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 **Brighton
Science**

Substrate Surface Chemistry Assessment via Water Contact Angle to Ensure Reliable Ink Adhesion

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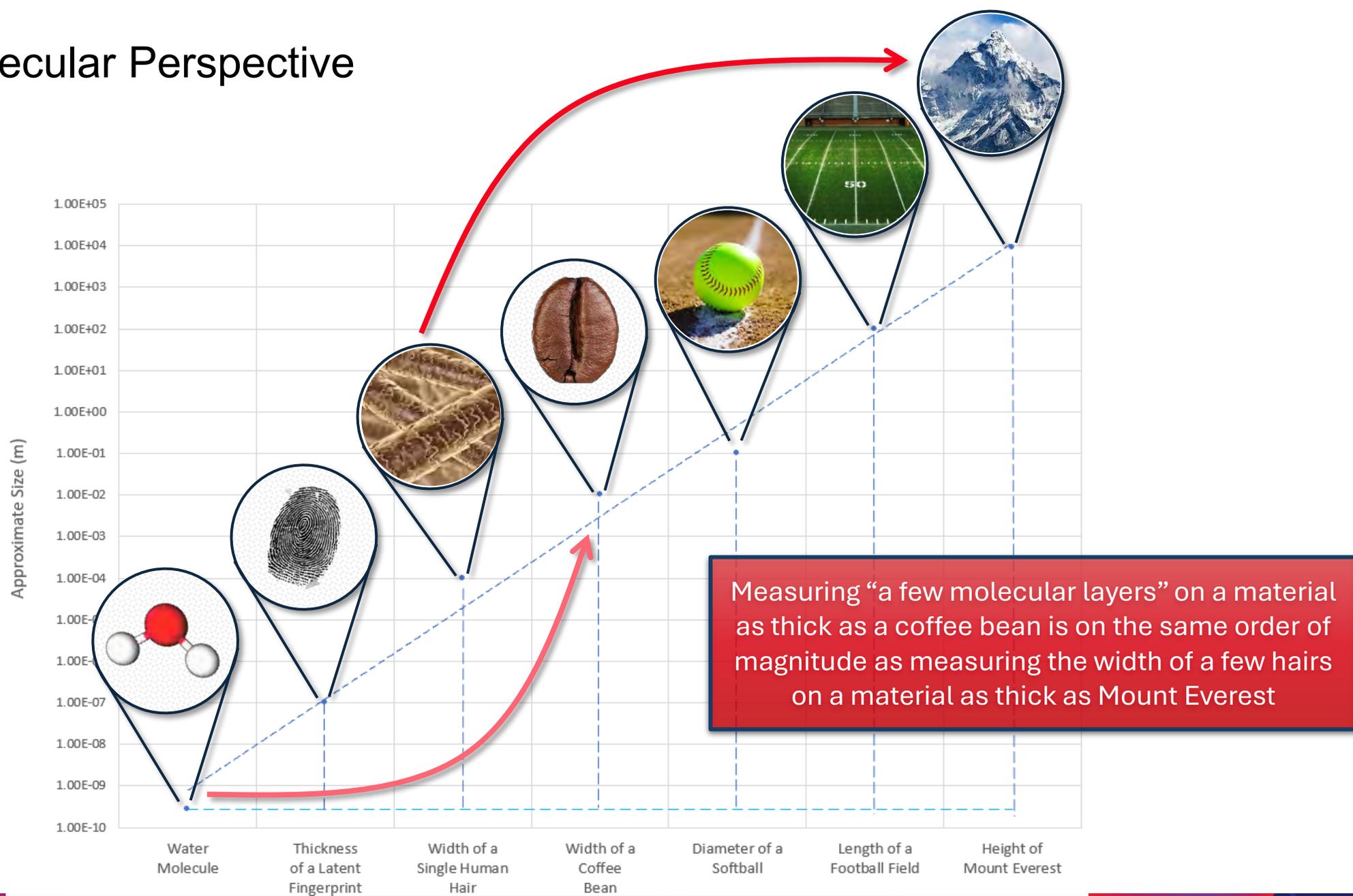
Outline

Polymer ***surface properties*** profoundly affect printing, coating, bonding, and sealing

- Surface properties depend on:
 - Incoming material *composition*: PE, BOPP, PET (Mylar), metallized, corona/flame
 - What we *do* to the surface: surface treatments and levels
 - How we *control treatment processes*: effects of day-to-day process variability
 - How materials are *stored and handled*
- Quantitative process monitoring during setup and production is vastly preferable to finished product testing
- This presentation discusses science-based methods for monitoring and controlling surface properties during film processing:
 - Wetting tension measurements using dyne solutions
 - Surface energy measurements via contact angle techniques

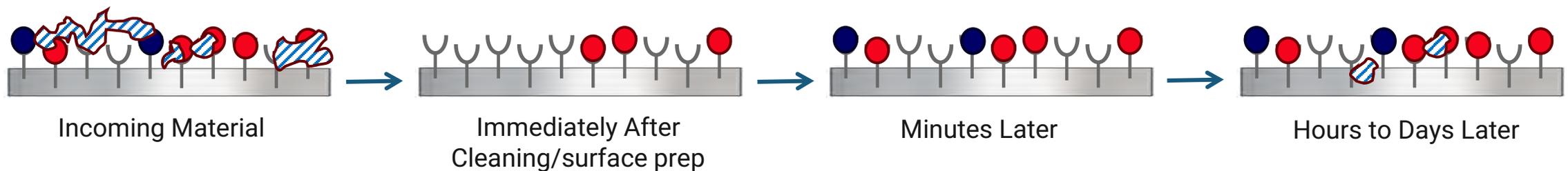
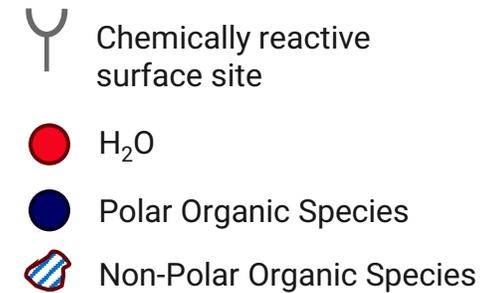


Surfaces: A Molecular Perspective



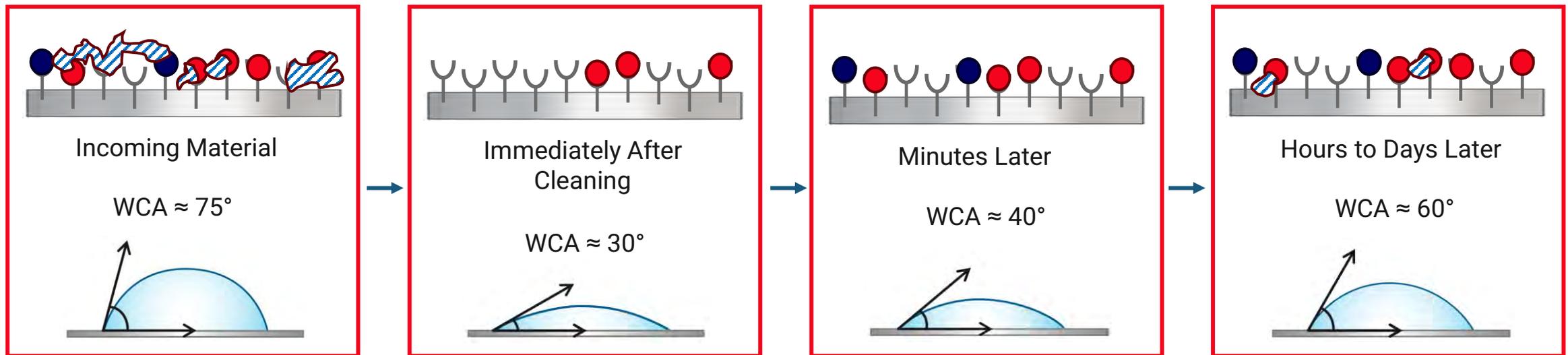
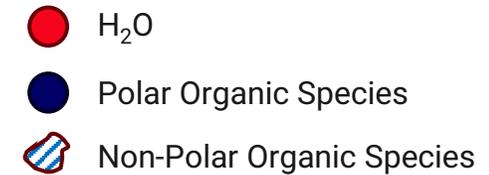
Surfaces from the perspective of adhesion of inks, coatings, adhesives

- Surfaces are composed of individual molecules
- The type of molecule determines the ability of the surface to interact with an ink or adhesive (*adhesion*)
- Anything that changes the top molecular layer of a surface changes its ability to interact with an ink or adhesive
 - **Surface energy** is a measure of the ability of a surface to interact with another substance



How do surfaces interact with liquids?

- The shape of a liquid drop on a surface is determined by the balance of forces acting on the liquid
 - If the liquid molecules are more strongly attracted to each other than to the surface, the drop will 'bead up' and not spread and not adhere
 - If the liquid molecules are more strongly attracted to the surface, they will spread out and adhere
- The shape of a small drop can be defined by the contact angle
- The contact angle is a function of the surface energy



Surface Energy and Material Type

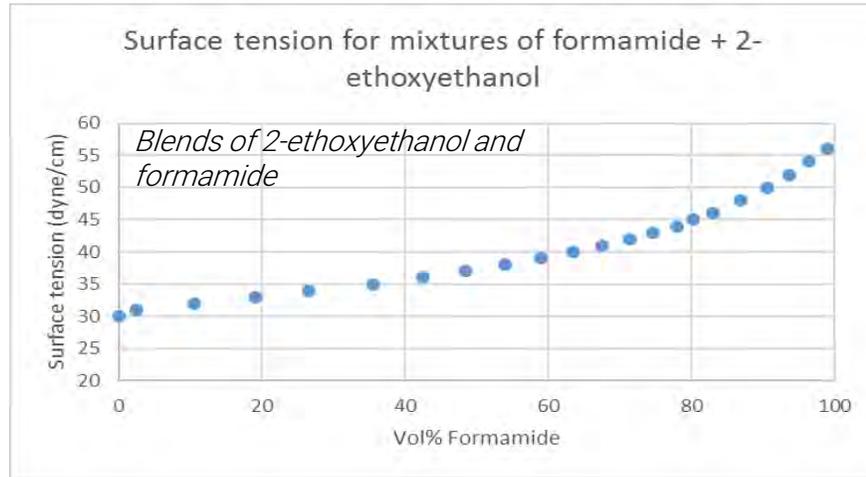
Material	Surface Energy (mJ/m ²)	Relative adhesion of inks and adhesives
PTFE	18	Lowest
Polyethylene (PE)	31	
Epoxy	42	
Corona/flame treated PE	50	
Silica (SiO ₂)	287	
Aluminum oxide	638	Highest

Weak interaction with inks, adhesives

Strong interaction with inks, adhesives

- Thermoplastic polymers tend to have low surface energies: lower than thermosets and much lower than inorganic materials
- Surface treatment can increase these

Estimation of Wetting Tension via Dyne Solutions (ASTM D 2578)



- Surface tension of the liquid mixture that ‘just spreads’ is taken as the wetting tension of the surface
- This is used as an estimator of Critical Wetting Tension γ_c



“Dyne solutions”: A mixture of two fluids with different surface energies that create a range of surface tensions (γ_l)

- Spread the test fluid over approximately 1in² of specimen
- Note time it takes for continuous film of ink to break into droplets.
 - T < 2 seconds indicates a lack of wetting; repeat with lower surface tension fluid
 - T > 2 seconds indicates , a higher numbered test fluid should be tried.
- Target: lowest surface tension fluid that remains continuous for at least 2 seconds



This is not a 0° contact angle

Estimation of Wetting Tension via Dyne Solutions (ASTM D 2578)

- Dyne solutions are widely used despite well-known limitations:
 - Manual, semiquantitative measurement not suitable for statistical process control
 - Controlled interlaboratory studies show 10-15 dyne/cm differences between laboratories and technicians^{1,2}
 - Valid only with polyolefin polymers (e.g. polypropylene and polyethylene)³.
 - Test fluids will dissolve and mask contaminants⁴
 - Dimethyl formamide/2-ethoxyethanol are toxic and teratogenic
- New technologies for rapid, practical measurement of contact angles are replacing wetting tension measurements for quantitative, automated control of surface engineering processes

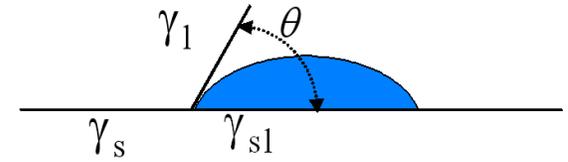
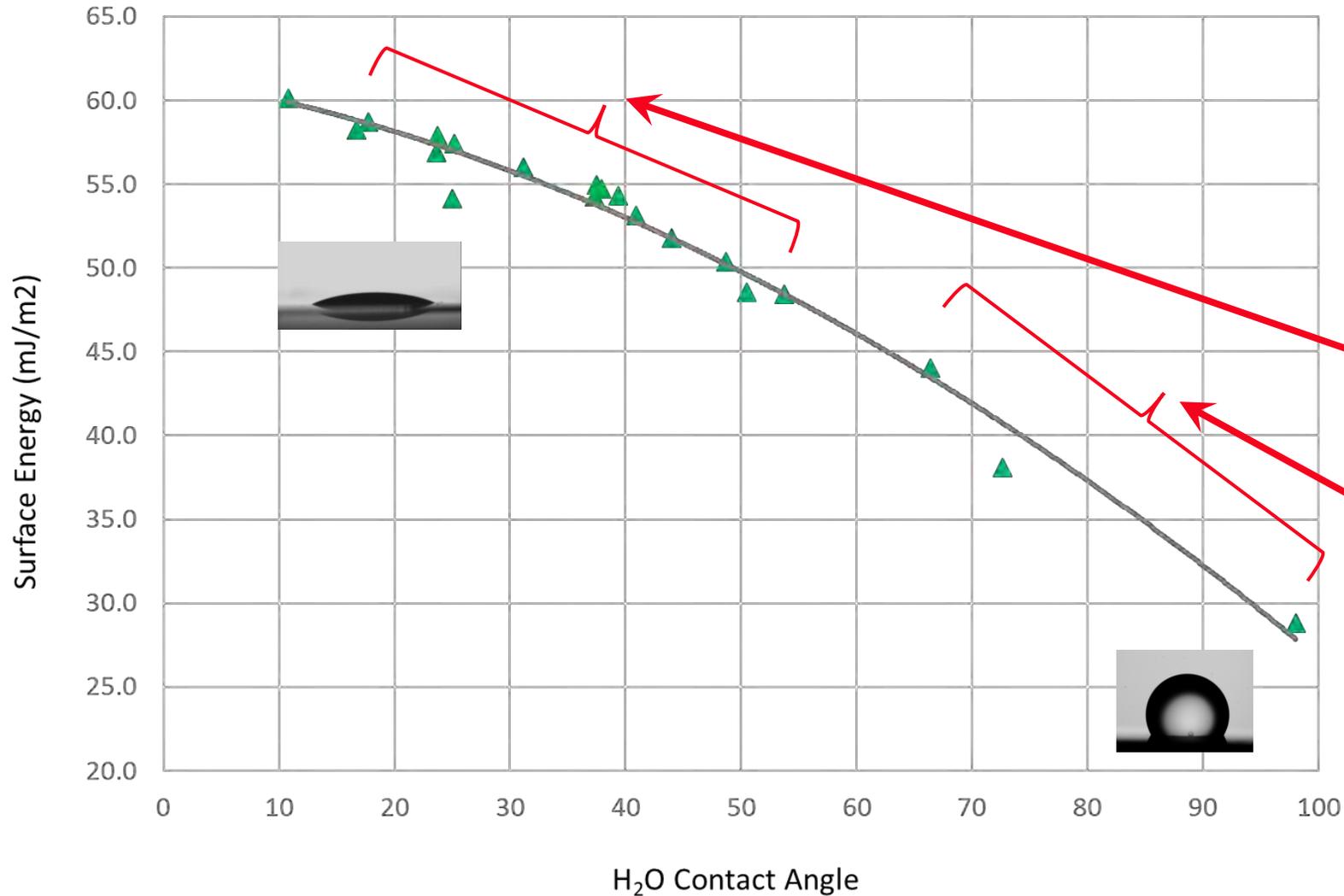
¹Caimi, R.J., Derr, L.K., Dunn, T.J., *Converting Magazine* 10 (6): 62 (1992)

²ASTM D5946 *Standard Test Method for Corona-Treated Polymer Films Using Water Contact Angle Measurements*

³ASTM D2578 *Standard Test Method for Wetting Tension of Polyethylene and Polypropylene Films*

⁴Blitshteyn, M., *Tappi Journal* vol. 78 No. 3 pp. 138-143 (March 1995).

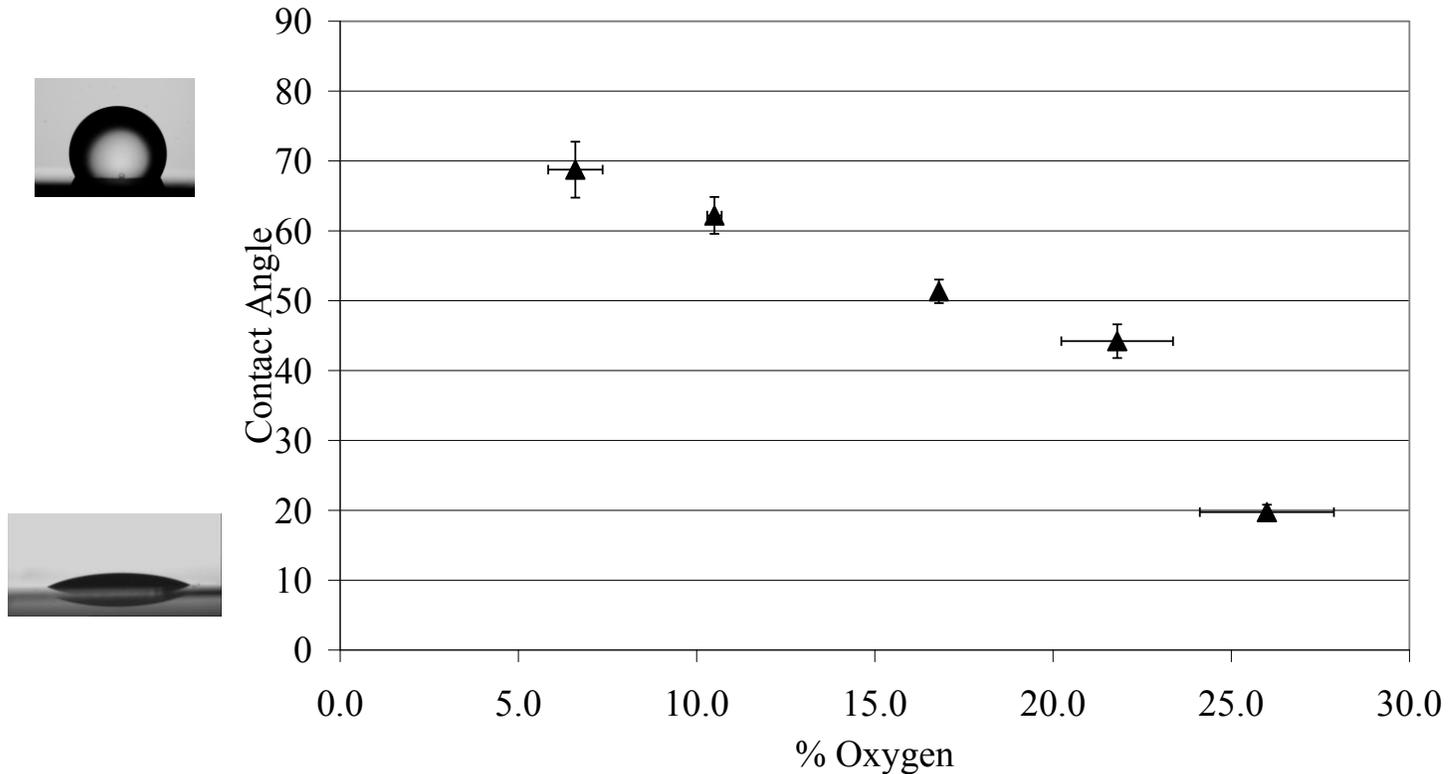
Contact angles and surface energy



$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta$$

- High energy (reactive) surface
- Good adhesion
- Low energy (non-reactive) surface
- Poor adhesion

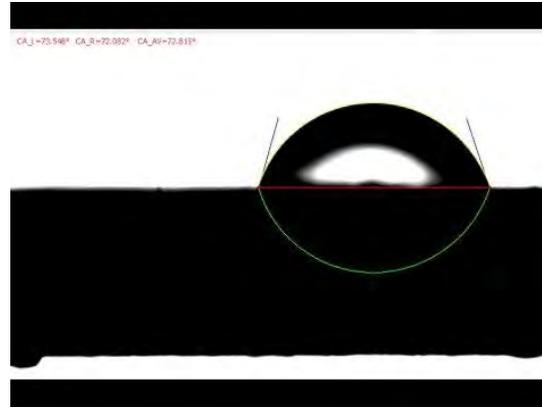
Contact angles and surface chemistry



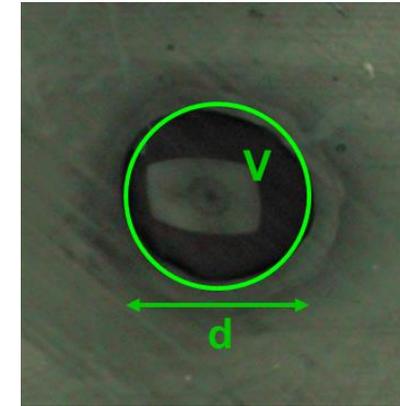
- The contact angle strongly correlates to the amount of oxygen incorporated in the surface by plasma treatment
- **It can be used as a quantitative measure of the surface composition**

Measurement of contact angles

- Side view:
excellent for
planar surfaces
- Top view:
excellent for non-
planar (curved)
substrates,
restricted space
access,
imperfectly round
drops
encountered on
'real' surfaces

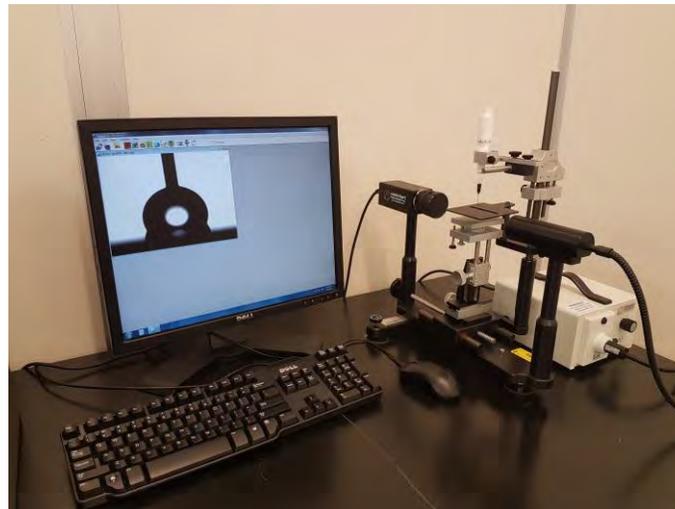


Side view:
Direct measurement



Top view:
Calculated from diameter and volume

$$\frac{d^3}{V} = \frac{24 \sin^3 \theta}{\pi(2 - 3 \cos \theta + \cos^3 \theta)}$$

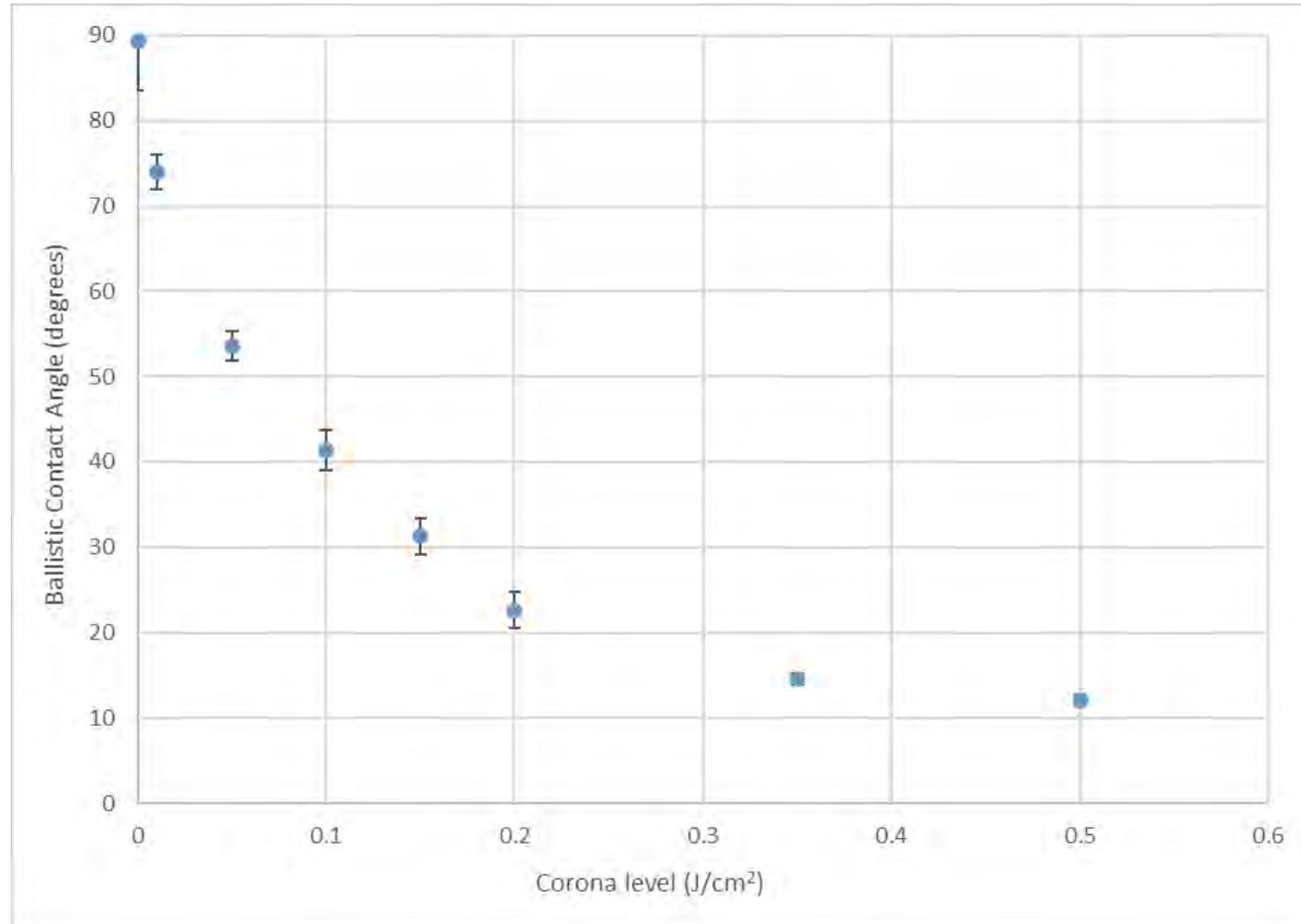


How does the Surface Analyst Work?

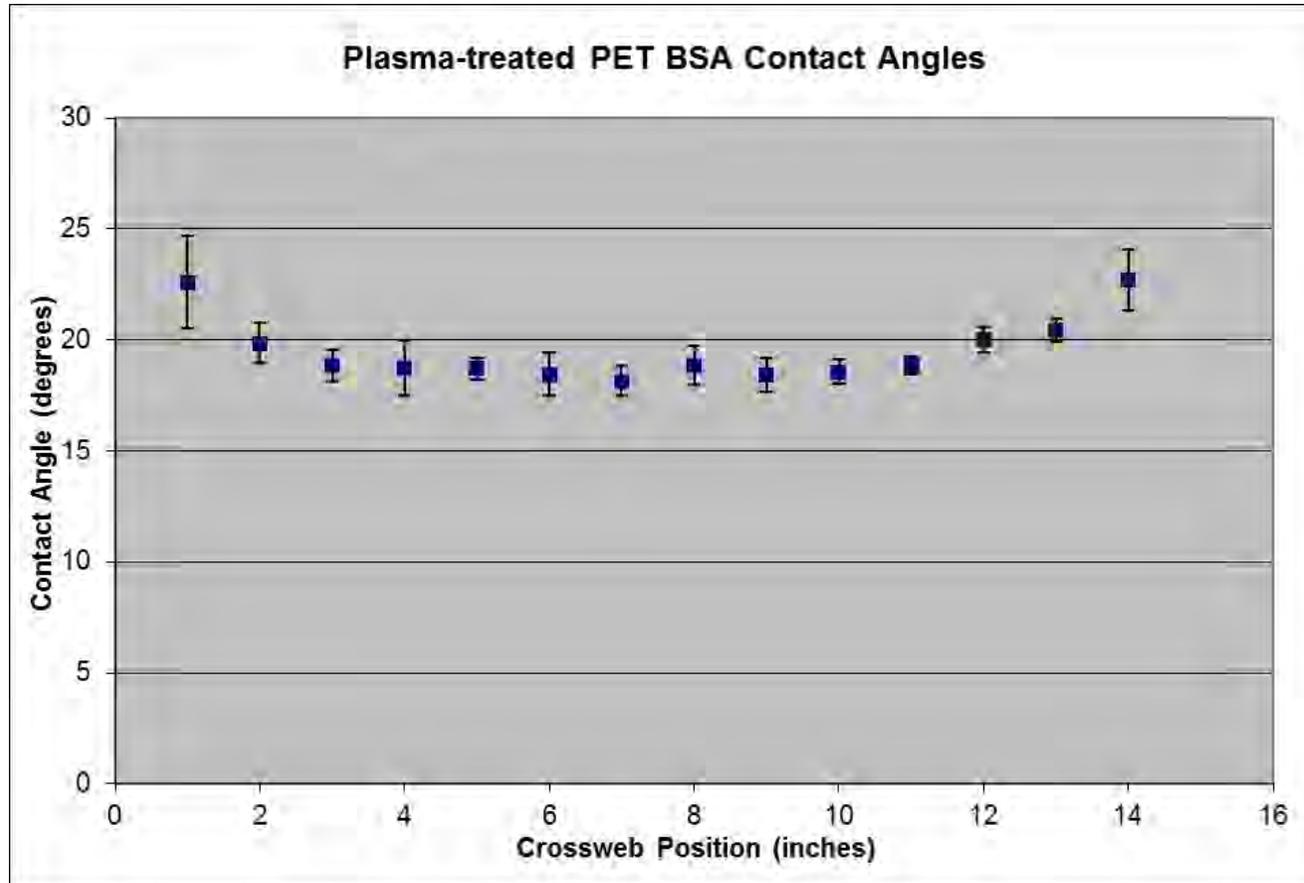
The Surface Analyst measures the contact angle of a fluid drop on your surface to determine the surface energy.



Process control via contact angle measurement: corona treatment level



Process control via contact angle measurement: corona treatment level variation



- This sort of process variation can profoundly affect product quality
- Data is rapidly and objectively obtained using contact angle methods

Beyond the 'Dyne Pen'

Substrate	Dyne Pen (dynes/cm)	WCA (degrees)
A	32	74,84,81
B	34	84,71,89
C	32	118,110,120
D	32	20,31,22
E	32	73,70,77

Water Contact Angle (WCA) shows broad surface distinctions not captured by the Dyne Pen as a means for understanding effects of specific substrate film surface on bonding performance.

Following Substrate Surface Changes



Water Contact angle (WCA) of BOPP Film Substrate as a function of corona treatment

Corona Treatment - 1 kW per pass

Note the continued changing and increased uniformity as additional corona passes were done.

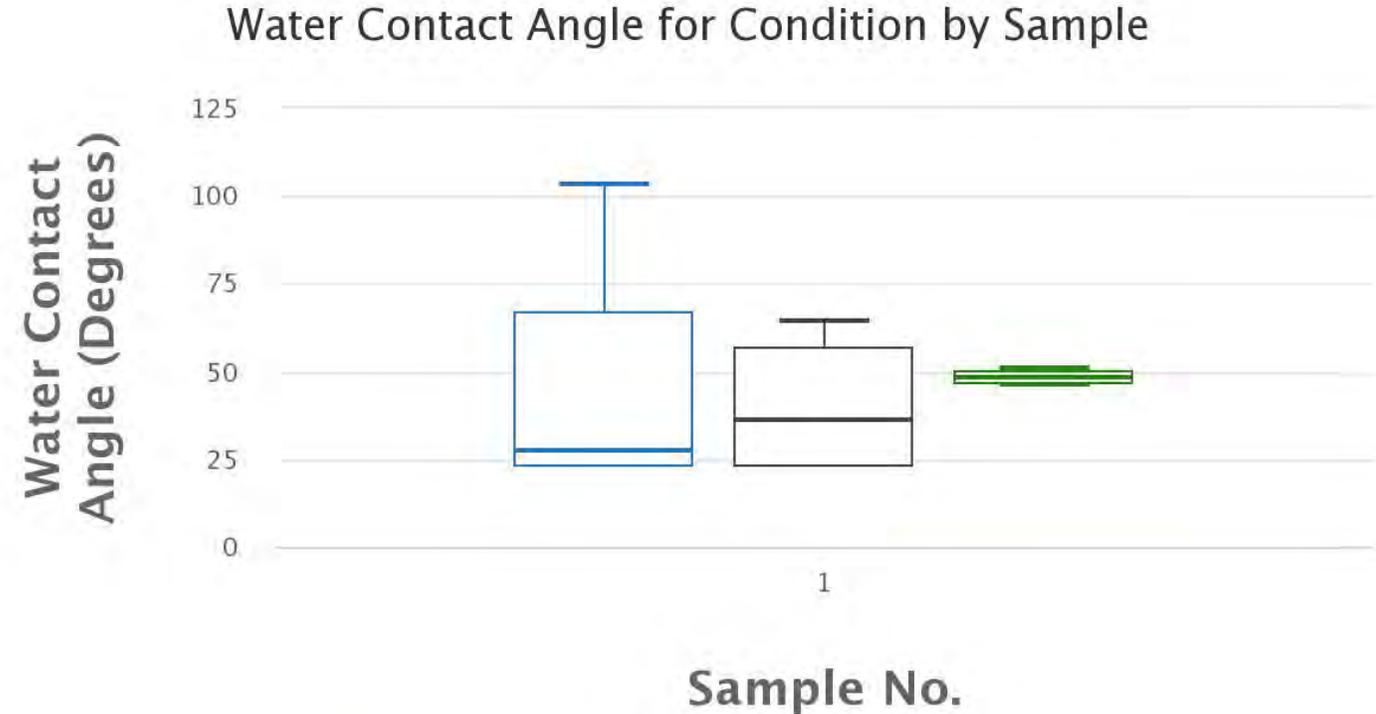
Substrate Treatment over Time

BConnect WCA as Function of Time after Corona (1 kW)



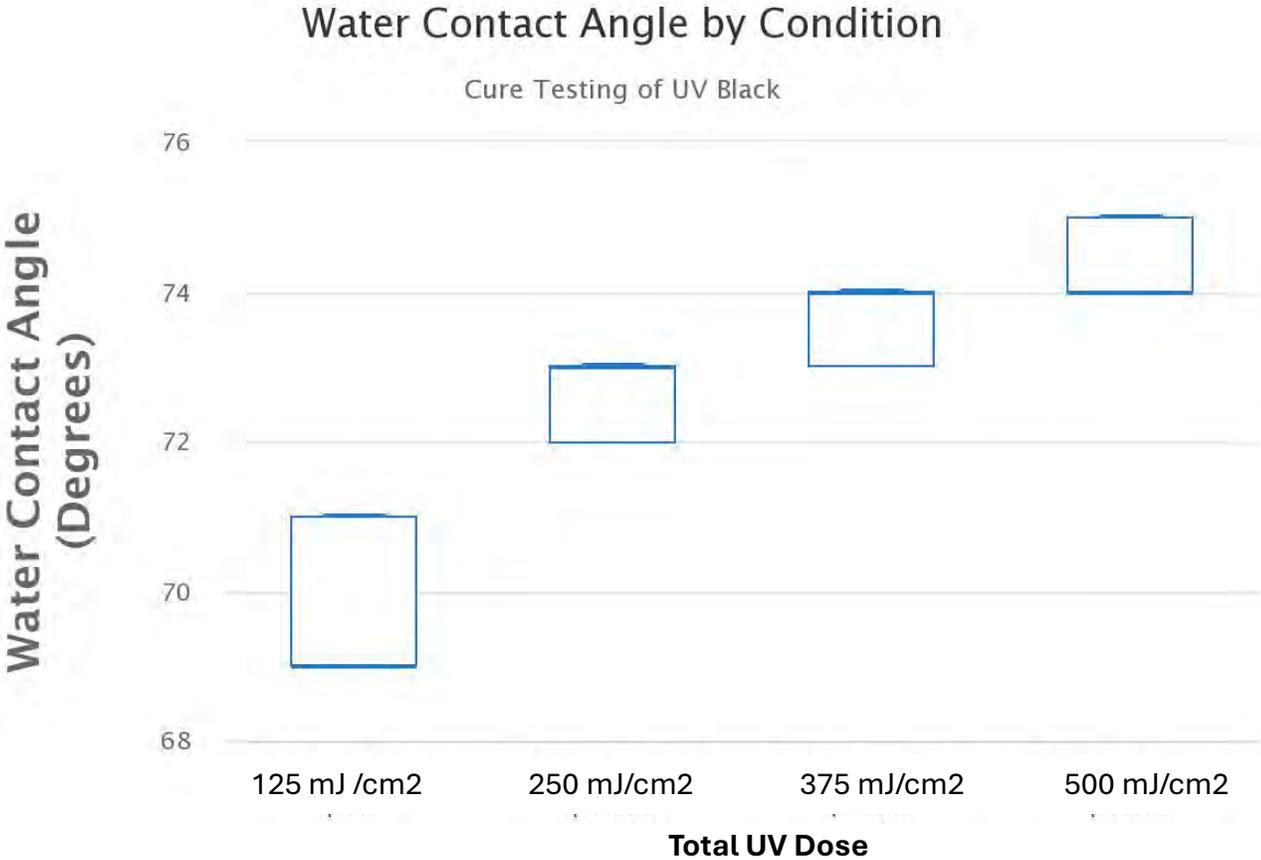
Behavior of two different BOPP films over time from treatment

Application to Unusual Surfaces



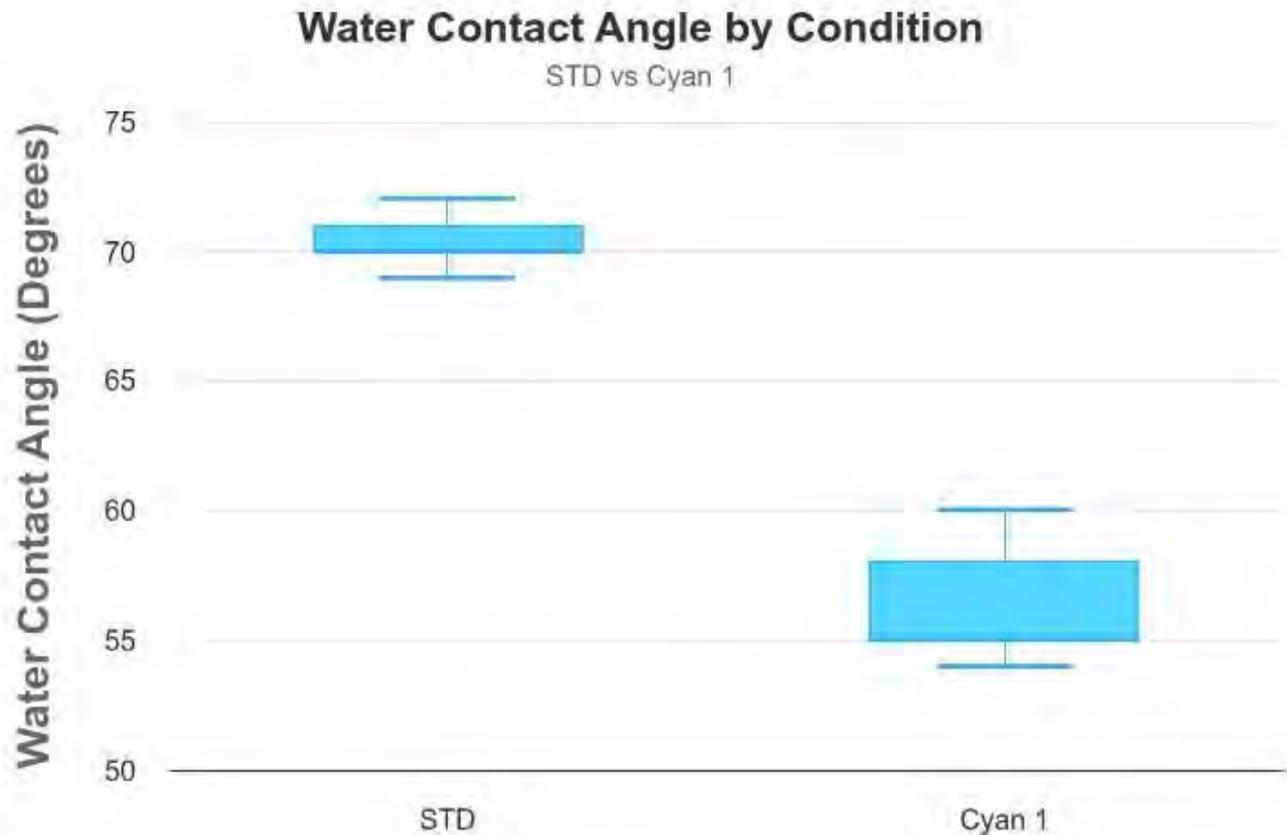
- Non Treated Non Cleaned Bottle - As received
- IPA Cleaned - Cleaned
- Sprayed with Green Ink - Sprayed with Green Ink

Water Contact Angle and Ink Performance



	1	2	3	4
125 mJ /cm2 per pass				
# Passes	1	2	3	4
IPA Rubs	7	10	13	18
Contact Angle Deg.	69.7	72.7	73.7	74.3
Std Deviation (Deg.)	0.9	0.5	0.5	0.5

Effects of Ink Formulation on WCA



Wettability Assessments and Ink Surface Properties

The Standard (STD) had a distinctly lower set off response than Cyan1 for these fully cured inks. This seems to be in line with relative water wetting which notes a clear surface distinction. Lower values indicating less hydrophobicity at surface.

Conclusions

- The properties of the uppermost few molecular layers of a surface determine the performance of coated/printed/bonded structures
- Surface energy is an excellent metric for monitoring and controlling the effects of this critical region
- Dyne solutions, the historic approach for probing surface energy, are hampered by a range of deficiencies
- Recent advances in contact angle measurement technology make this approach viable for high-rate, high-precision manufacturing where quality control is paramount for product performance and cost savings