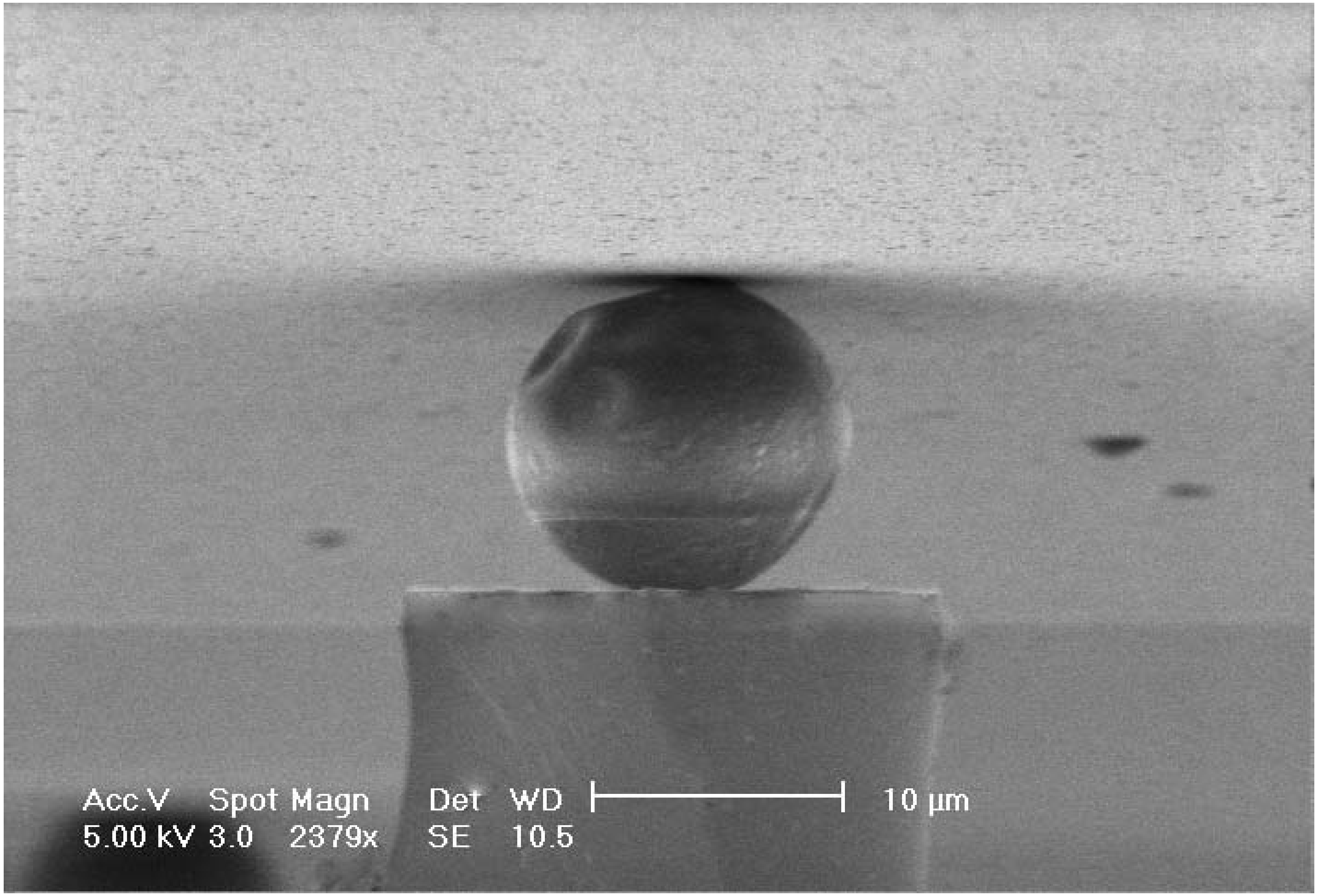


Mercadé-Prieto et al. (2012) *AIChEJ*

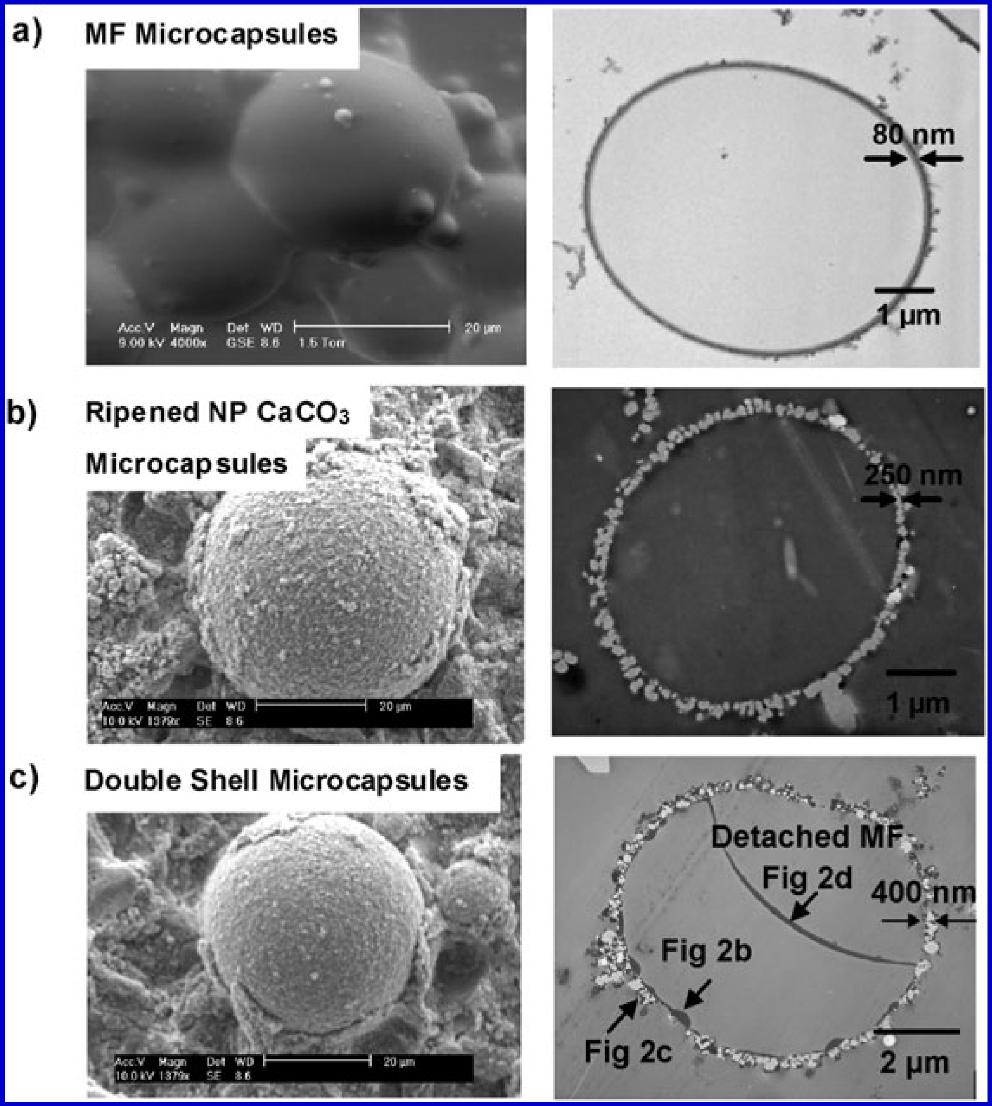


Schematic diagram of the nano-manipulation device in an ESEM

Liu, Donald and Zhang (2005) *Materials Sci. Technol.*

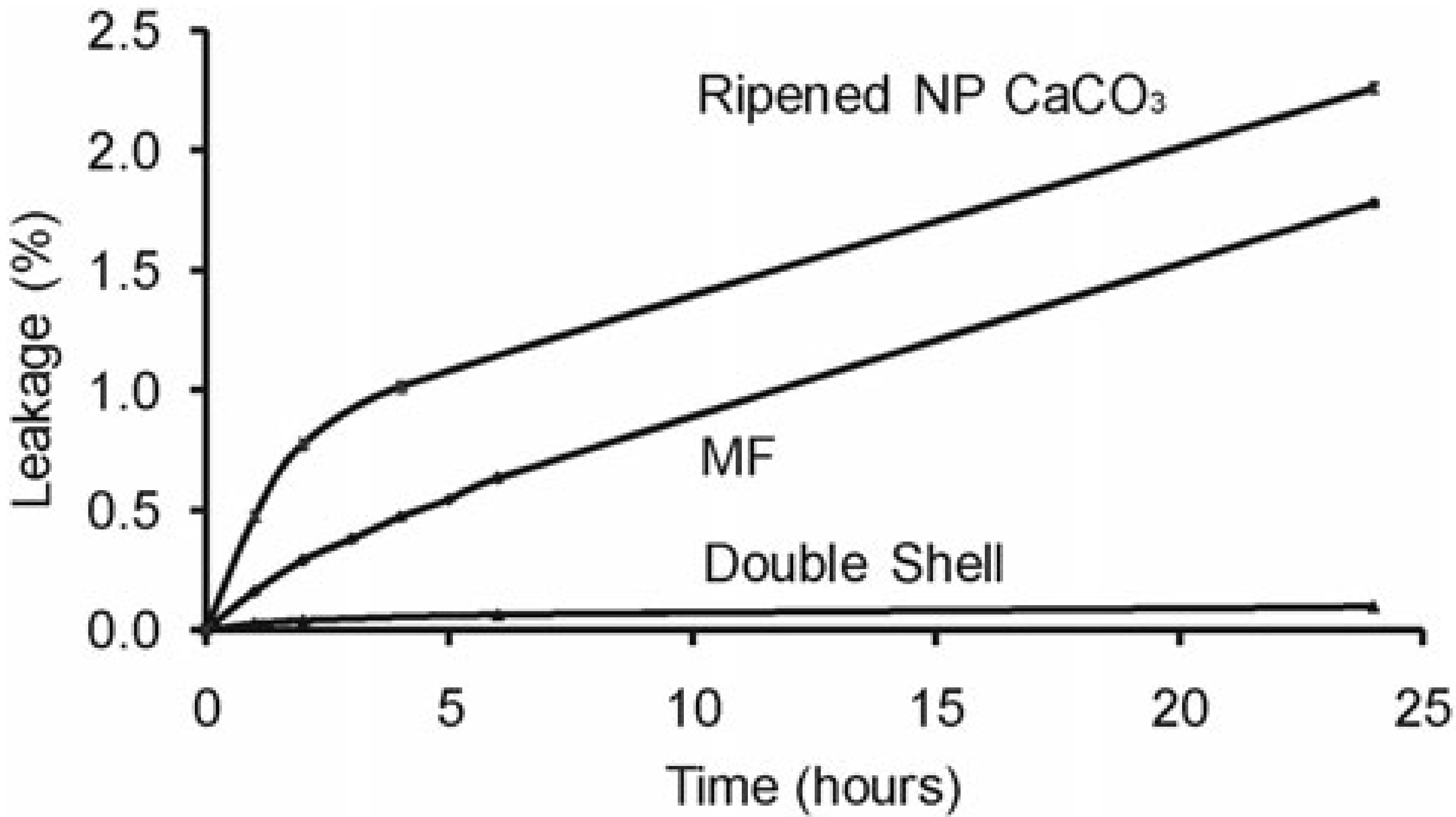


Ren, Donald and Zhang (2007) ***Materials Sci. Technol.***

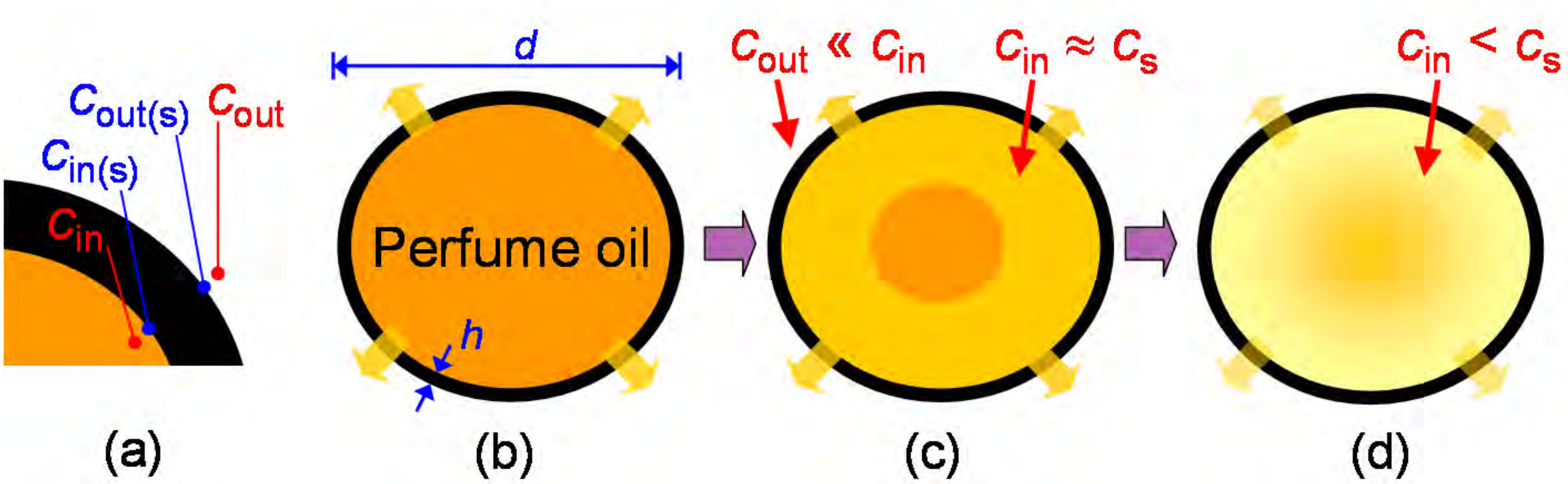


ESEM (LHS) and TEM (RHS) images of the MF, ripened NP CaCO3 and double shell composite microcapsules

Long, Vincent, York, Zhang and Preece (2010) *Chem. Commun.*



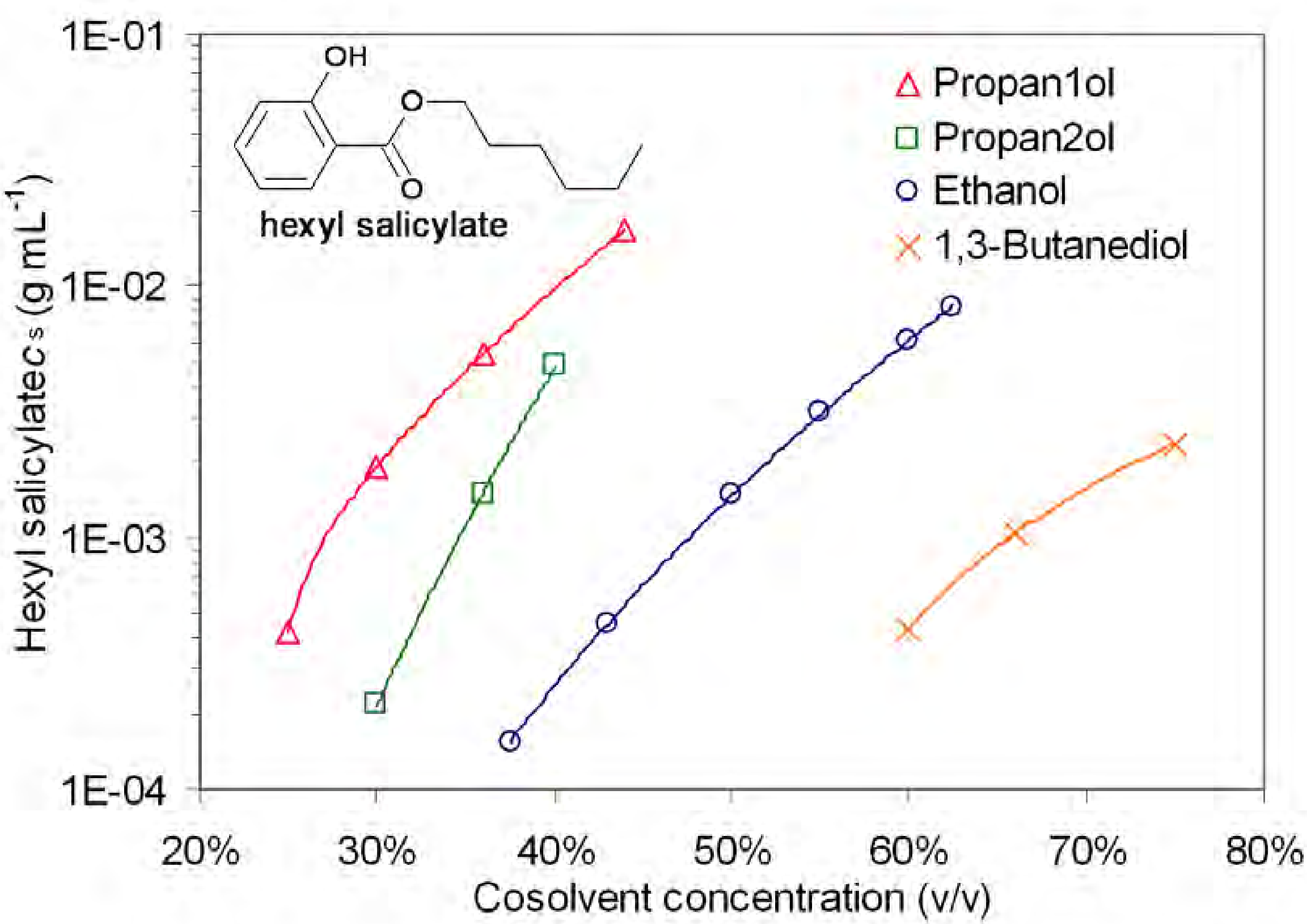
Percentage leakage of the core oil from the MF, ripened NP CaCO3 and double shell composite microcapsules over 24 hours



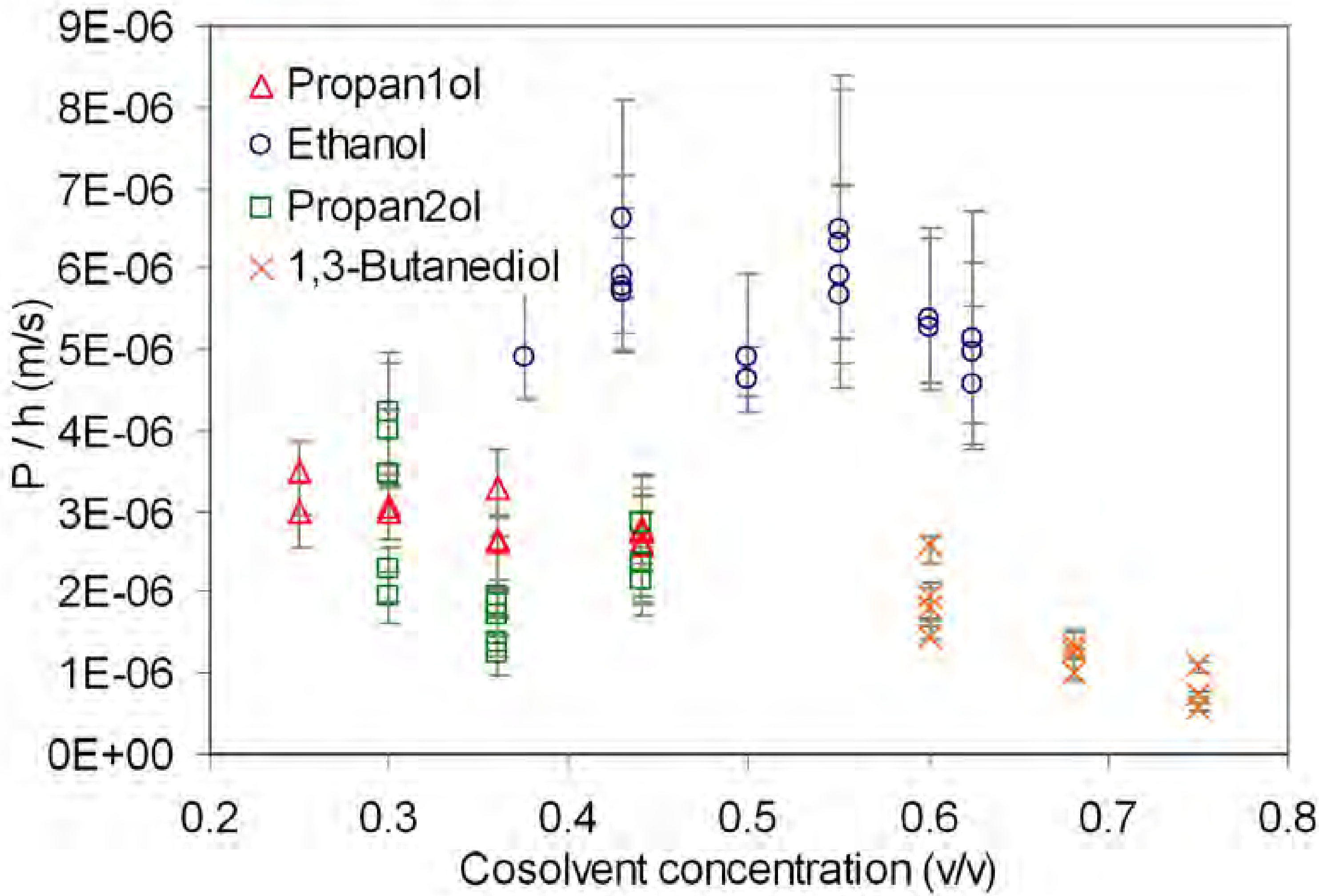
$$J = \frac{D}{h}\left(c_{in(s)} - c_{out(s)}\right) = \frac{P}{h}\left(c_{in} - c_{out}\right)$$

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

Mercadé-Prieto et al. (2012) *J. Microencapsulation*



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



The corresponding mean P/h values obtained using different cosolvents.

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

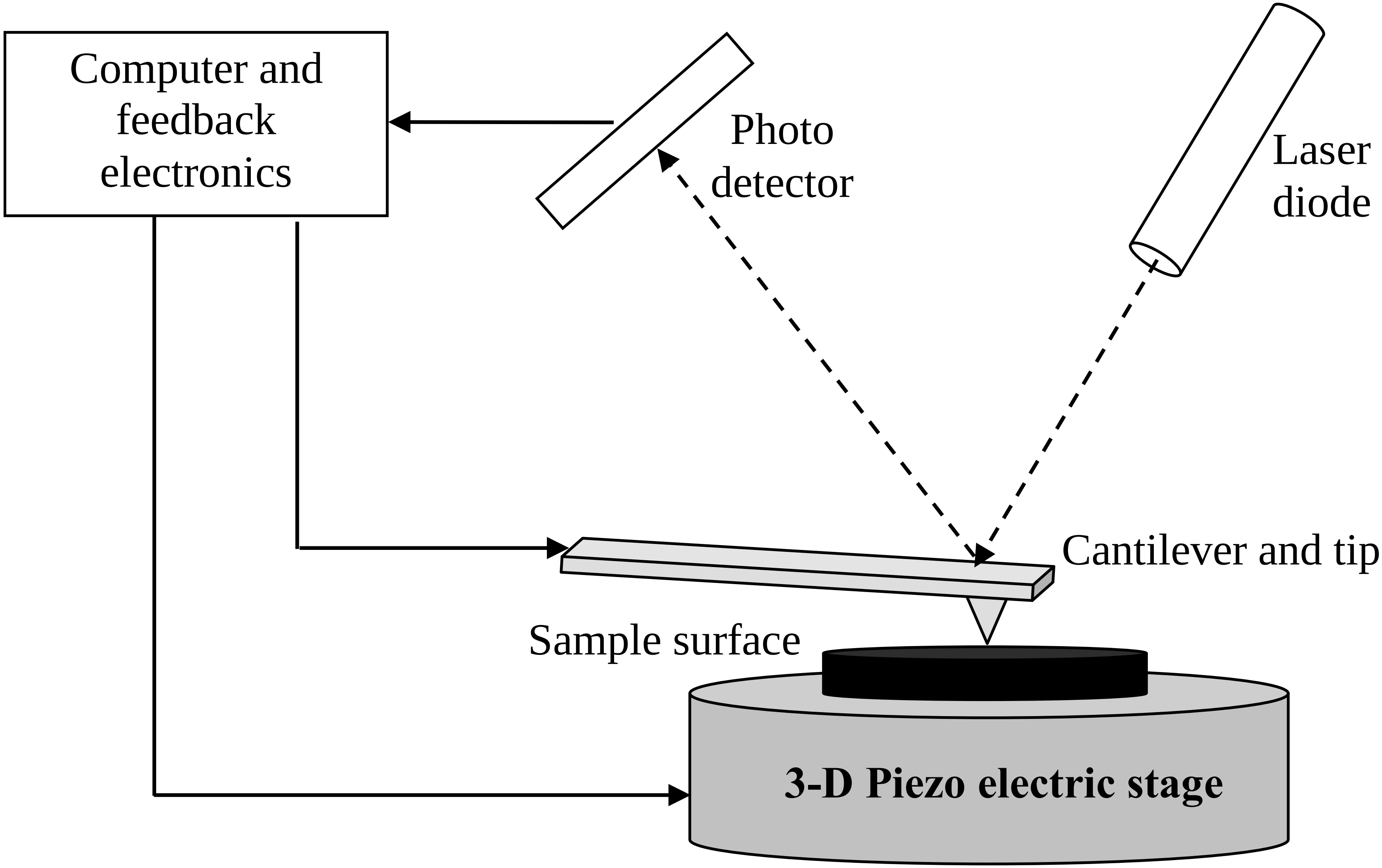
The fracture strength is mainly determined by the macro-structure.

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

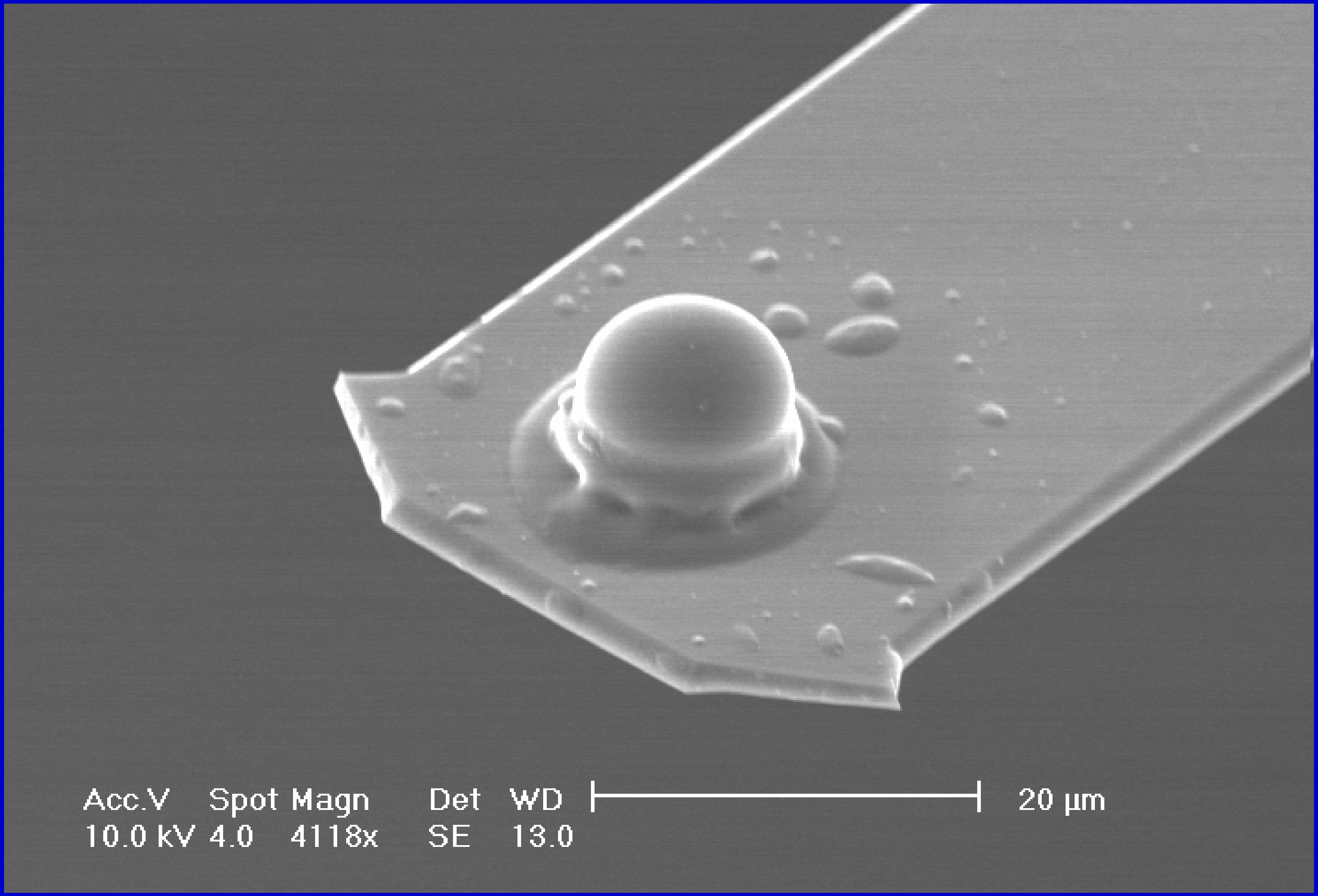
The oil release rate is dominated by the fine structure, particularly for small molecules.

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

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



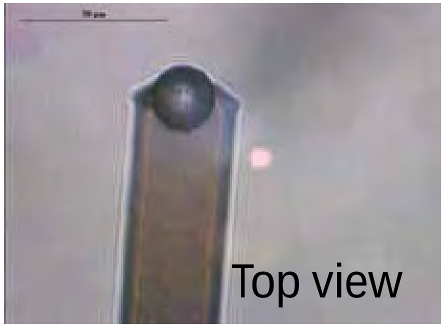
Schematic of an AFM set up.

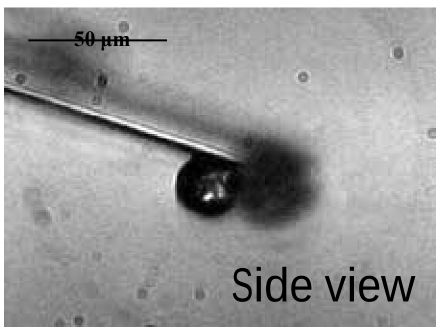


SEM image showing an encapsulate (11.9 mm) was attached to a tipless cantilever

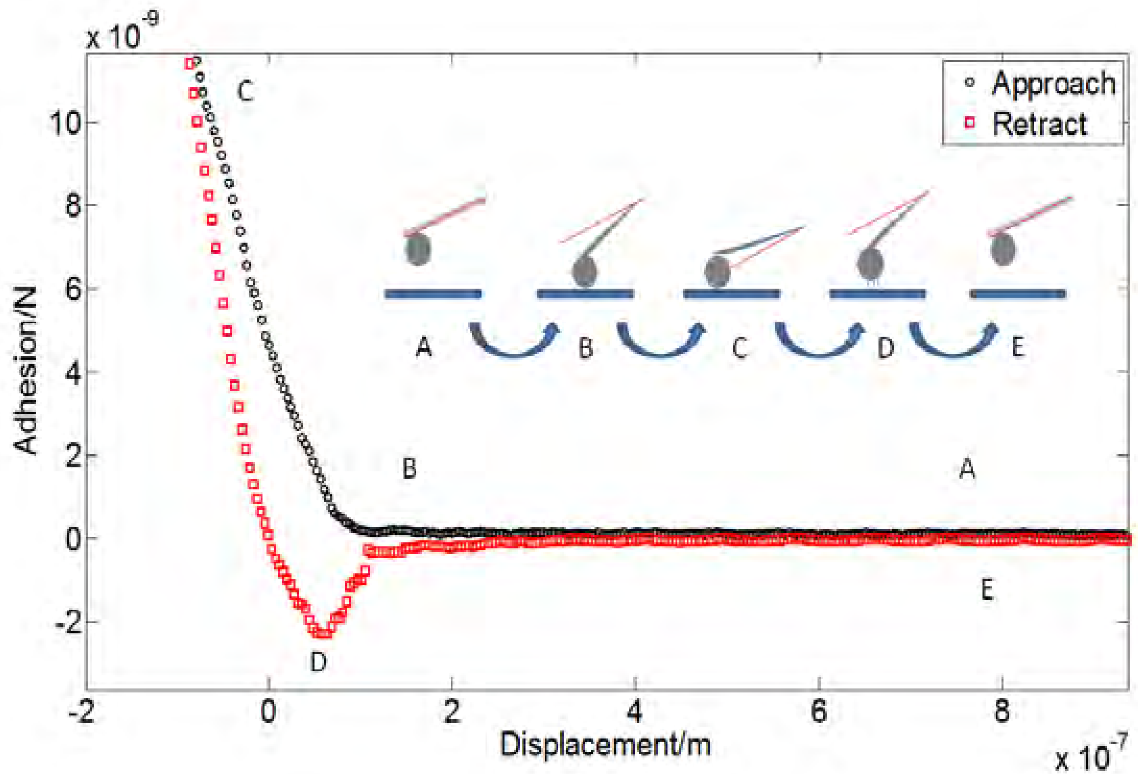
Liu et al. (2013) *J. Adhesion Sci. Technol.*

Adhesion Investigation by AFM





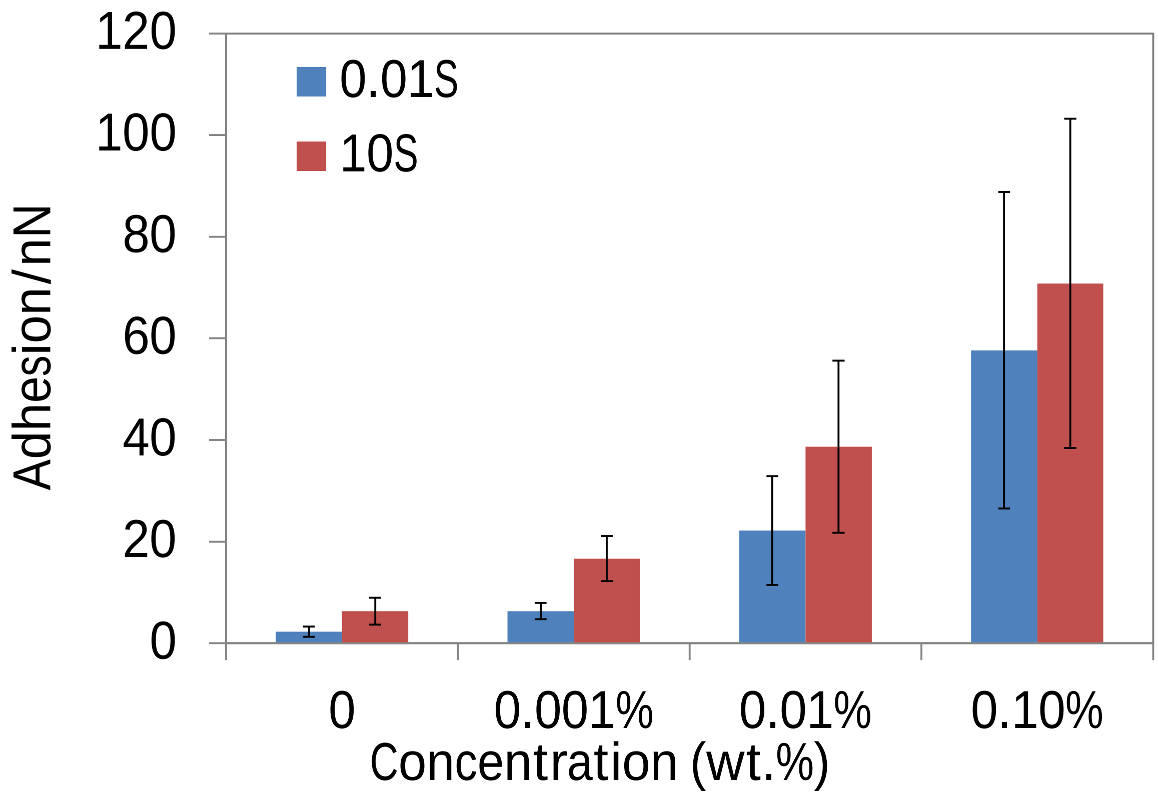
Encapsulate colloidal probe



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

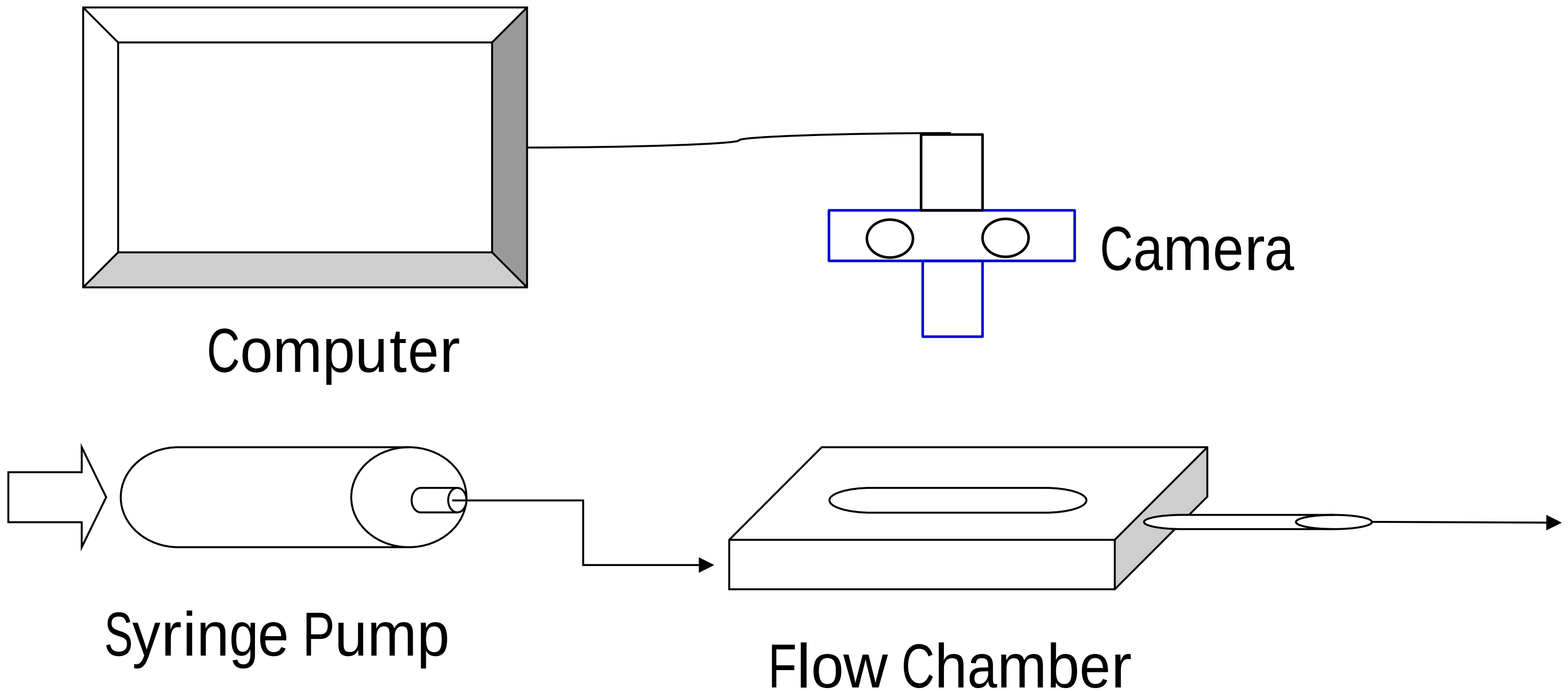
He et al. (2014) *J Microencapsulation*

Adhesion Force between encapsulates and Cellulose Films



Mean adhesion between 5 encapsulates and a cellulose film before and after being modified with chitosan solution.

Schematic Diagram of the Flow Chamber



Fabric care R&D in Procter & Gamble

Laundry Liquid Detergents (HDL)

Fabric Enhancers

Laundry UnitDose

Conclusions

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- Perfume microcapsules are required to have non/low permeability, strong adhesion on fabric surface and optimum mechanical strength.
- Functional perfume capsules with different size, structure, surface property, mechanical strength and permeability have be prepared using various formulation and processing conditions to meet industrial needs.
- Micromanipulation has been demonstrated to be a very powerful tool to characterise the mechanical properties of capsules and to infer their structure, and their mechanical strength can be used as a trigger to control the release of core materials, e.g. perfume.

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- Lesaffre France
- International Favours and Fragrances, USA
- DSM, Switzerland
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