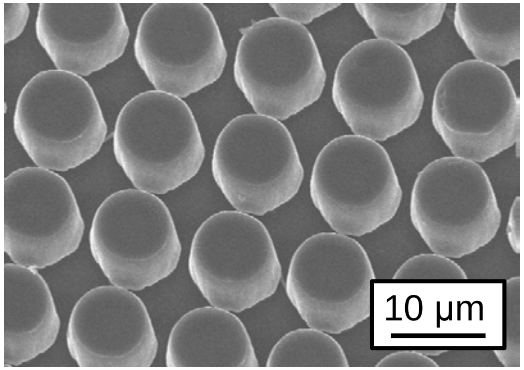
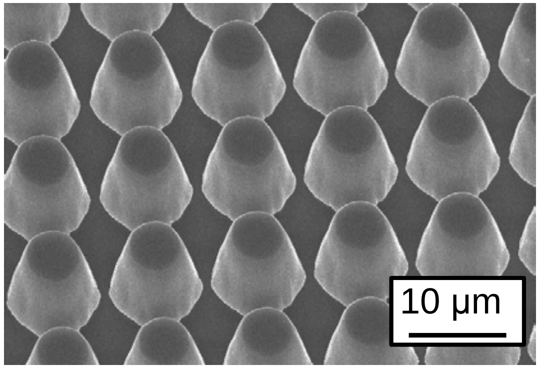
PURDUE CHEMICAL ENGINEERING

Advances in Trace Detection



~8 µm pillars



~12 µm pillars

Steve Beaudoin

Director , Purdue Energetics Research Center

Purdue University

September 19, 2017

- NSF ERC for Structured Organic Particulate Systems
- Department of Education GAANN program in Pharmaceutical Engineering
- This material is based upon work supported by the U.S. Department of Homeland Security, Science and Technology Directorate, Office of University Programs, under Grant Award 2013-ST-061-ED0001. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

Checkpoint Detection

- Checkpoint-based IED detection relies on contact sampling to harvest trace residue followed by ion mobility spectrometry (IMS) for detection of residue
  - IMS technology is highly advanced, studied in great depth
  - Swipes for contact sampling are commodities, customized to each manufacturer’s IMS
- Extent to which residue collection controls effectiveness of IMS-based detection is uncertain
- Key aspects
  - What controls residue adhesion
  - How to describe adhesion of residues
  - What controls residue removal
  - Electrothermal desorption - a better way

Roughness and van der Waals (vdW) Forces

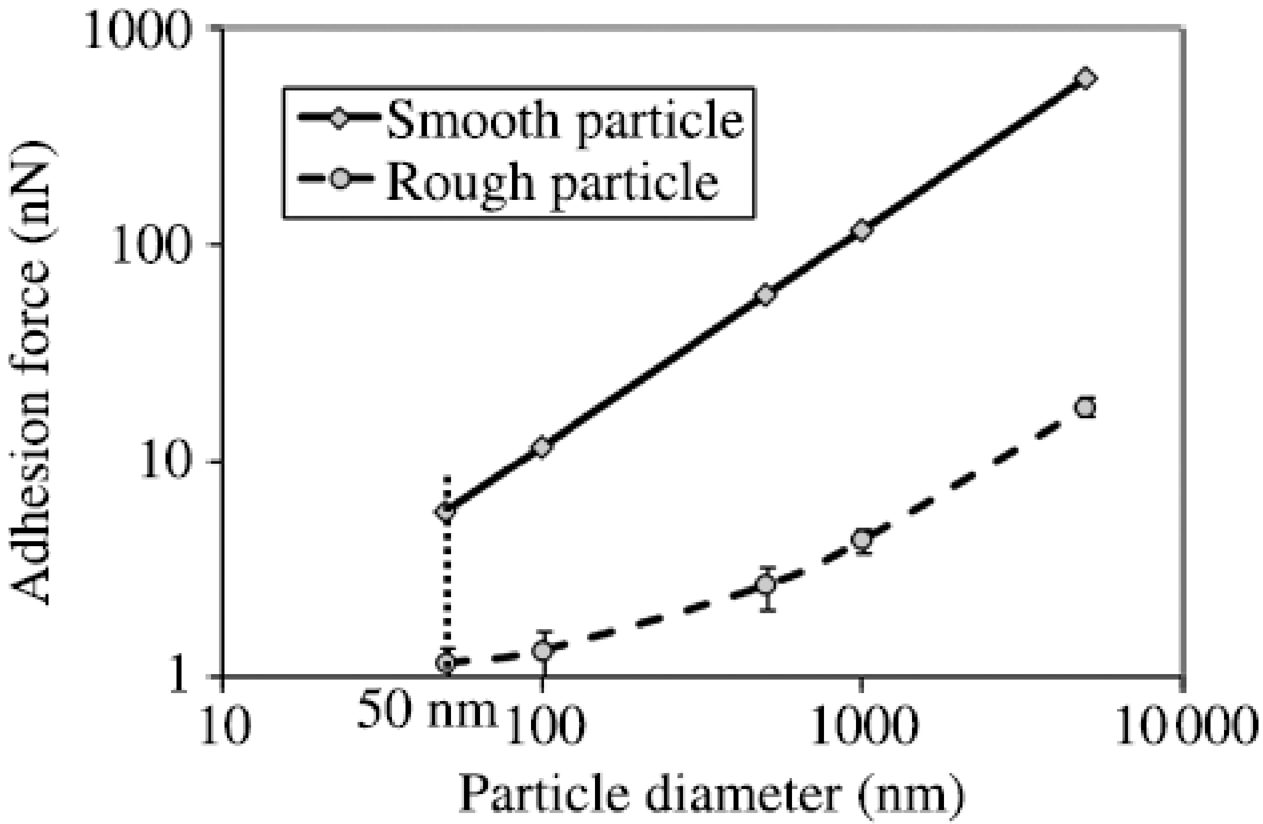
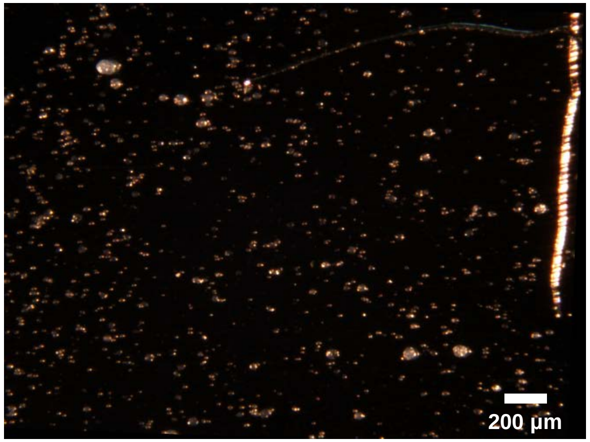


Figure 5. Predicted adhesion between a flat substrate and smooth and rough nano- and micrometer diameter particles (at separation distance = 0.4 nm). All rough particles have the same sinusoidal roughness imposed on their surfaces (amplitude of the sinusoidal roughness = 5 nm, wavelength of the sinusoidal roughness = 20 nm). $A_{132} = 1\times10^{-19}$ J

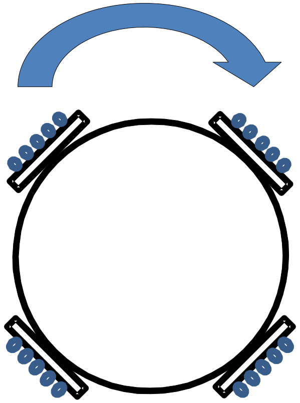
R. P. Jaiswal, S. P. Beaudoin / J. Adhesion Sci. Technol. 25 (2011) 781–797

Describing Residue Adhesion: vdW Force

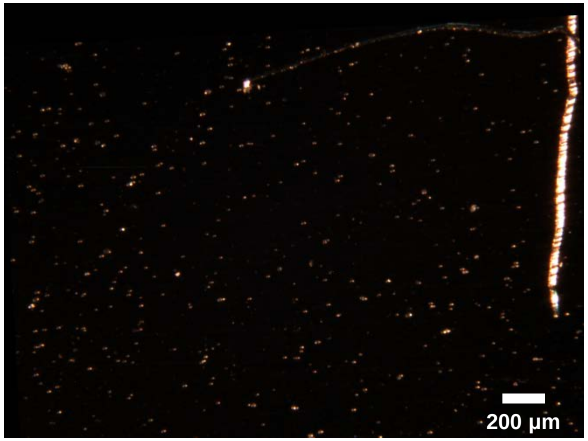
Initial Image



Centrifugal Rotation

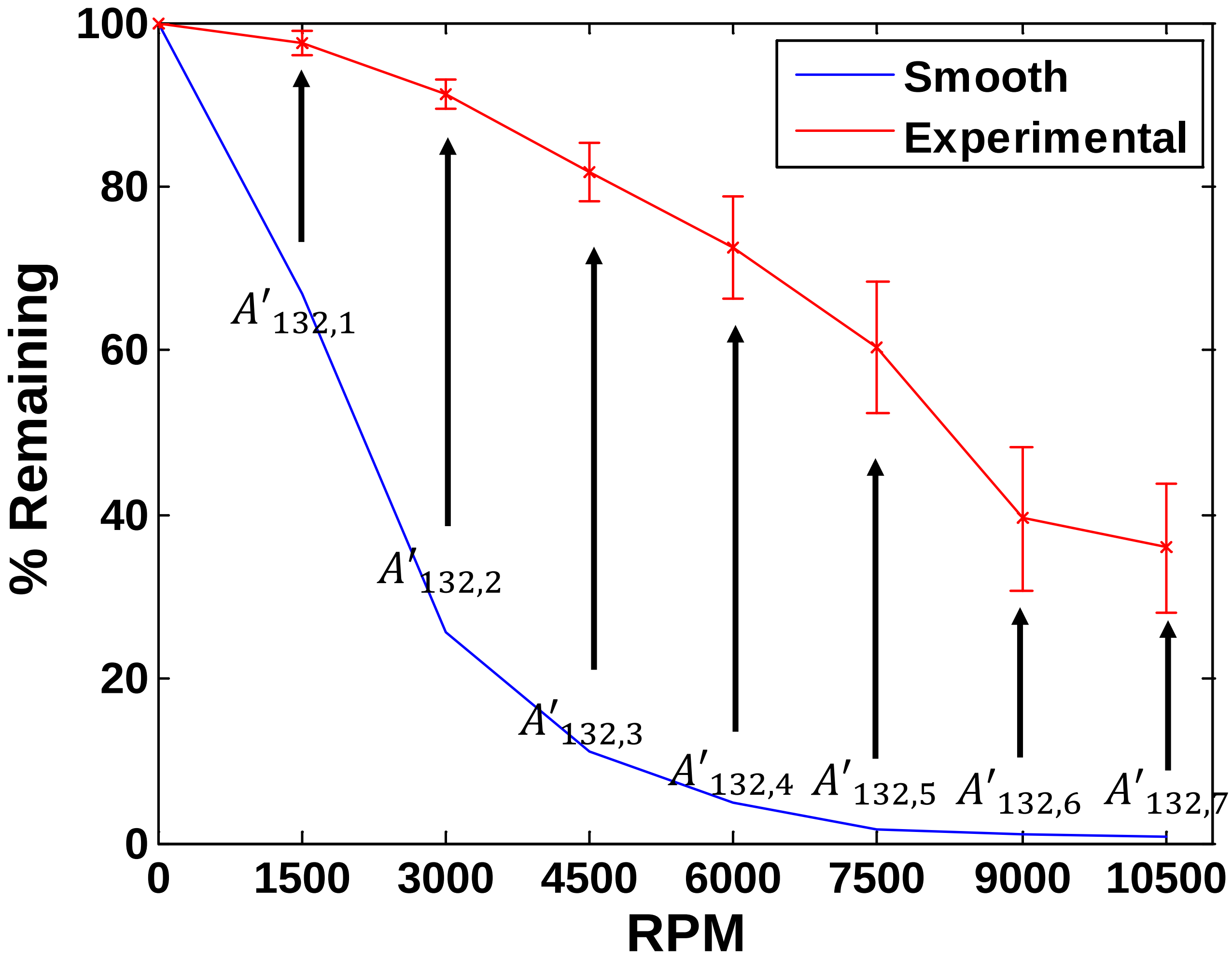


After 10500 rpm



- Silica particles dispersed on stainless steel plates
- Rotate plates in centrifuge
  - 1500 to 10500 rpm
  - One minute run time

Roughness Matters: vdW Force



Describe the adhesion of real silica powder to stainless steel in terms of a perfect silica powder

Perfect powder = all particles are perfect spheres with same size distribution as real powder

Link the Hamaker constant to the size and roughness of the particles in order to map the 'reality' onto the perfect powder

Roughness Matters: Capillary Forces

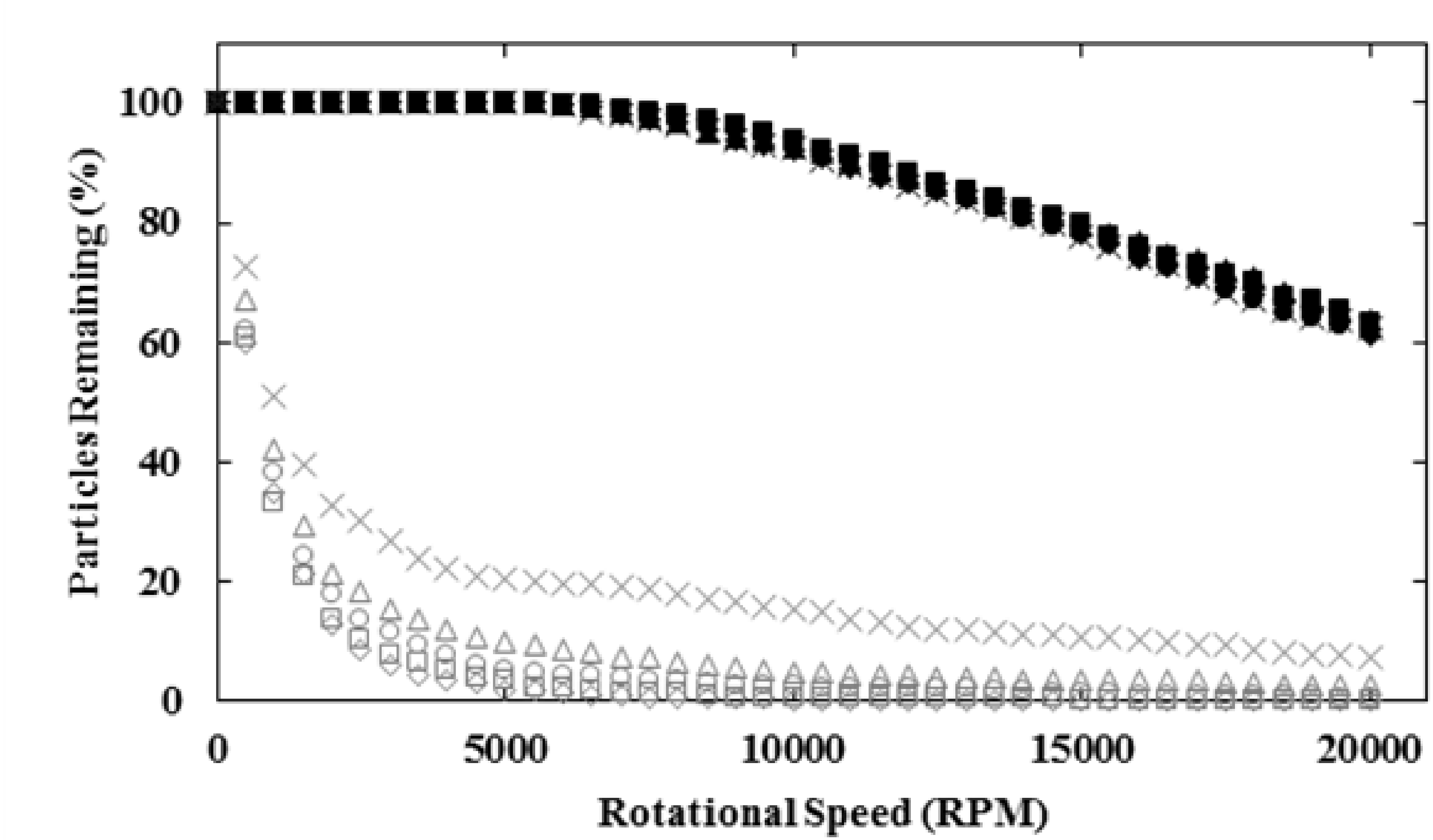
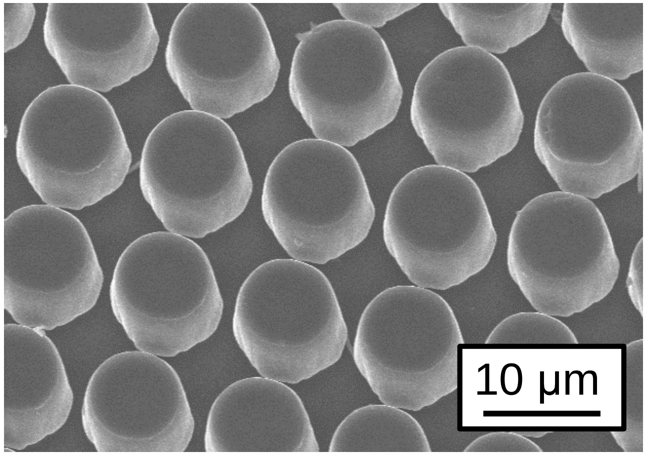


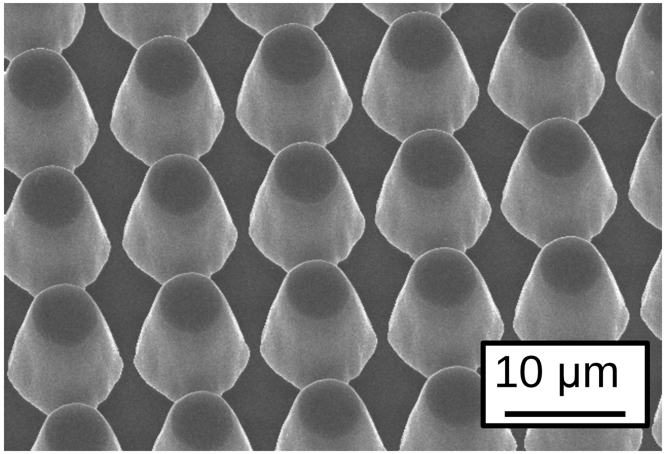
Figure 3. RAP curves of smooth particles adhered to smooth substrates (black, filled) and rough substrates (gray, not filled) at relative humidity values of (♦) 20%, (■) 35%, (●) 50%, (▲) 65%, and (x) 80%.

M. Thomas, E. Krenek, S. Beaudoin / MRS Advances, 1(31), (2016) 2237-2245

Polypyyrole (Conductive) Swabs

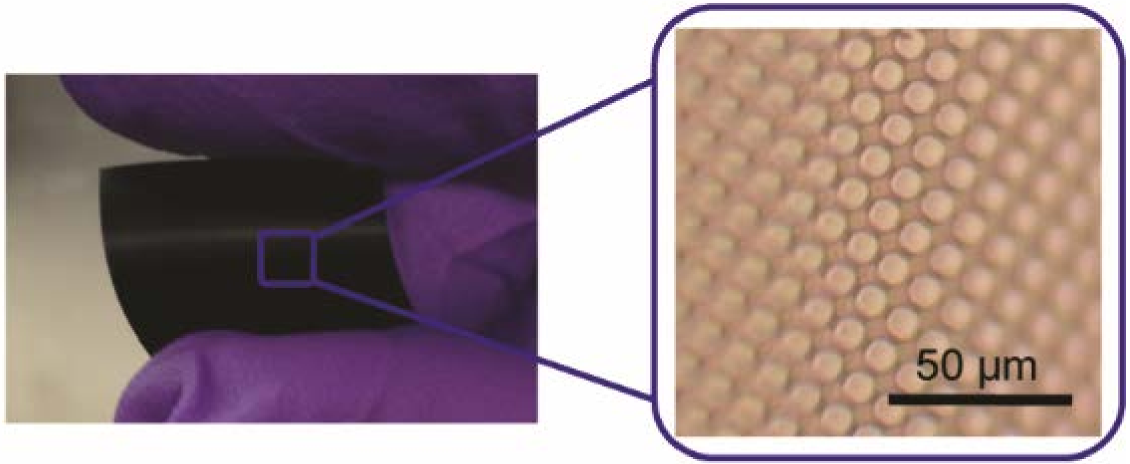


~8 µm pillars



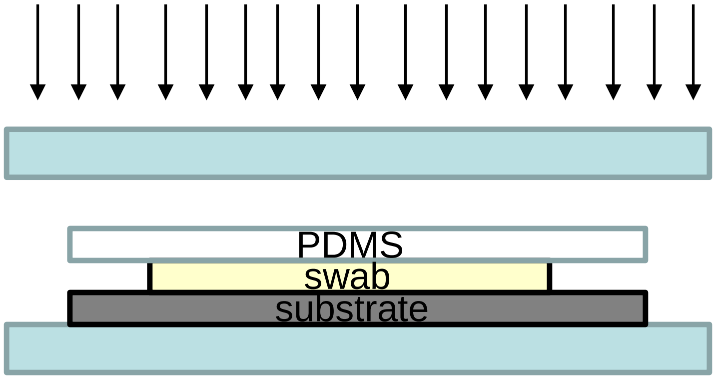
~12 µm pillars

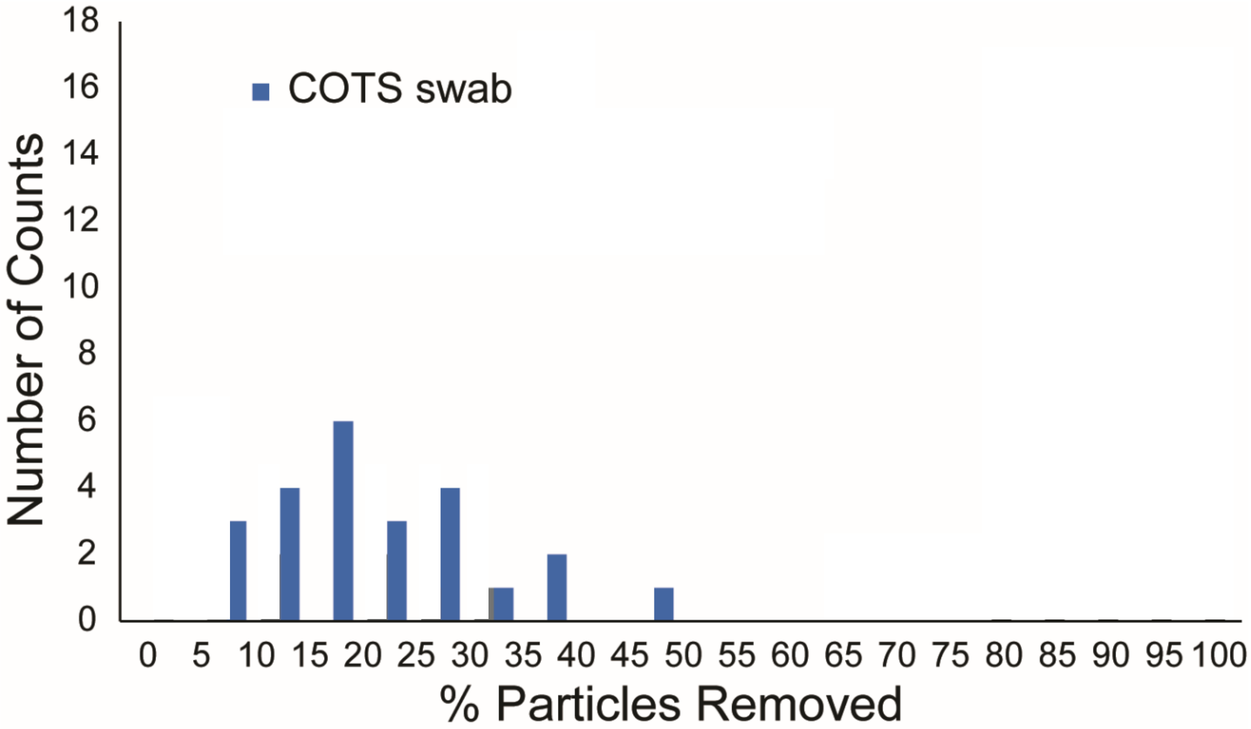
Can make pillars with range of sizes



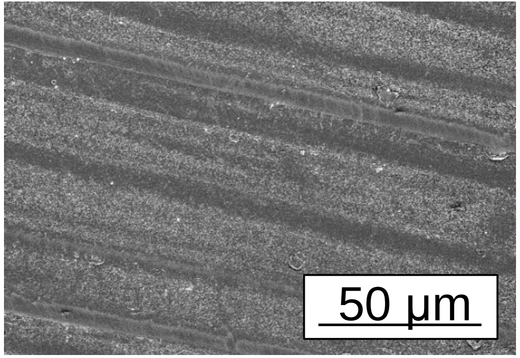
Contact Matters: Polypyyrole Swabs

Constant Normal Load Applied with Bench Top Press

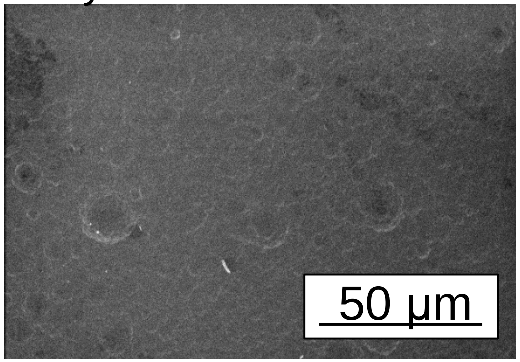




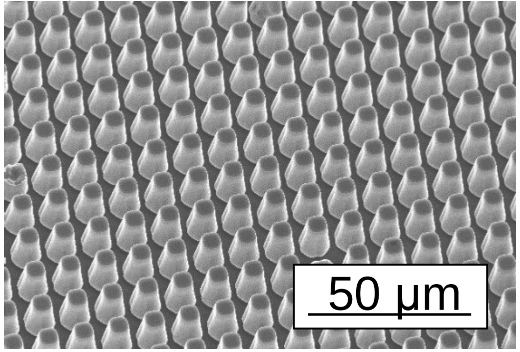
Woven COTS Swab



PPy-DBS Non-structured



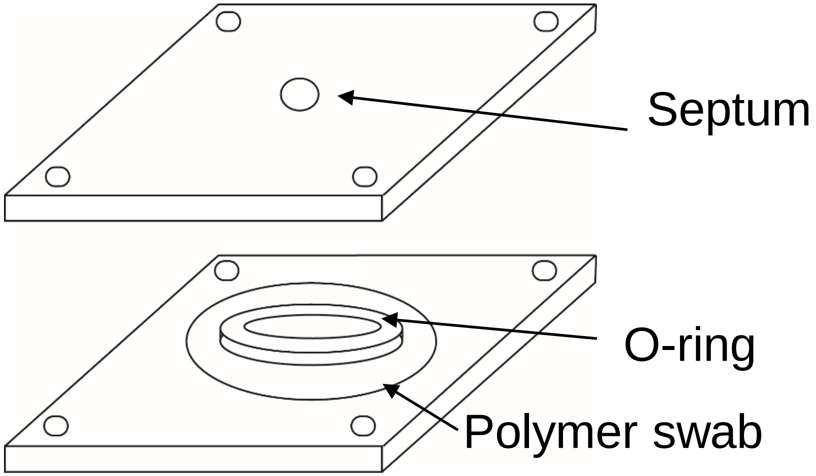
PPy-DBS Microstructured



Laster, J. S.; Deom, N. A.; Beaudoin, S. P.; Boudouris, B. W. / *Journal of Polymer Science Part B.,* 54 (2016) 1968-74

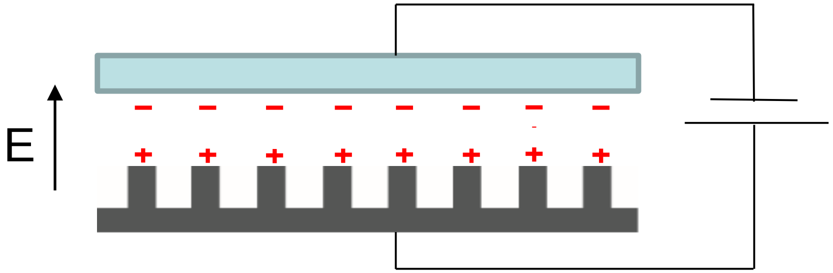
Enhanced Desorption of Residue by Electrical Biasing

Designed Experimental Sampling Chamber



Concentration of analyte determined though headspace solid-phase microextraction (SPME) – gas chromatography mass spectrometry (GCMS)

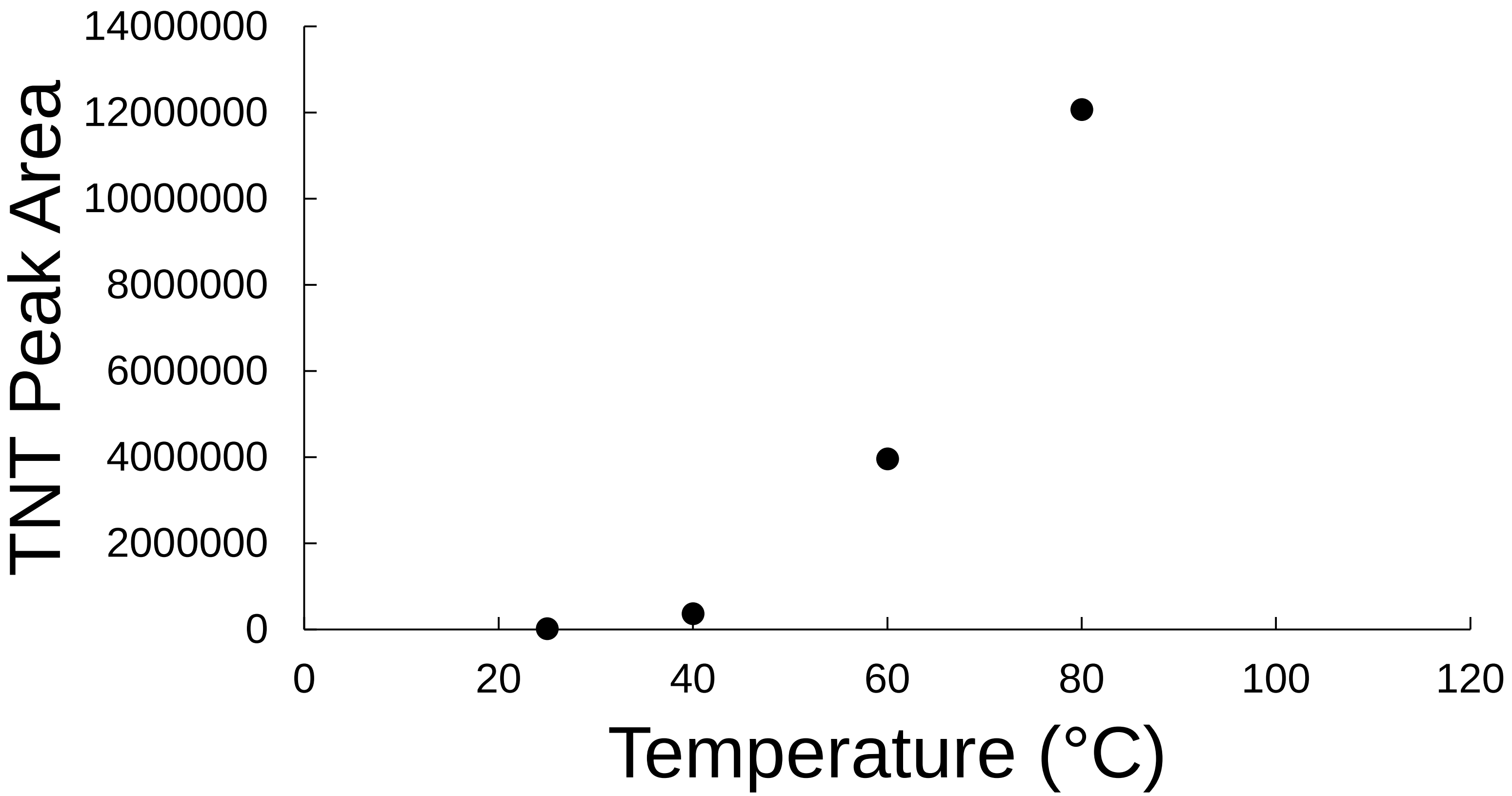
Electrothermal Desorption of Residue



An electric field generated between the polymer swab and the aluminum chamber through the application of an applied voltage

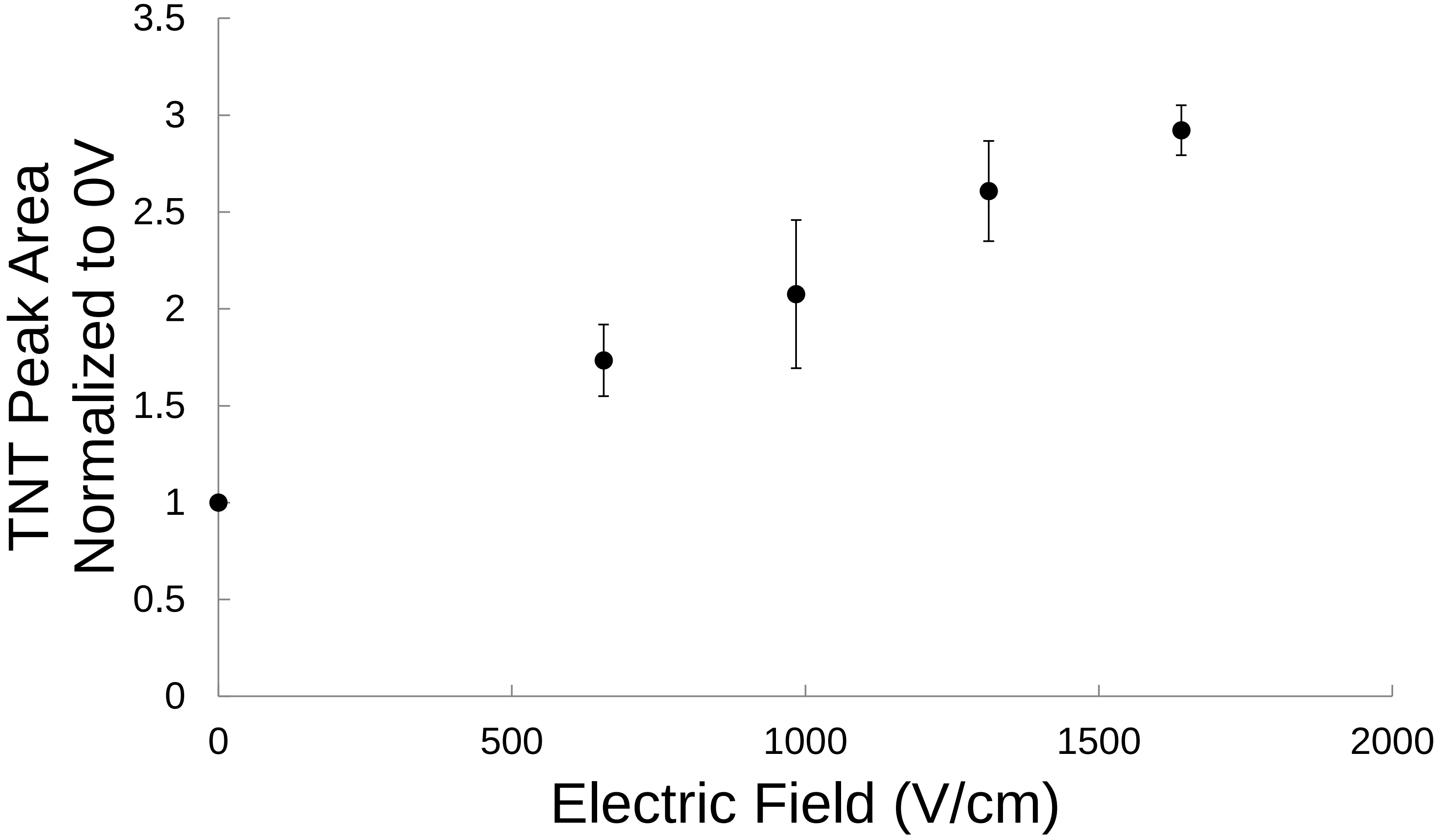
IF IT WORKS, we can evaluate new residues that can't be evaluated in IMS as currently implemented

Thermal Release of TNT from PPy Swab at 0V



- These are preliminary results
- Area is normalized to area at 25 °C

Electrothermal TNT Release from PPy Swab



- These are preliminary results
- Area is normalized to area at 0V
- Suggests that electrothermal desorption may be viable

Conclusions

- Particulate explosives vary substantially in their adhesion to surfaces based on the surface roughness
- Adhesion forces are not sufficiently long-range to allow residue removal without swab contact
- When conductive swabs are applied, it is possible to use electrothermal desorption to remove residues from the swabs at low temperatures
  - Opens the door to using IMS-based detection for inorganic residues

Acknowledgements

Colleagues:

- Myles Thomas
- Aaron Harrison
- Jennifer Laster
- Leo Miroshnik
- Melissa Sweat

Financial support:

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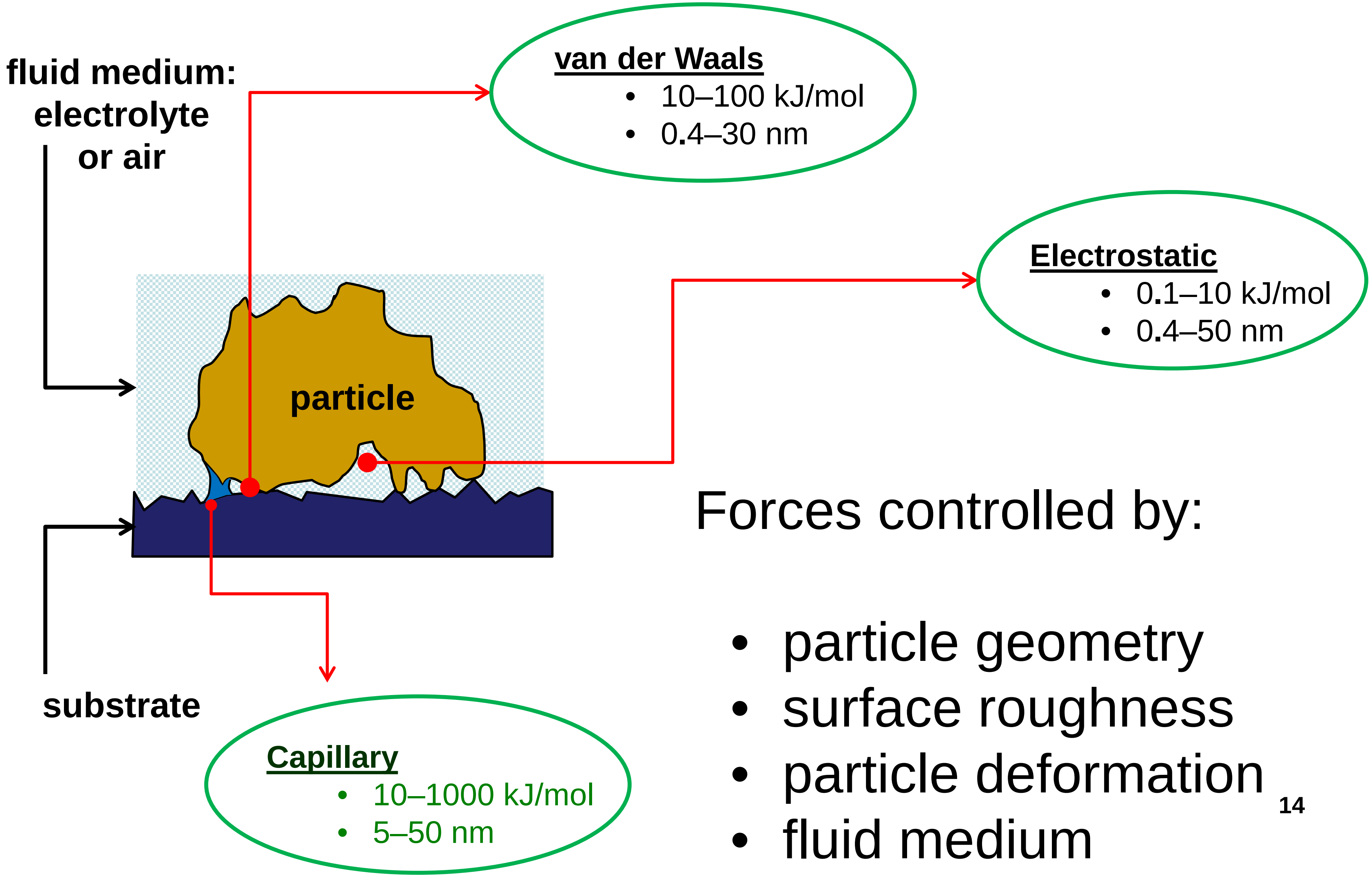
Forces in Residue Adhesion



fluid medium: electrolyte or air

particle

substrate

van der Waals

- 10–100 kJ/mol
- 0.4–30 nm

Electrostatic

- 0.1–10 kJ/mol
- 0.4–50 nm

Capillary

- 10–1000 kJ/mol
- 5–50 nm

Forces controlled by:

- particle geometry
- surface roughness
- particle deformation
- fluid medium

Roughness Matters

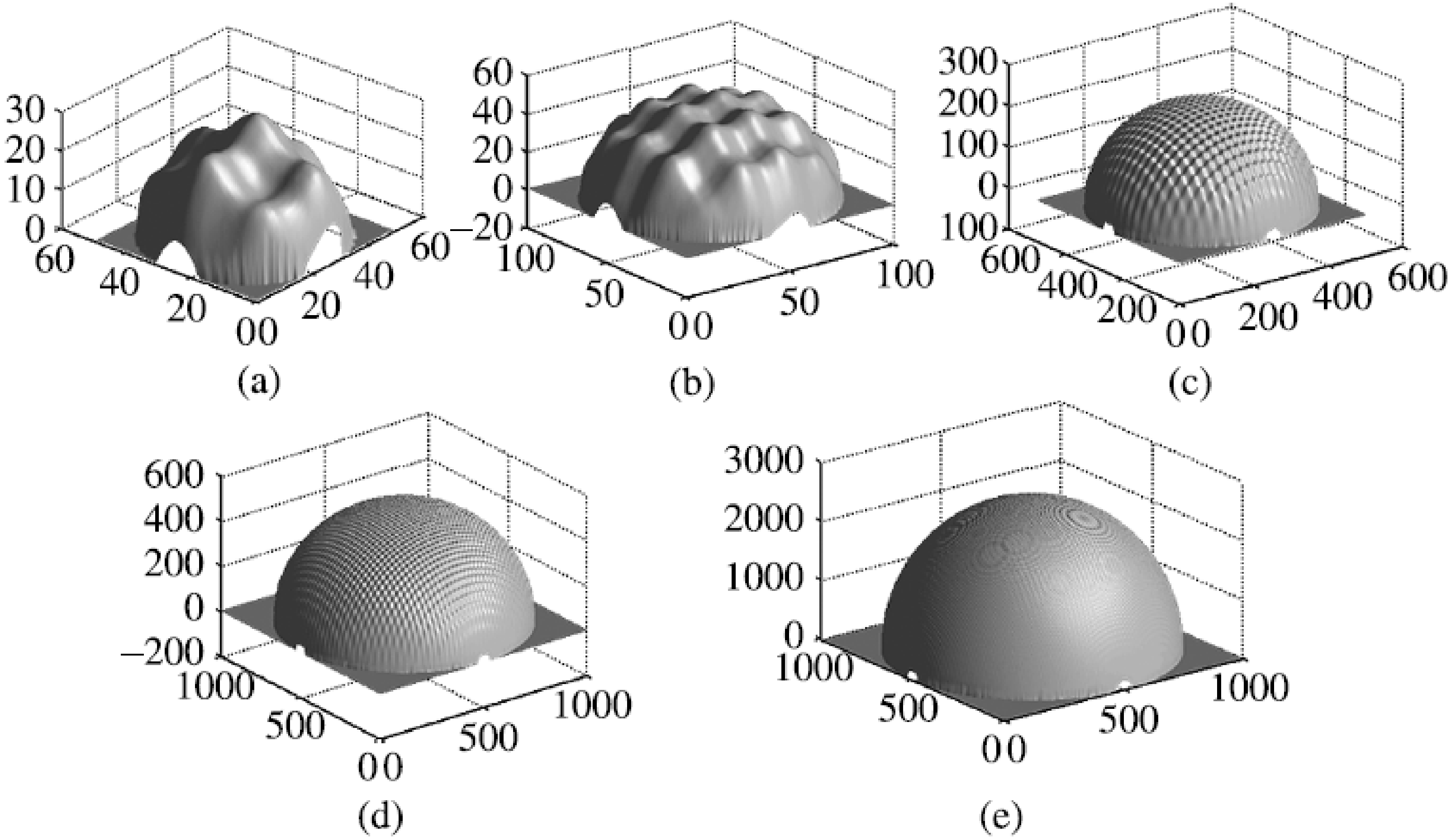
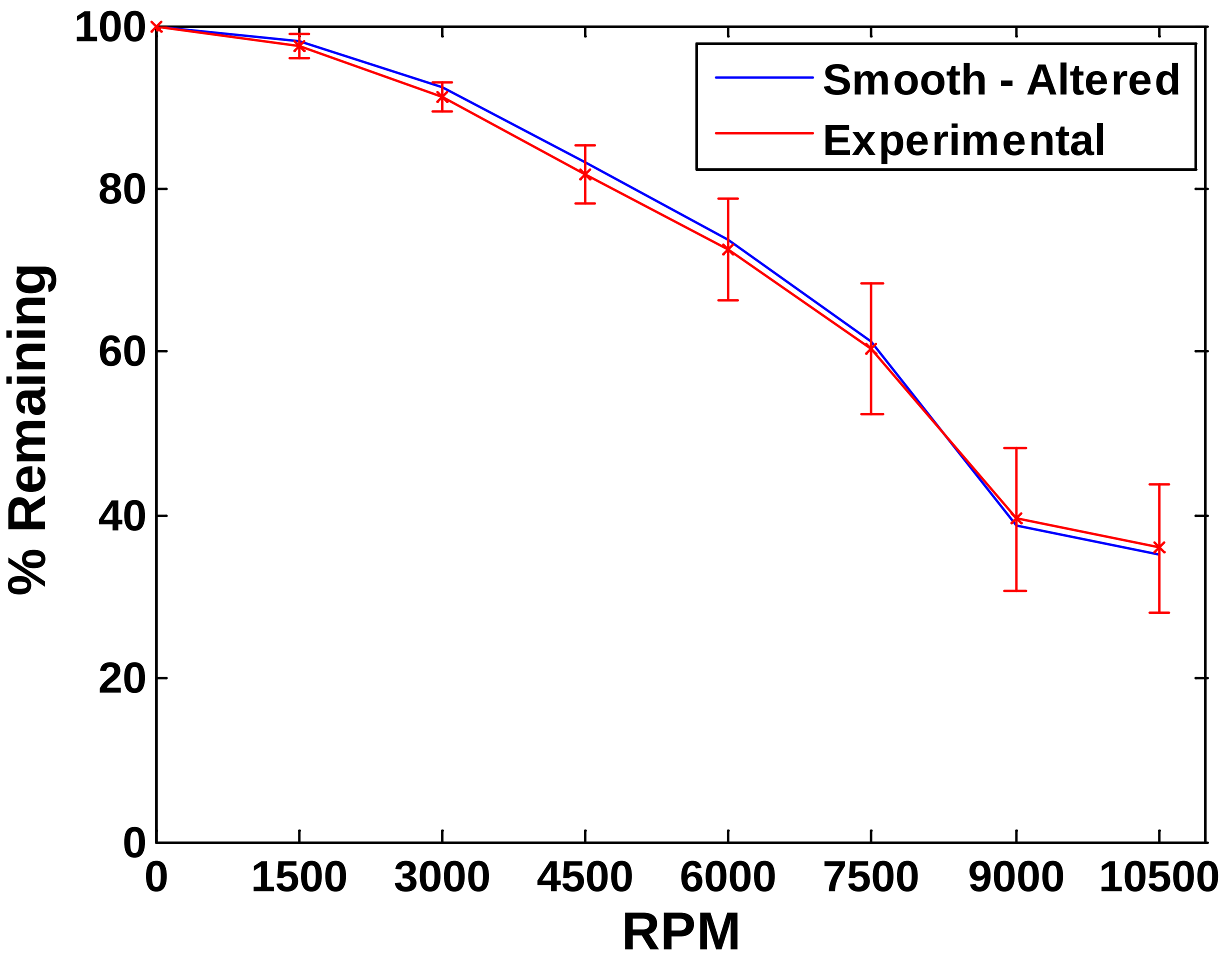


Figure 4. Hemispherical particles with sinusoidal roughness: roughness amplitude = $2a$ = 5 nm and wavelengths $\lambda_x = \lambda_y$ = 20 nm. D is the particle diameter. (a) D = 50 nm, (b) D = 100 nm, (c) D = 500 nm, (d) D = 1 μm and (e) D = 5 μm. All axes in nm. $A_{132} = 1x10^{-19}$ J

R. P. Jaiswal, S. P. Beaudoin / J. Adhesion Sci. Technol. 25 (2011) 781–797

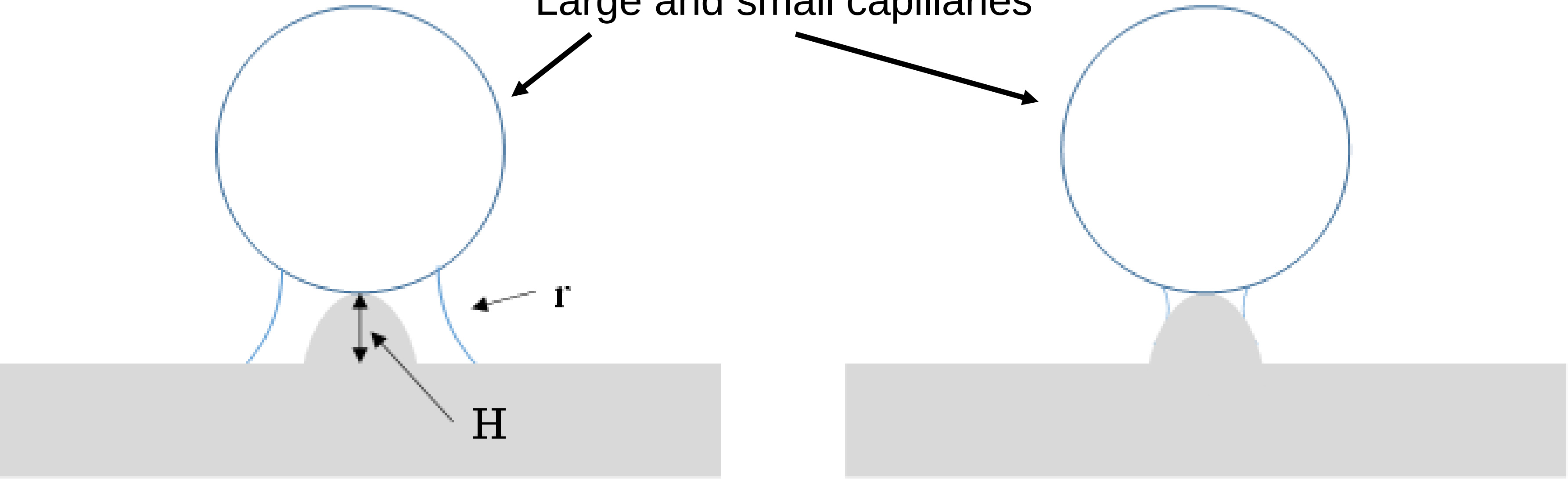
Map vdW Behavior of Real Residues onto Ideal Ones



Do it again for capillary forces?

M. Thomas, S. Beaudoin / Powder Technology 306 (2017) 96–102

Roughness Matters: Capillary Force

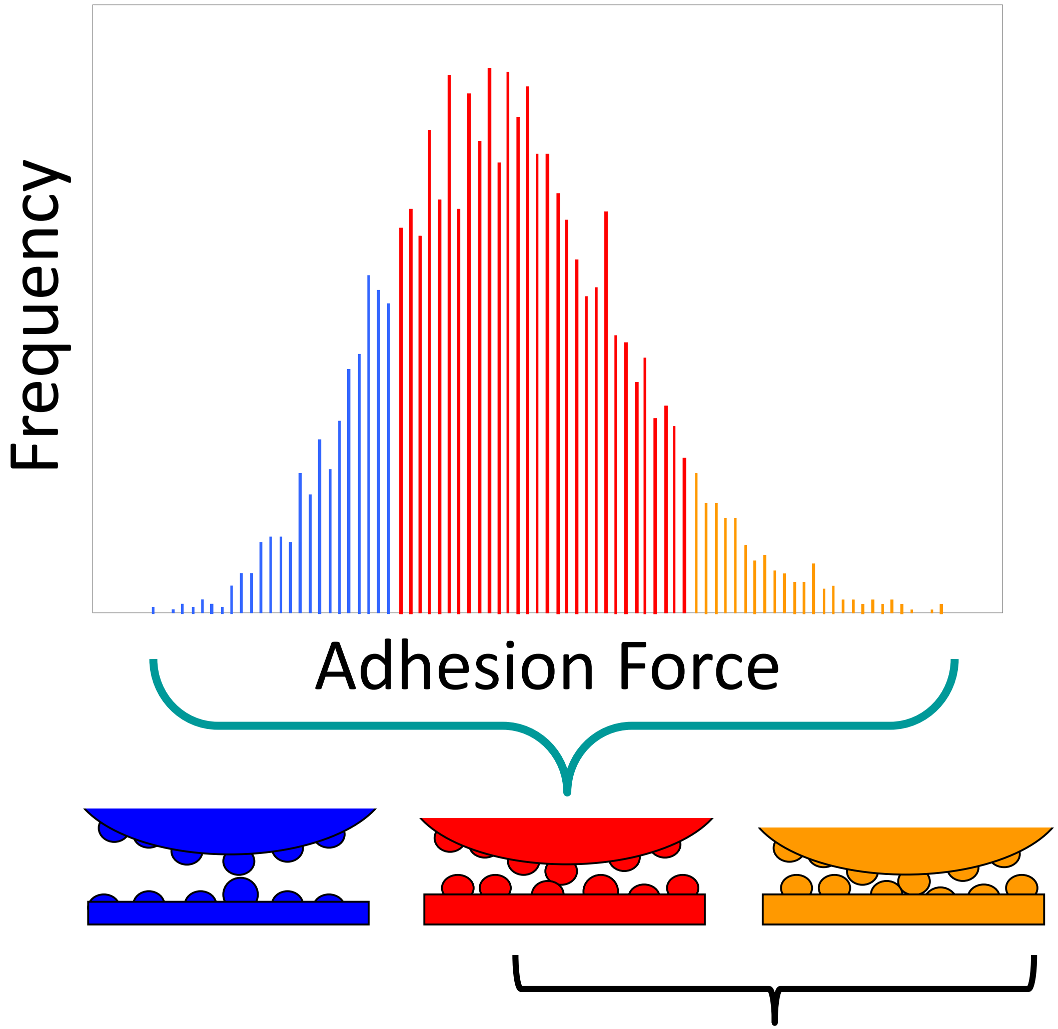


Limiting cases:
Large and small capillaries

- Repeat ‘force mapping’ exercise from vdW force
- Now consider capillary force
- ‘Effective contact angle’ becomes fitting parameter

M. Thomas, E. Krenek, S. Beaudoin / MRS Advances, 1(31), (2016) 2237-2245

Net Result: No Unique Force

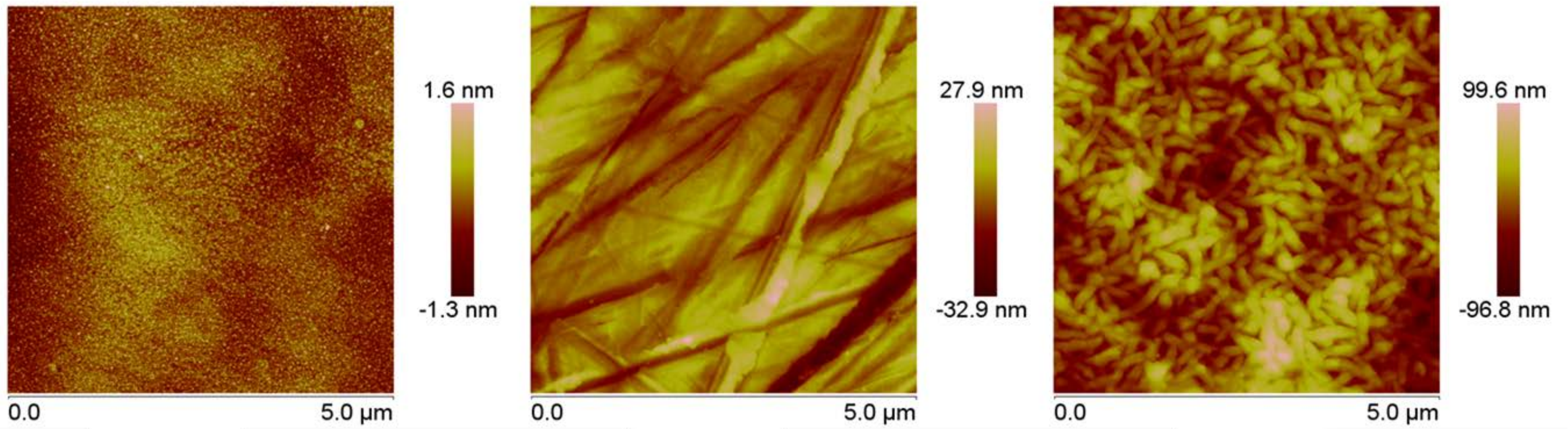


This variation is up to 1 – 1.5 ORDERS OF MAGNITUDE

How Rough Is Rough?

- Goal: Determine how many locations on a surface need to be evaluated to determine the adhesivity of the surface (the effect of the roughness)
- What did we do?
  - Measured roughness of 40 locations on each of 3 surfaces (silicon wafer, steel, Teflon)
  - Performed 1200 simulations of adhesion between a smooth, 10 micron silica bead and each scanned area to determine mean force
  - Used some statistics to clean up the distribution (bootstrap method)
  - Assessed ‘value’ of making more measurements of adhesion (more measurements of roughness)

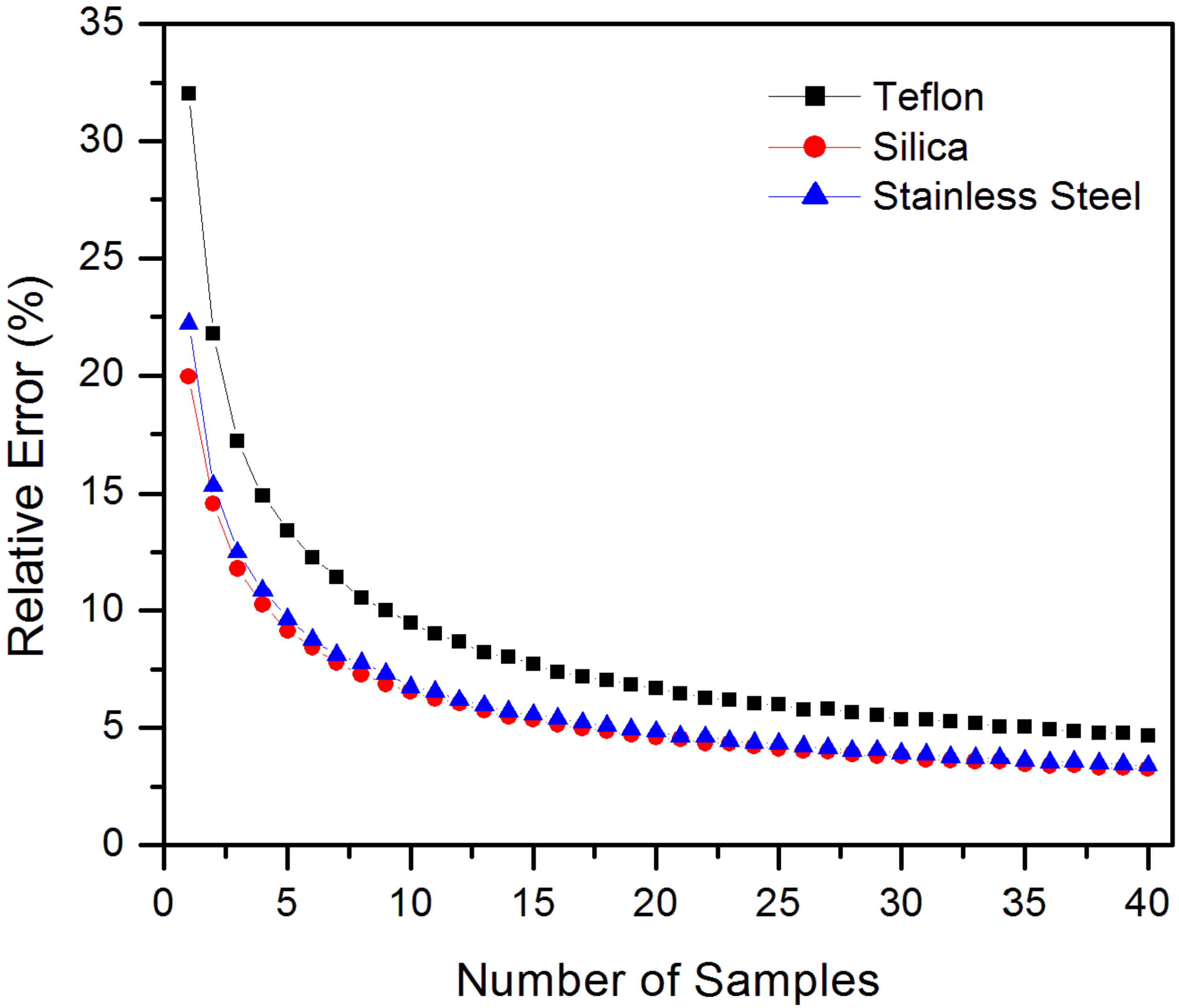
How Rough Is Rough?



40 areas (5 micron^2) scanned on (L→R) silicon wafer, stainless steel, Teflon

Substrate	RMS	Peak–Peak Distance
Silica	0.6 ± 0.2 nm	12.8 ± 7.9 nm
Stainless Steel	7.4 ± 1.9 nm	65.9 ± 17.9 nm
Teflon	24.3 ± 5.8 nm	181.2 ± 52.7 nm

How Rough Is Rough?

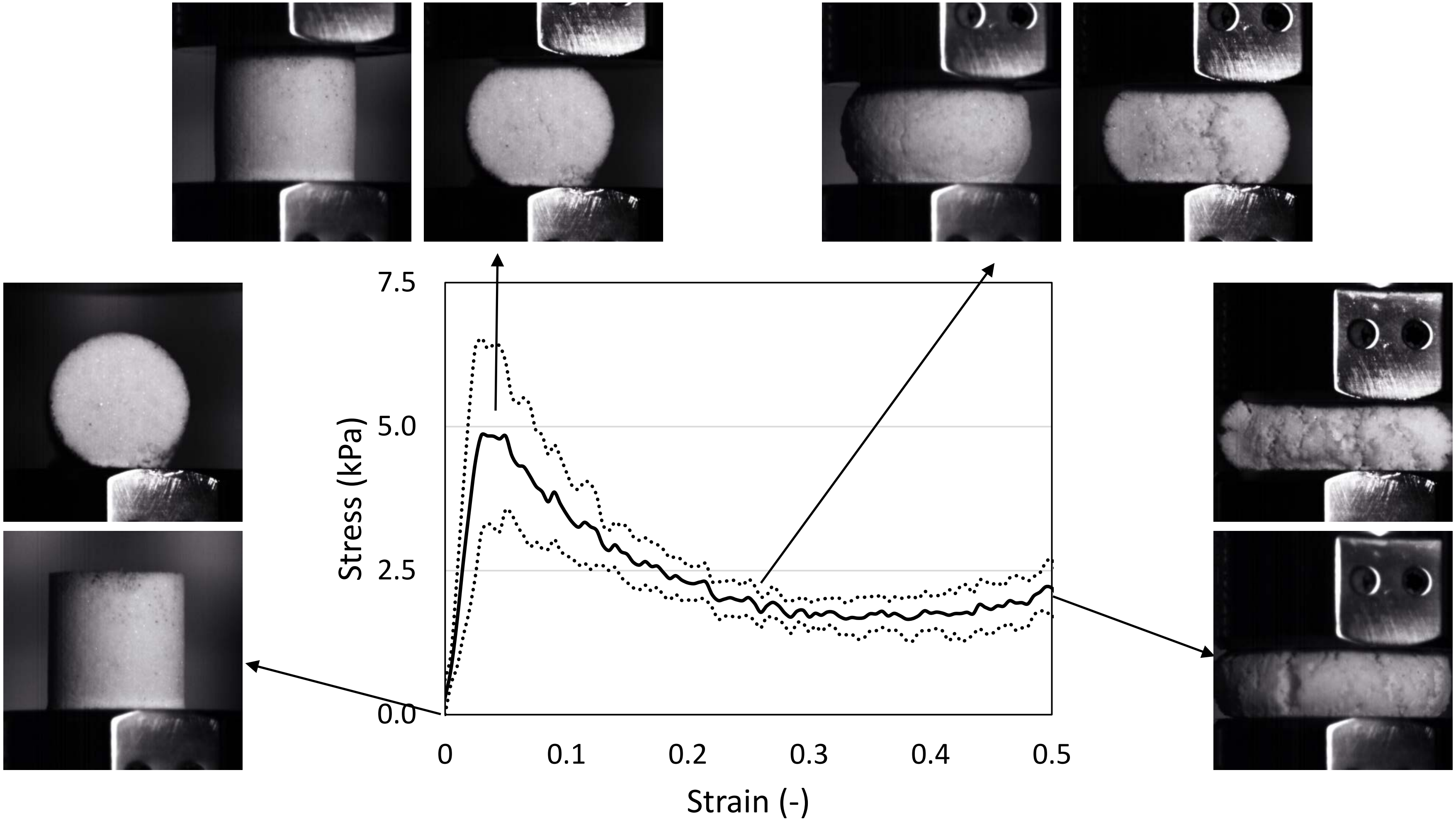


Fronczak, S., Thorpe, J., Thomas, M., Cassidy, M., Evans, J., Beaudoin, S., / J. Adhesion Science and Technology (In review, 2017).

How Rough Is Rough? Takeaway

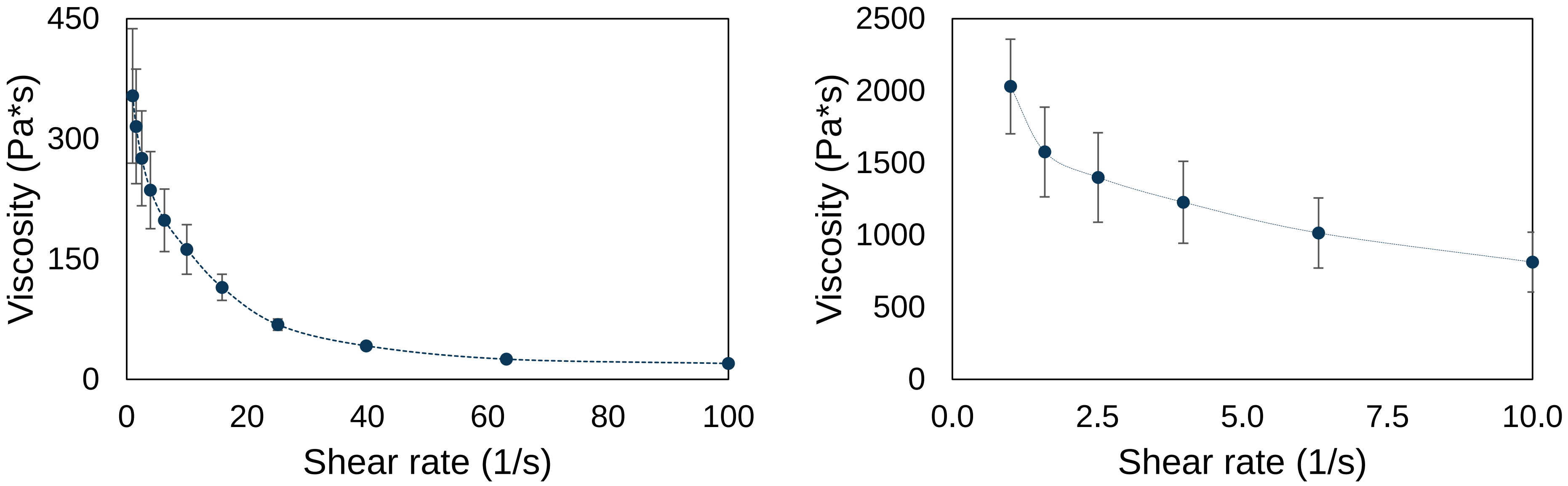
- For surfaces we care about in explosives sampling settings, it should be possible to quantify the residue adhesion
- Requires direct measurement of roughness and/or adhesion at ~ 15 locations on the surface

Adhesion and Removal of Compounded Explosives



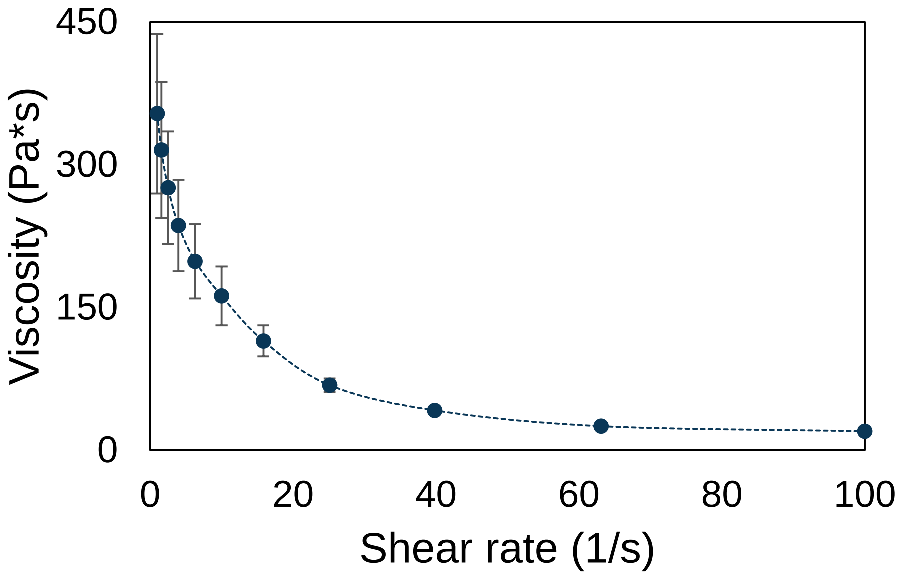
Stress-strain curve (with error regions) for silica particles (40-150mesh) in PDMS (60 Pa·s viscosity) at 10mm/s compression rate. Axial images shown bottom and left; diametrical are top and right.

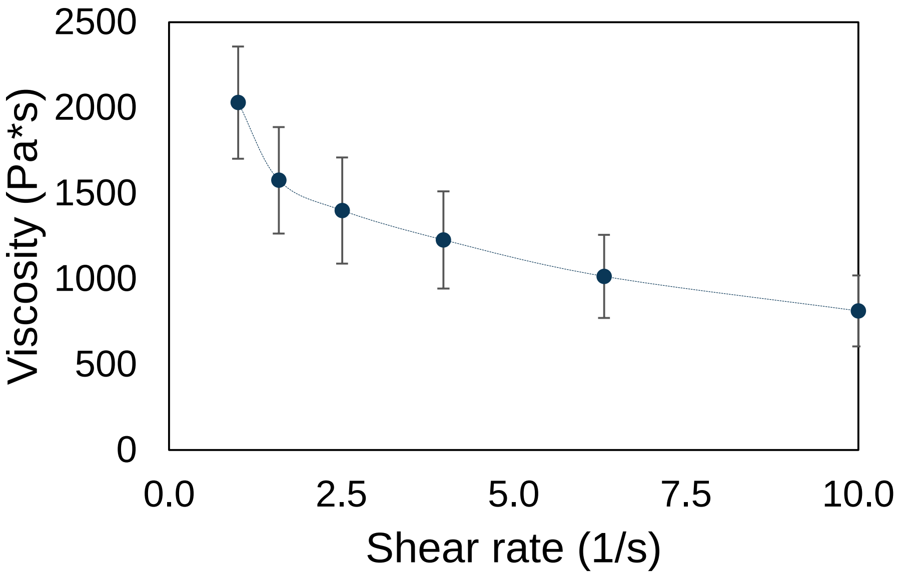
Viscosity of Compounded Explosives

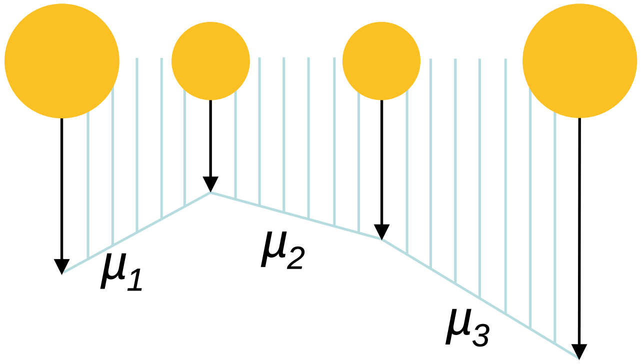


Viscosity profiles for simulated C-4 binder (top left) and simulated Semtex H (top right). Bottom images are simple schematics for binder viscosity effects in a granular mixture.

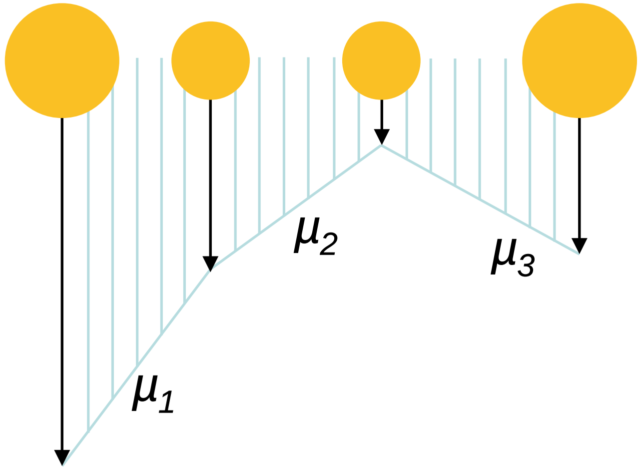
Viscosity of Compounded Explosives





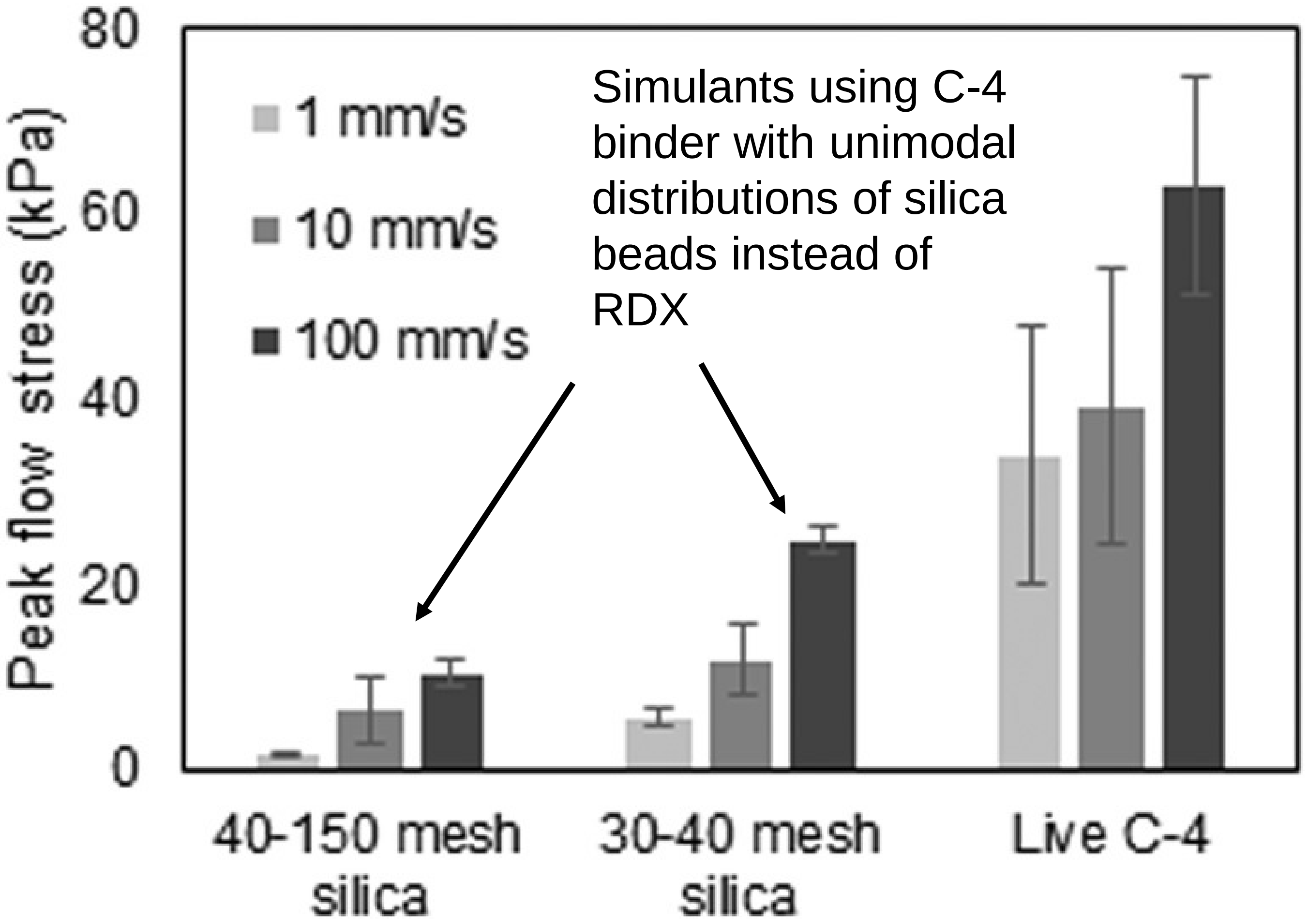


High shear causes very viscous residue to flow like water



Viscosity profiles for simulated C-4 binder (top left) and simulated Semtex H (top right). Bottom images are simple schematics for binder viscosity effects in a granular mixture.

Composition of Binder Controls



Simulants using C-4 binder with unimodal distributions of silica beads instead of RDX

Figure 14. Peak flow stress as a function of compression rate for simulated and live C-4. Note that 1, 10, and 100 mm s^{-1} correspond to strain rates 0.042±0.004, 0.431±0.076, and 4.651±1.752 s^{-1}.

M. Sweat, A. Parker, S. Beaudoin / *Propellants, Explosives, Pyrotechnics*, 41 (2016) 855-863.

Composition of Binder Controls

Simulants use C-4 binder with bimodal distributions of silica beads instead of RDX

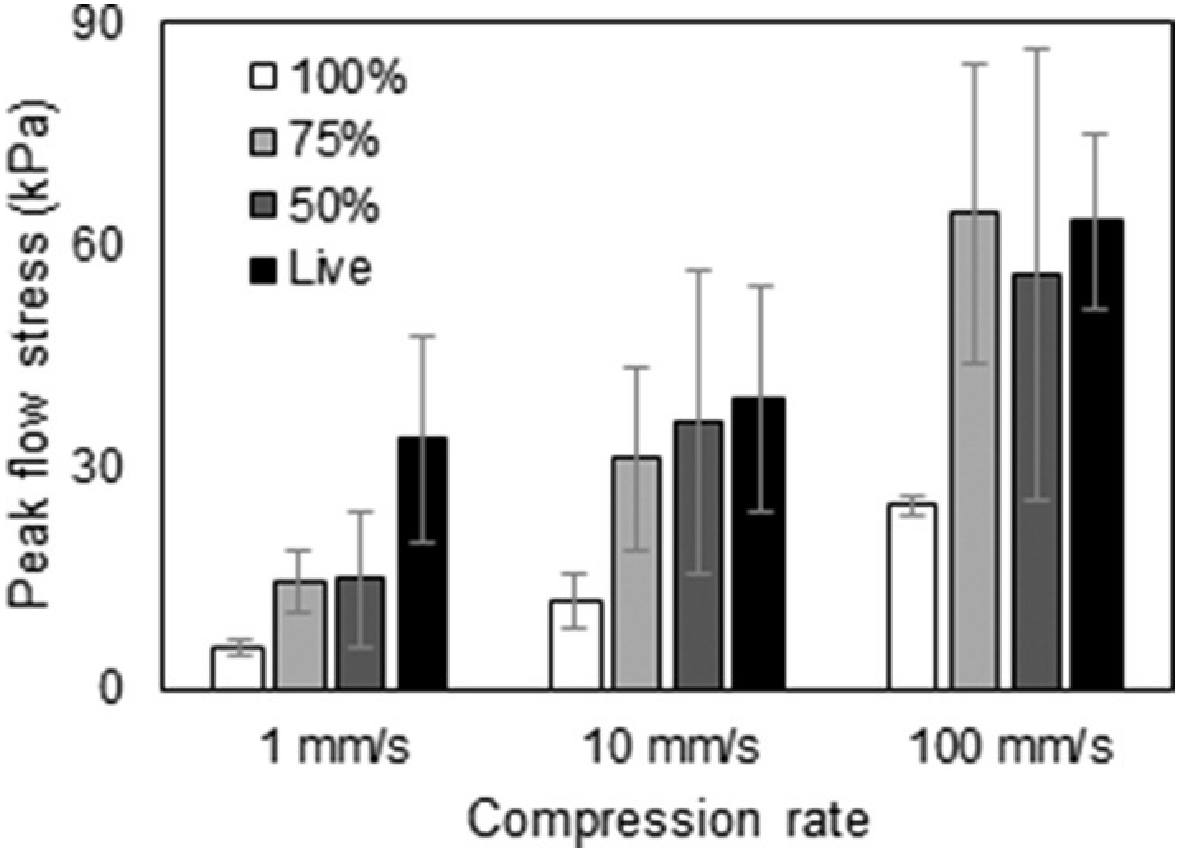


Figure 16. Peak flow stress as a function of increasing compression rate for simulated C-4 compared with live C-4. For the bimodal distributions, the percentage refers to the mass fraction of 30–40 mesh silica, with the remaining mass fraction comprised of the >230 mesh silica. Note that 1, 10, and 100mm s^{-1} correspond to strain rates 0.042±0.004, 0.431±0.076, and 4.651±1.752 s^{-1}.

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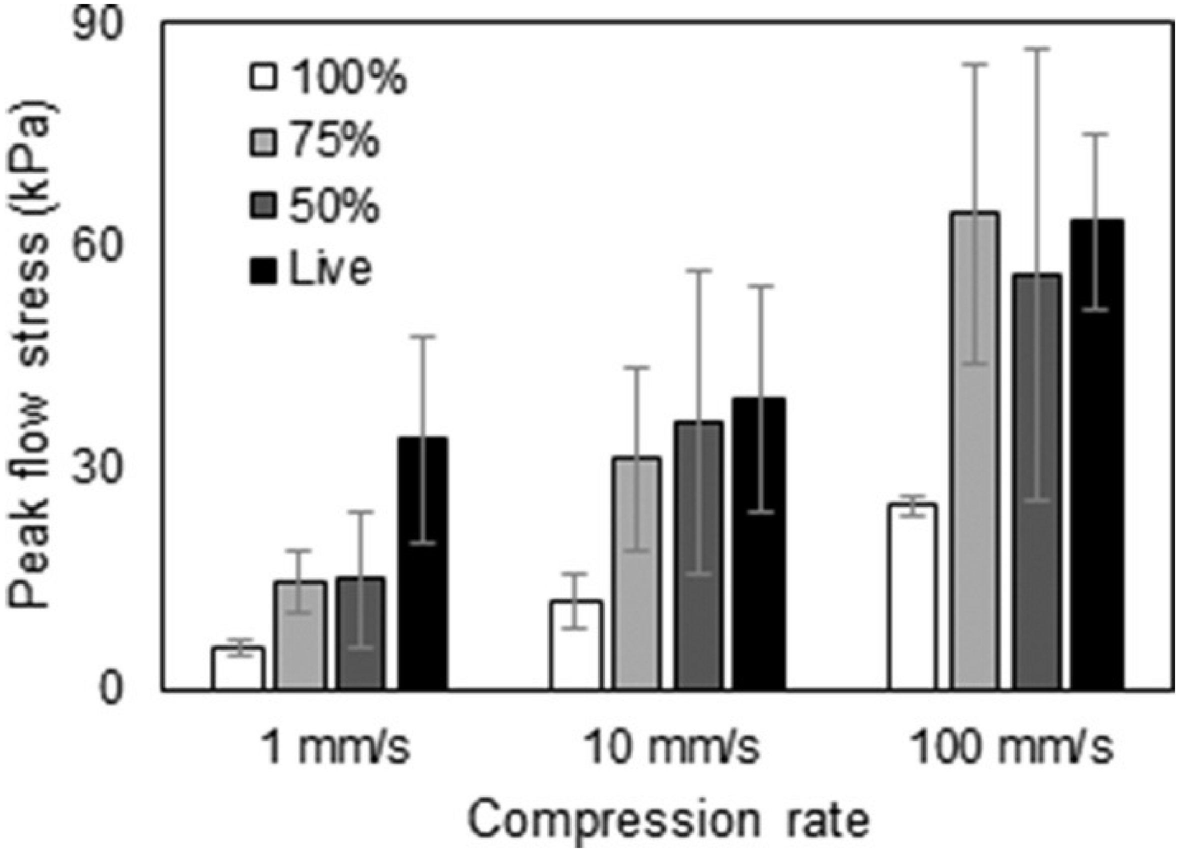

Simulated C-4 using bimodal distribution of silica beads in place of RDX behaves (mechanically) like C-4

Figure 16. Peak flow stress as a function of increasing compression rate for simulated C-4 compared with live C-4. For the bimodal distributions, the percentage refers to the mass fraction of 30–40 mesh silica, with the remaining mass fraction comprised of the >230 mesh silica. Note that 1, 10, and 100mm s^{-1} correspond to strain rates 0.042±0.004, 0.431±0.076, and 4.651±1.752 s^{-1}.

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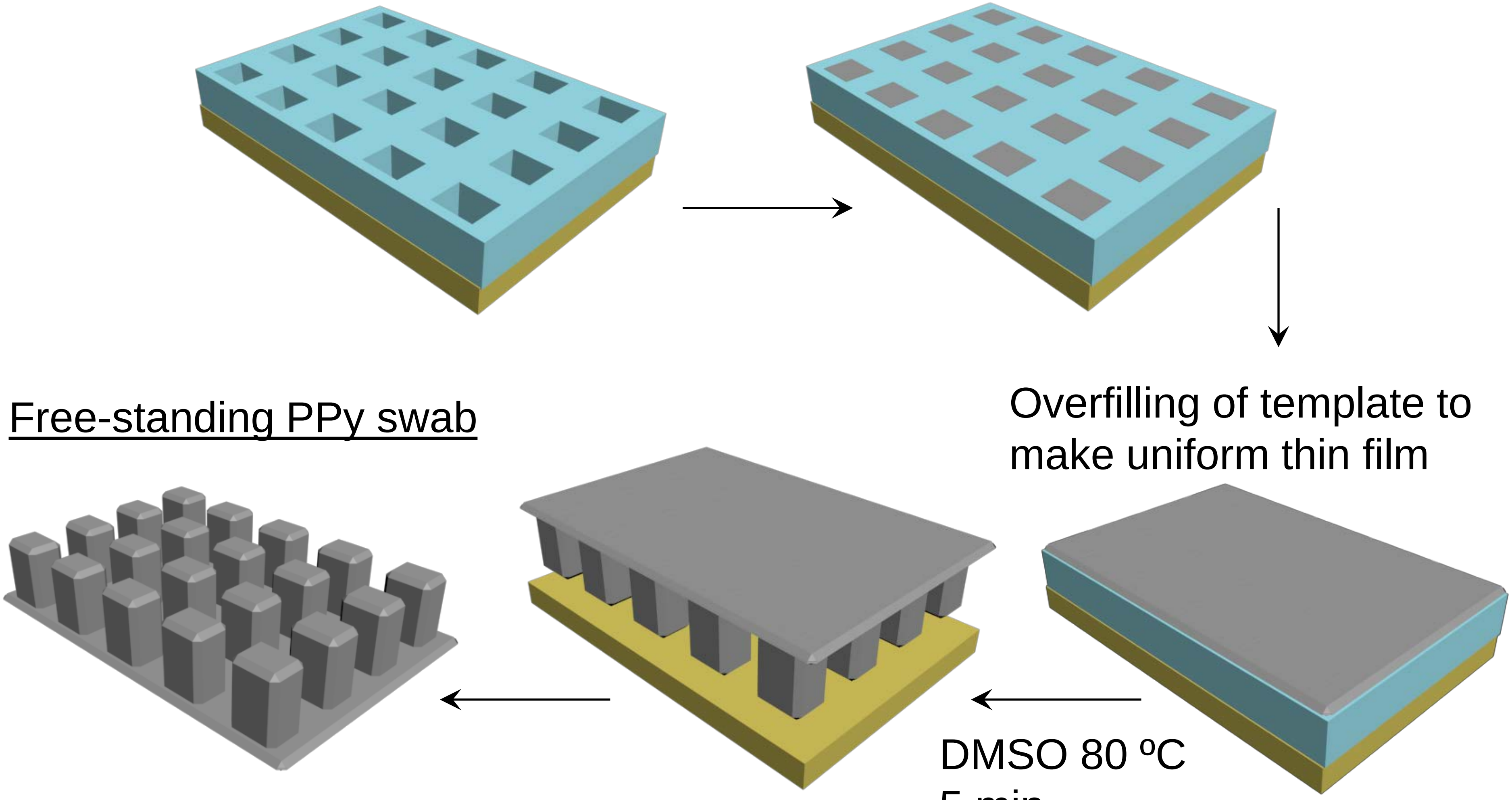
Polypyyrole (Conductive) Swabs



Photolithography to make ordered template

Electropolymerization of Py through pores of template

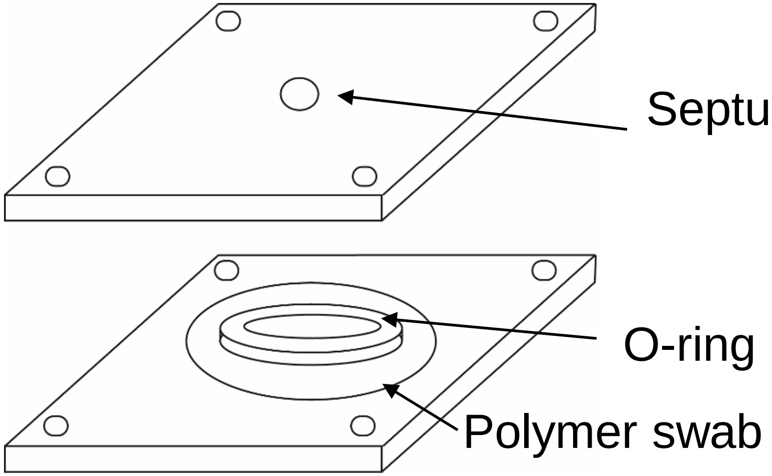
Overfilling of template to make uniform thin film

DMSO 80 ºC
5 min

<u>Free-standing PPy swab</u>

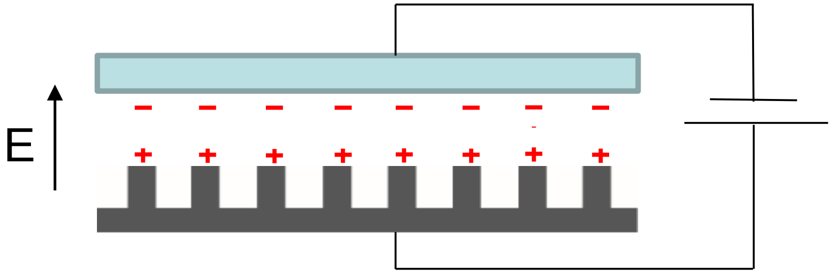
Enhanced Desorption of Residue by Electrical Biasing(!)

Designed Experimental Sampling Chamber



Concentration of analyte determined though headspace solid-phase microextraction (SPME) – gas chromatography mass spectrometry (GCMS)

Electrothermal Desorption of Residue



An electric field generated between the polymer swab and the aluminum chamber through the application of an applied voltage

Explosives Adhesion in Contact Sampling

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PURDUE CHEMICAL ENGINEERING

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