Rheometers: not just for rheology any more

Looking beyond rheology

Gavin Braithwaite

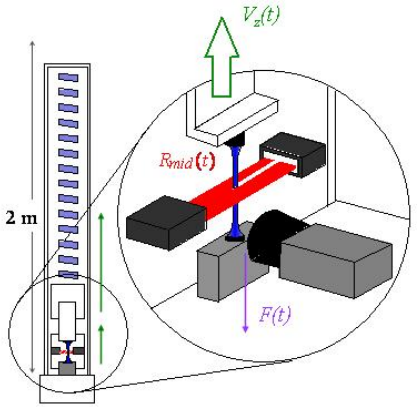
Cambridge Polymer Group,
56 Roland Street, Suite 310
Boston, MA 02129

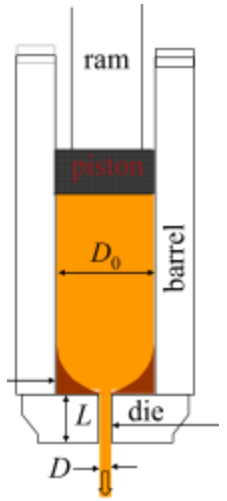
Cambridge Polymer Group, Inc.

Testing, Consultation, and Instrumentation for Polymeric Materials

Rheology

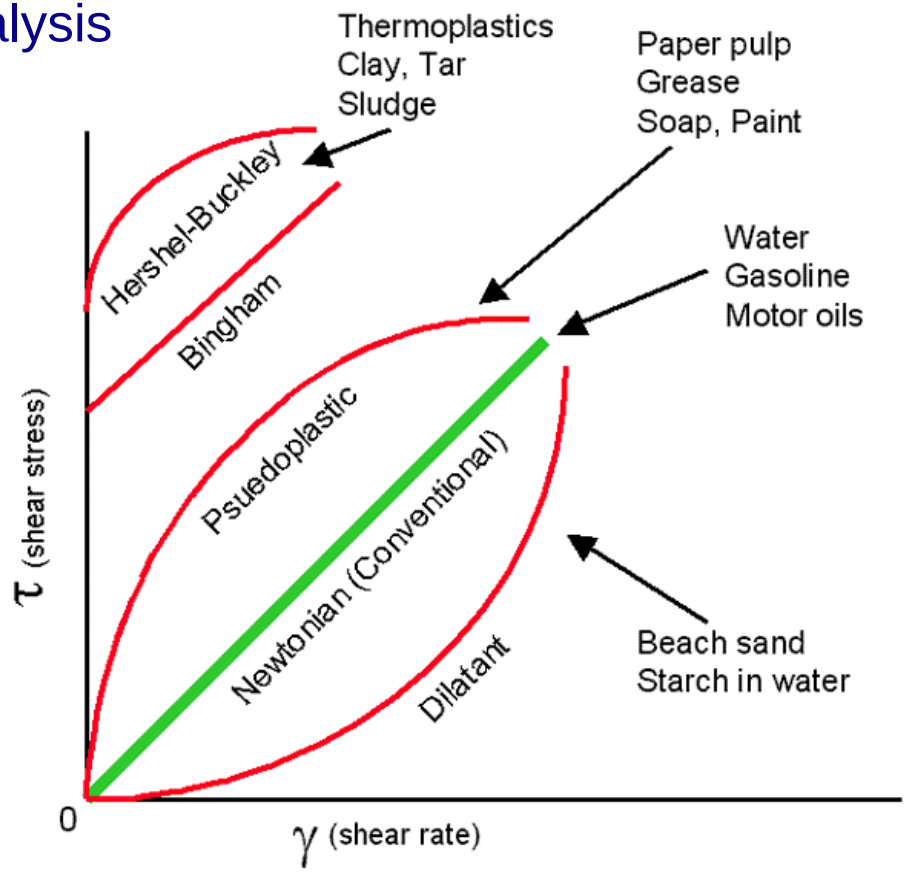
- Modern shear rheometers exceptionally robust tools
  - Wide torque and strain range
    - Many orders of magnitude
  - Robust control systems with wide dynamic range
  - Well understood flow-fields
  - Industry accepted instrumentation and models
- Other geometries
  - Capillary
  - Vane
  - Extensional
- Simplifying flows aids characterization





Quantitative characterization

- Simplifying flow-fields aids analysis
  - Shear flows
    - Viscosity
    - Shear thinning/thickening
    - Elasticity
    - Temporal evolution
    - Relaxation times
    - Yield stress
  - Pipe flow
    - Extensional properties
    - Melts
  - Extensional rheometers
    - Breakup times
    - Relaxation times
  - Reduce flow-fields and deformations to tractable situations



“Psycho-rheology”

- Where analytical rheology doesn’t provide the complete answer
  - Rheology invaluable as a method for reliably analyzing and ranking materials
  - Consumer perception arises from the overall response of the material
    - “psycho-rheology”
- Real-world usage is rarely one deformation
  - “performance” based tests often useful in linking “real world” experience with fluid properties
  - Tests that inherently use multiple relevant deformations can sometimes provide better insight in to consumer perception
  - Almost certainly non-linear
  - Less “transferable”

Case studies

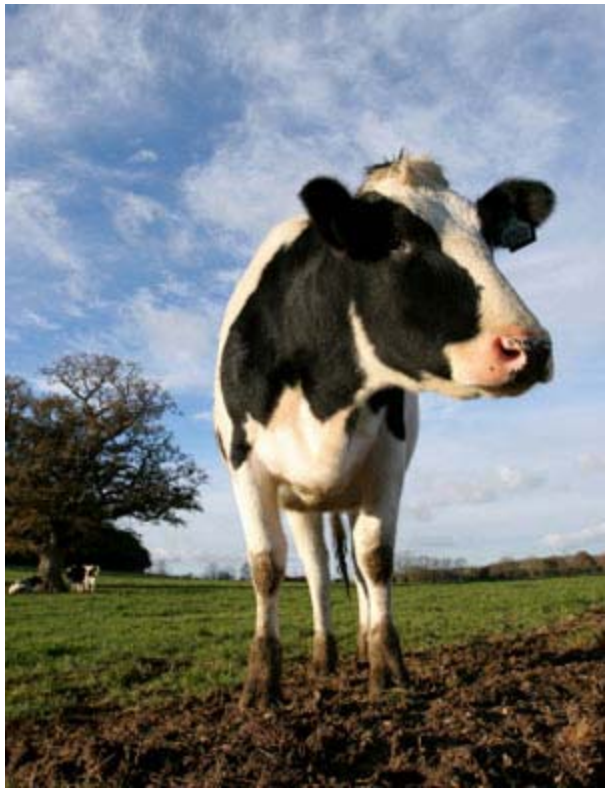
1. Food products
   - Differentiating milk products
2. Consumer healthcare
   - Tactile feel of personal care fluids
3. Cardiovascular applications
   - Implantation of catheters

Case 1: Food products

- Perception of food “feel” is driven by all senses
  - Partially sight and smell but substantially taste and “feel”
  - Consumer test panels are costly and time consuming
    - Intensive training required
    - Subjective
    - Can have difficulty describing differences
    - Outcomes can be ambiguous
    - Need big sample group
- Rheology provides tools
  - rapid and cost effective screening

Milk rheology

- Bovine milk similar composition, with breed variations
  - Fat
    - Holstein/Friesian - 3.6wt%, Jersey - 5.2 wt%
  - Proteins
    - 3.4-3.9 wt%
  - Lactose
    - ~5 wt%
- Proteins act to stabilize fat globules
  - Strongly influence feel and behavior
  - Agglomeration and separation important
  - Other solids impact shear viscosity
- Normally considered Newtonian
- Motivation: Replacement of fats and sugars
  - Desirable for health reasons
  - Need to preserve consumer perception

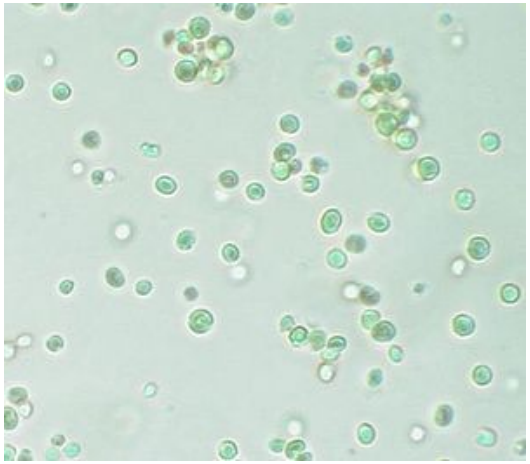


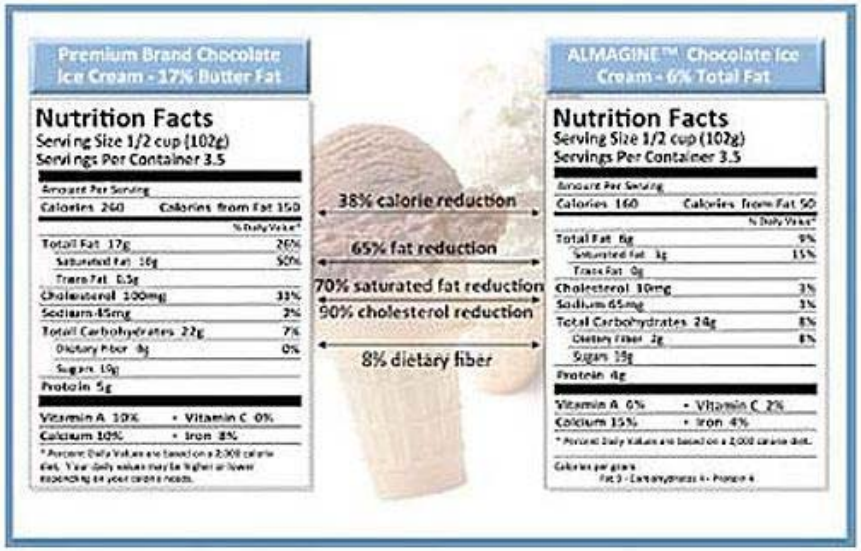
Experimental

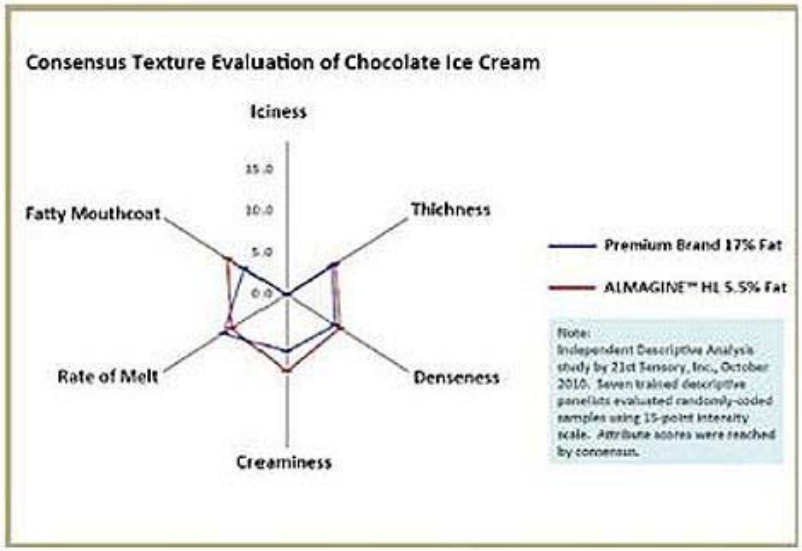
- AR-G2 cone-and-plate
  - 60 mm 1º SS cone, 25 ºC
  - Stepped shear 0.1-1000 s^{-1}
- Milk (fresh)
  - Whole (~4% fat)
  - Skimmed (2% fat)
  - Skimmed (1% fat)
  - Non-fat (0.5 wt% fat)
- Starch solutions
- Sugar solutions
- Proprietary food additives
  - Consumer testing indicates best alternative

Microalgal flour

- Microalgal biomass contains nutrition-providing materials
  - carotenoids
  - dietary fiber
  - tocotrienols and tocopherols
  - varying lipid compositions
  - low levels of saturated lipids

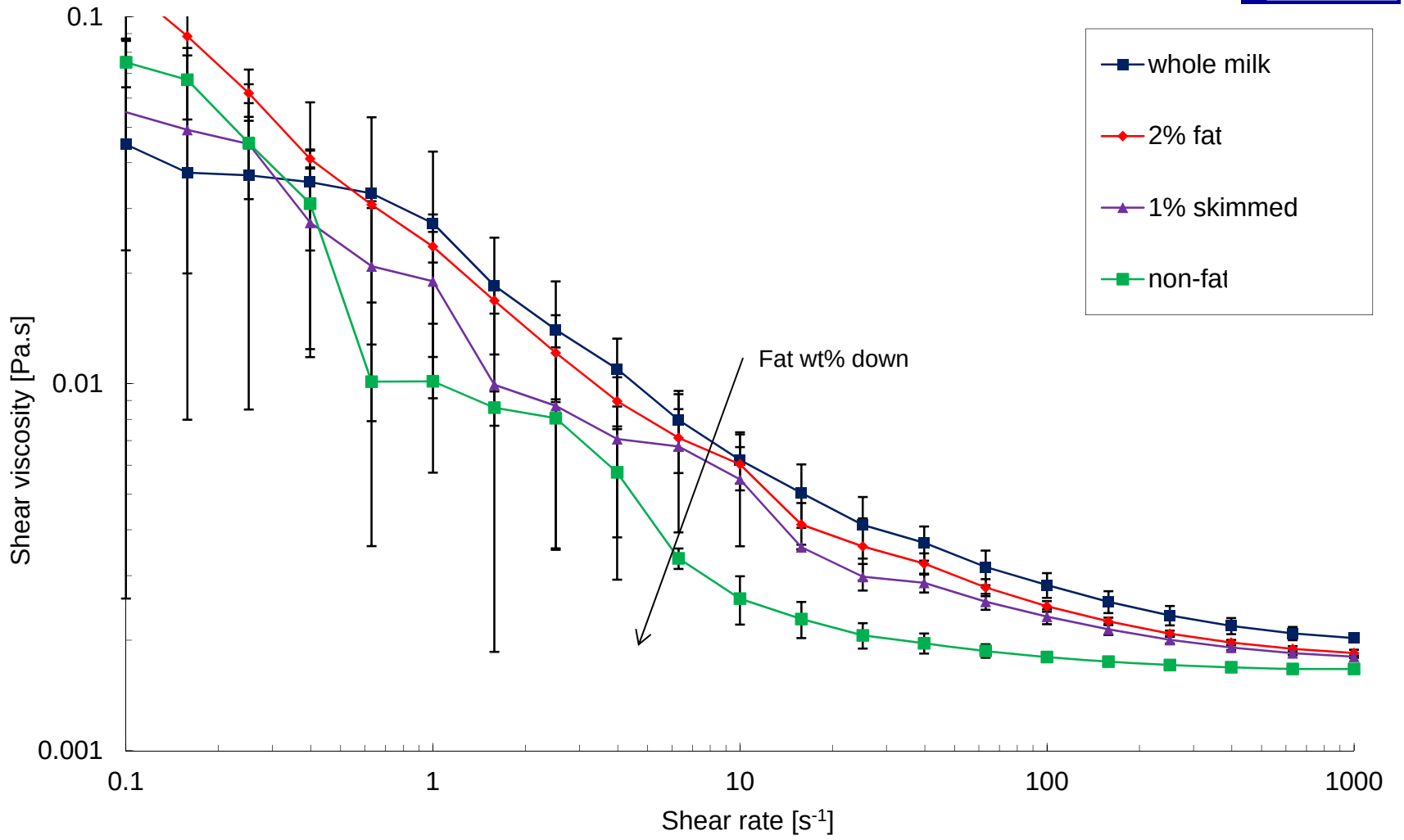






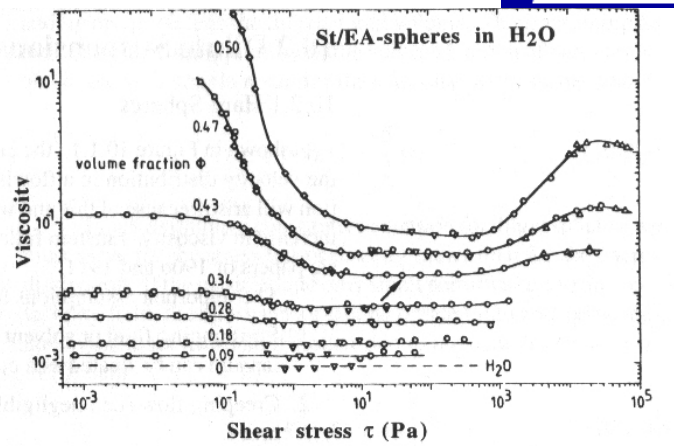
Milk

Error bars SD for three runs

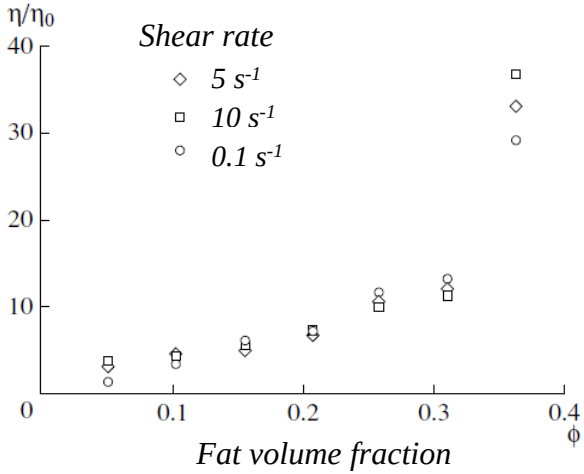


Impact of composition

- Milk normally considered “newtonian”
- Stabilized fat globules
  - Deformable spheres
  - Hydrodynamic interactions dominate
- Einstein/Taylor/Schowalter etc
  - Spheres in Newtonian solution
  - Packing fraction depends on proteins and sugars (~10%)
  - Not mono-disperse
  - Globules prone to cluster
- Critical response for mouth-feel
  - Shear thinning with zero-shear plateau
  - Fat provides viscosity
  - Fat % does not change behavior

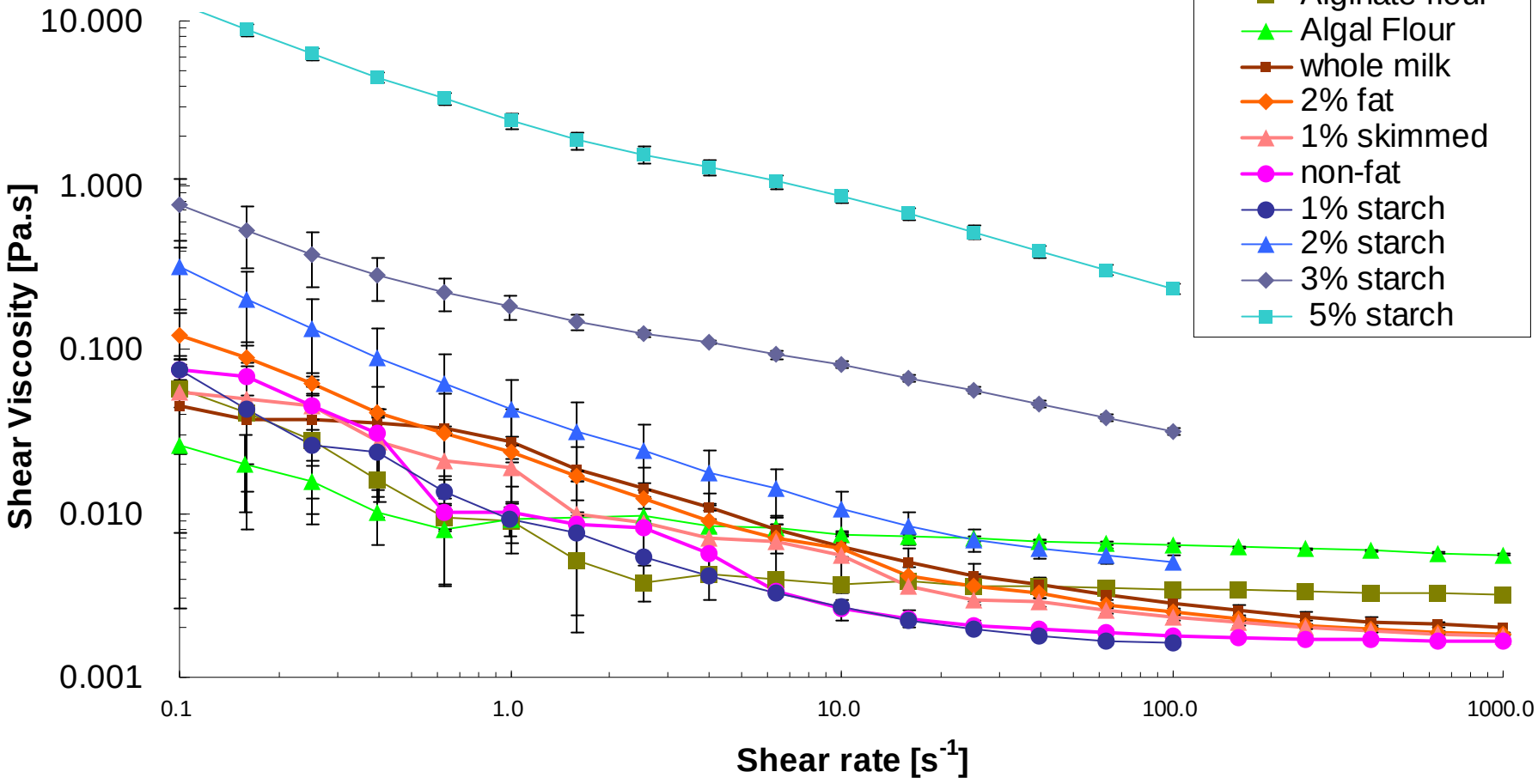


C.W. Macosko *Rheology: Principles, Measurements, and Applications*, VCH Publishers Inc., New York, 1994.



Kyazze, G. and Starov, V., *Viscosity of Milk: Influence of Cluster Formation*. Colloid Journal **66**(3),316-321 (2004)

Reducing fat



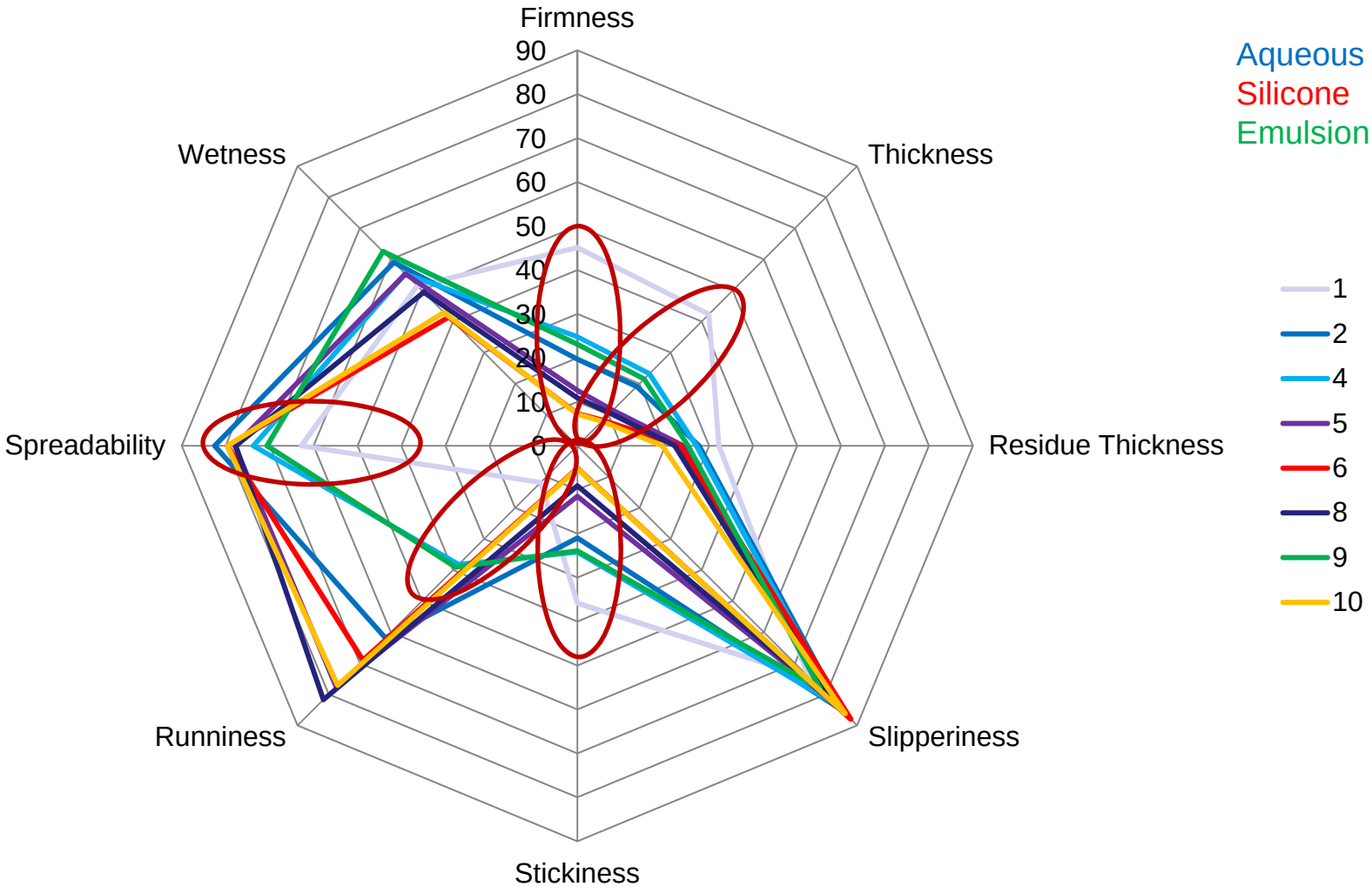
Conclusions

- Consumer testing implies
  - Algal flour closest to milk response
  - Shear rheology indicates starch is the best
- Complex fluids can yield deceptively simple responses
  - Milk (stabilized fat globules)
    - Shear thinning
    - Shear rate response controlled by fat content plus proteins and sugars
  - Choosing “dominant” deformation does not always allow replacement of ingredients
    - Milk “feel” expected to be dominated by shear viscosity
    - Corn syrup, algal flour and starch all provide reasonable rheological responses
    - But rheology does not provide separation between systems
  - So where is the difference?
    - Wrong deformation?

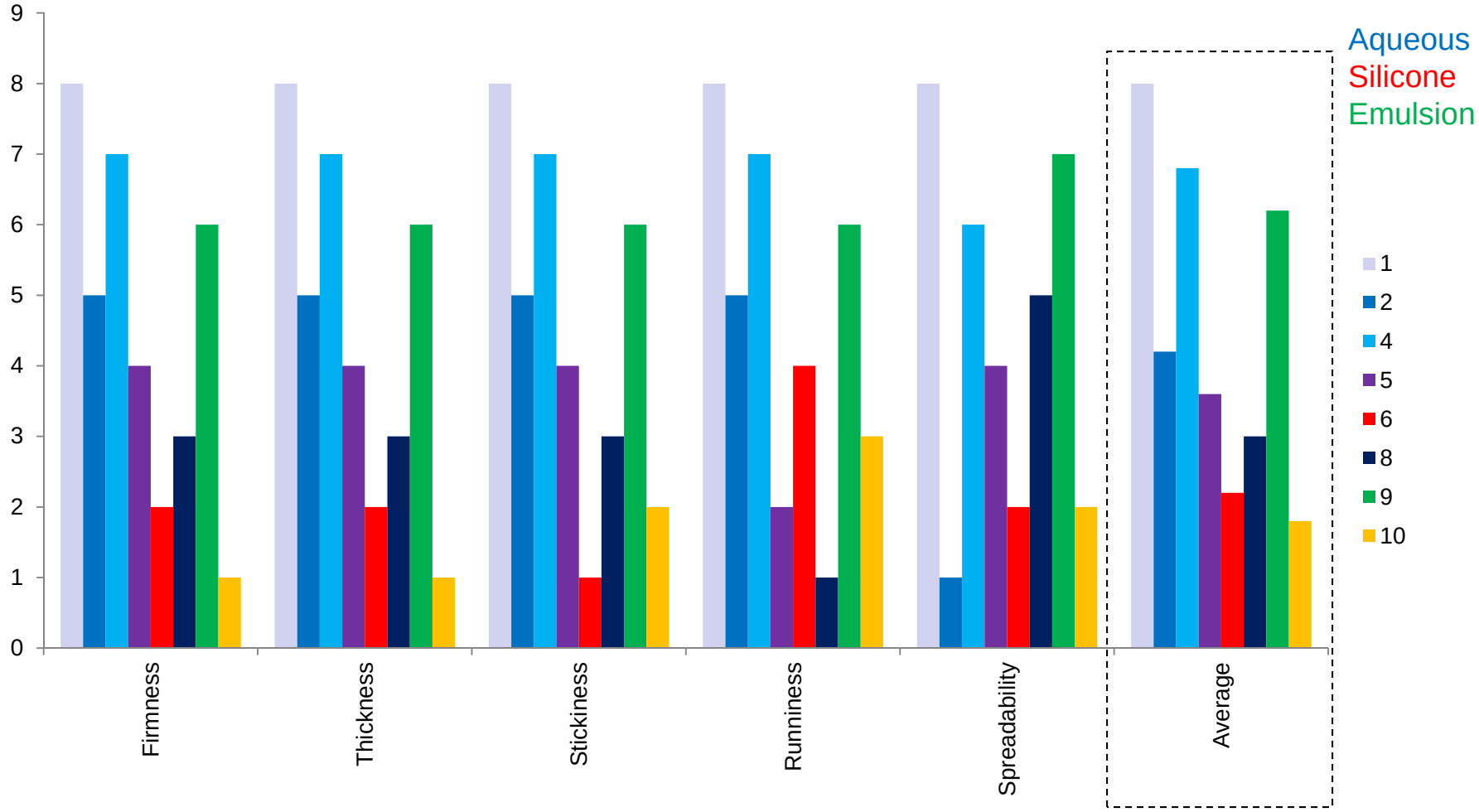
Case 2: Consumer Products

- Consumer products represent a massive market in US
  - Emulsions, emollients, moisturizers and personal lubricants
- Perception of efficacy influenced by “feel” and “look” of system
  - Complex interplay of
    - Viscosity
    - Yield stress
    - Absorption
    - Wetting
    - Elasticity
    - Loading

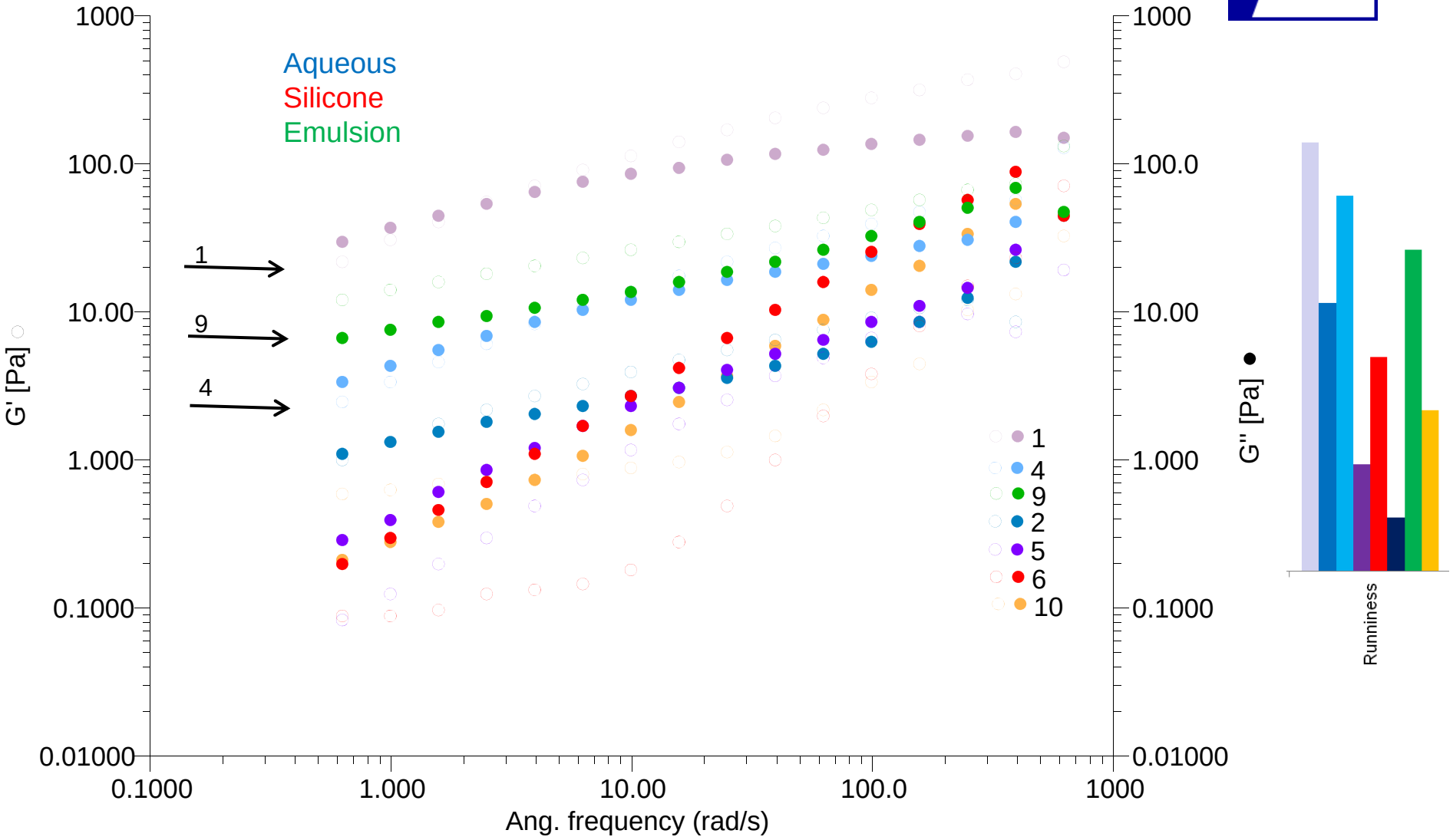
Personal Lubricants



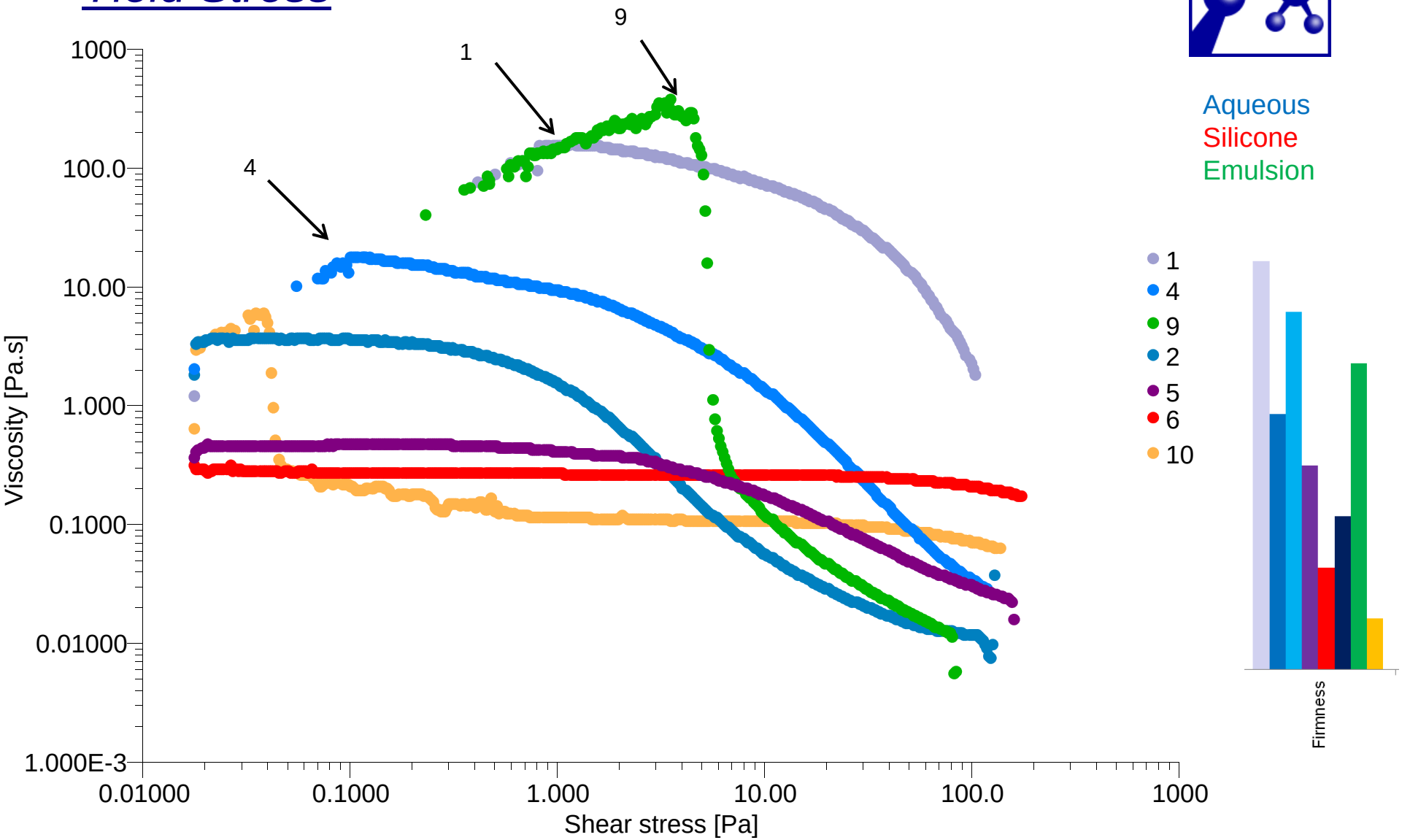
Consumer ranking (selected)



Small Amplitude Oscillatory Shear



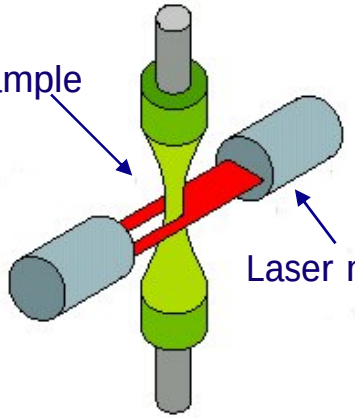
Yield Stress

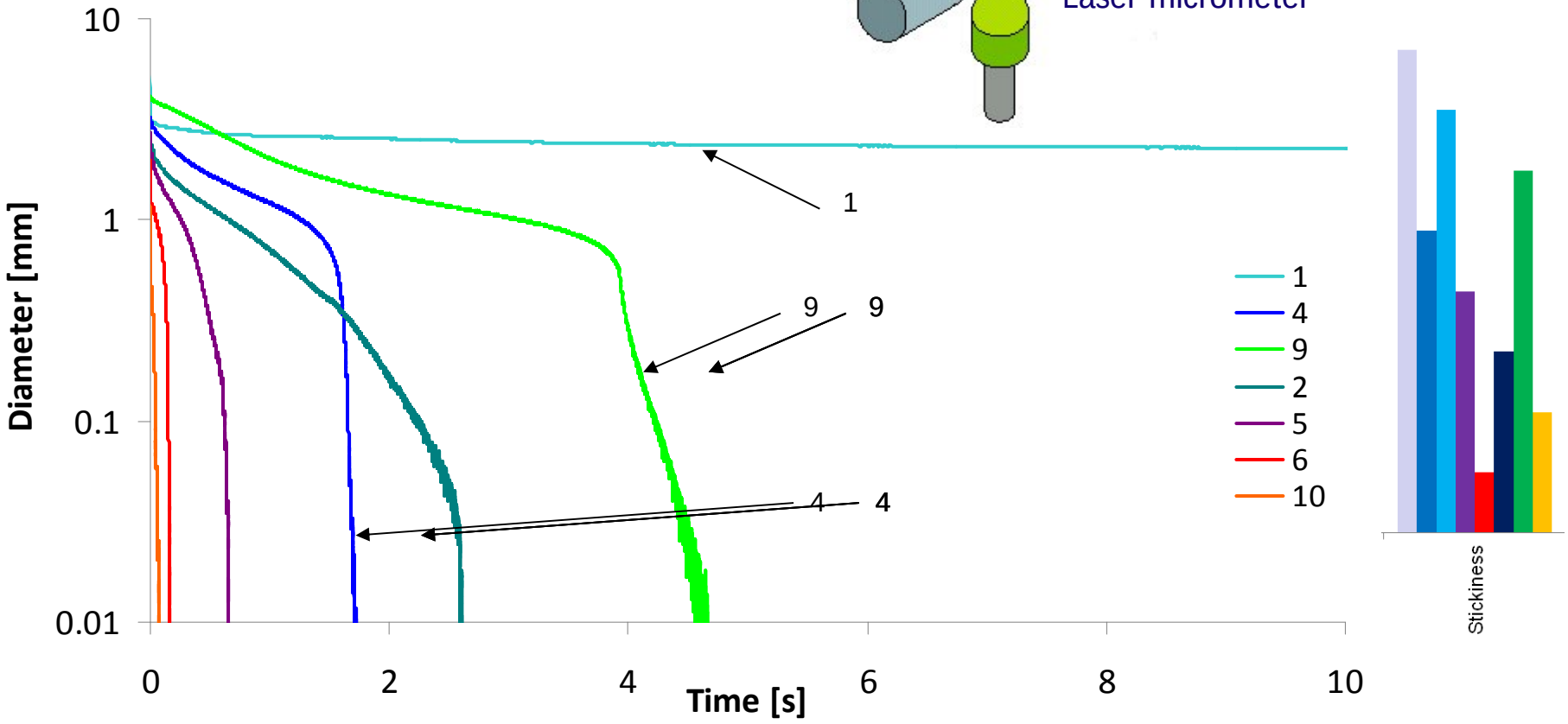


Aqueous
Silicone
Emulsion

Capillary Breakup

- Thermo Haake CaBER



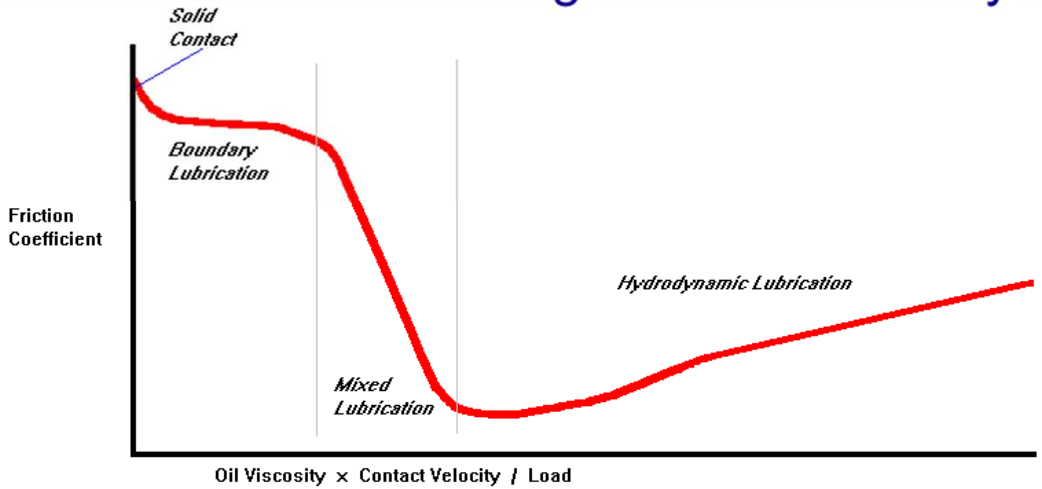


Observations

- High ranking materials appear to have
  - High low-shear viscosity and low high-shear viscosity
  - High shear viscosity seems to be more important
  - Elasticity less important
  - Extensional properties appear related
- What is missing?
  - “slipperiness” (lubricity)
    - Related to shear viscosity and surface chemistry
    - “Thin” film with gap governed by shear properties
    - Coefficient of Friction
  - “stickiness” (tack)
    - Related to elasticity and adhesion
    - Large contact area, dependent on pull speed and fluid properties
    - Tack test

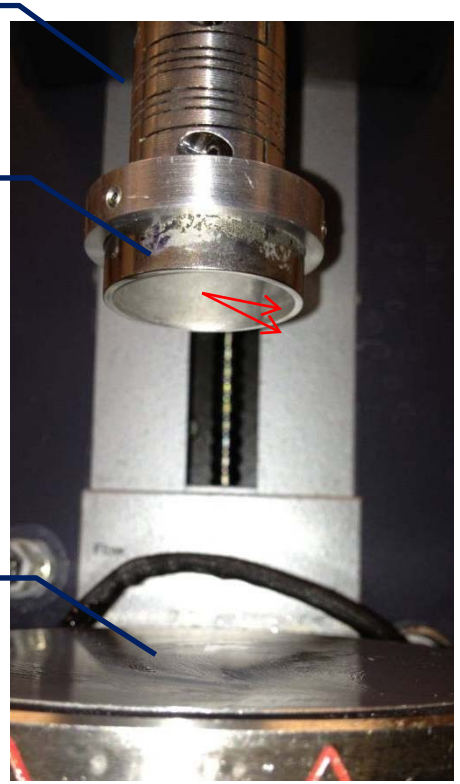
Lubricity

- Conventionally measure of effort required to slide two objects past each other: Coefficient of Friction
  - $CoF = \frac{F_{shear}}{F_{normal}}$
- Despite this simple formulation, difficult to produce equipment invariant tests
  - ASTM D 1894 describes one such standard
    - Sled dragged across surface
- Characterization of lubrication regimes described by a "Stribeck" curve



CoF on a rheometer

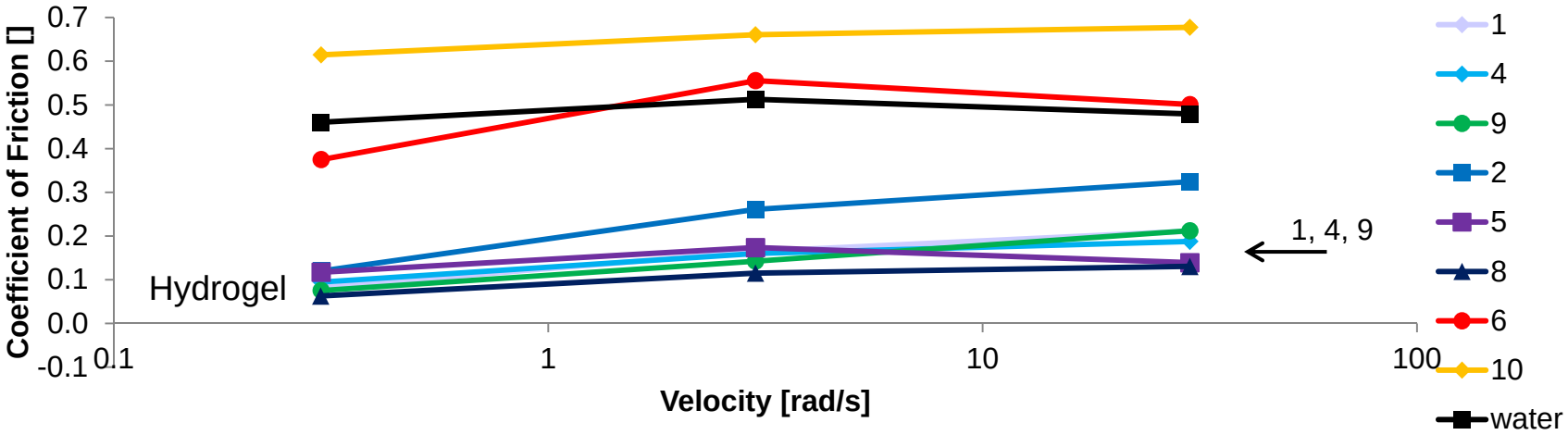
- Fundamental parameters required
  - CoF: shear and normal forces
  - Lubrication parameter: velocity, viscosity and normal force
- Natural for a rheometer, with the correct configuration [1]
  - Annulus geometry approximates a line contact
    - ID and OD: R_1 and R_2
    - Velocity "constant" across geometry
    - Coefficient of Friction: $\mu = \frac{\tau_{\bar{R}}}{\sigma_N} = \frac{\pi T (R_1 + R_2)}{F_N (R_1^2 + R_2^2)}$
    - Gumbel Number: $Gu = \frac{\Omega \eta}{\sigma_N}$
- Addition of a spring coupling allows the fixture to compensate for non-parallel alignment

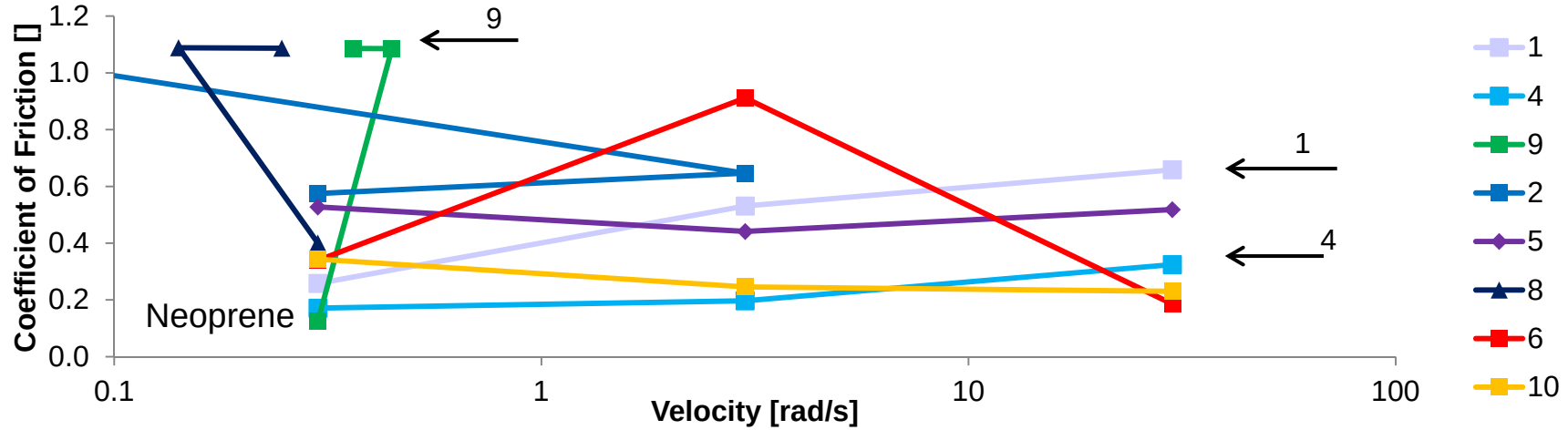


[1] *Kavehpour and McKinley "Tribo-rheometry: from gap-dependent rheology to tribology" Tribology Letters (2004) 17(2) 327-335*

Coefficient of Friction

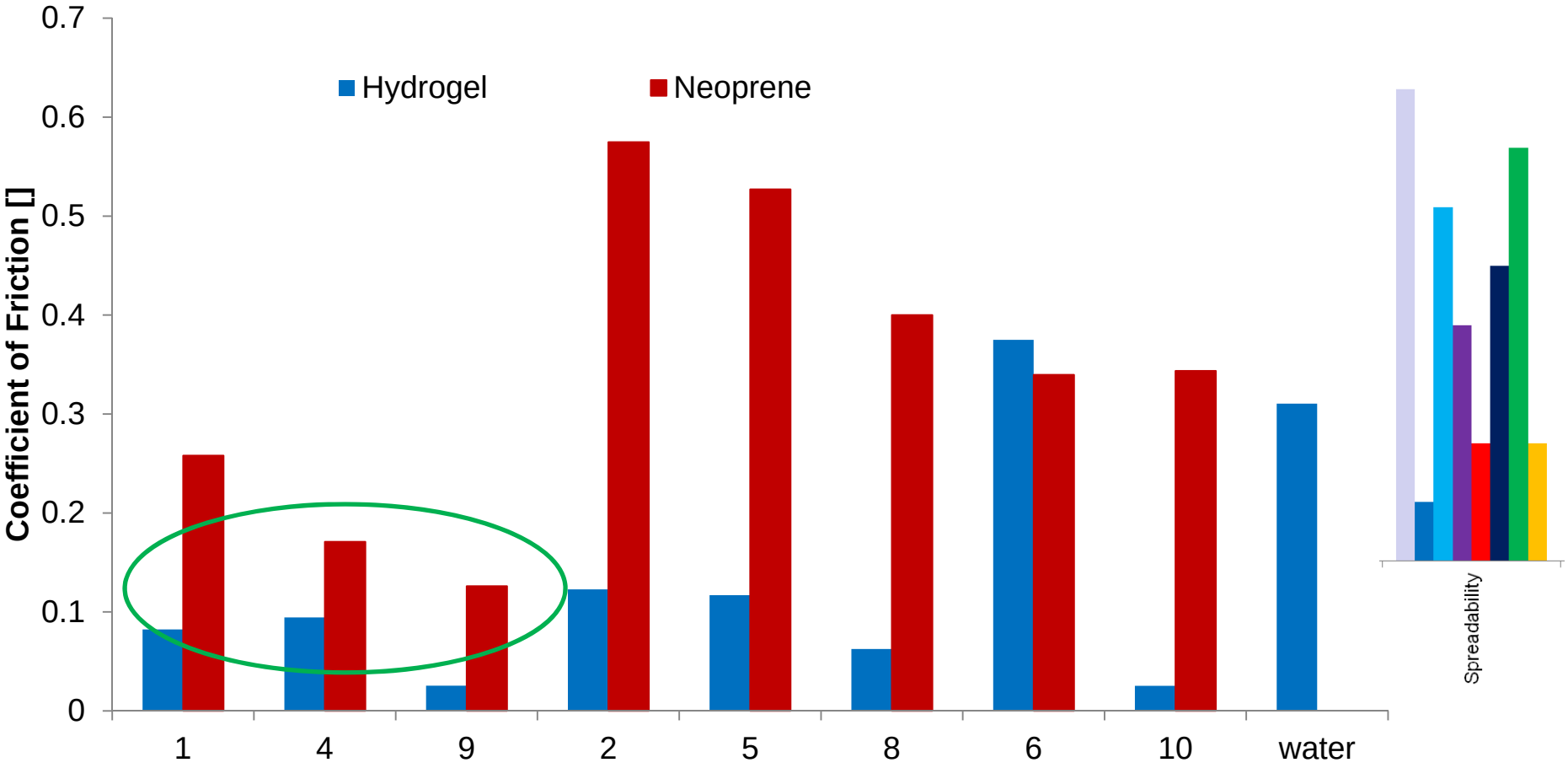
- CoF fixture on AR-G2. Controlled normal stress (82 kPa) and rotation rate





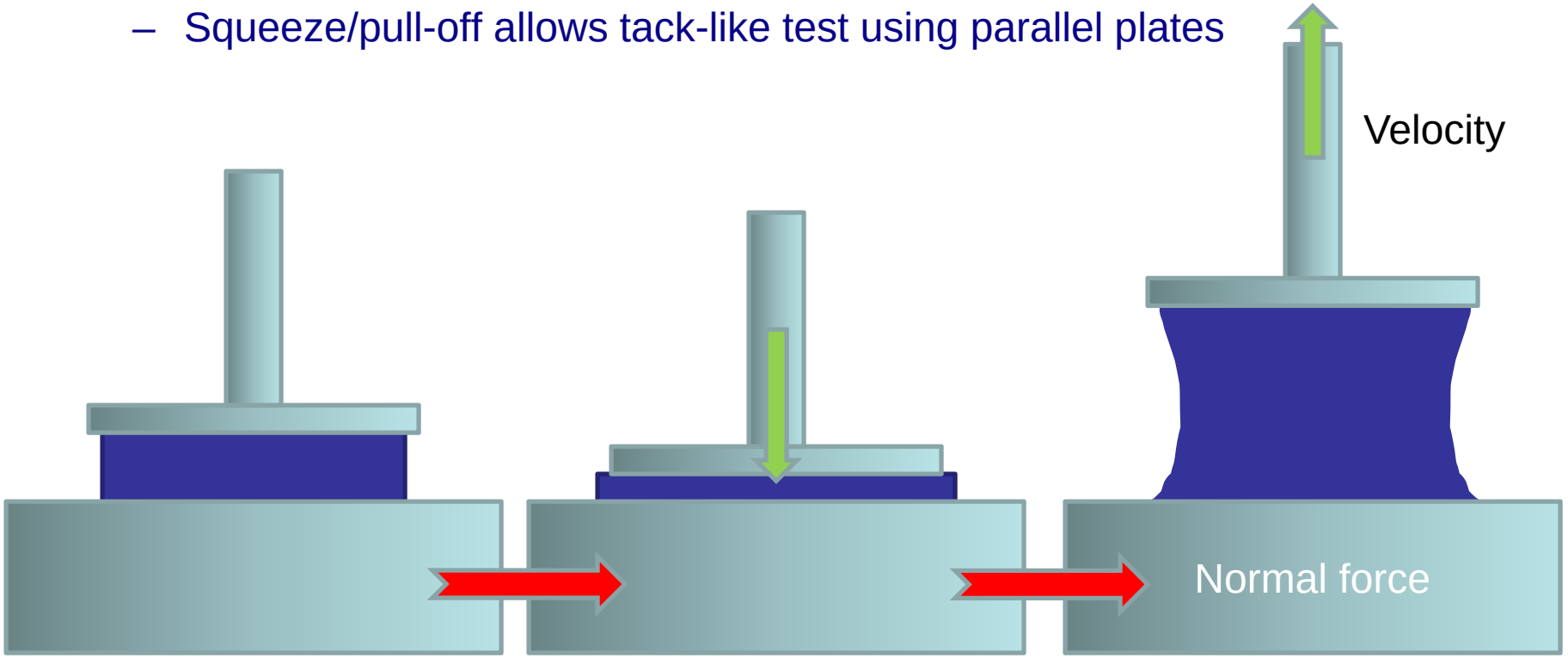
Comparisons

- CoF fixture on AR-G2. Controlled normal stress (82 kPa) and rotation rate (0.3 rad/s)



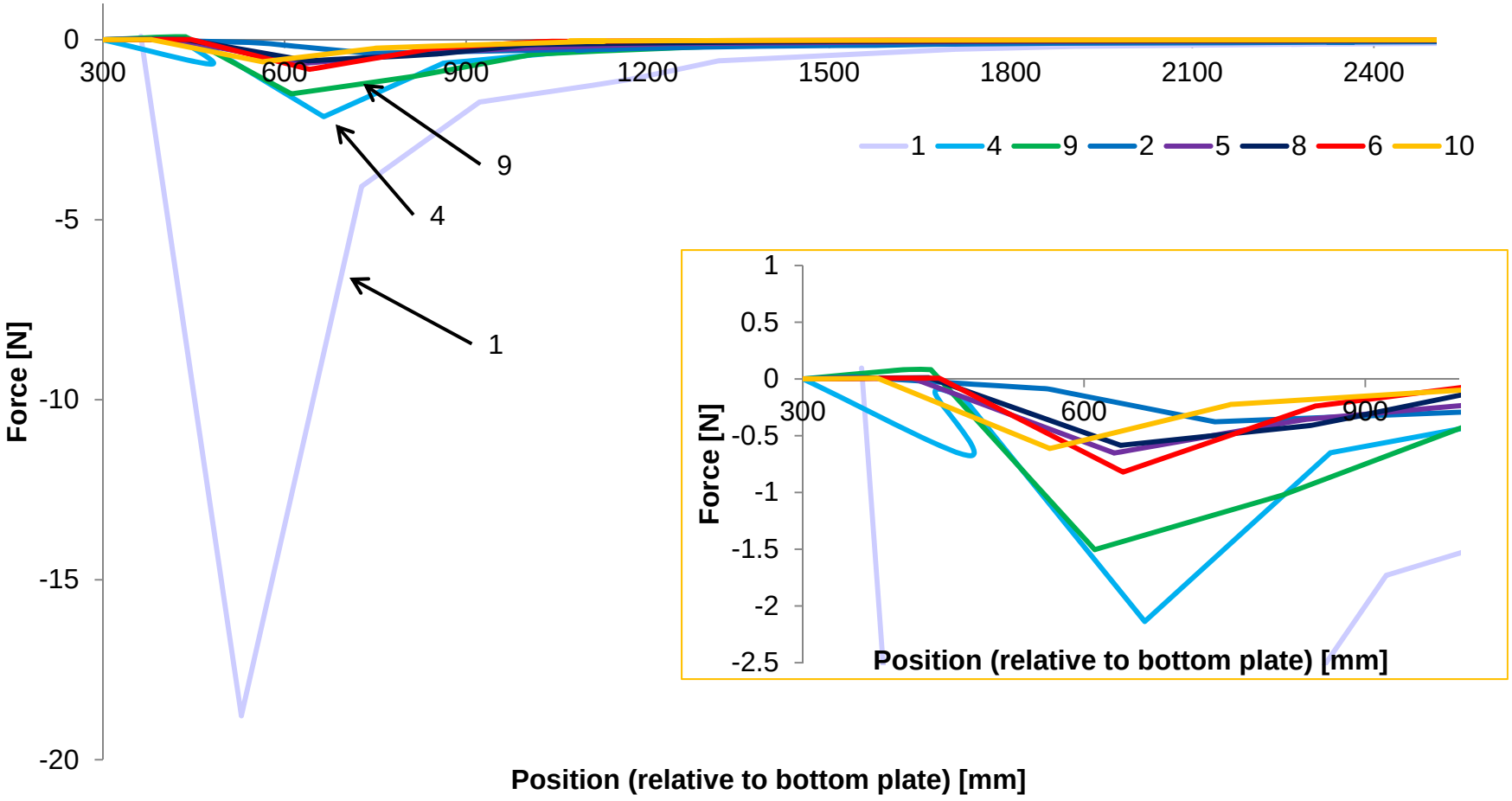
Tackiness

- Combination of accurate vertical position and normal force allow tack to be measured on a conventional rheometer
  - AR-G2 has a “fast sampling” mode that allows 250 Hz
  - Squeeze/pull-off allows tack-like test using parallel plates

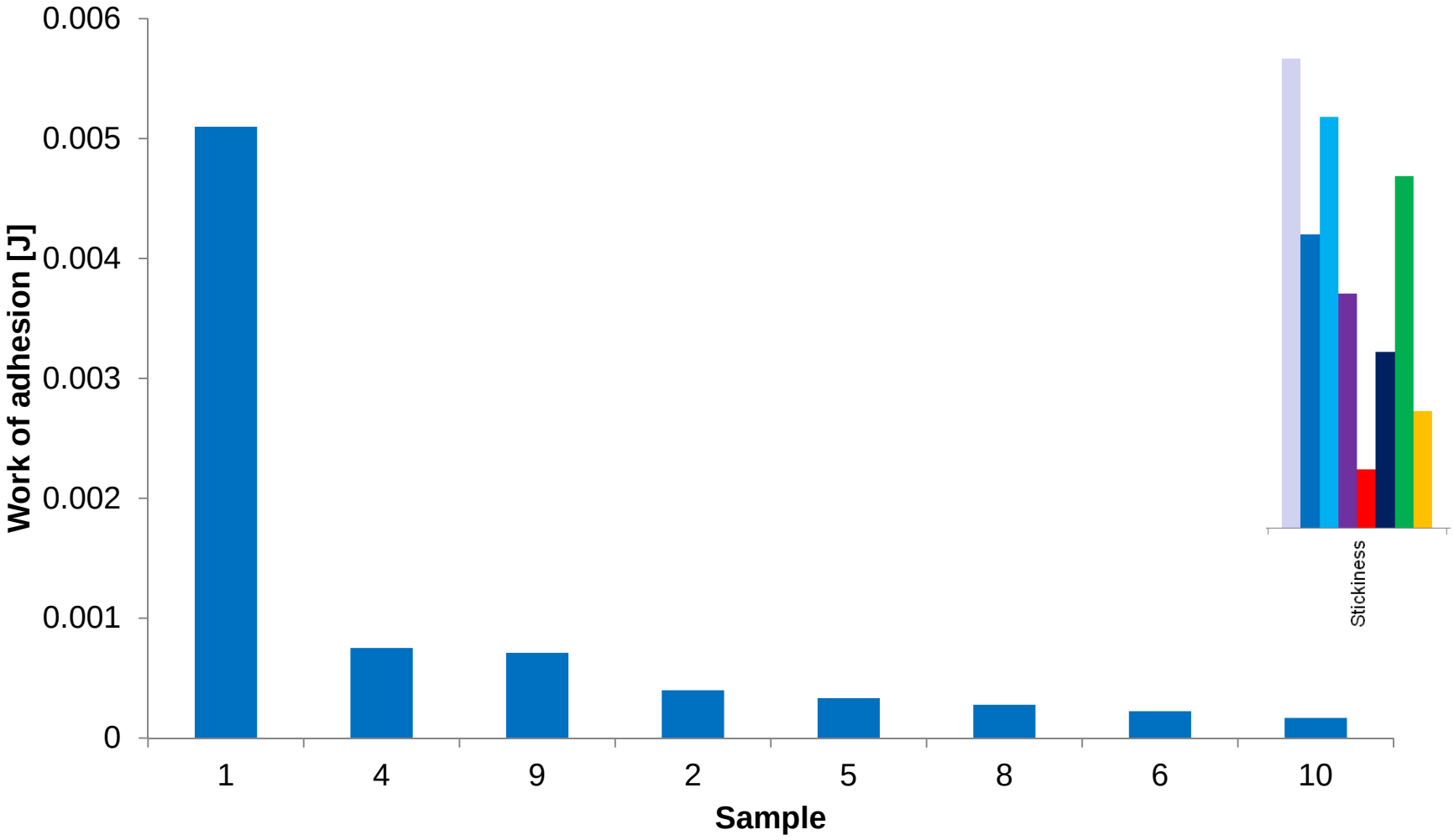


Tackiness

- 4 cm parallel plate loaded to fixed gap and pulled at 500 micron/s

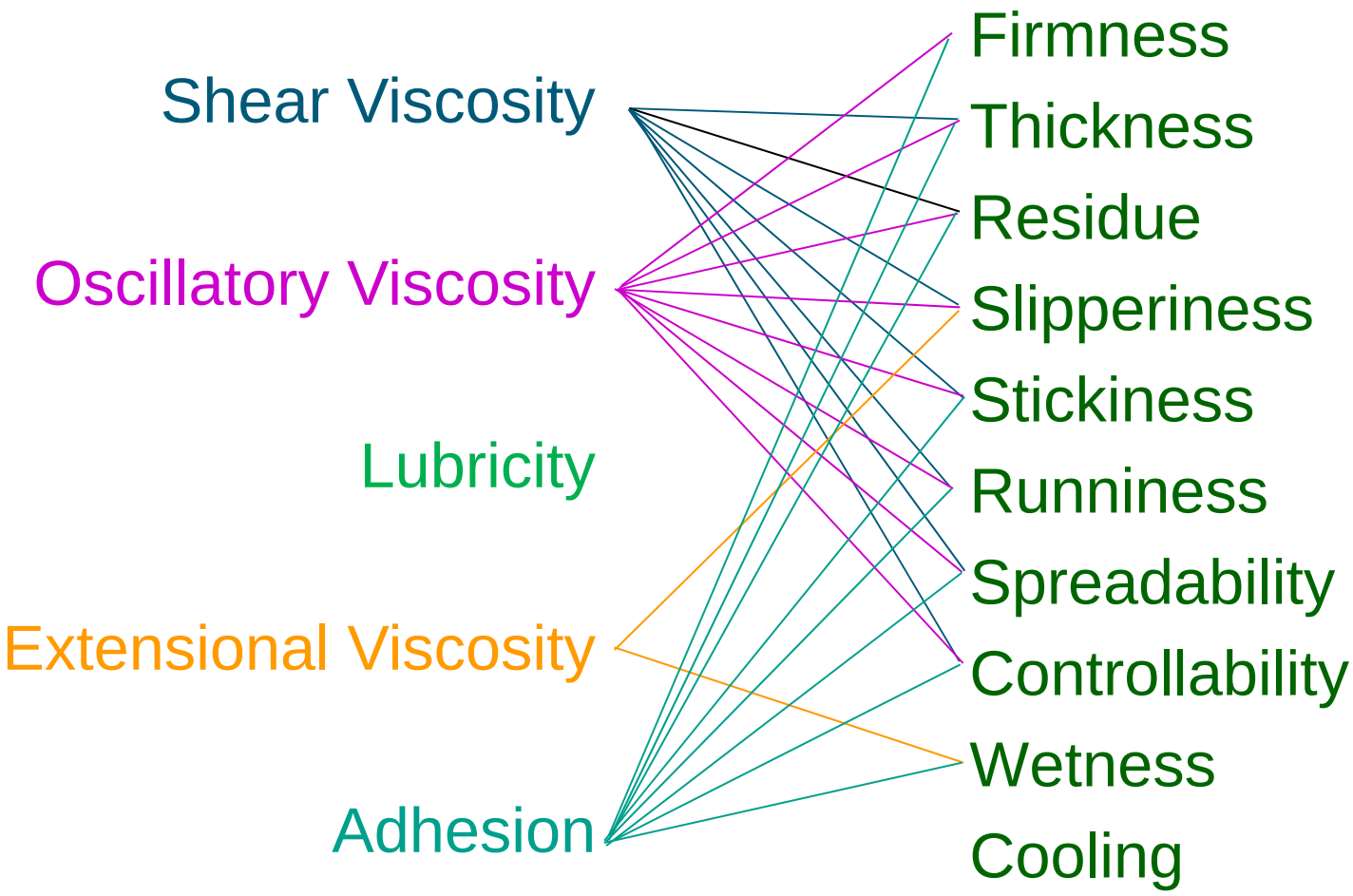


Work of Adhesion



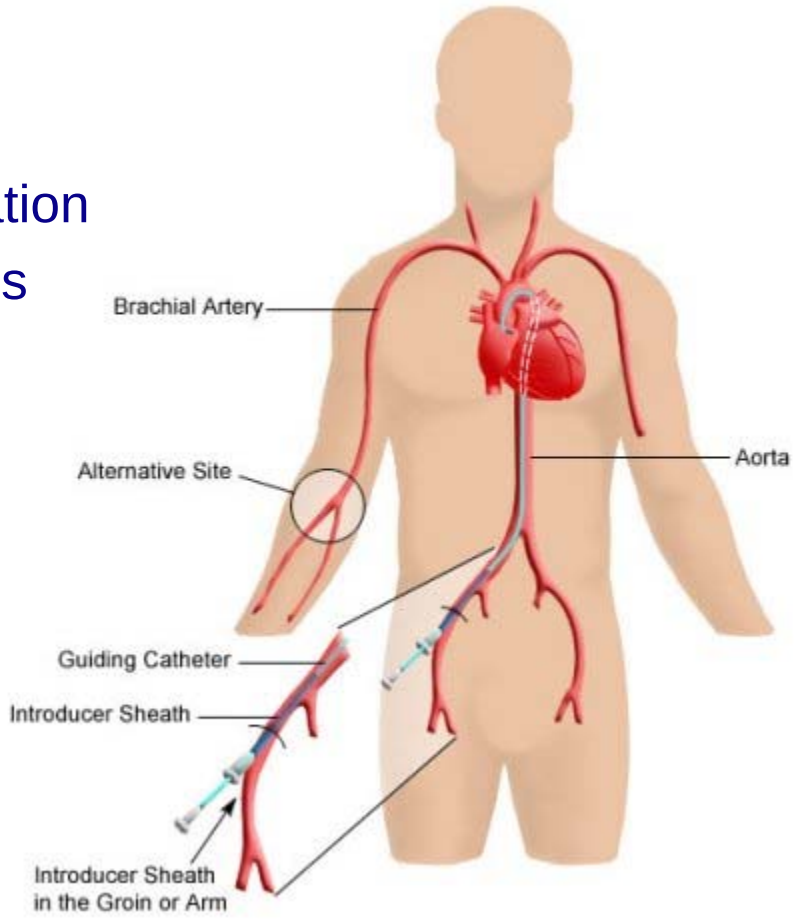
Conclusions

Correlation between physical and sensory measures
Intimate Health products, (p<0.05)



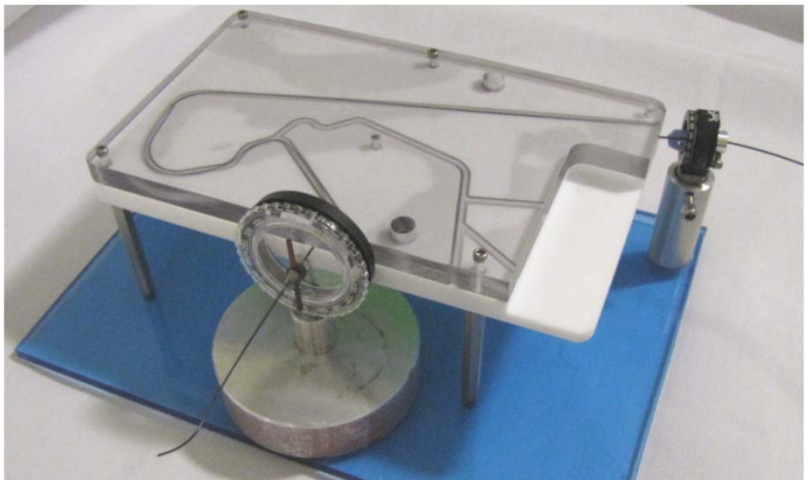
Case 3: Implantation of catheters

- Cardiovascular catheters are used for access, surgery and drug delivery
- Usually inserted through the femoral artery and then guided to their destination
- Device is “steered” through the arteries along tortuous pathways and around sharp corners
- Guidewire is used to direct catheter
- Surgical feel of device influenced by
  - Coating friction on walls
  - Level of wetting/lubrication
  - Varying contact area due to bends



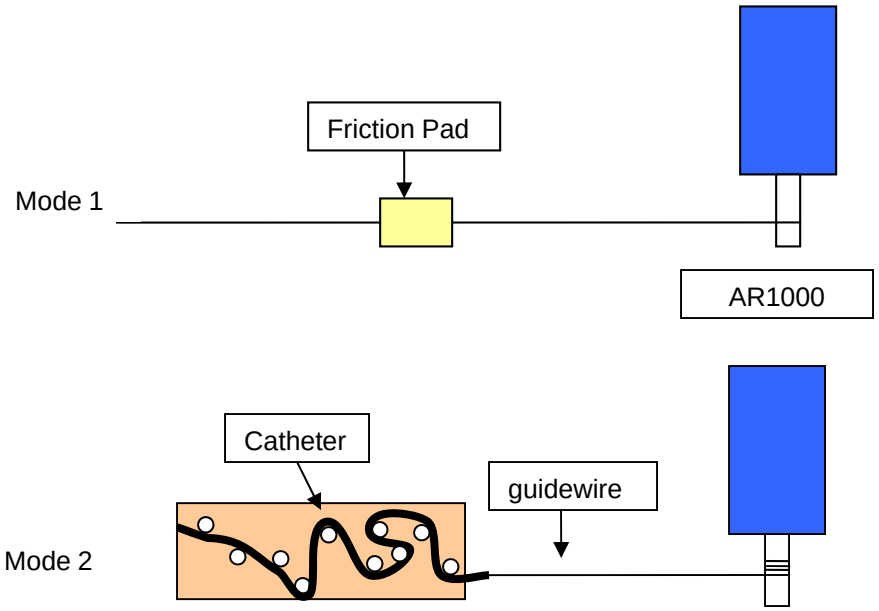
Testing of catheters

- Surgical feel of the device controlled by
  - Physiological fluids present
  - Absorption of species
  - Wettability of the coating
  - Intrinsic coefficient of friction
  - Bending elasticity of the composite catheter
- ASTM F2394: Expandable Vascular Stents
  - Tortuous path for testing of catheter insertion and rotation



Friction and lubricity of catheters

- Effective friction a function of pull-force and displacement
  - AR1000 provides accurate measures of both
    - Testing through “friction pad” decouples tortuosity
    - Testing through fixture allows effect of tortuosity to be determined

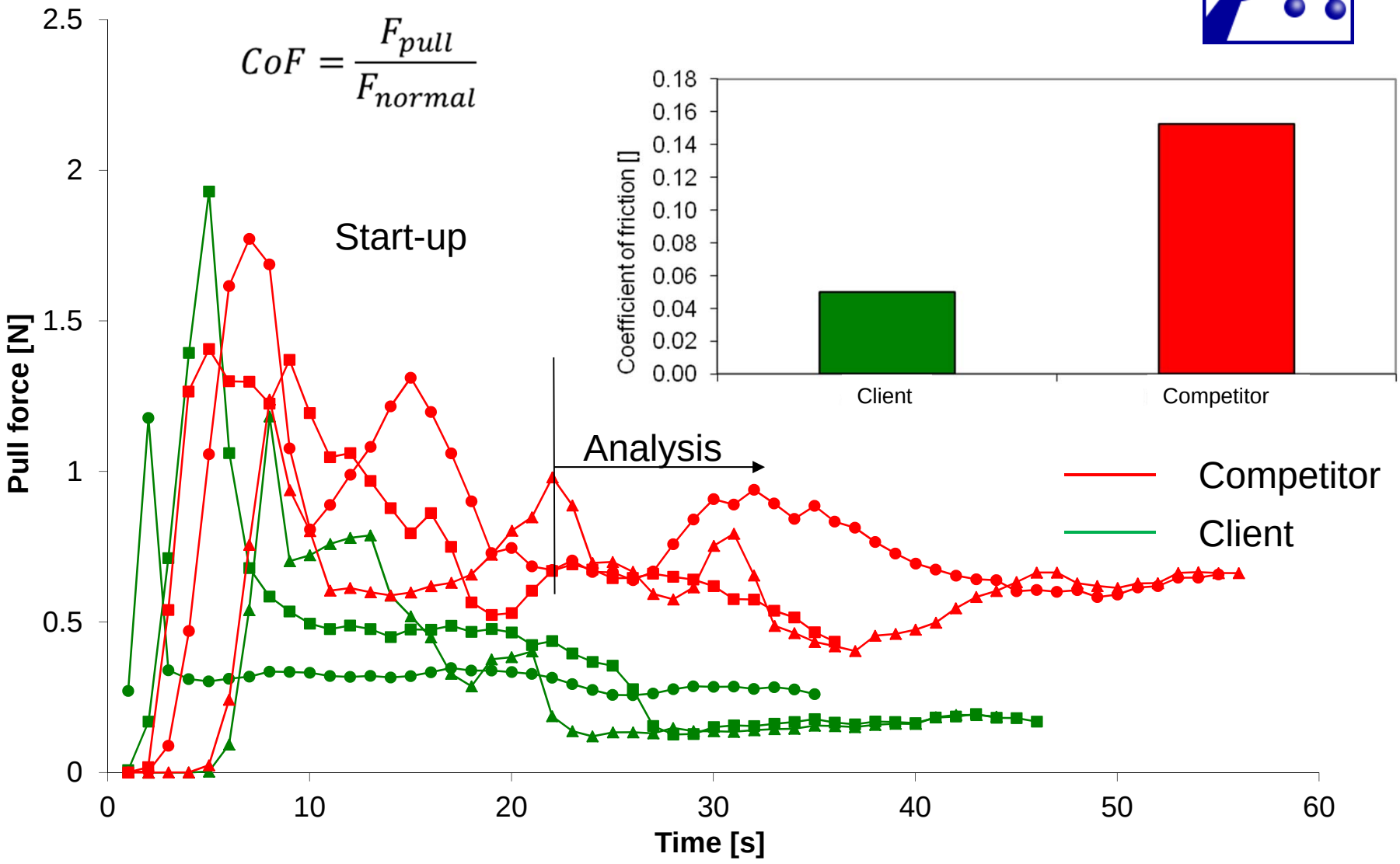


Direct measure of friction between guidewire and model surface

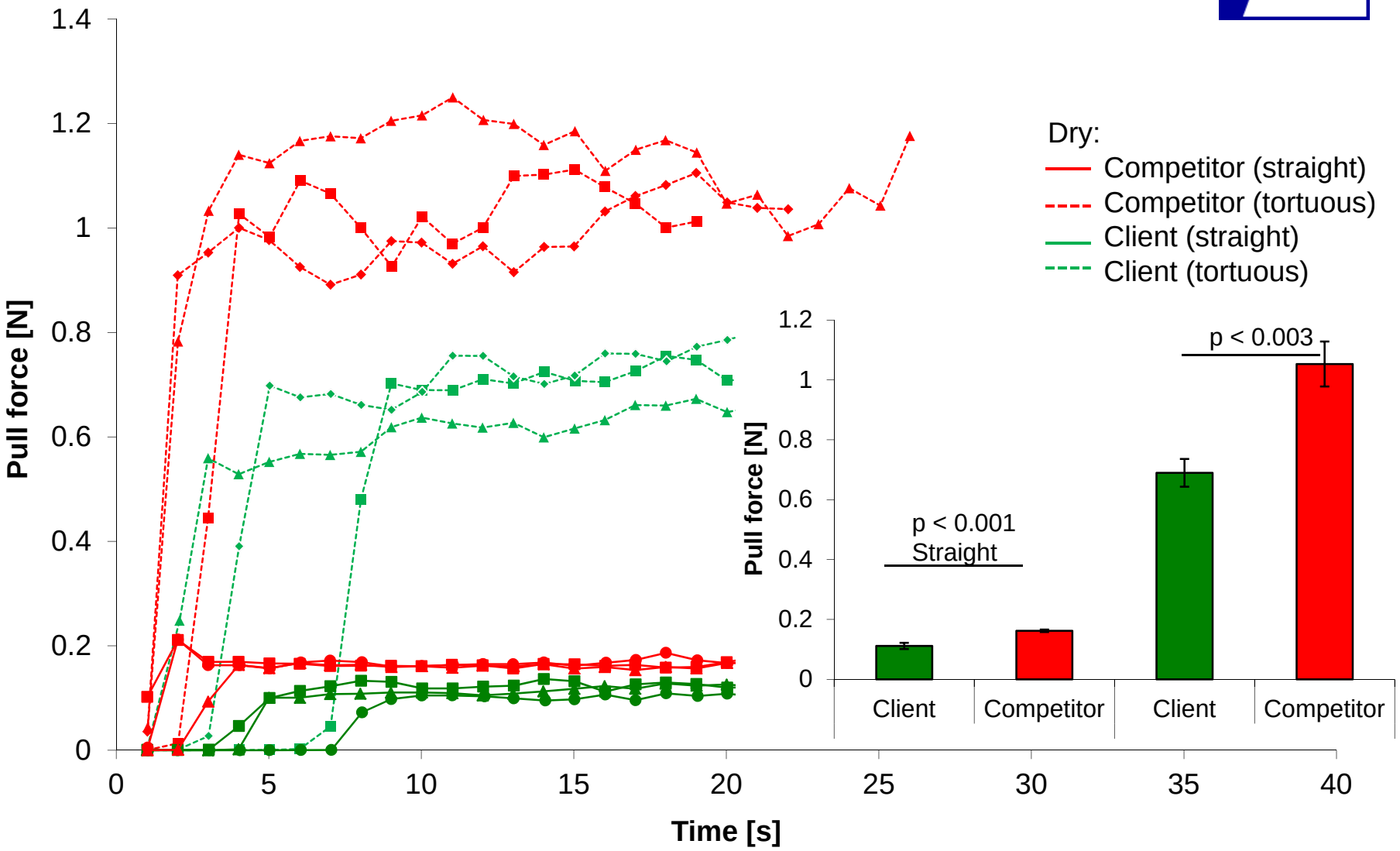
Measure of friction between guidewire and catheter in tortuous contour

Mode 1: Friction pad

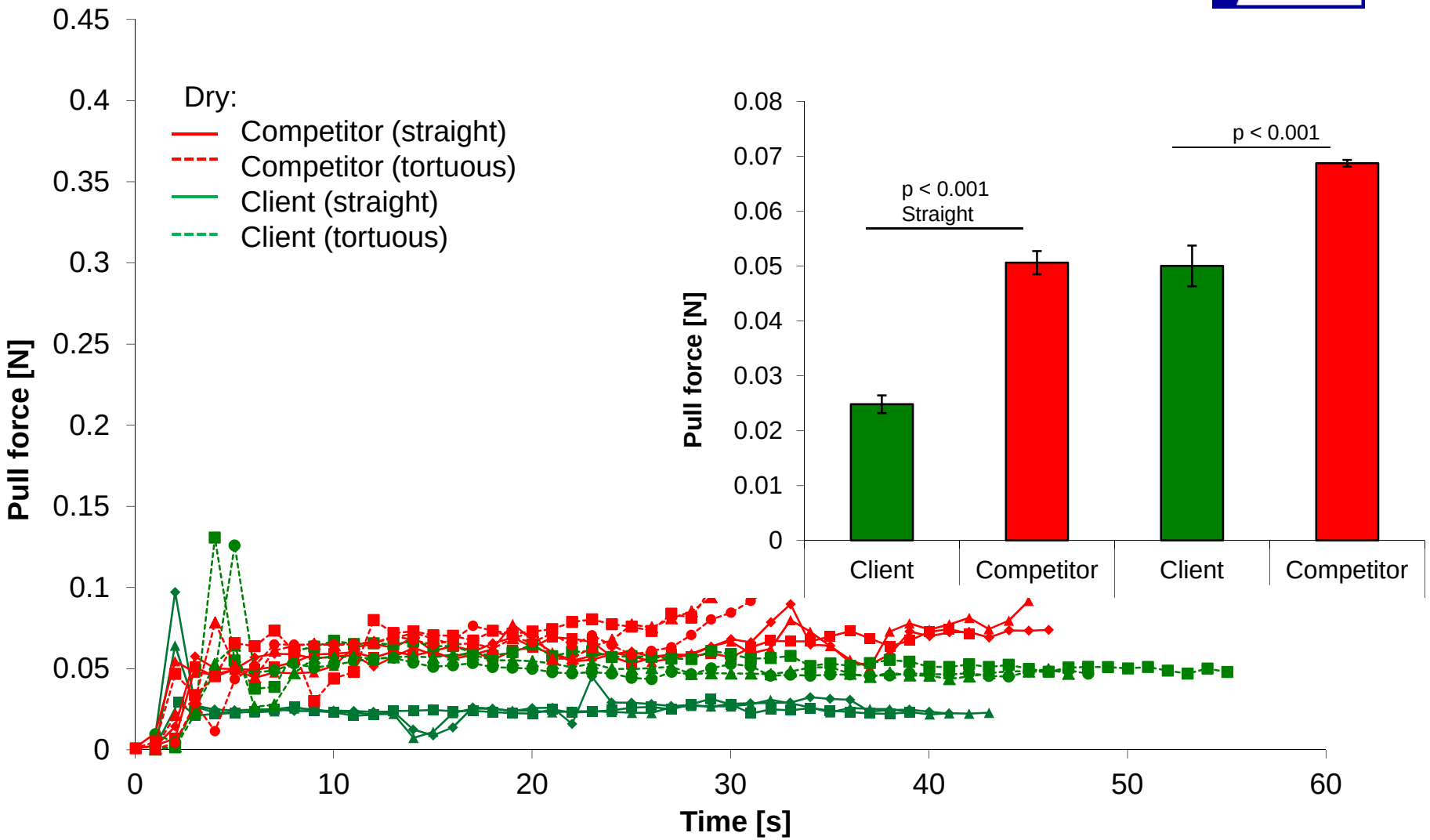
$$CoF = \frac{F_{pull}}{F_{normal}}$$



Mode 2: pull-force in catheter (dry)

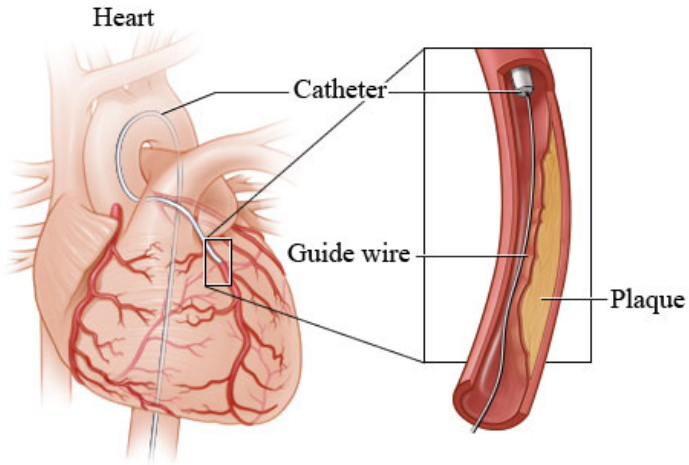


Mode 2: pull-force in catheter (wet)



Conclusions

- In a crowded market place surgeon impressions drive sales
- Reducing “impressions” to quantitative numbers allows direct competitive comparisons
- Using conventional rheological techniques and instruments in unconventional manners allows differentiation of materials in physiologically relevant conditions
  - Test structure that is familiar to users
  - Numbers that are easily correlated



Lessons and comments

- Understanding the rheology of fluids critical for understanding consumer perception and use
- But mode of use can be just as important
  - Usage rarely simple shear
  - Perception is therefore governed by response to variety of deformations
    - Simple shear
    - Compression
    - Extension
    - Pipe-flow etc
- Collating data in more relevant configurations can provide useful correlations with field data
- Superb force and position control of a conventional rheometer still useful
- Sometimes the tests need to be modified to help act as consumer screening tests

Thank you

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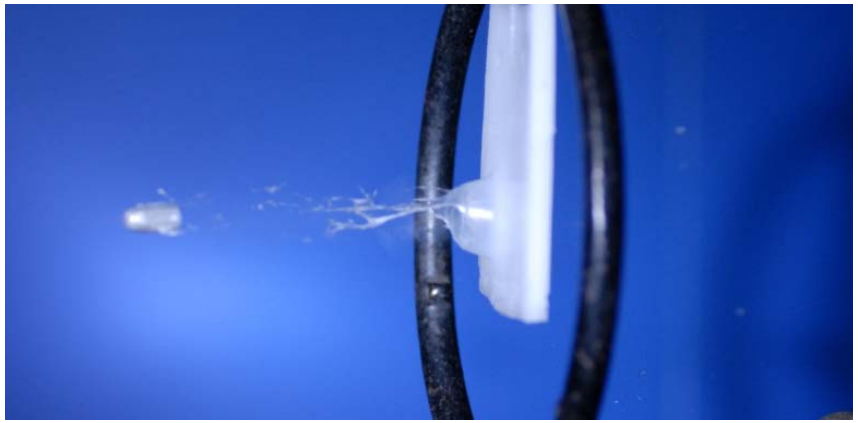

Cambridge Polymer Group, Inc.
56 Roland St., Suite 310
Boston, MA 02129
(617) 629-4400
http://www.campoly.com
info@campoly.com