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Direction Measurement of the Mechanical Strength of Single Microcapsules by Micromanipulation

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Why do we need to characterize capsules mechanical strength?

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

Techniques for Characterizing

Capsule Population

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

Single Capsules

- **Micropipette aspiration (only for very soft solids)**
- **Micromanipulation based on diametrical compression**
- **Atomic force microscopy (AFM)**

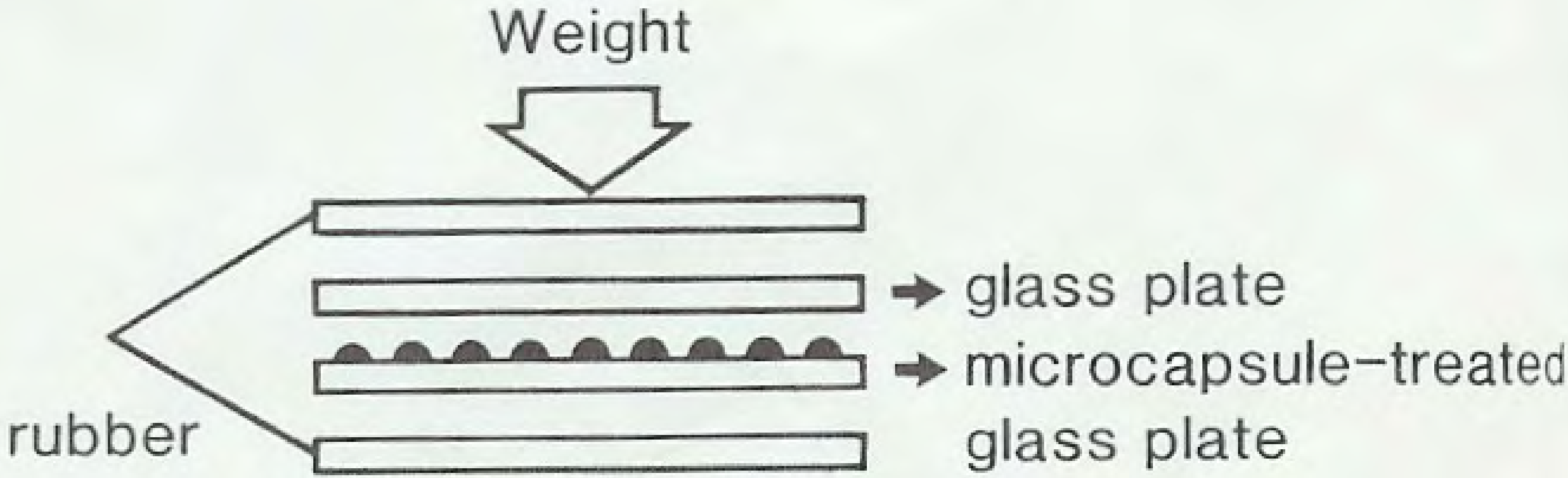


Figure 1 Method for the breaking test

Compression of a population of microcapsules between two plates.

Ohtsubo et al. (1991) , *Polymer*, 32: 2395-2399.

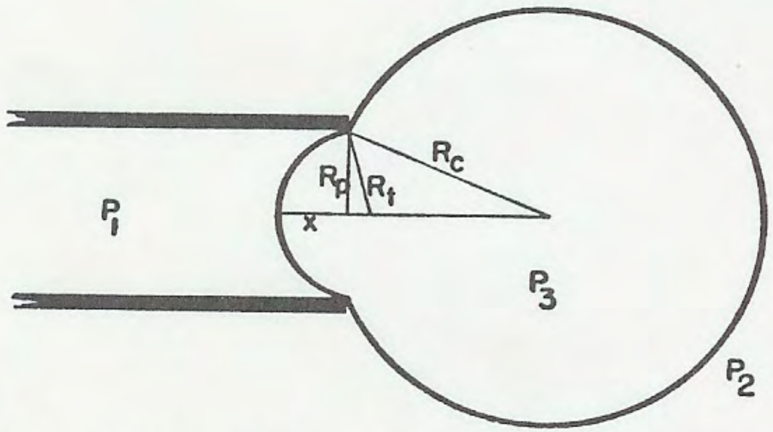
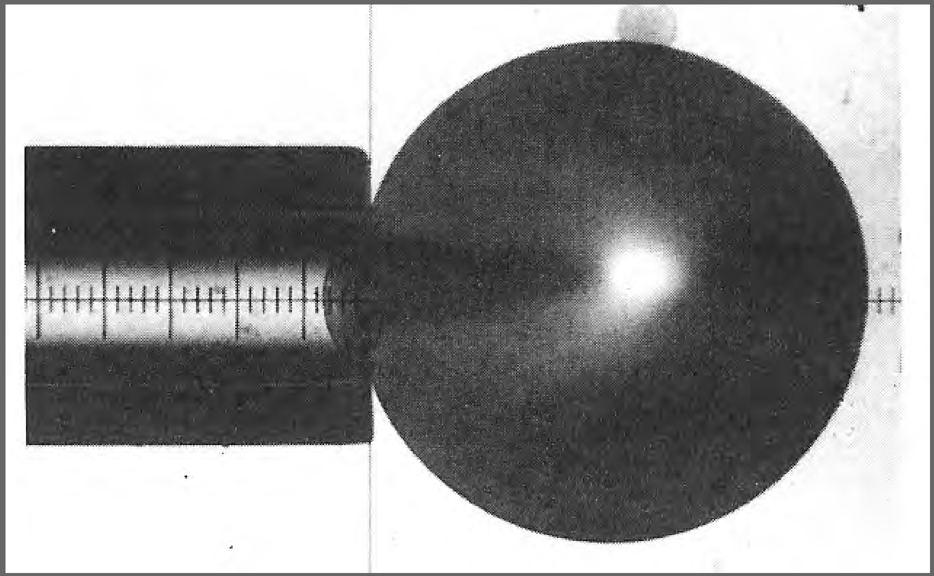


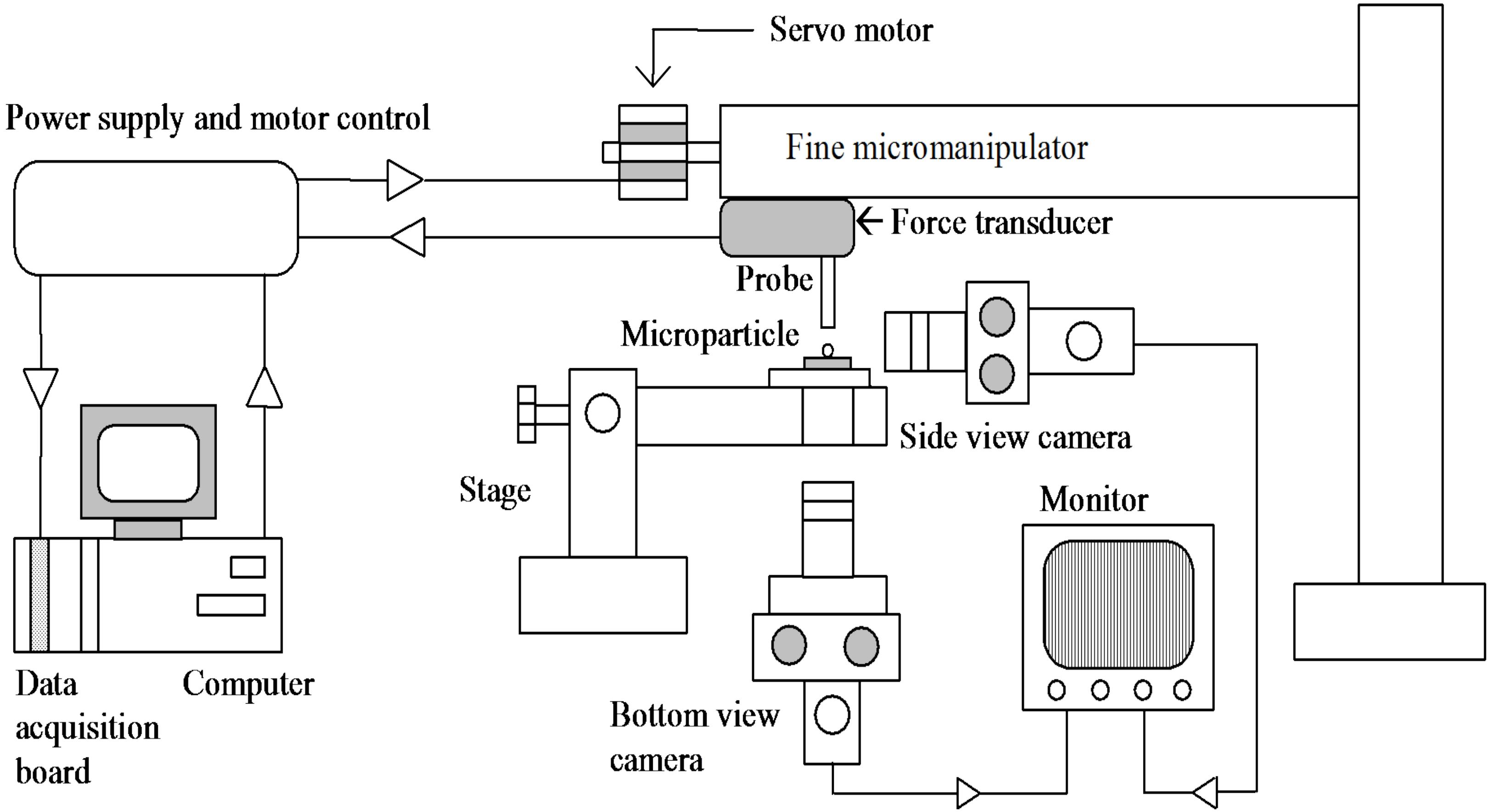
FIG. 1. Schematic of capsule showing parameters involved.



$$P_2 - P_1 = 2T\left(\frac{2x}{x^2 + R_p^2} - \frac{1}{R_c}\right)$$

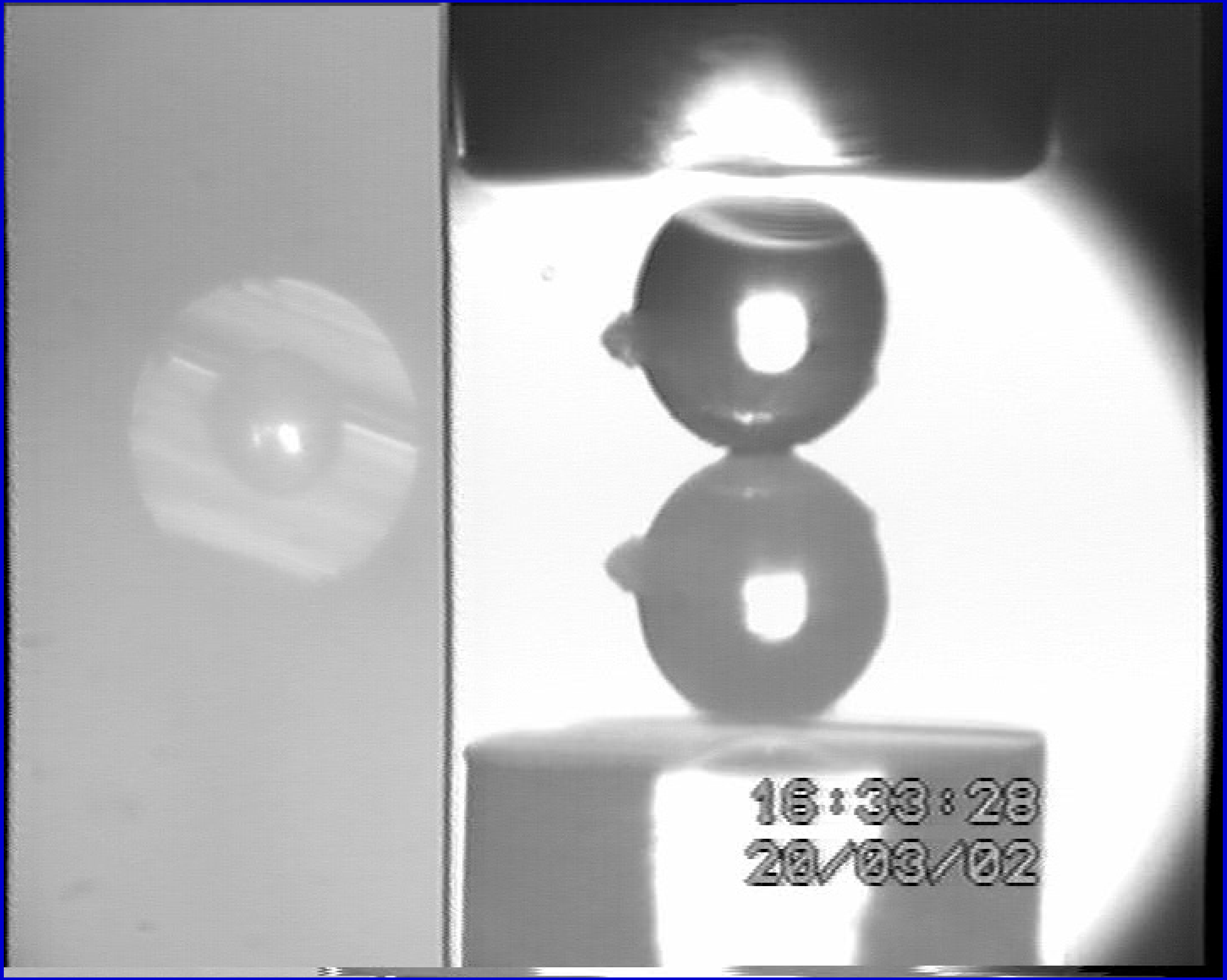
Pipette aspiration of single microcapsule.

Jay and Edwards (1968), *Can. J. Physiol. Pharm*. 46: 731-737.



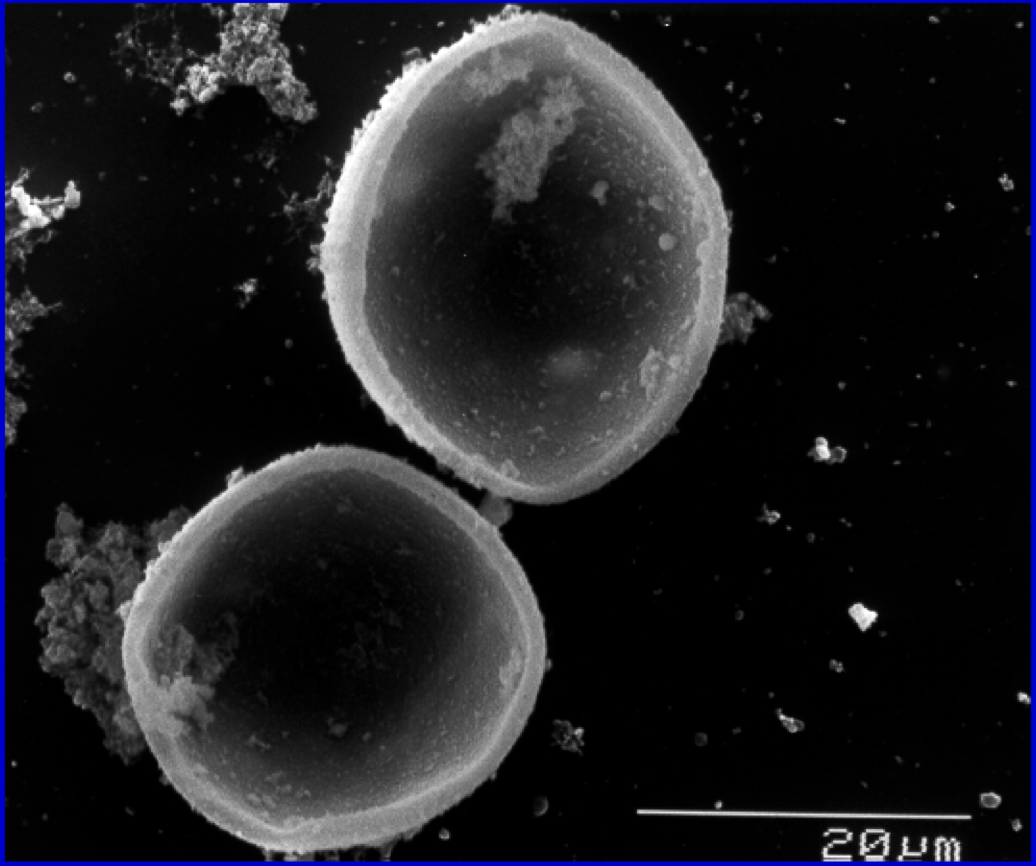
Schematic diagram of the micromanipulation rig

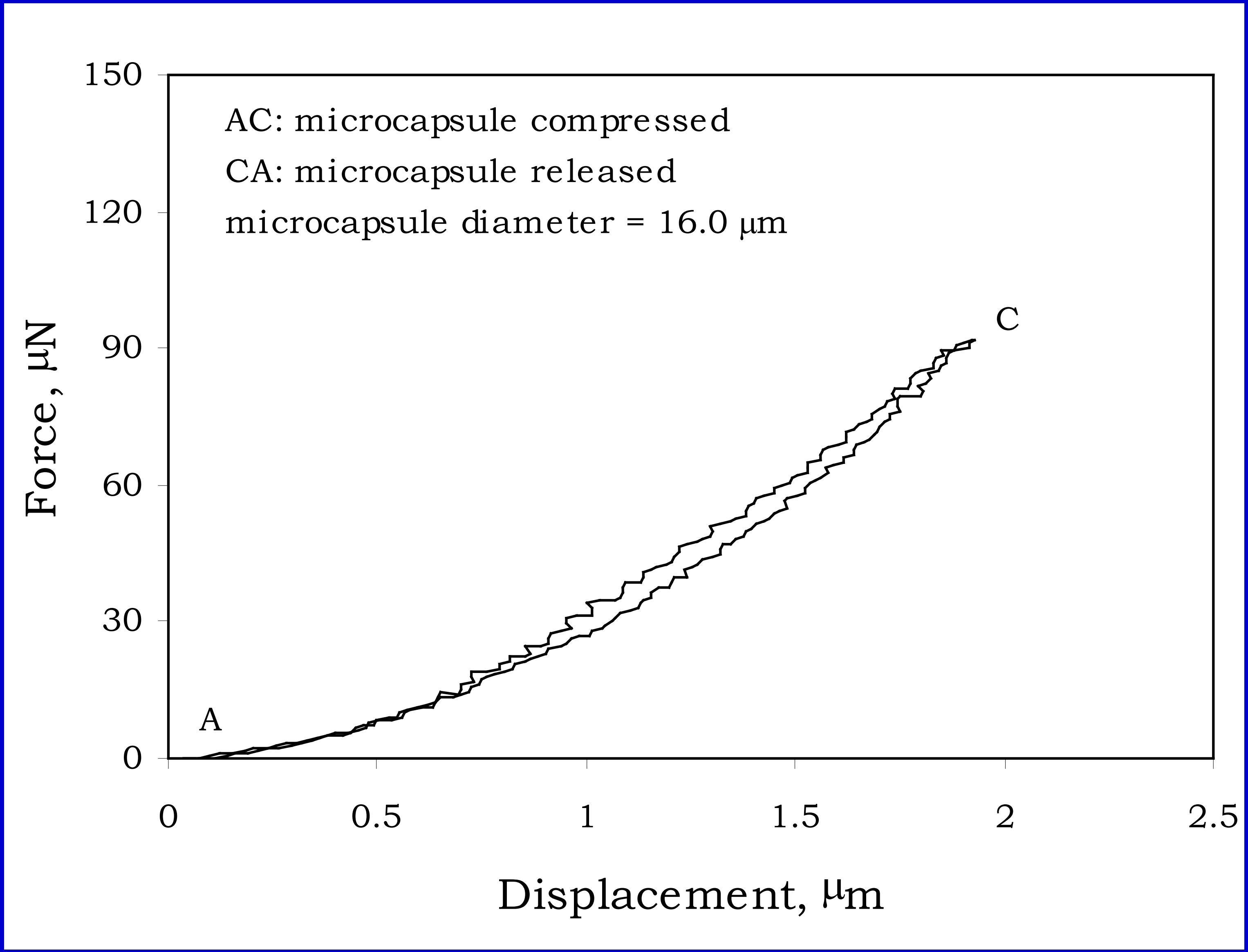
Sun and Zhang (2001), *J Microencapsulation* 18: 593-602



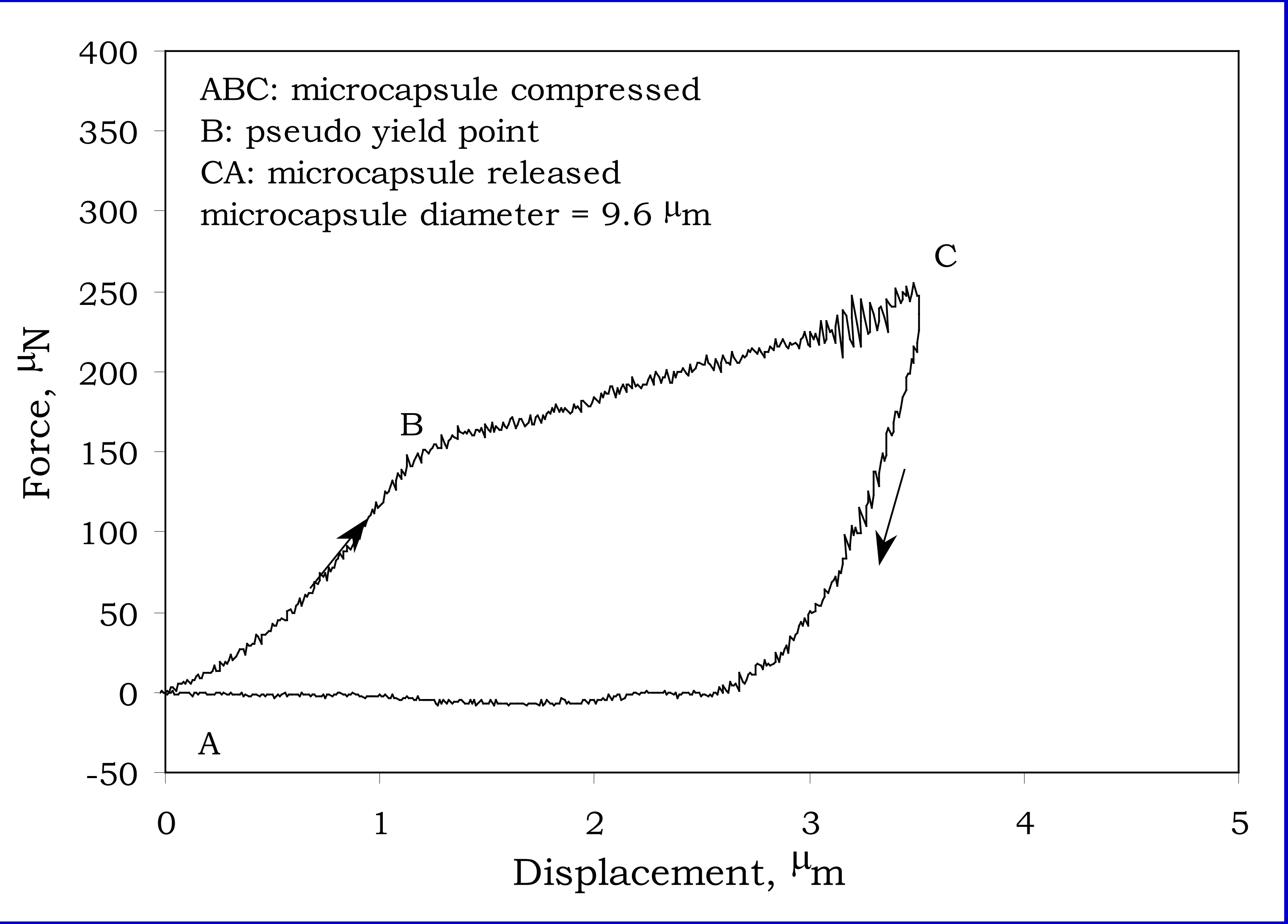
Single MF microcapsule (20μm) held between a force probe and slide.

Ruptured melamine-formaldehyde (MF) microcapsules with a core of oil released

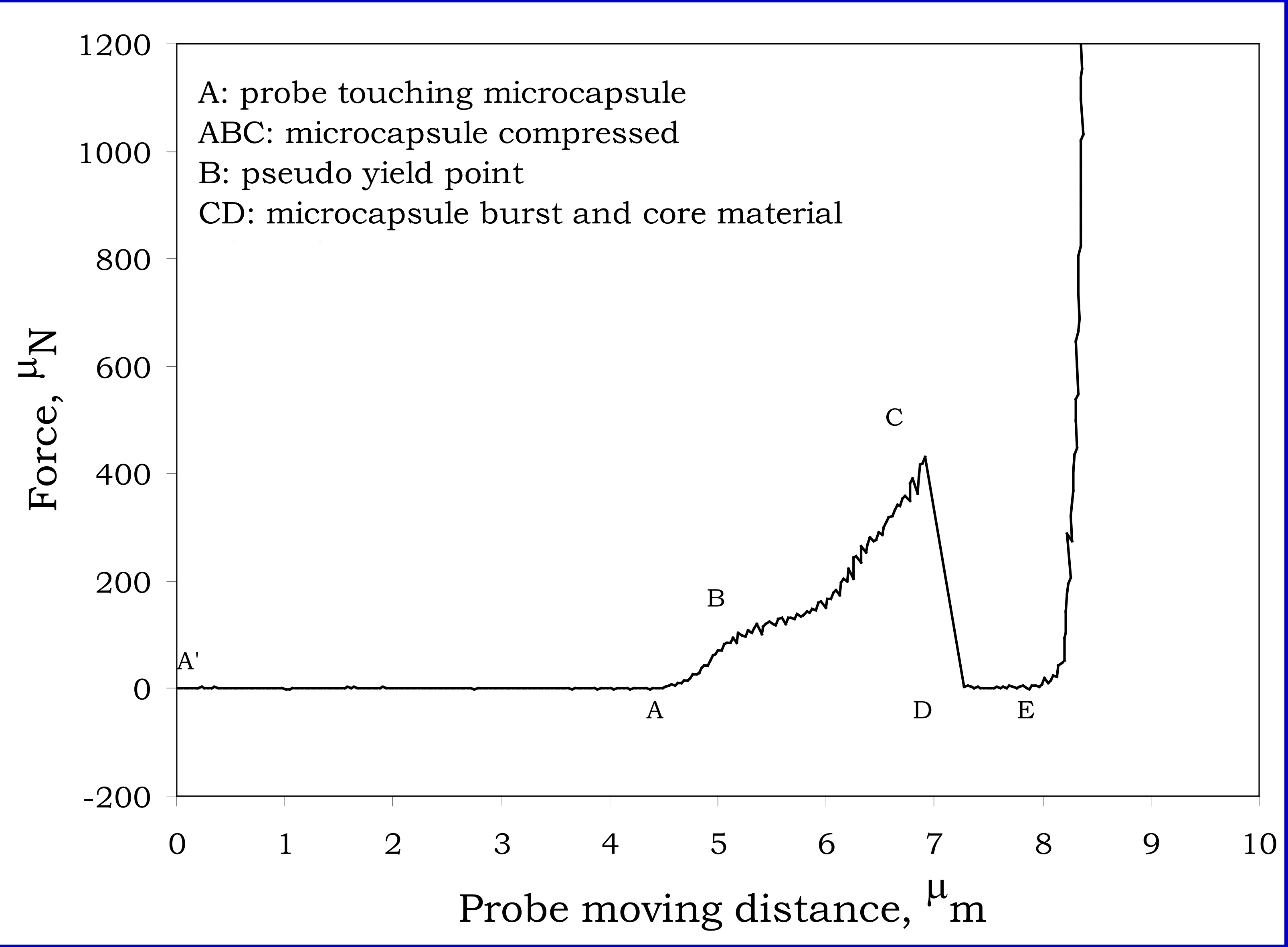




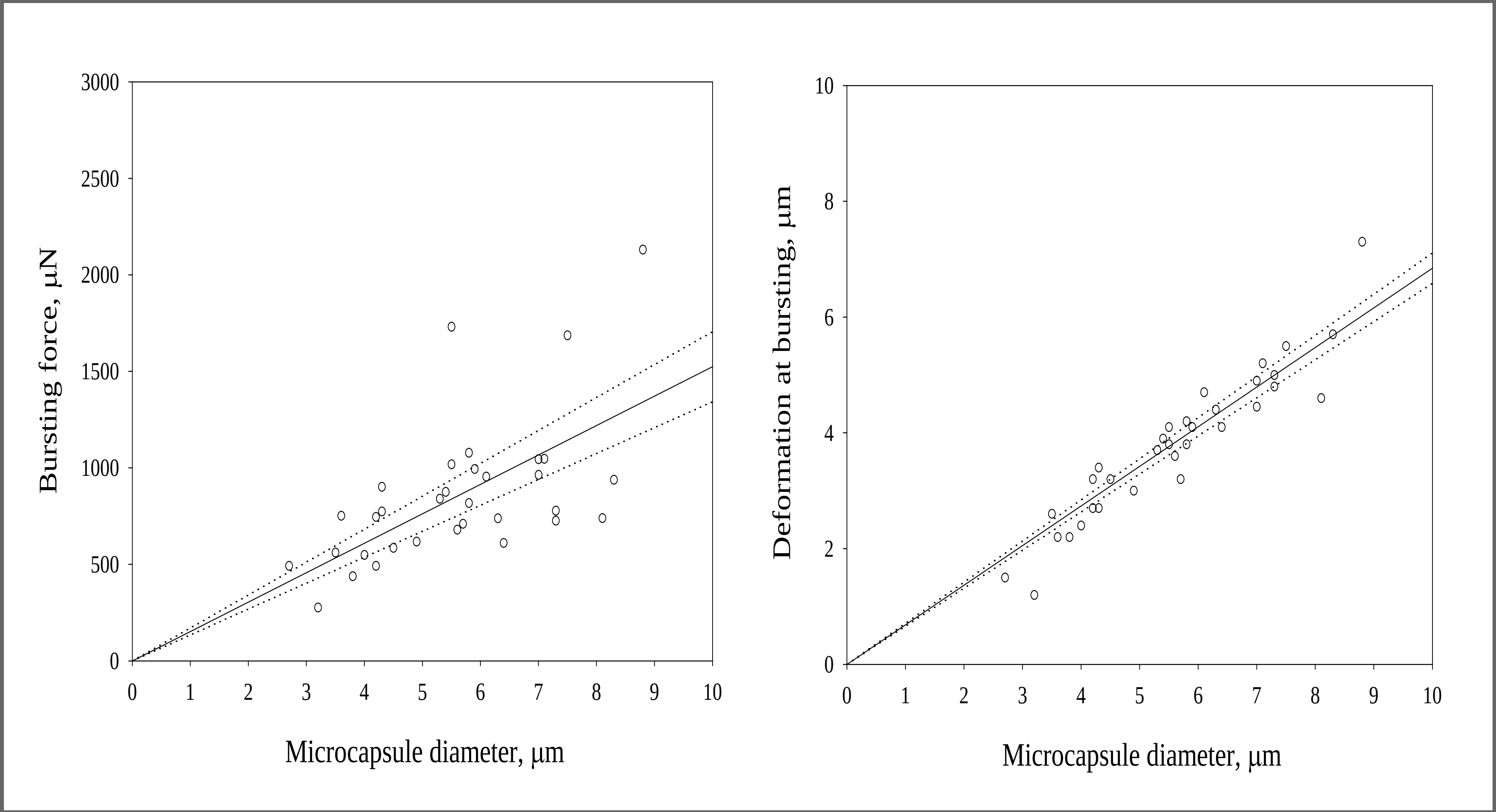
Force versus displacement curve for compression of a MF microcapsule to a small deformation and then release.



Force versus displacement curve for compression of a MF microcapsule to a large deformation and then release.



Force versus displacement curve for compression of a MF microcapsule to bursting.



Bursting force and deformation at bursting vs. diameter for melamine-formaldehyde microcapsules

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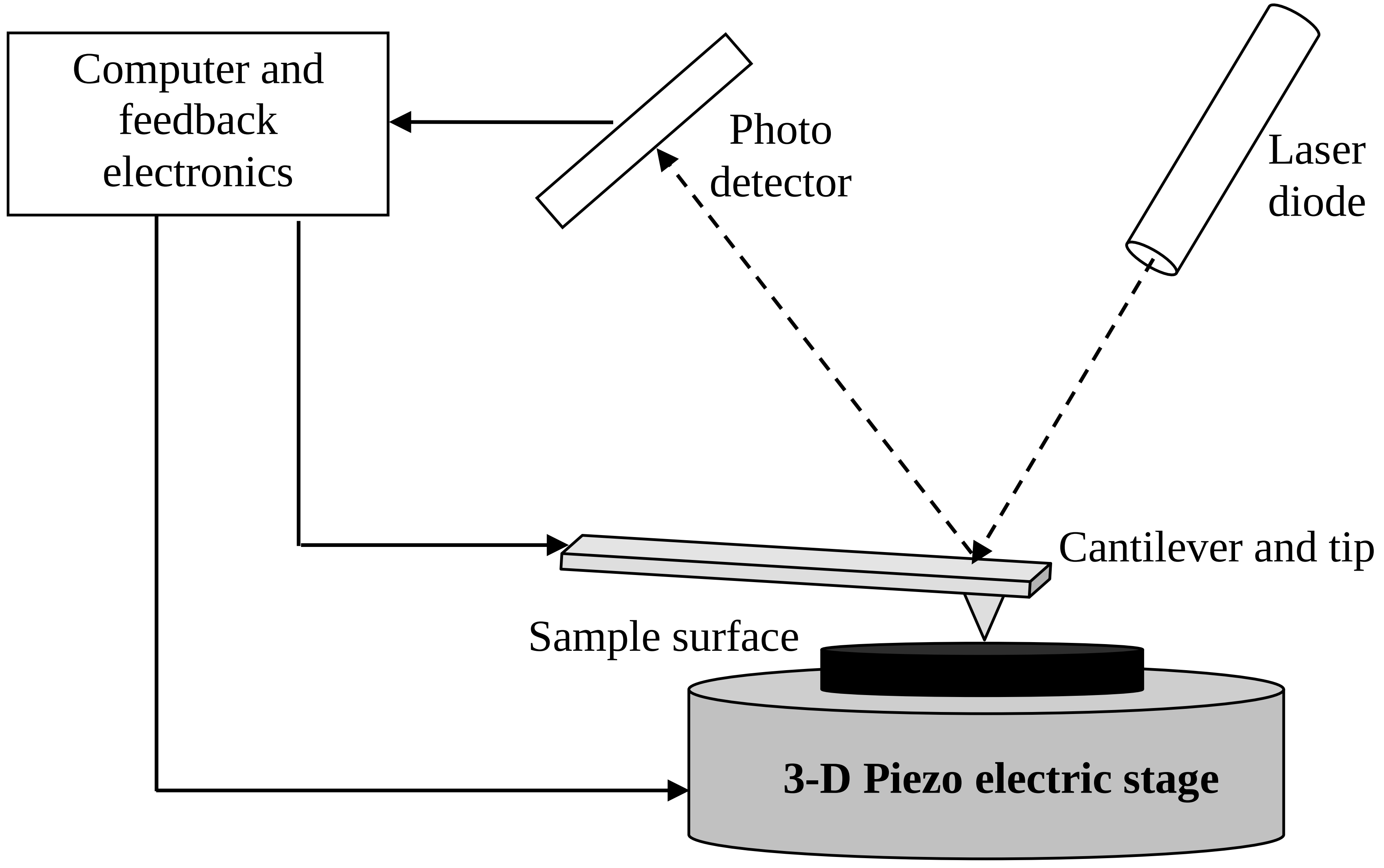
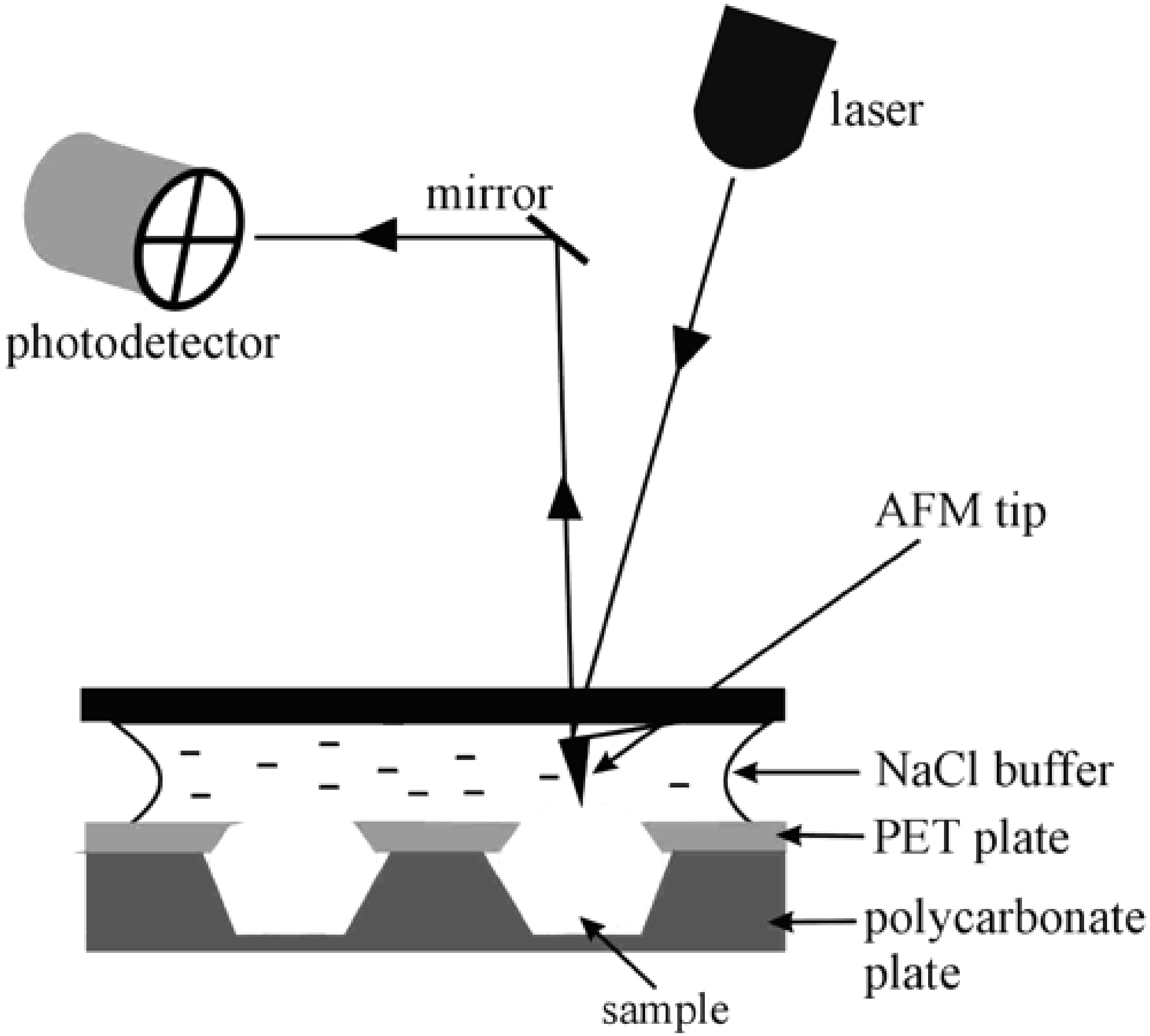
Table 1. *K* values including 95% confidence intervals under different compression speeds.

Compression speeds, µm/s	Number of samples	K for displacement at yield point, µm/µm	K for displacement at bursting, µm/µm	K for bursting force, µN/µm
0.5	34	0.17 ± 0.01	0.68 ± 0.02	142 ± 8
1.0	33	0.19 ± 0.01	0.68 ± 0.02	152 ± 18
3.0	58	0.19 ± 0.01	0.70 ± 0.02	146 ± 14
6.0	57	0.19 ± 0.01	0.71 ± 0.02	149 ± 8
Average		0.19 ± 0.01	0.70 ± 0.01	148 ± 6



Schematic of an AFM set up.



Indentation of a microcapsule with an AFM probe

Lekka et al. (2004), *Langmuir* 20: 9968-9977.

Polyelectrolyte Microcapsules 2833

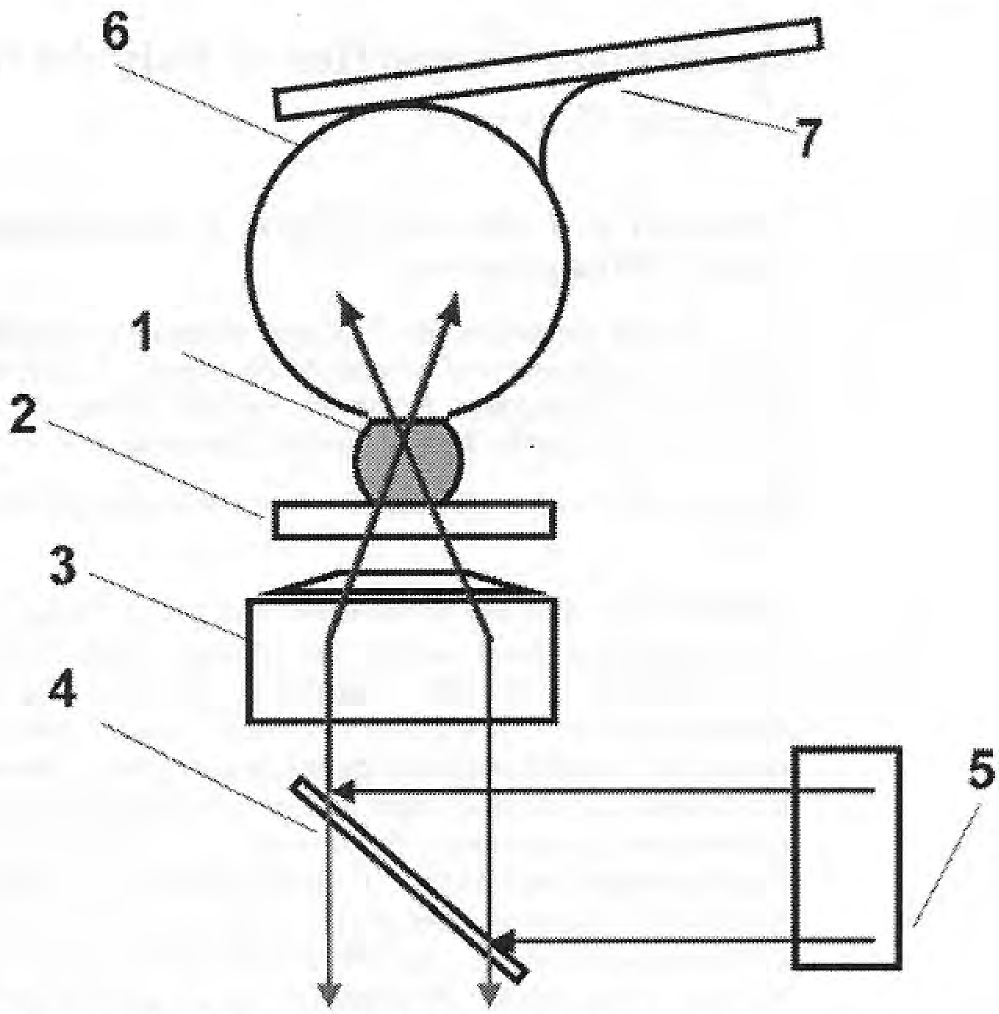
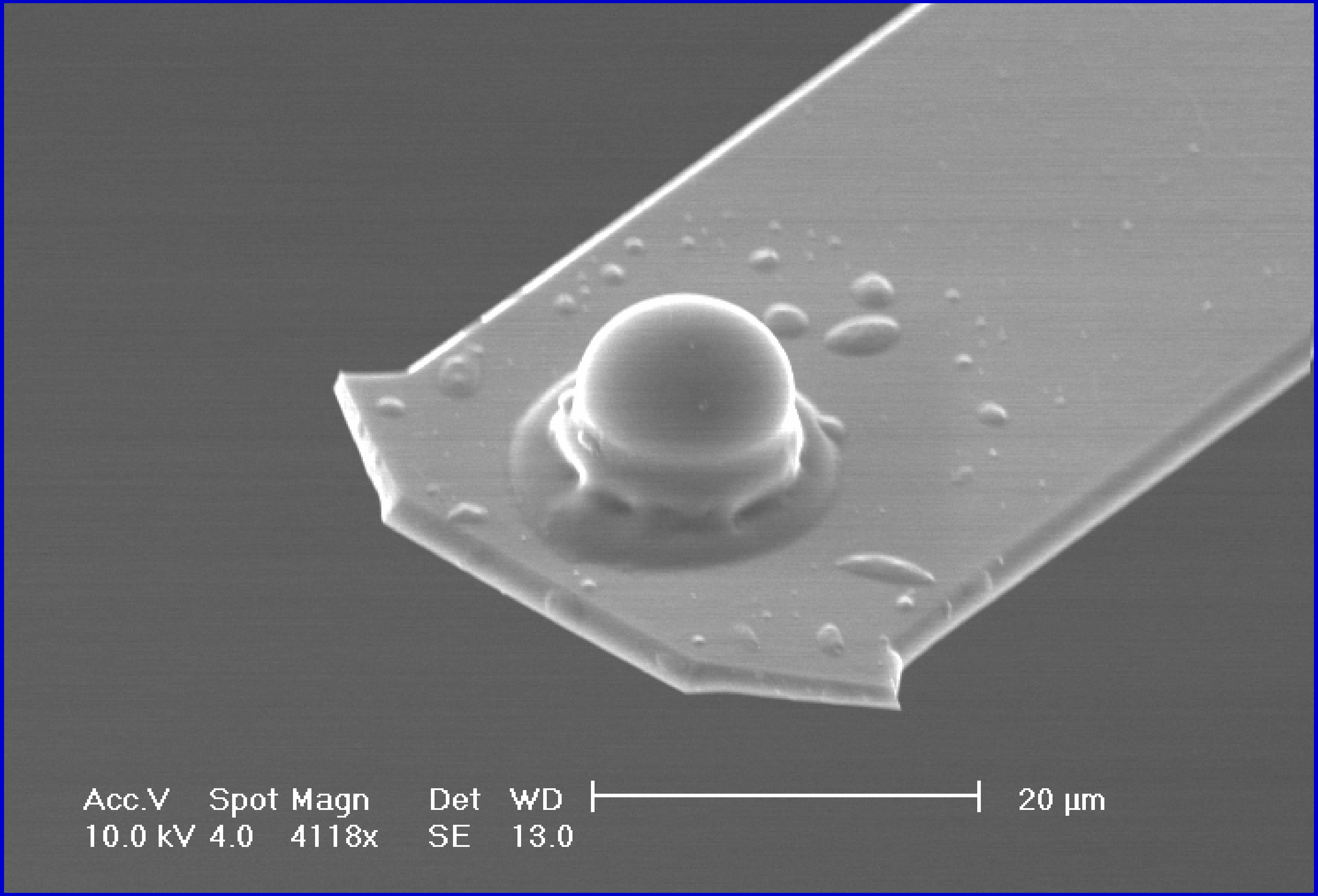


Figure 2. Schematic of the AFM force experiment.

Lulevich et al. (2003), *Macromolecules* 36: 2832-2837.



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

Liu et al. (2013), *J. Adhesion Sci. Technol*. 27: 973-987.

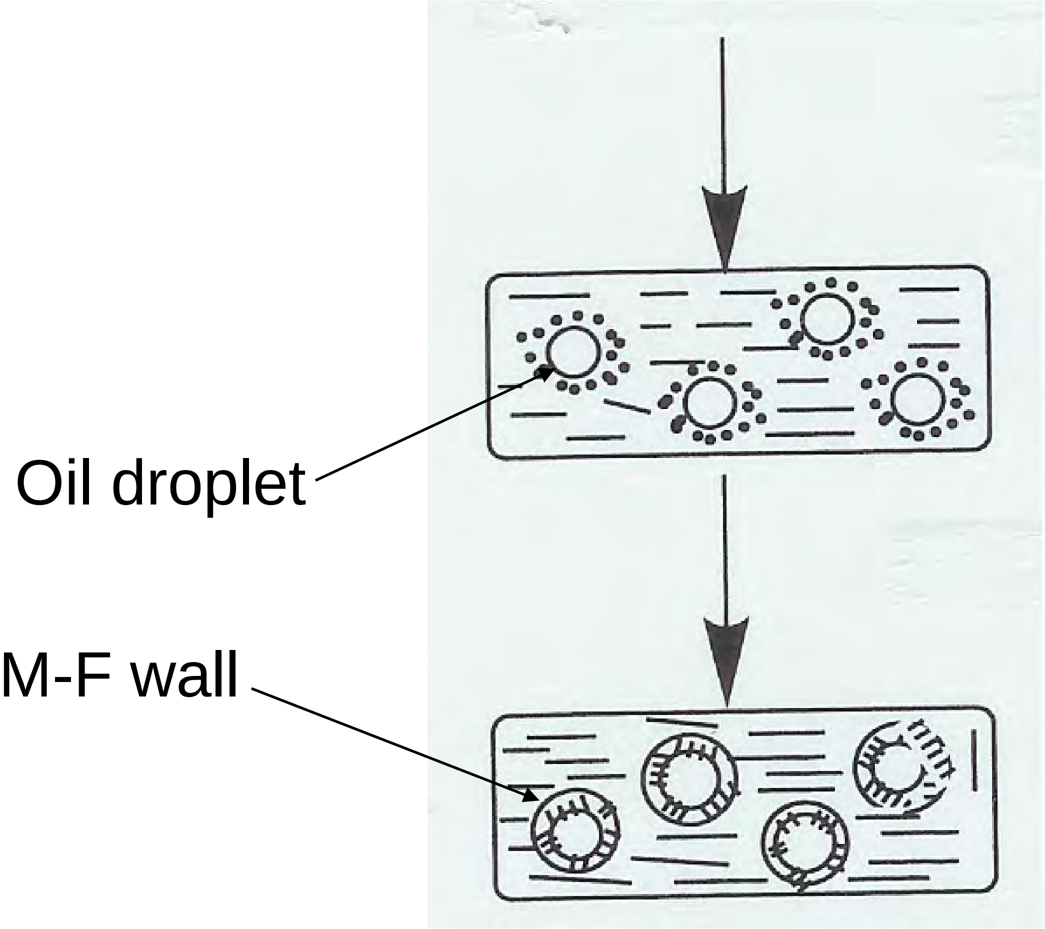
http://www.scienceinthebox.com/laundry-perfumes-provide-fresh-scents

Perfume Microcapsules

- The microcapsules may be incorporated into various functional products, e.g. laundry detergents.
- They should have desirable size, structure, surface property and mechanical strength.
- The perfume may be released by rupturing the microcapsules.

<u>Mechanical characterization of microcapsules</u>

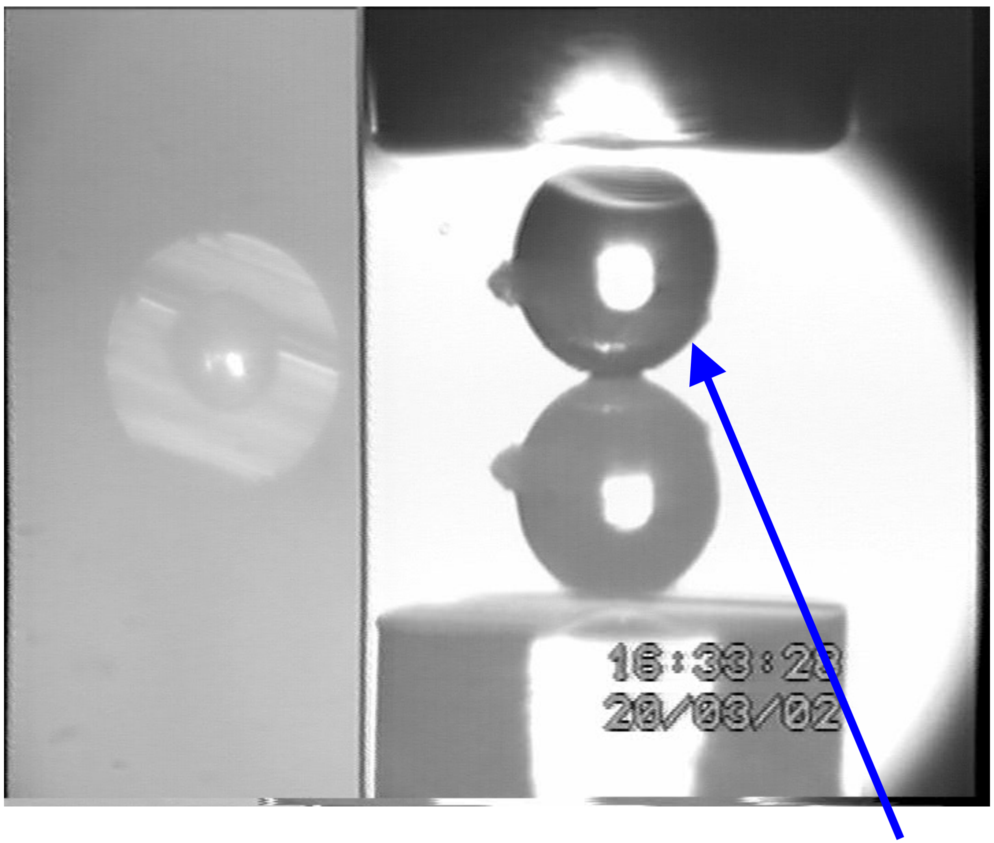
- To prevent the damage to microcapsules in processing equipment (e.g. stirred vessel, pump, extruder, mixer).
- To control their quality and maintain long-term mechanical stability.
- To realise triggered release of active ingredients by mechanical forces.



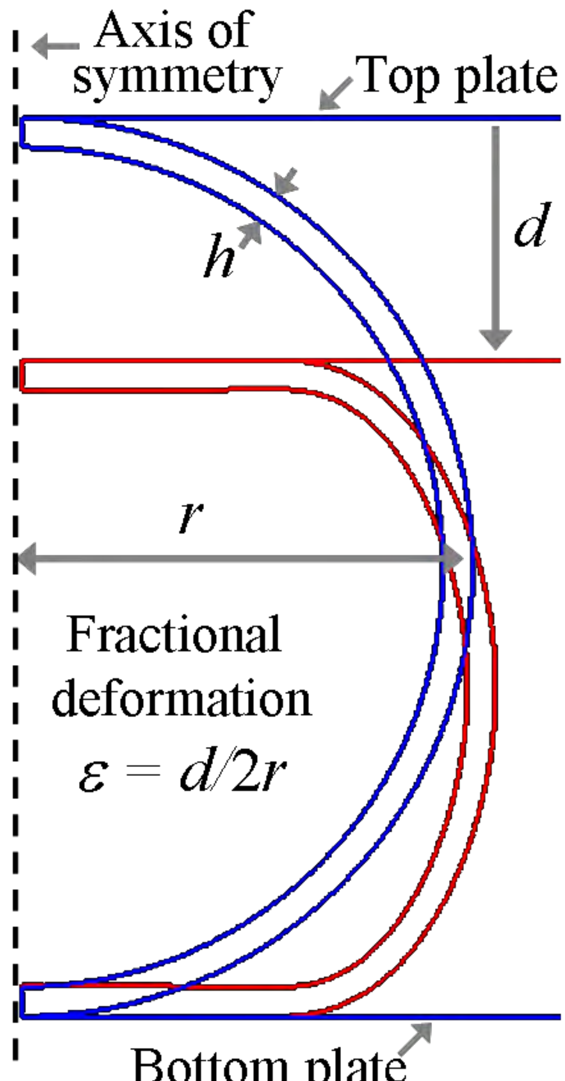
Formation of a melamine formaldehyde (M-F) wall on the surfaces of oil droplets.

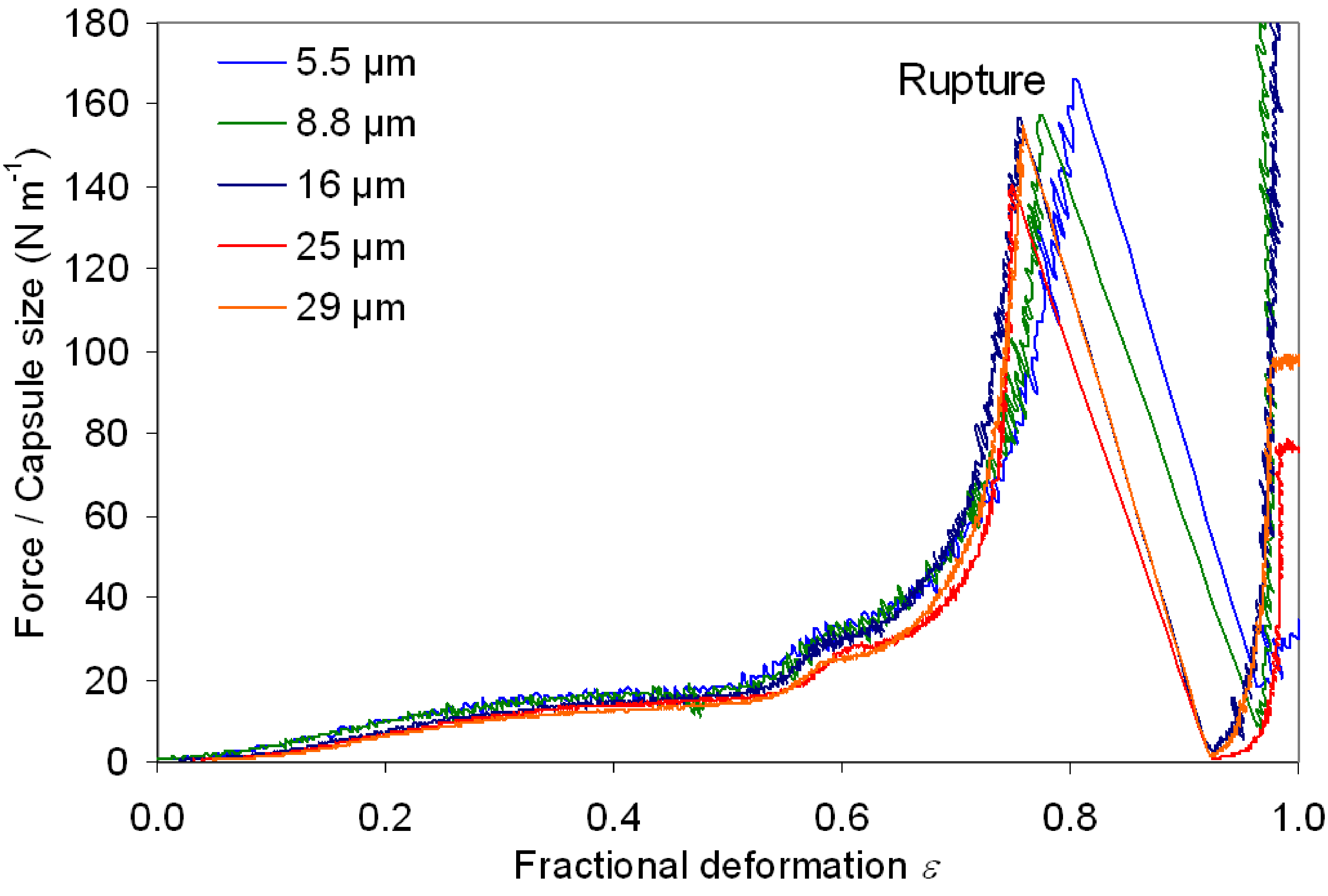
Sun and Zhang (2001), *J. Microencapsulation* 18: 593-602.

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

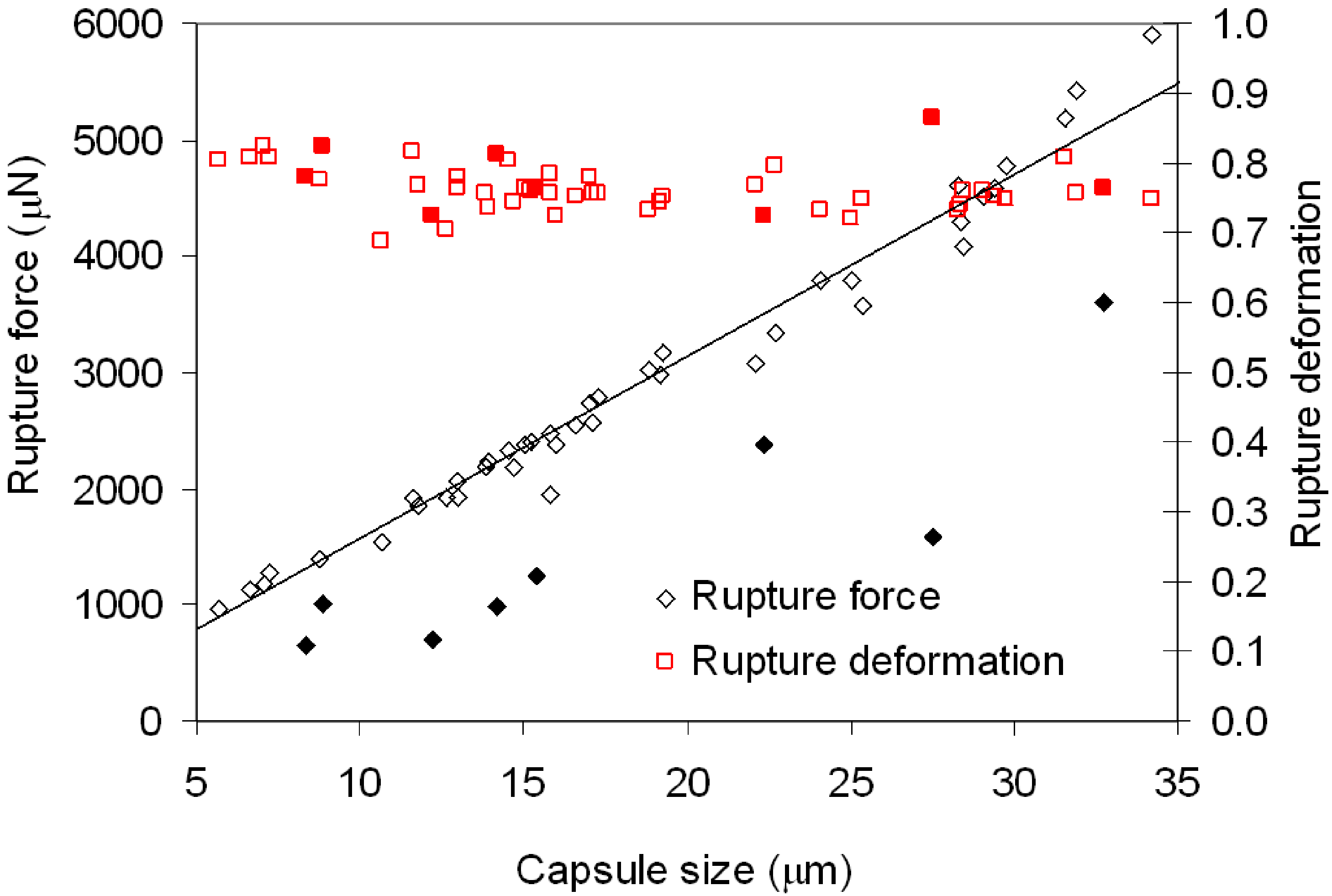


20 µm





Force normalized with the capsule size (diameter) versus fractional deformation for capsules of different sizes



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

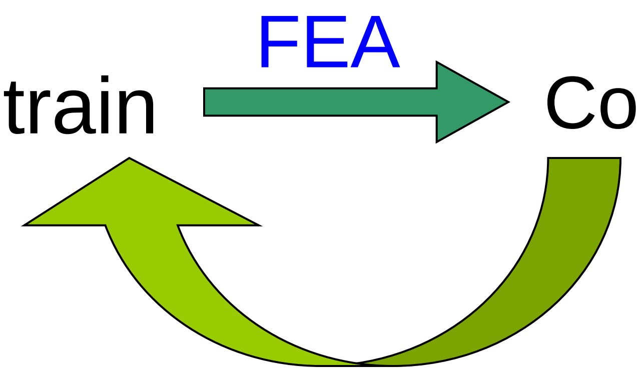
Finite Element Modelling

- Micromanipulation force data provides information that depends on the geometry
- How to obtain intrinsic mechanical property parameters?

STRESS – STRAIN relationship

Modelling
- Theoretical (simple cases – Hookean)
- Numerical (FEA with ABAQUS®)

Stress – strain

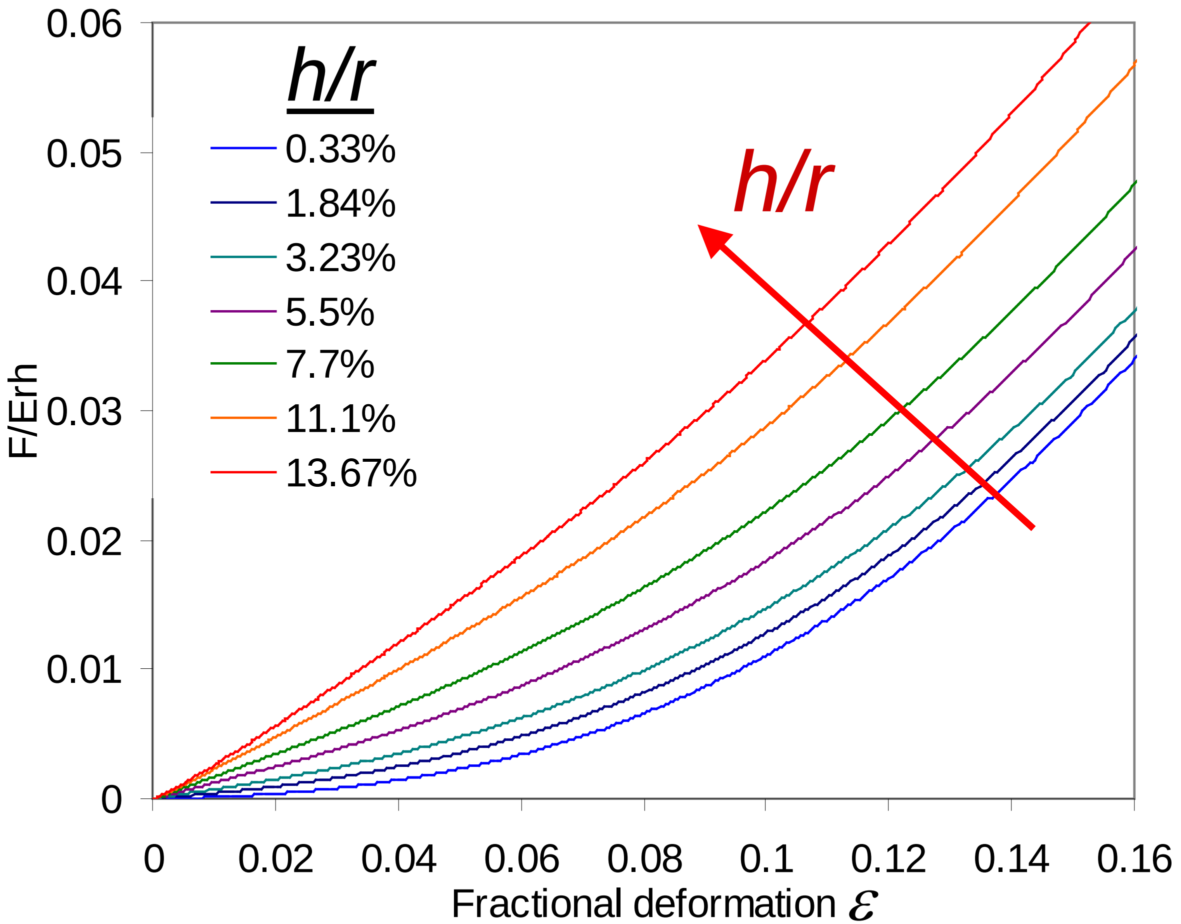


Compression force profile

FEM – Elastic shell

Determination of the Elastic Modulus (*E*):

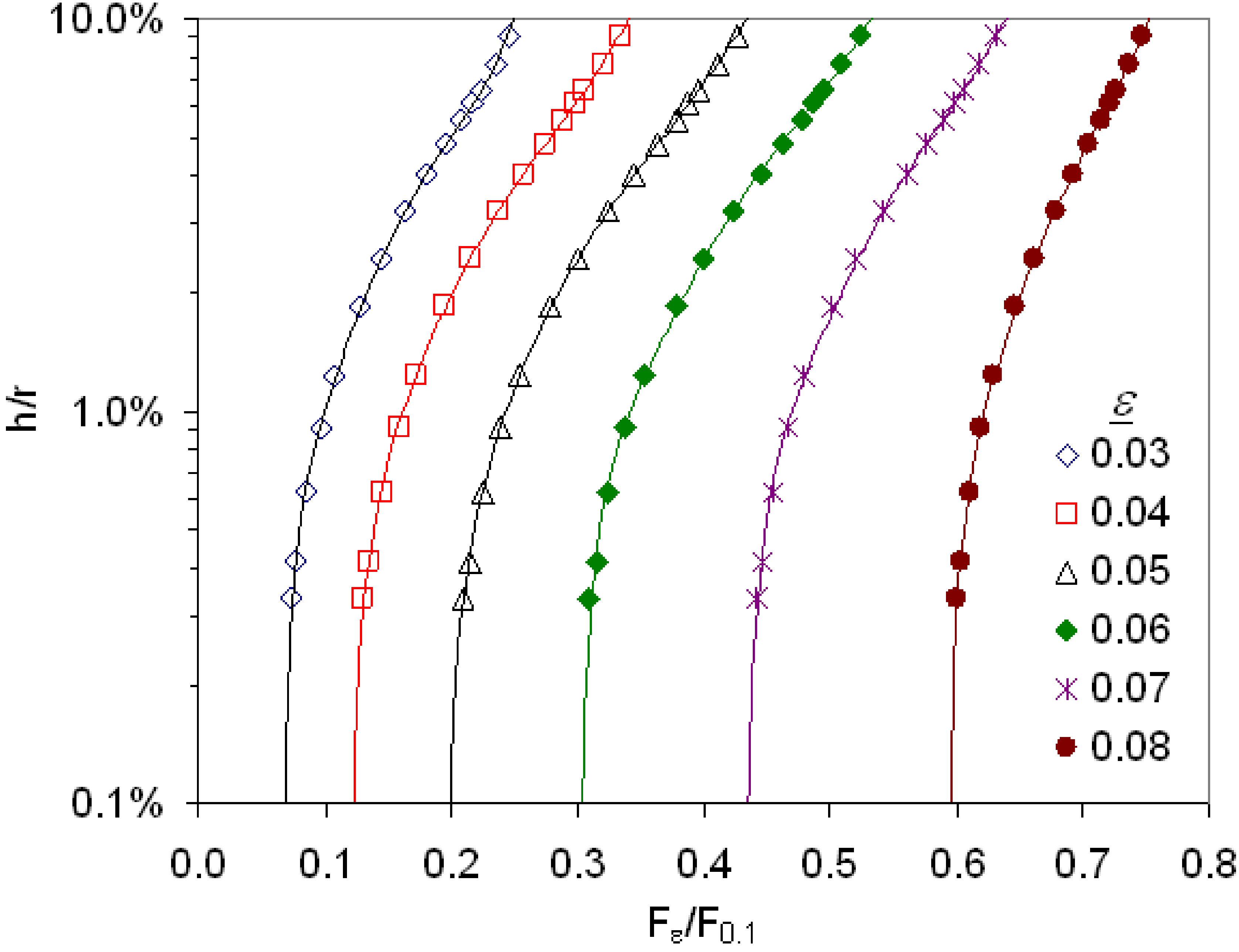
- MF microcapsules are known to be elastic at small fractional deformations $\varepsilon < 0.15$



- 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.



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
Fε/F0.1
ε
0.03
0.04
0.05
0.06
0.07
0.08

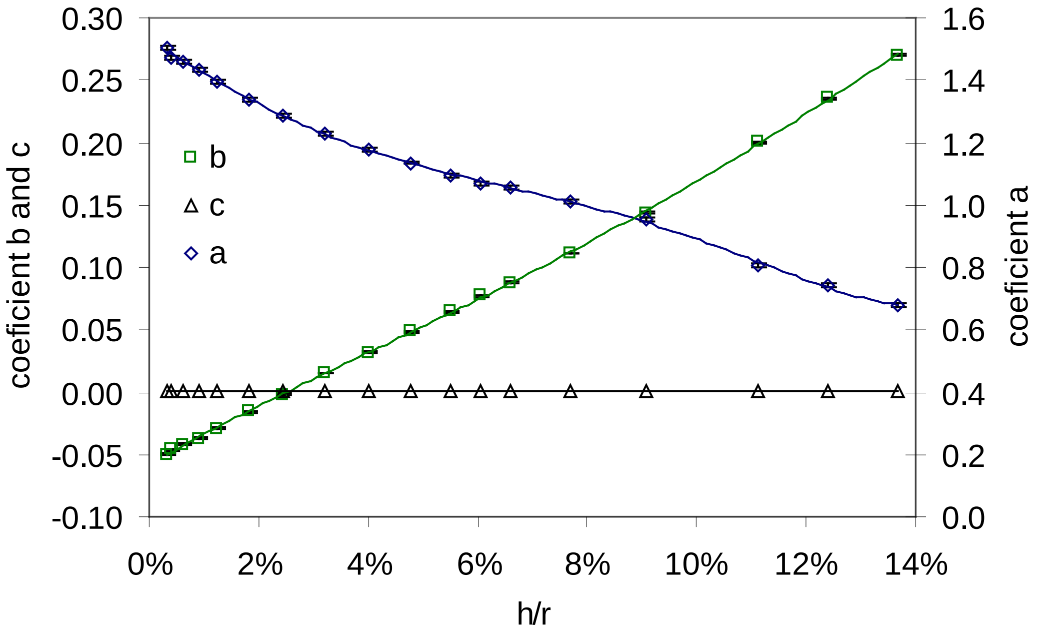
FEM – Elastic shell – Estimate *Eh*

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

FEA results:

$$\frac{F}{Erh} = a\varepsilon^2 + b\varepsilon + c$$

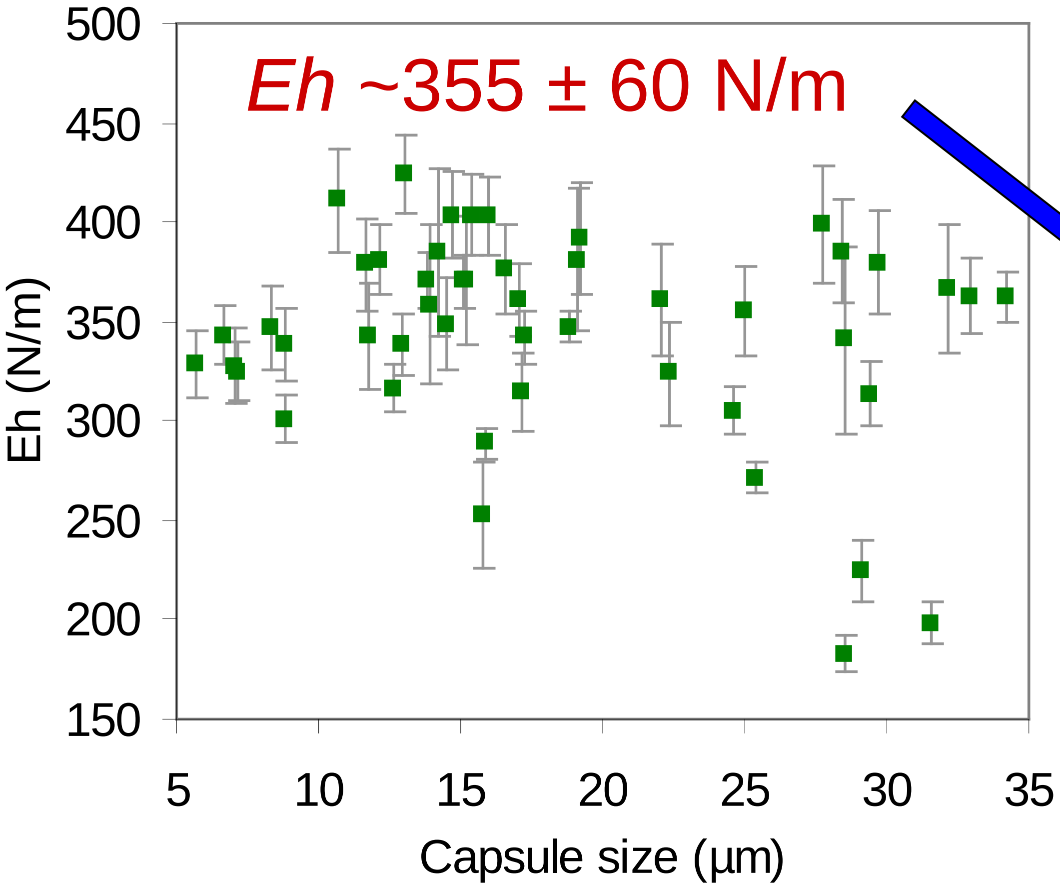
$$0.03 < \varepsilon < 0.1$$



The experimental *Eh* is calculated at different fractional deformations

$$Eh_\varepsilon = \frac{F_\varepsilon / r}{a\varepsilon^2 + b\varepsilon + c}$$

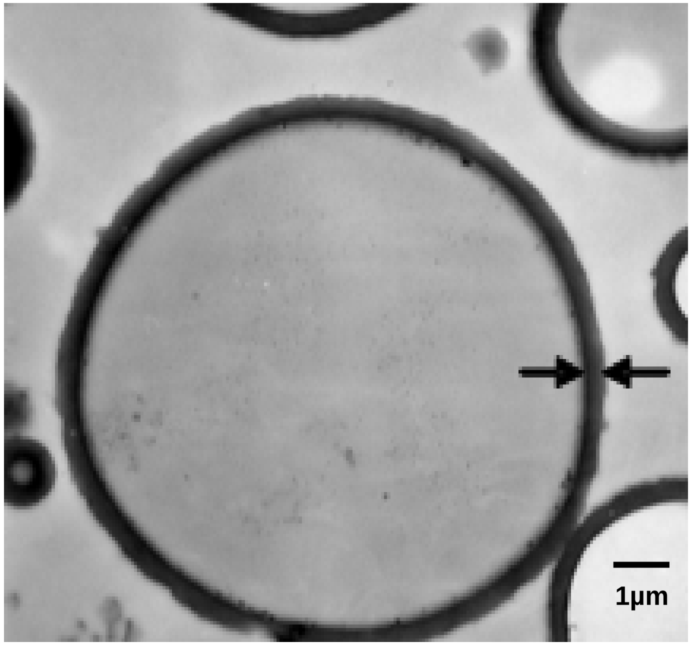
MF capsules – Elastic shell – Estimate *Eh*



Eh ~355 ± 60 N/m

h ~0.2 µm

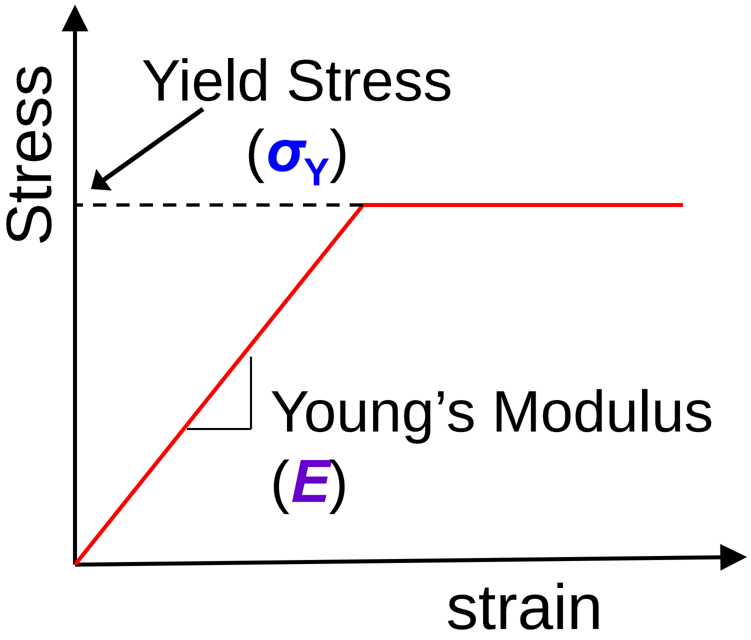
E ~1.8 ± 0.3 GPa

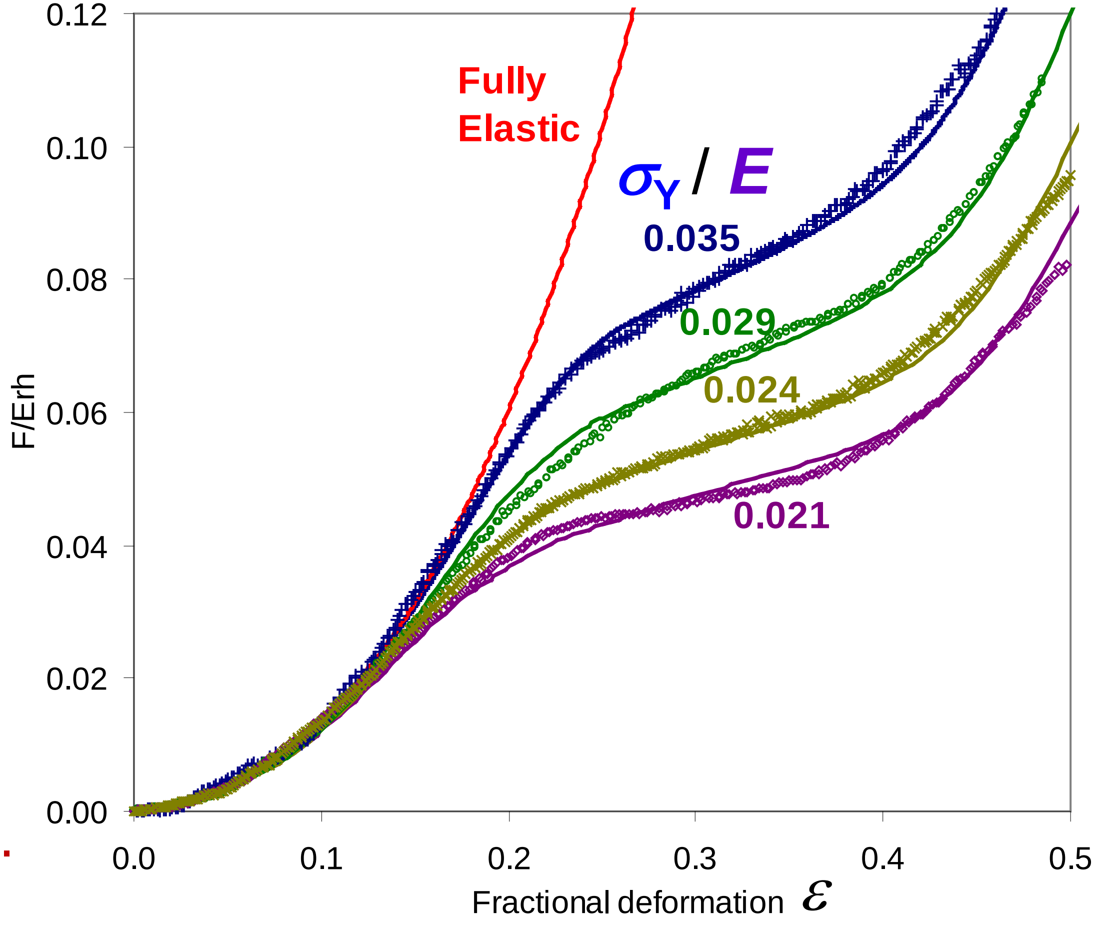


Eh is independent of the capsule size.

MF capsules – Elastic perfectly-plastic shell

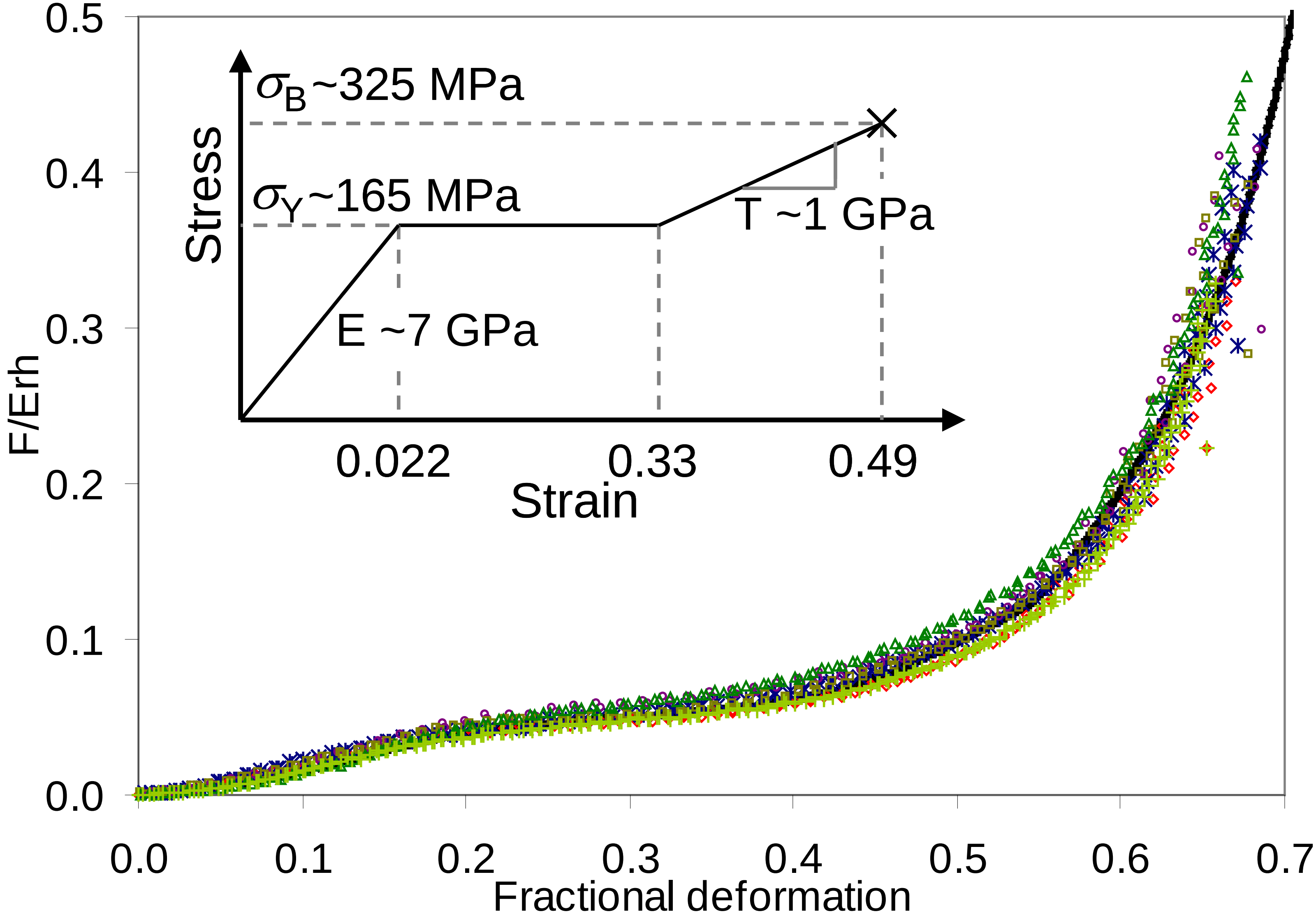
- At high deformations (*e.g.* $\varepsilon > 0.1$), MF microcapsules deform plastically
- Consider the simplest plasticity scenario: Perfect plasticity



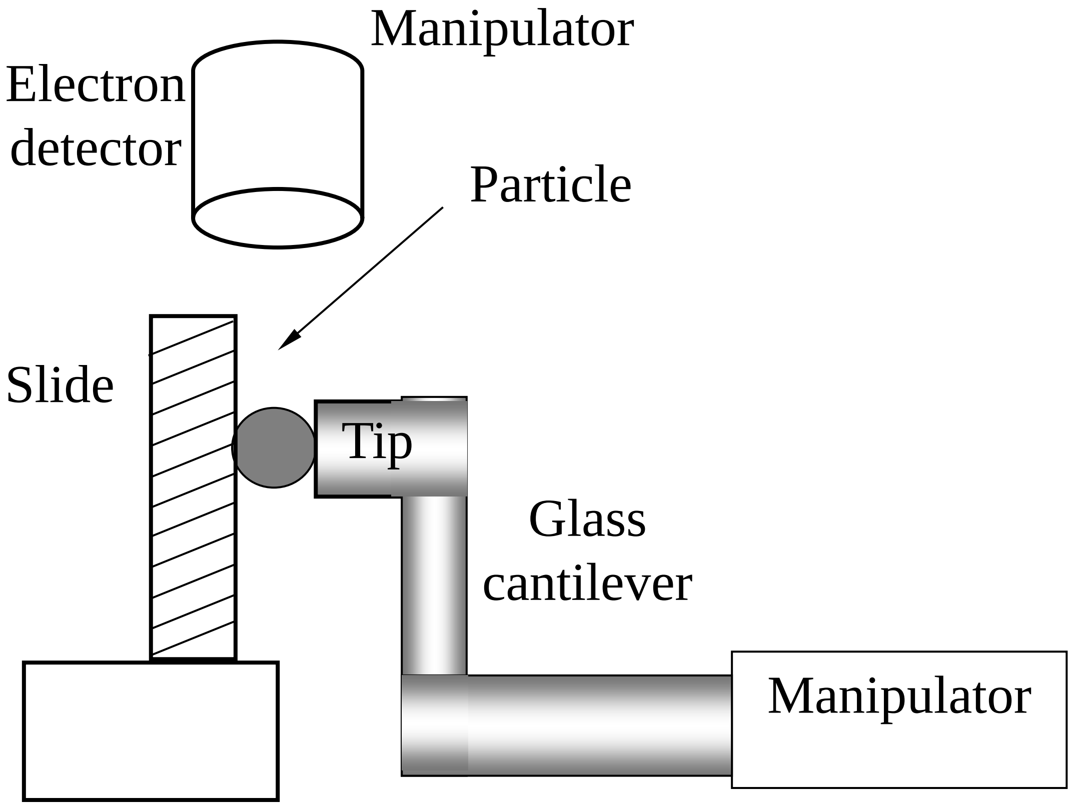


Mercadé-Prieto et al. (2011), *Chem. Eng. Sci*. 66:1835-1843.

FEM – Determination of rupture parameters

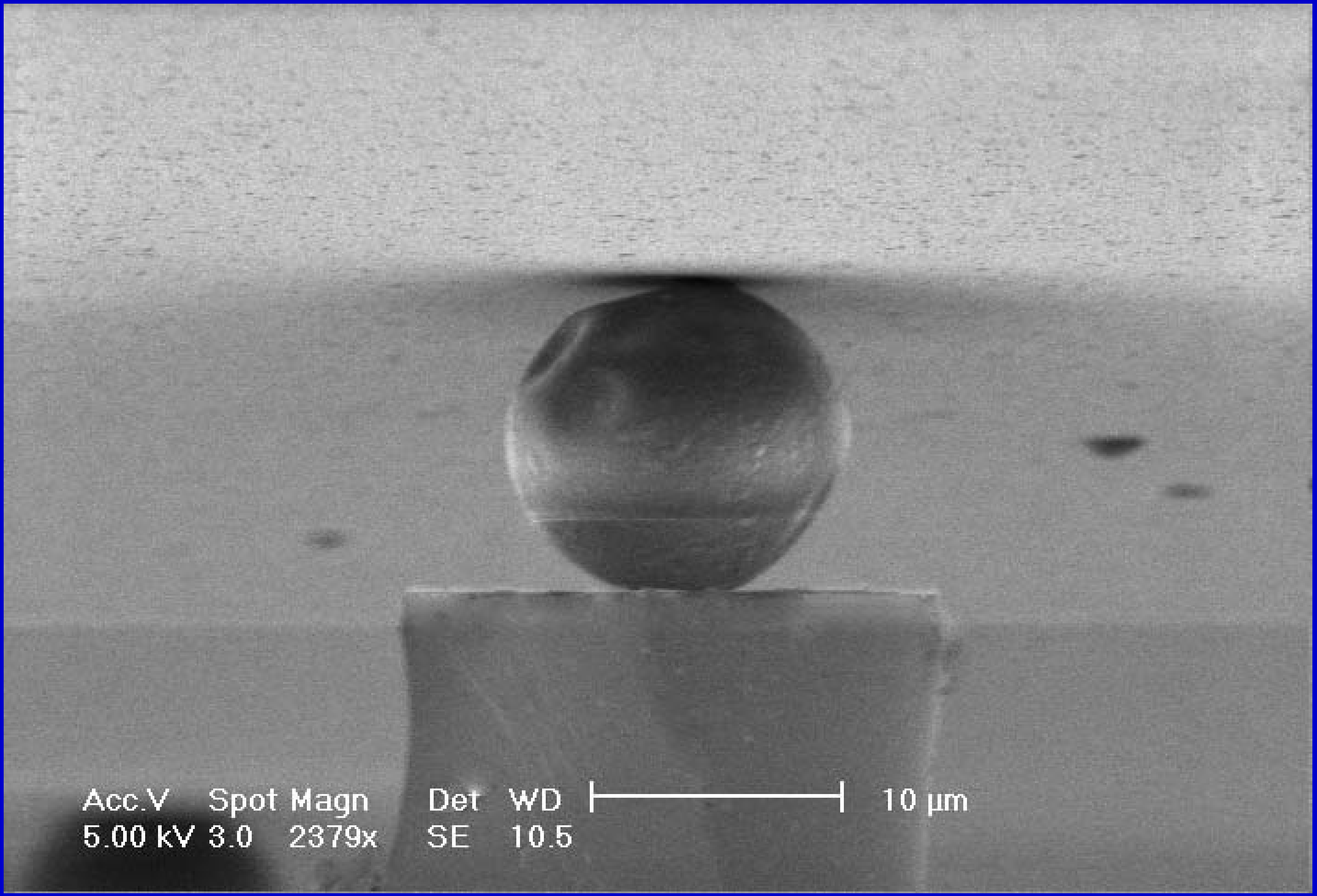


Mercadé-Prieto et al. (2012), *AIChEJ* 58: 2674–2681.

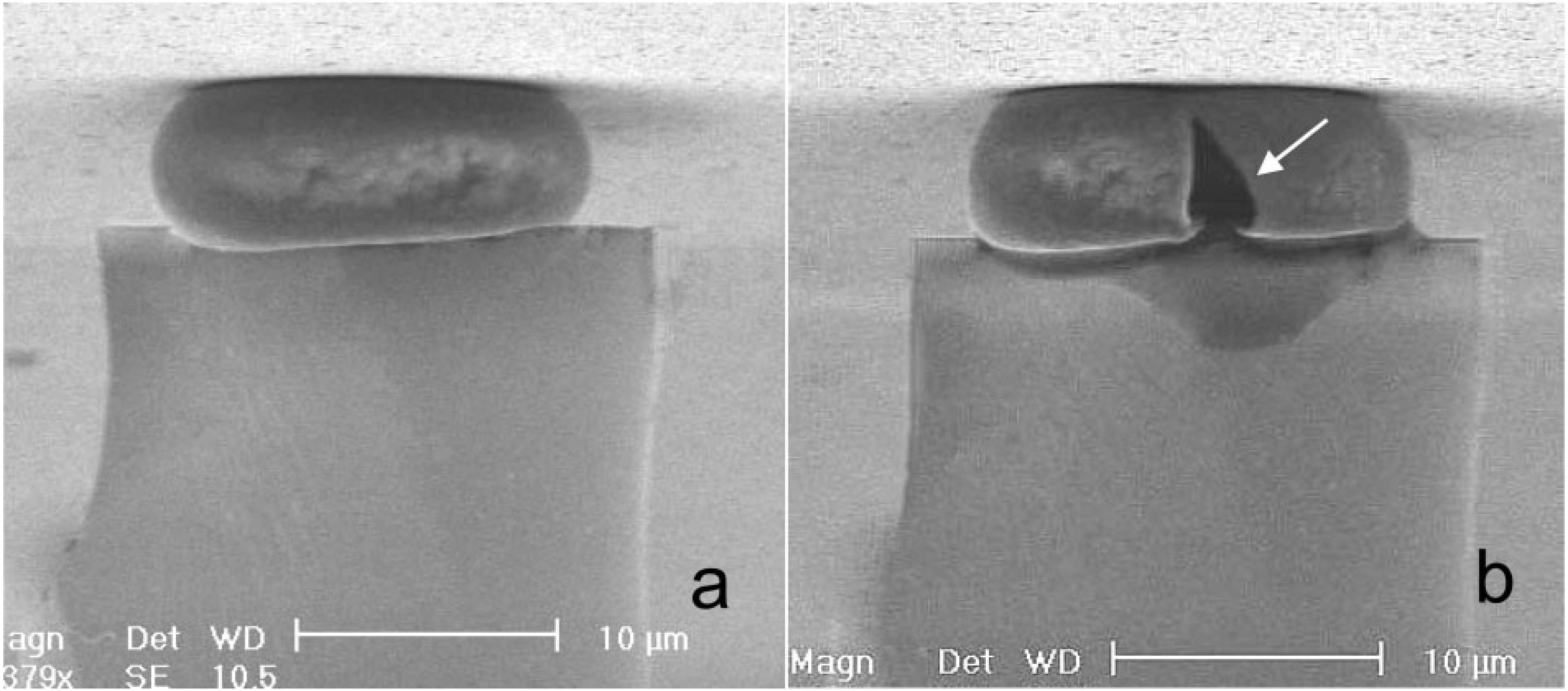


Schematic diagram of a nano-manipulation device in an ESEM

Liu et al. (2005), *Mat. Sci. Technol*. 21: 289-294.



Single MF microcapsule held between a force probe and slide in ESEM..



Ren et al. (2007), *Materials Sci. Technol.* 23: 857-864.

Conclusions

- ✓ Understanding the mechanical strength of capsules is essential to a wide range of industrial applications.
- ✓ The principle and limitations of different characterization techniques have been described.
- ✓ A case study on using micromanipulation based on diametrical compression of single capsules to characterize their mechanical strength leading to an industrial application has been presented.

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