KRÜSS

Measurement of Surface Free Energy & Surface Cleanliness

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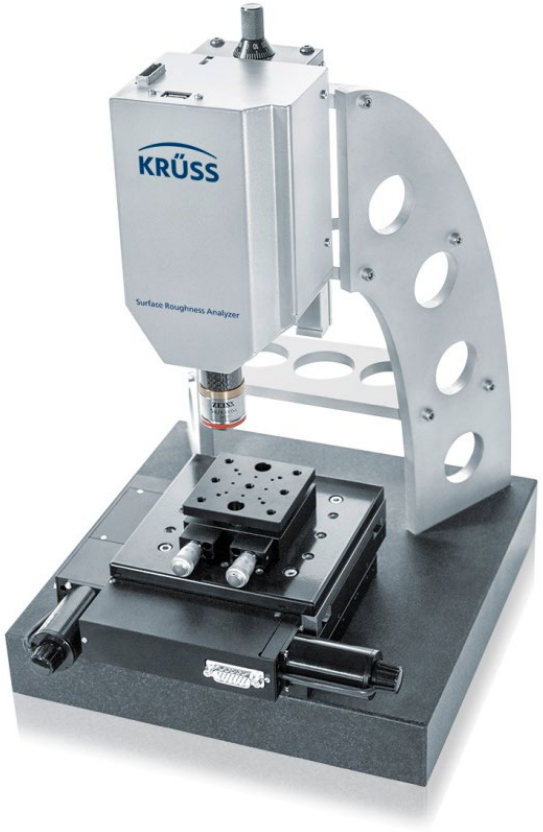
TOPCON 2019, Franklin, TN

KRÜSS – global market leader in the field of surface and interfacial tension

Surface Tension

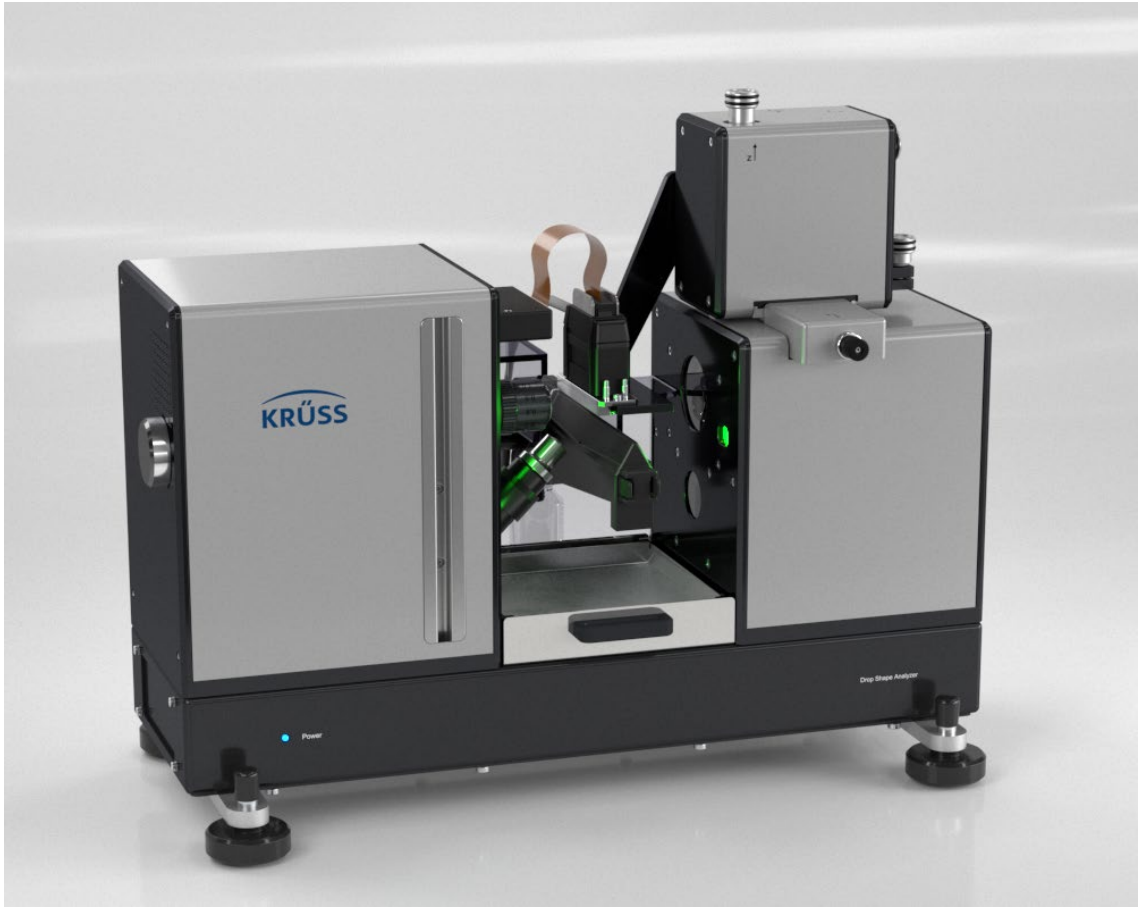
Contact Angle/SFE

Surface Roughness



KRÜSS – global market leader in the field of surface and interfacial tension

Ink Jet Development



Motivation – Why measure surface free energy?

Surface activation of plastic and composite materials promotes wetting and adhesion of coatings and glues

Activation of bumpers, panels, housings, etc.

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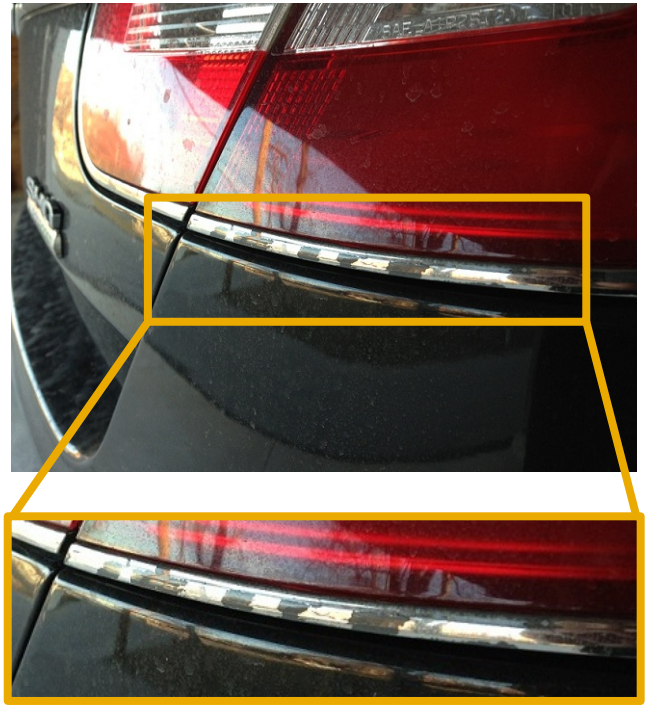
Some surface treatments don‘t have desired effect!

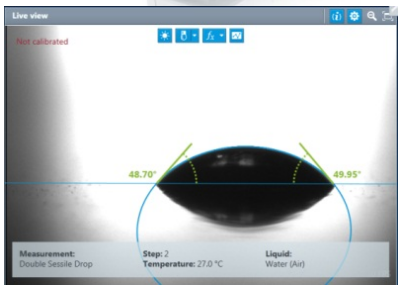
Surface activation of plastic and composite materials promotes wetting and adhesion of coatings and glues

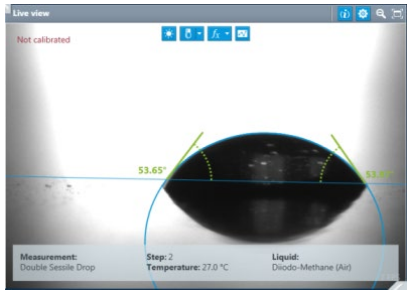
Increasing the plastic's SFE prior to coating prevents peel-off effects and adhesive failure

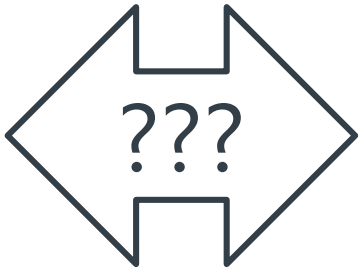


The SFE of an Solid can be measured with *test inks* or *contact angle* measuring devices

Are results comparable? What are the benefits/limitations of each method?







Comparative study – Contact angle measurements vs. Test inks

We took a quite large number of rather different samples

Mica

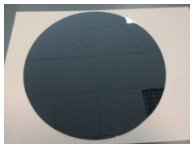
Polyamide 6(PA-6)
Akulon® K222-D

Polypropylene(PP)

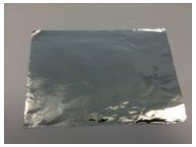
PA6 + 3% CLOISITE® 30B

Glass

Wafer



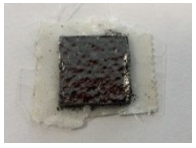
Aluminum foil



Polyethylene (PE)

Polytetrafluoroethylene
(PTFE /Teflon)

Highly ordered pyrolytic
graphite (HOPG)



Polyvinyl chloride (PVC)
- PVC table cloth

Polyethylene terephthalate
(PET)-PET bottle flake

Acrylonitrile butadiene
styrene (ABS)

Polydimethylsiloxane
(PDMS)

A proper cleaning procedure was applied before measurements were conducted

1. Clean the sample with detergent.
2. Rinse it under hot and cold tap water until all the surfactant residues are removed.
3. Rinse with distilled water.
4. Rinse with isopropanol (IPA).
5. Dry off the IPA by using compressed air stream.

We measured all samples with a KRÜSS CA device using at least two test liquids and with two different types of test inks

KRÜSS Drop Shape Analyzer

- Norm: DIN55660
- Test liquids: Water, diiodo methane, ethylene glycole,..

DyneTEC Test Ink /Formamide

- Norm: ISO8296
- Color: blue
- Substances: formamide and ethylene glycol monoethyl ether

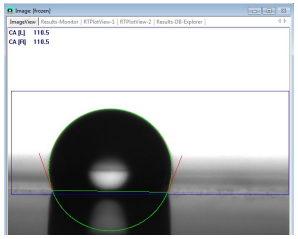
DyneTEC Test Ink /Ethanol

- Norm: Tantec development
- Color: yellow
- Substances: ethanol and deionized water

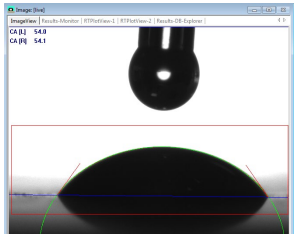
For the example of polypropylene (PP) everything seems to be fine

Measurement data for Polypropylene

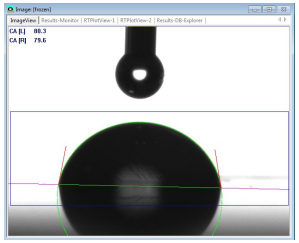
CA of Water



CA of diiodo methane

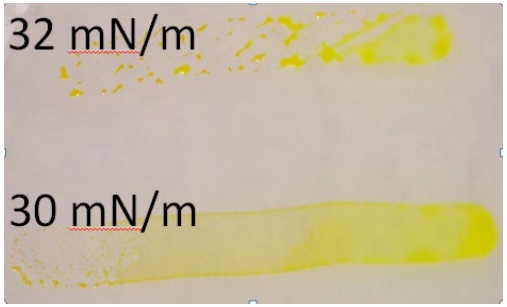


CA of ethylene glycol



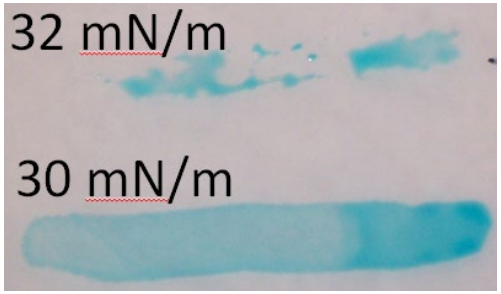
OWRK → SFE = 29.6 mN/m

Ethanol based test ink



→ SFE ≤30 mN/m

Formamide based test ink



→ SFE = 30 mN/m

But what about all the other tested materials?

Surface free energy in mN/m (=dyn/cm) determined with different methods

Samples	Contact angle	Test ink yellow (ethanol based)	Test ink blue (formamide based)
Mica	53.7	»56	»56
PA 6	50.6	≥56	≥56
PP	29.6	≤30	30
PA 6+3% C30	52	≥56	≥56
Glass	64.6	>56	>56
Silicon wafer	48.5	46	42
Aluminium foil	55.9	≥56	≥56
PE	32.2	30	30
Teflon	16.1	«30	«30
HOPG	44.8	56	40
PVC	47.1	30	32
PET	44.2	34	34
PDMS	22.64	«30	«30
ABS	37.1	34	34

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Surface free energy in mN/m (=dyn/cm) determined with different methods

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PP	29.6	≤30	30
PA 6+3% C30	52	≥56	≥56
Glass	64.6	>56	>56
Silicon wafer	48.5	46	42
Aluminium foil	55.9	≥56	≥56
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Teflon	16.1	«30	«30
HOPG	44.8	56	40
PVC	47.1	30	32
PET	44.2	34	34
PDMS	22.64	«30	«30
ABS	37.1	34	34

But a solid's SFE is more than *one* value: $\sigma = \sigma_{disperse} + \sigma_{polar}$

Contact angle measurement determine also the polar and dispersive parts of a solid's SFE

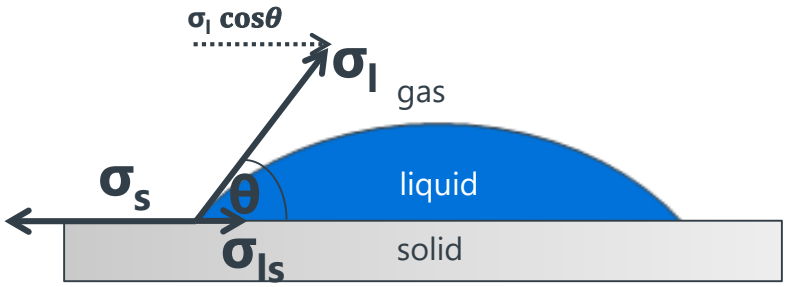
Samples	Contact angle SFE [polar part in %]	Test ink yellow (ethanol based)	Test ink blue (formamide based)
Mica	53.7 [24%]	»56	»56
PA 6	50.6 [19%]	≥56	≥56
PP	29.6 [0%]	≤30	30
PA 6+3% C30	52 [24%]	≥56	≥56
Glass	64.6 [50%]	>56	>56
Silicon wafer	48.5 [39%]	46	42
Aluminium foil	55.9 [46%]	≥56	≥56
PE	32.2 [0%]	30	30
Teflon	16.1 [0%]	«30	«30
HOPG	44.8 [71%]	56	40
PVC	47.1 [3%]	30	32
PET	44.2 [3%]	34	34
PDMS	22.64 [0%]	«30	«30
ABS	37.1 [16%]	34	34

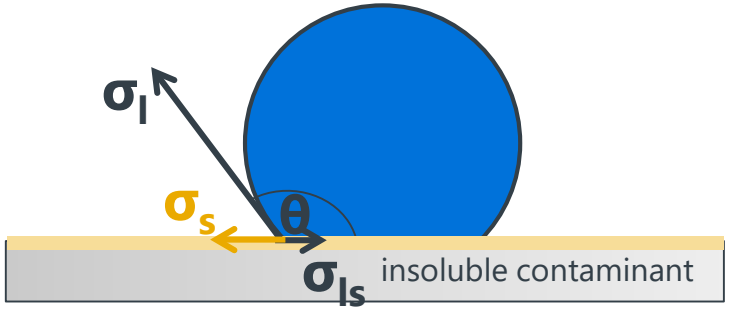
Cleanliness of Surfaces affects surface energy

Contact angle measurements as a method to investigate the cleanliness of a surface

Basic concept of the method

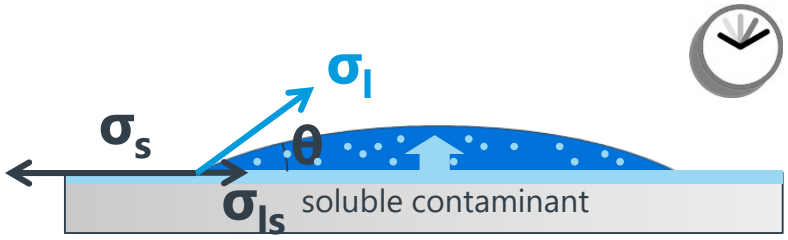
- The Young equation describes the shape that a drop forms on a solid surface:





$$\sigma_s = \sigma_{ls} + \sigma_l \cos\theta$$

σ_l = liquid's surface tension
σ_s = solid's surface free energy
σ_{ls} = liquid-solid interfacial tension
Θ = contact angle



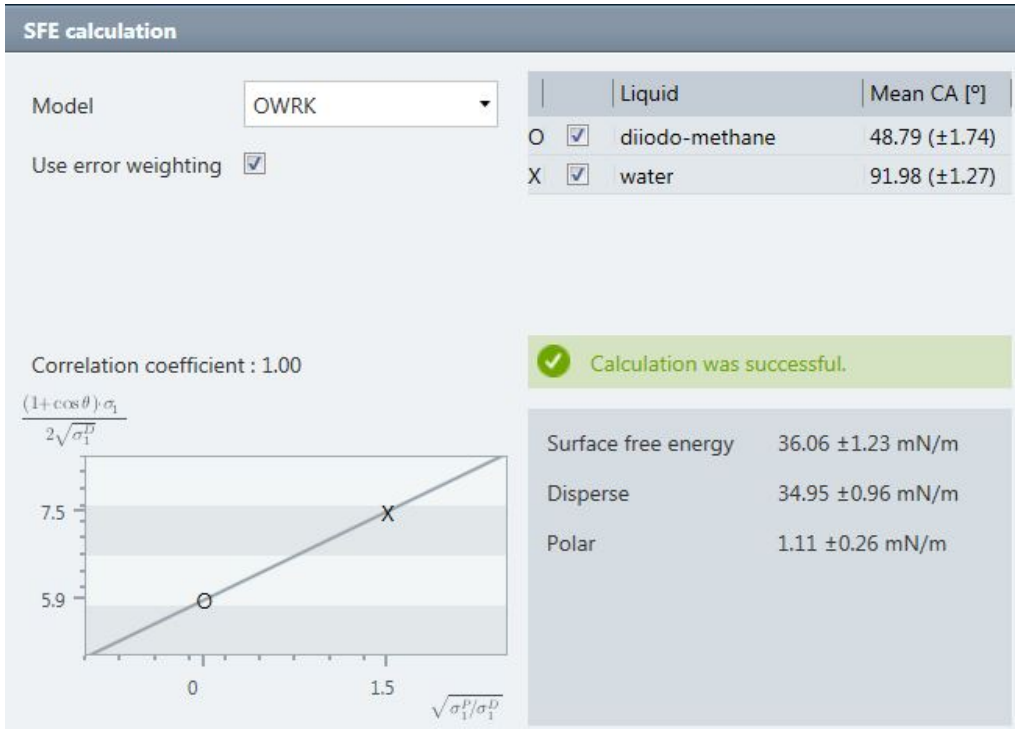
Polar and disperse parts of surface free energy reveal additional information about the analyzed surface

Dosing of at least two different test liquids is mandatory for this approach

- Based on contact angle data of at least two different test liquids, the surface free energy of a solid sample can be determined with respect to polar and disperse parts:

$$\sigma = \sigma^p + \sigma^d$$

- What type of contaminant can be found on my sample surface? (Oil, surfactant,…)
- Allows prediction of the adhesion properties of subsequent layers (coating, adhesive, varnish,…)



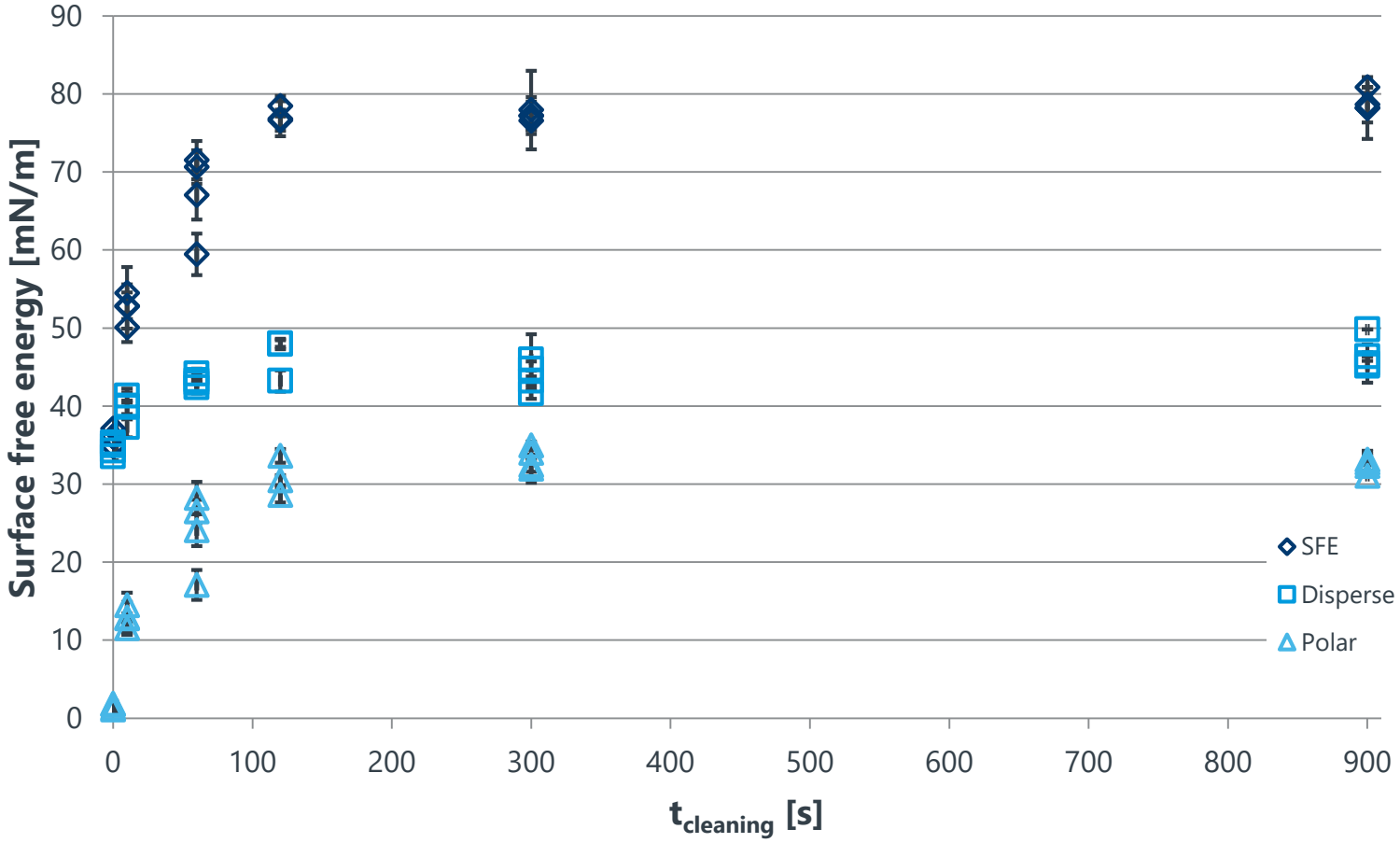
We‘ve tested steel sheets that were cleaned in an ultrasonic bath with different dwell times

Only after extended cleaning time a difference appears to the eye

Increasing cleaning time

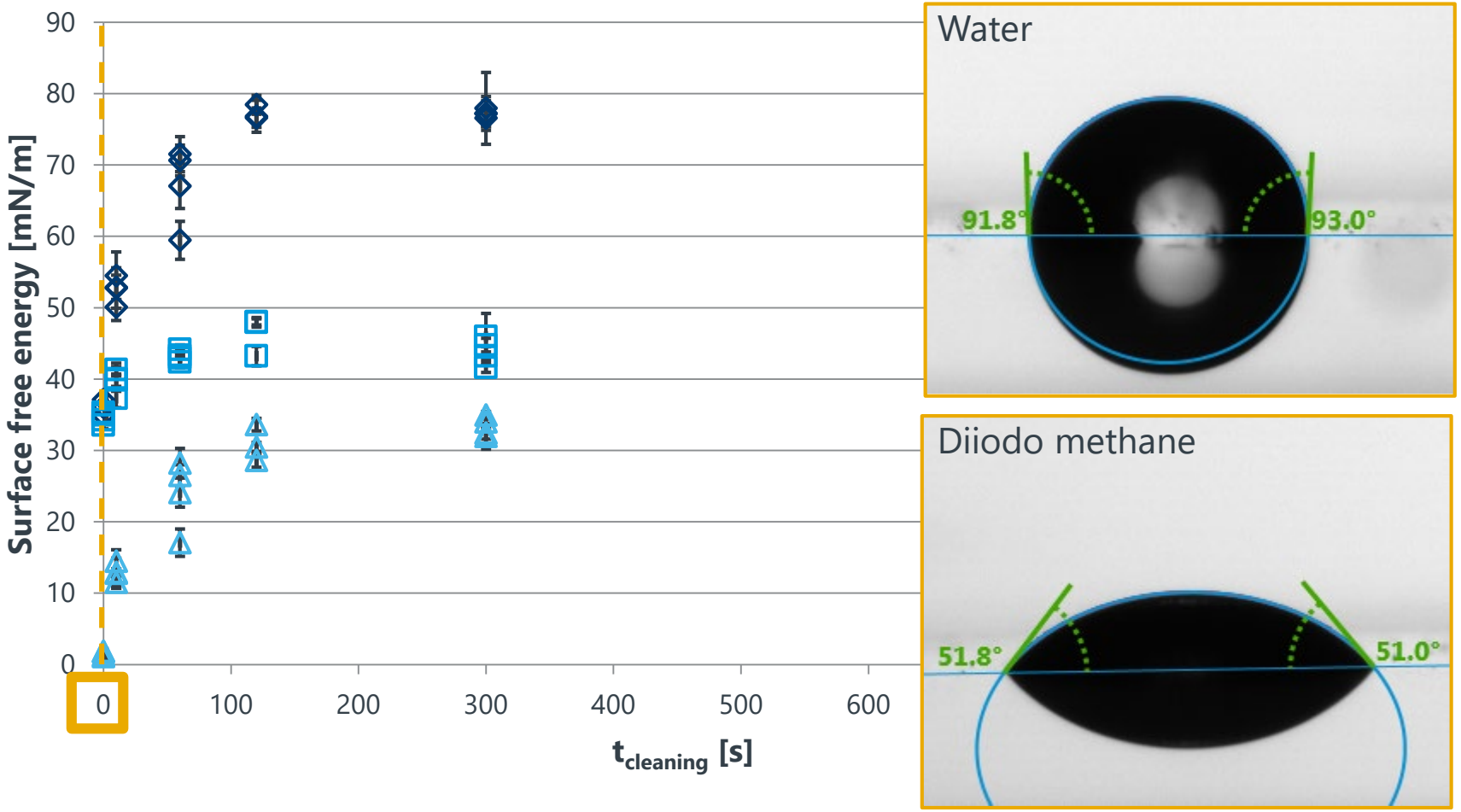
After 120 s an optimum cleaning is reached – further cleaning doesn't show any effect

After only 10 s of cleaning, significant differences in surface free energy can be observed



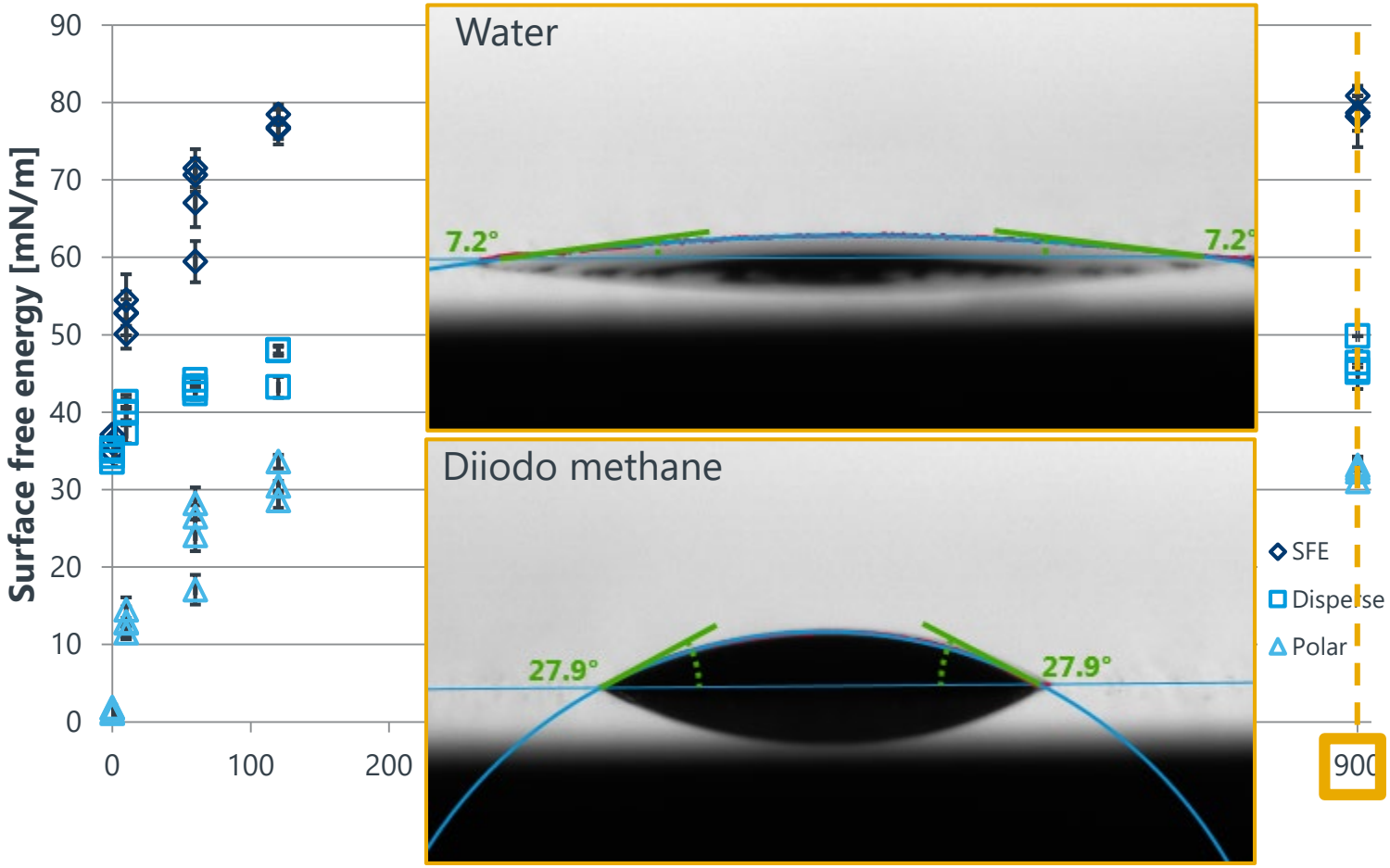
After 120 s an optimum cleaning is reached – further cleaning doesn't show any effect

Exemplary drop images from the contaminated sample (0 s)



After 120 s an optimum cleaning is reached – further cleaning doesn't show any effect

Exemplary drop images from the cleaned sample (900 s)

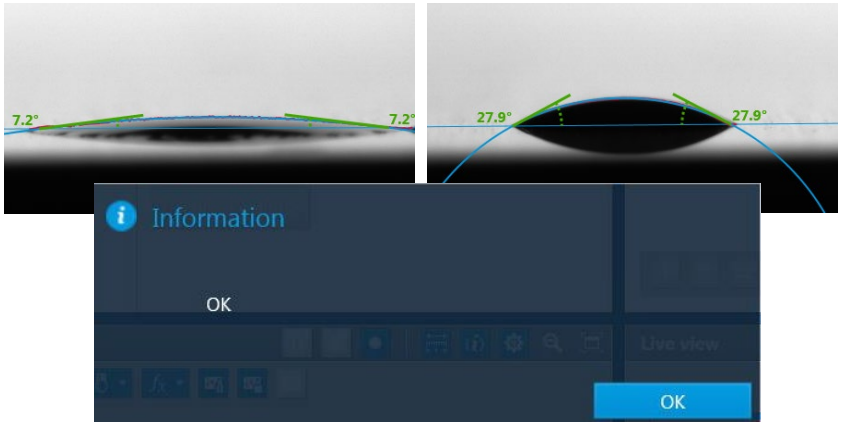


Once the dwell time has been optimized, the method can be used for quality control

Controling the cleanliness of processed parts

Automation program

Proc.	Wait until	Delay	Action	Mode	Interval
☑ 1			Dose left 2 µL	Next when comple...	
☑ 2			Dose right 2 µL	Next when comple...	
☑ 3		1 s	Measure left	Next when comple...	
☑ 4			Measure right	Next when comple...	
☑ 5			Validate SFE Polar | > 30 mN/m	Next when comple...	
☑ 6			Data export Excel | C:\		



Contact angle measurements as a tool for quality control of cleaning processes

Advantages of the method at a glance

- **Simple:** One click and the measurement is executed automatically
- **Fast:** Dose and measure within a second
- **User-independent:** The high degree of automation in combination with the patented *Liquid Needle* dosing provides best results
- **Local:** Spatially resolved information about the surface cleanliness
- **Mobile:** Check large samples of complex geometry in place, no need to transfer samples to the lab
- **Non-invasive:** No need to cut samples into smaller pieces, drops of test liquids evaporate completely
- **Documented measurement:** Drop profile images are stored

⇒ **Safe time and money, optimize the use of ressources**

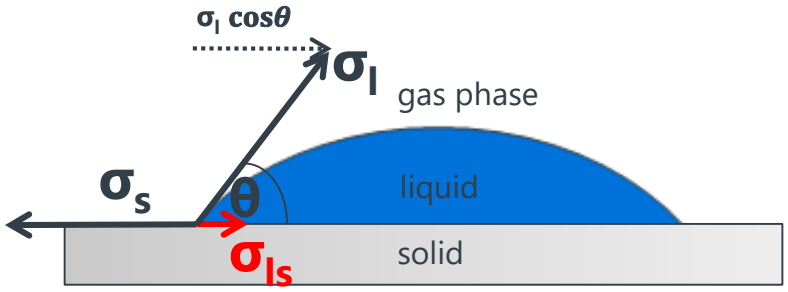
⇒ **Monitor the cleaning results in a reliable manner**

Back to Test Ink Study

Test inks neglect interfacial tension

But σ_{ls} vanishes only if SFE = SFT **and** the polar-disperse ratios for solid and liquid are equal

$$\sigma_s = \sigma_{ls} + \sigma_l \cos\theta$$

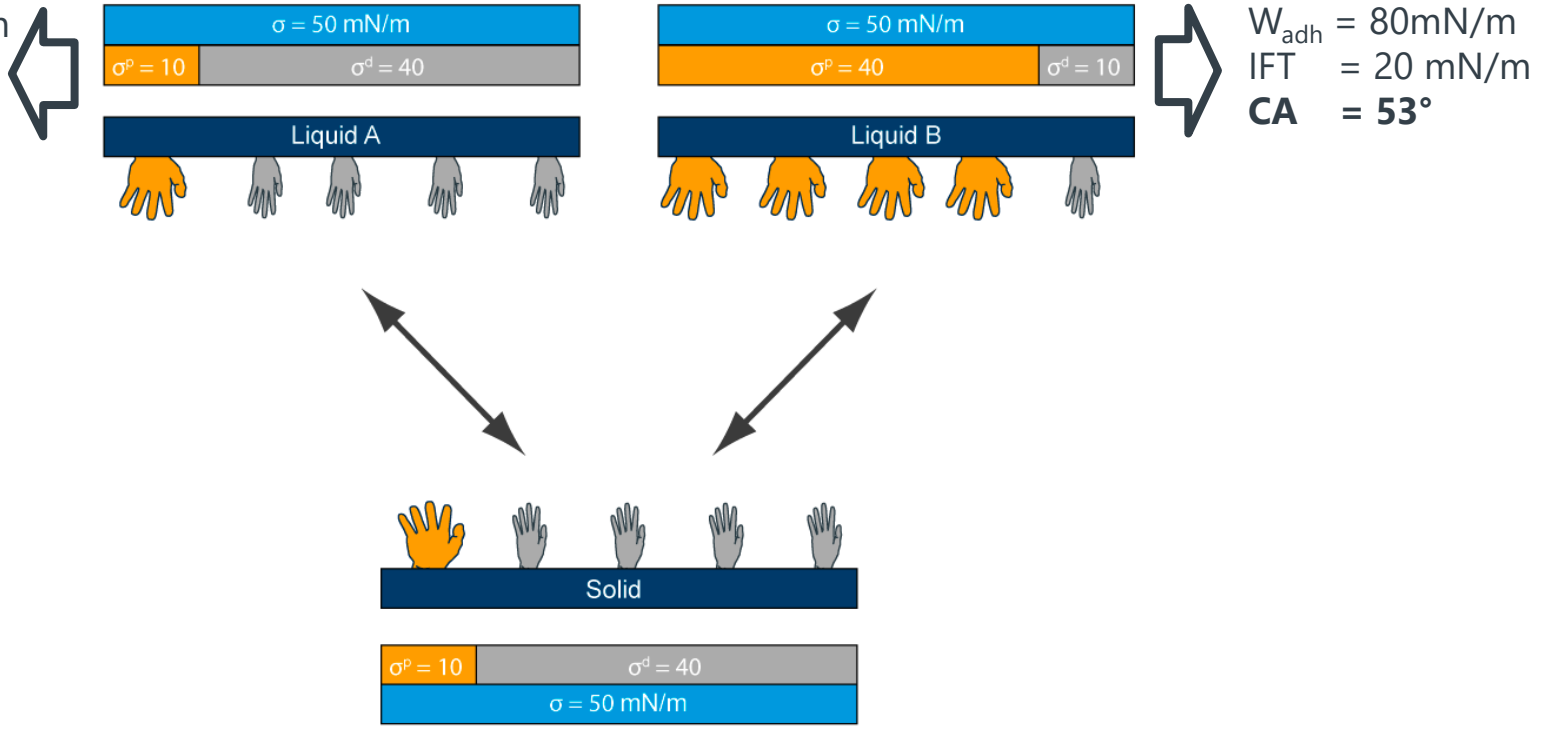


Interfacial tension according to OWRK theory:

$$\sigma_{ls} = \sigma_s + \sigma_l - 2 \cdot \left(\sqrt{\sigma_s^d \sigma_l^d} + \sqrt{\sigma_s^p \sigma_l^p} \right)$$

If the polar-disperse ratio is not the same a test ink does not spread on a solid even though its SFT matches the solid's SFE

W_{adh} = 100mN/m
IFT = 0 mN/m
CA = 0°



W_{adh} = 80mN/m
IFT = 20 mN/m
CA = 53°

So the surface polarity is the really interesting part!

The „fathers of adhesion science“ had a similar opinion

But even supposing that γ_S^{TOT} somehow could in general be approximated via only one equation in one independent variable, i.e., by measuring contact angles with only one liquid (and that approximation is by coincidence, occasionally, surprisingly close when using the equation of state), the question may be raised, what can one do with γ_S^{TOT} once its value is known? The answer is not much. It does, of course, allow one to calculate the energy of cohesion of the solid (eq 9 and 11). But contrary to γ_L^{TOT}, which is an essential factor in the Young equation (see also Figure 1), γ_S^{TOT} plays no role in that or any equation other than eq 11 and is in itself of no direct use in the determination of interaction energies between a solid and a liquid (eq 3, 6, 7) or between a solid and other solids (eq 3, 6, 7, 16).

van Oss, Good, Chaudhury, *Langmuir* **1988**, *4*, 884.

9.1. Use of Liquid Mixtures

W. A. Zisman was adamant against the use of mixtures of liquids in the Fox-Zisman method of determining γ_c, and he was unhappy with the American Society for Testing and Materials (ASTM) recommendation[49] to do so. We strongly support the condemnation of the use of liquid mixtures, particularly when one of the liquids is capable of hydrogen bonding. Adsorption of at least one component

Good, van Oss, in: Modern approaches to wettablity, **1992**.

Based on contact angle data, according to OWRK, physical parameters that describe adhesion can be calculated

Spreading coefficient:

$$S = \sigma_s - \sigma_l - \sigma_{sl}$$

Work of adhesion:

$$W_A = 2\sqrt{\sigma_s^d \sigma_l^d} + 2\sqrt{\sigma_s^p \sigma_l^p}$$

Interfacial tension:

$$\sigma_{sl} = \sigma_s + \sigma_l - 2\sqrt{\sigma_s^d \sigma_l^d} - 2\sqrt{\sigma_s^p \sigma_l^p}$$

Parameter	Effect	Critical value
S	spontaneous wetting	≥ 8 mN/m
W_A	bonding strength	≥ 65 mN/m
σ_{sl}	long term stability	≤ 1 mN/m

Test inks cannot deliver these parameters!

According to KRÜSS AR 260 *Optimizing Automotive Coatings* **2007**.

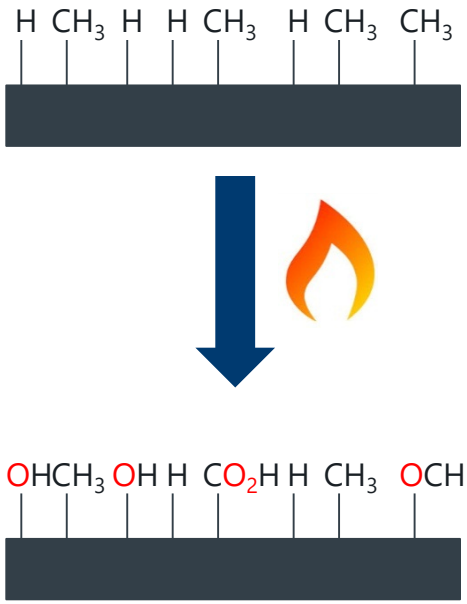
What about activated surfaces? We tested plasma activated surfaces with both contact angle and dyne pen methods

A flame plasma is formed when a flammable gas and atmospheric air are combined and combusted to form an intense blue flame. The surface of materials are made polar as species in the flame plasma affect the electron distribution and density on the surface. This polarization is made through oxidation. In addition, functional groups are deposited on the surface.

Used with permission from Enercon Surface Treating Systems

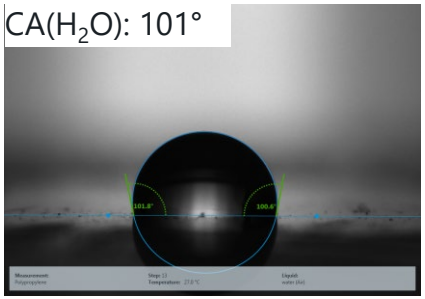
Reactive oxygen species form during combustion and are integrated into the polymer surface

Flame activation results in an increase in SFE

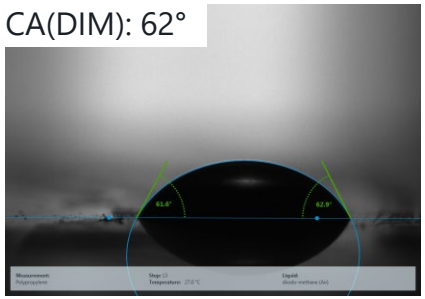


Polypropylene (PP):

CA(H_2O): 101°

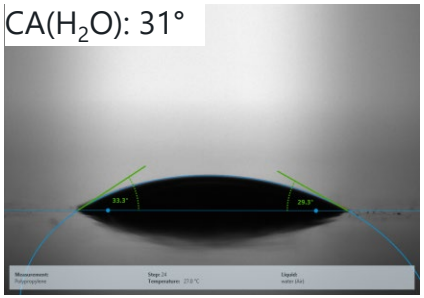


CA(DIM): 62°

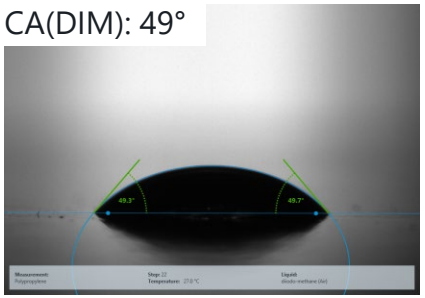


untreated: SFE = 27.9 mN/m (0.5 mN/m polar)

CA(H_2O): 31°



CA(DIM): 49°



treated: SFE = 66.0 mN/m (31.5 mN/m polar)

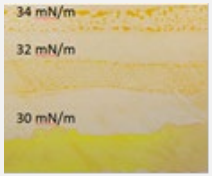
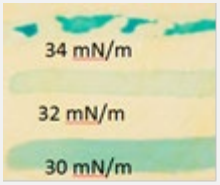
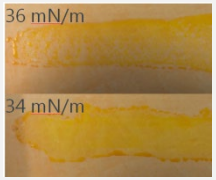
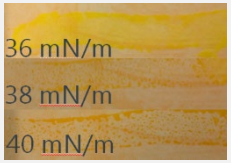
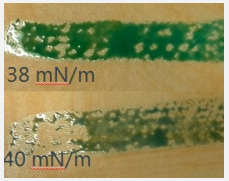
Test inks fail in monitoring the efficiency of plasma treatments

SFE of PDMS treated with atmospheric plasma (*Piezo Brush*® – Reylon Plasma)

Plasma treatment	Contact angle [mN/m]	Yellow test ink [mN/m]	Blue test ink [mN/m]
0 seconds	Total: 21.7 Polar: 0.0 Dispersive: 21.7	Total SFE< 30	Total SFE< 30

Test inks fail to monitor the efficiency of plasma treatments

SFE of PVC treated with atmospheric plasma (*Piezo Brush*® – Reylon Plasma)

Plasma treatment	Sessile drop method [mN/m]	Ethanol tesk ink [mN/m]	Formamide test ink [mN/m]
raw PVC sample	Total SFE: 47.1 Polar part: 1.3 Dispersive part: 45.7	Total SFE: 30 	Total SFE: 32 
PVC sample after 40 s plasma treatment	Total SFE: 54.08 Polar part: 6.36 Dispersive part: 47.72	Total SFE: 34 	Total SFE: 34 
PVC sample after 60s plasma treatment	Total SFE: 61.69 Polar part: 14.25 Dispersive part: 47.44	Total SFE: 36 	Total SFE: 38 

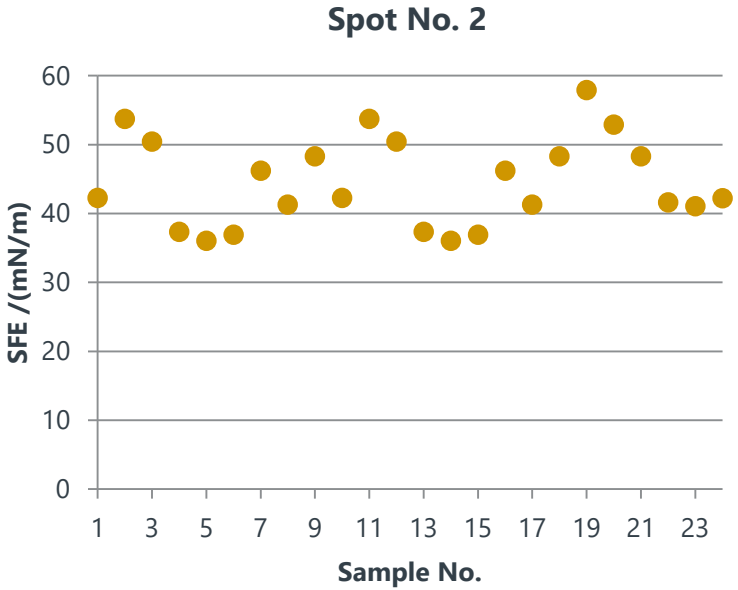
Case study – flame activation

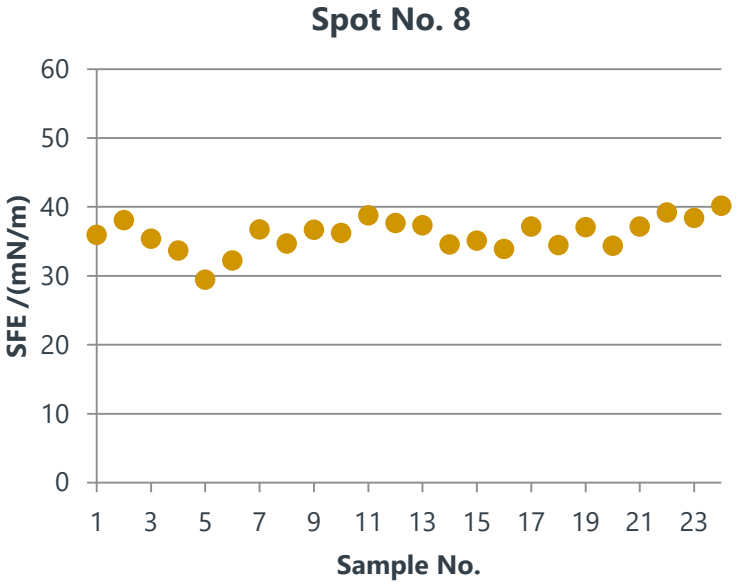
A major Tier 1 supplier tested mobile CA measurements to optimise their flame treatment process

Flame treatment of dashboard tops made from PP

Different flame treatment parameters resulted in varying surface free energy values

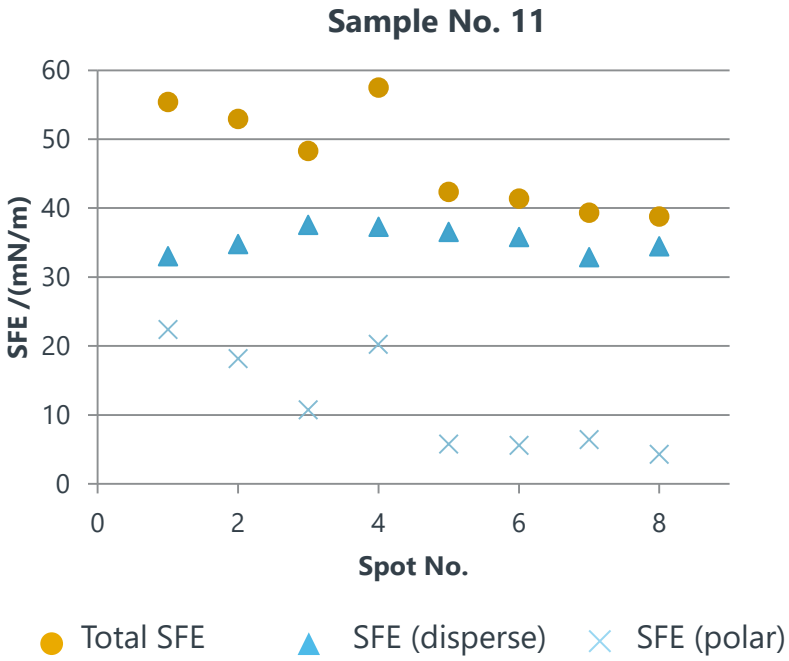
- **8** different spots per sample („Spot 1-8“)
- **8** different flaming-parameters
- **3** different samples per each tested flaming condition (8 x 3 = 24 samples)

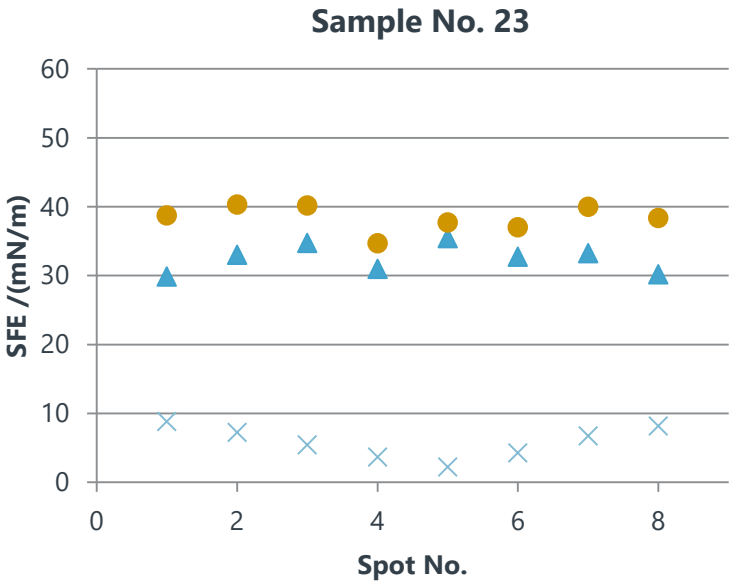




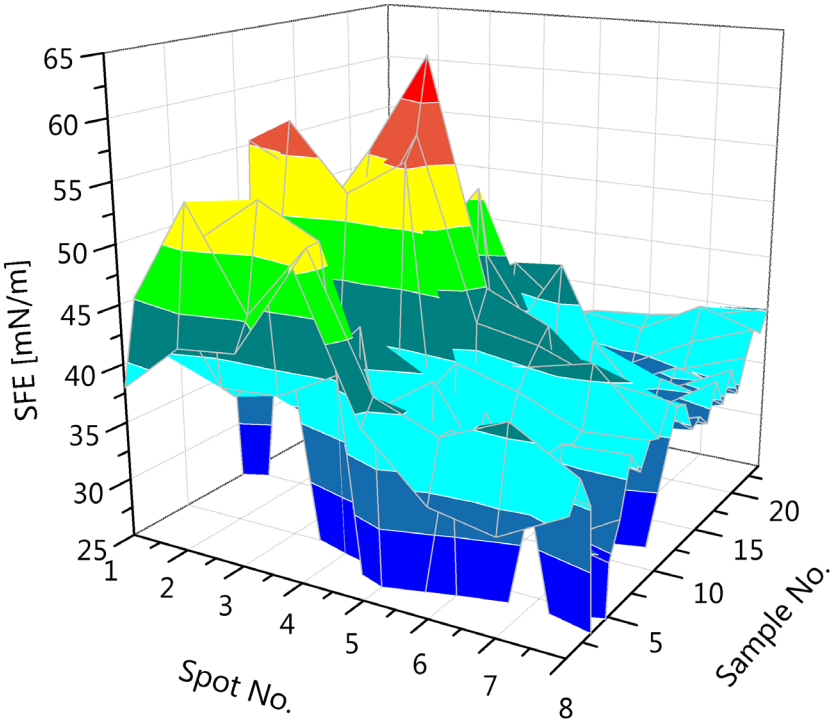
Some samples showed a very heterogeneous surface activation

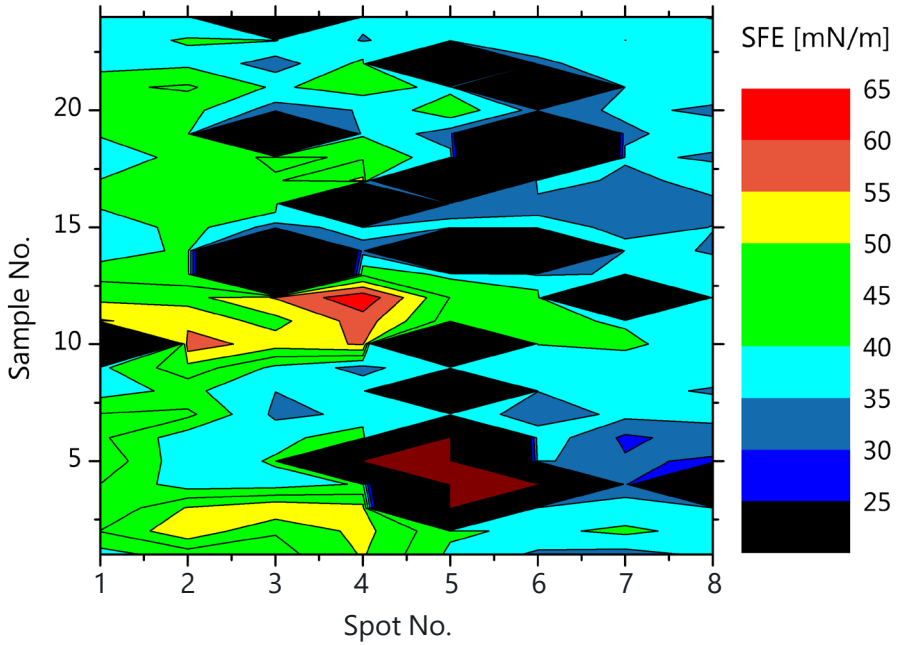
- **8** different spots per sample („Spot 1-8“)
- **8** different flaming-parameters
- **3** different samples per each tested flaming condition (8 x 3 = 24 samples)





Some samples showed a very heterogeneous surface activation





Result: - Improvement of the flame treatment process by adjusting single parameters => Reduction of rejection rate!

- CA-measurements as a QC-tool to predict possible delamination/"peel-off"-effects early and spatially resolved

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Advancing your Surface Science

Do you have questions?

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