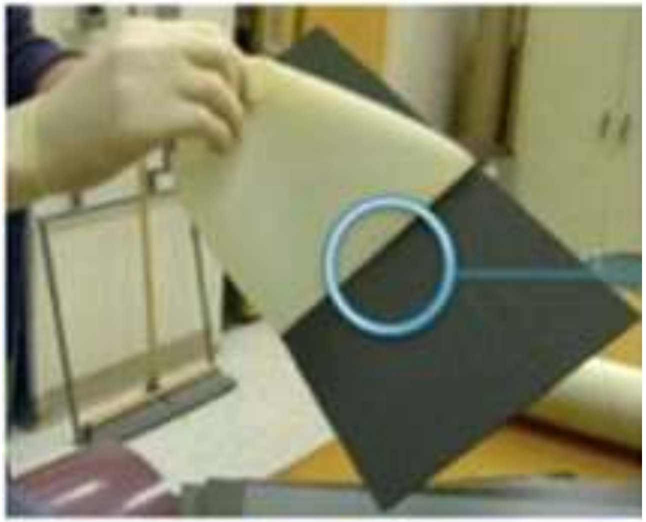
Factors affecting quality and consistency of plasma treatments for composite materials

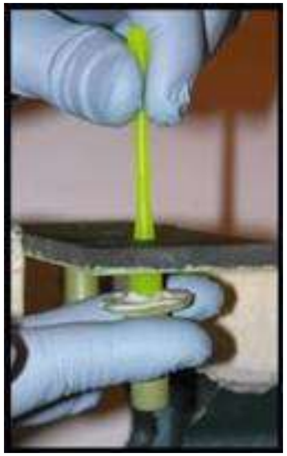
Automated surface treatment processes for aerospace composites

- Atmospheric pressure plasma treatment is a viable option for composite material surface preparation
- Plasma treatment affects a very limited depth: how do variations in incoming surface affect treated surface properties?
- Automated surface treatments have been successfully deployed in packaging, printing, and semiconductor manufacture for years
  - Highly automated operations: little handling
  - Substrate consistency is generally well controlled
  - Maintaining constant process parameters without feedback is frequently acceptable

Surface treatment processes for aerospace composites

- Aerospace bonding processes are still manual
- Implications for process control:
  - Variable out time prior to or after treatment due to process interruptions
  - Handling variance
  - Exposure to aerosol and contact contaminants



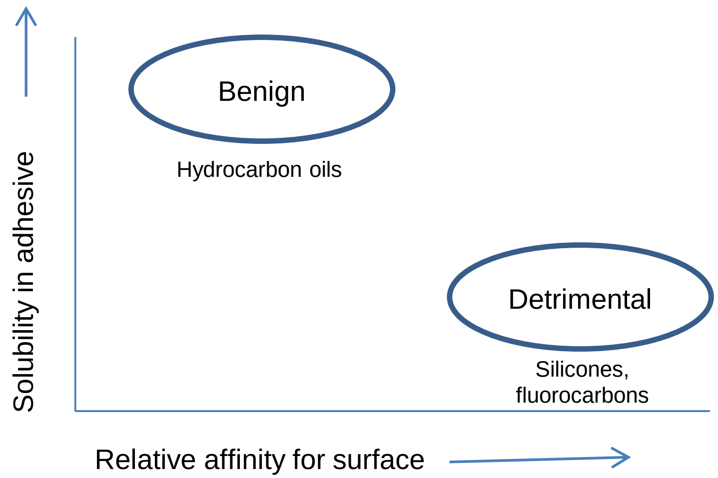


Surface treatment processes for aerospace composites

- How much variability in the composition of the surface prior to treatment can be tolerated?
  - ‘Variability’ can be variation in resin chemistry
  - Usually, variability = variability in the *bond surface* (e.g. amount of contamination, treatment level)
- Maintaining constant process parameters may not be sufficient to produce a consistent surface
  - Excessive variability in incoming material ≡ variability in treated surface
  - Process parameter monitoring (plasma power, gas flow, surface temp) does not inform surface state post-plasma

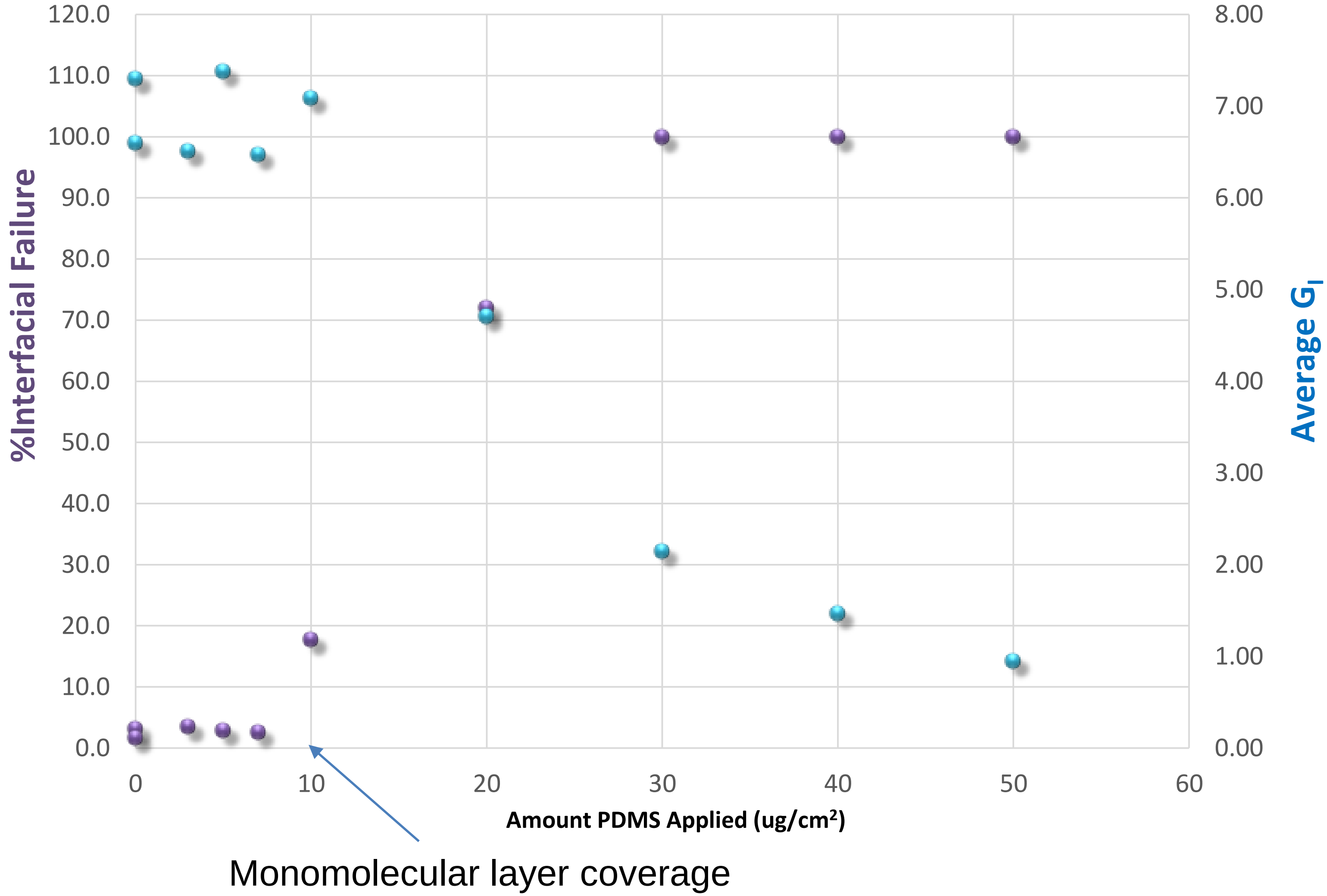
Characteristics of substances detrimental to adhesive bonding: contaminants

1. Presence in the environment
2. Affinity for the critical surface: will it adsorb to the substrate more strongly than the adhesive?
3. Solubility in the adhesive: will it tend to be absorbed and displaced?

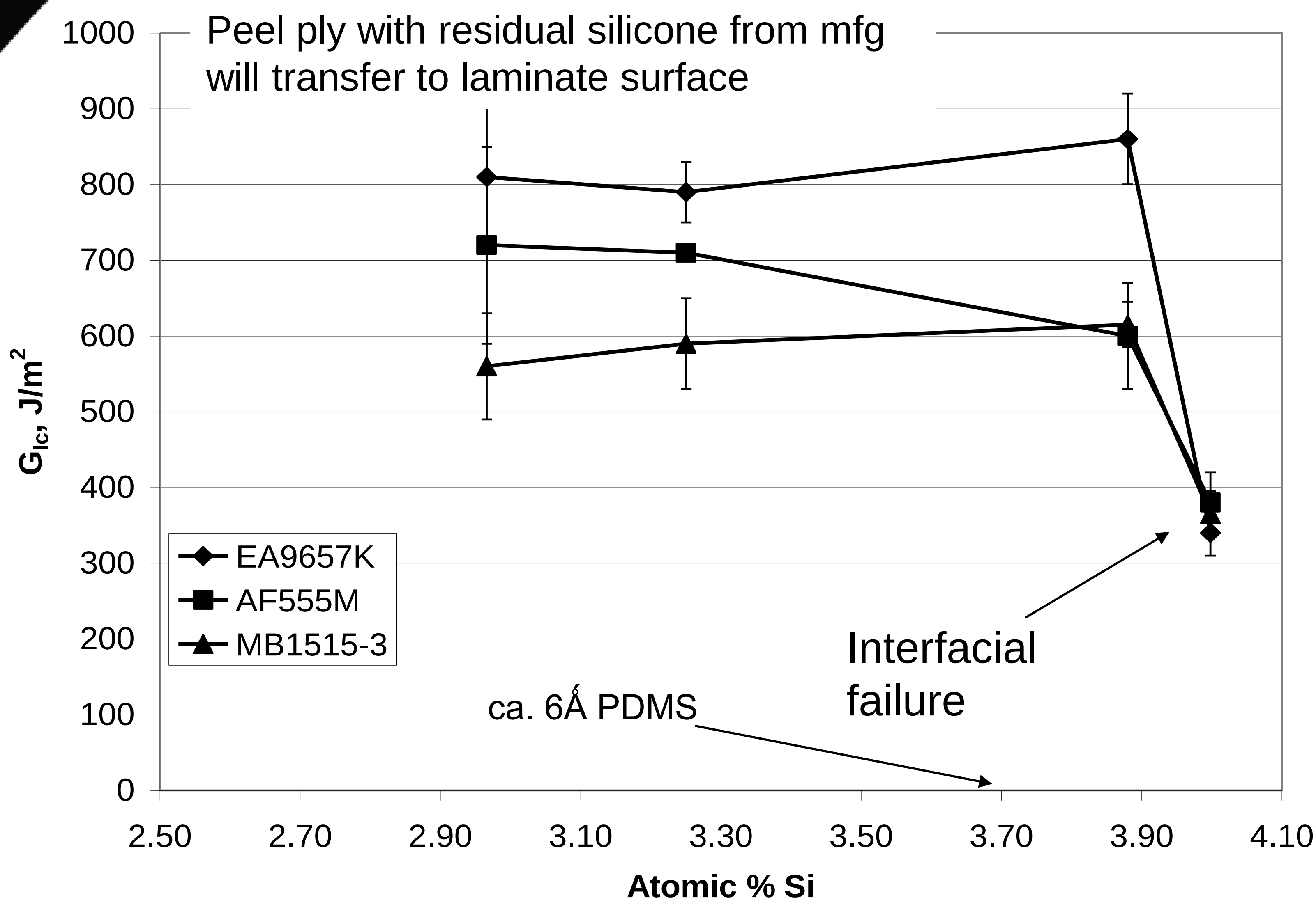


Many aerospace adhesive systems can tolerate a remarkable amount of organic contaminants ***except*** silicones

Effect of silicone contamination on fracture toughness and failure mode

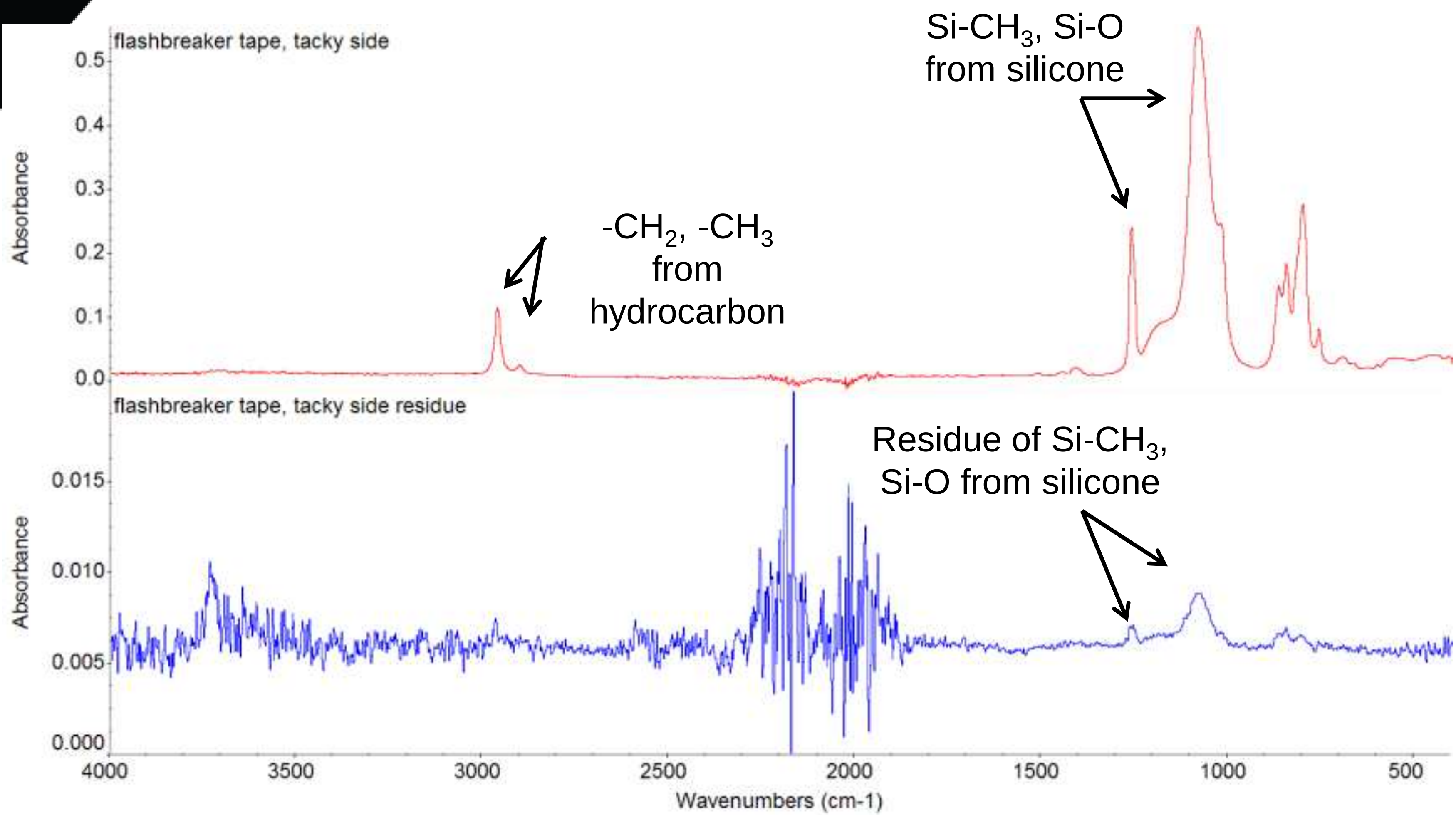


Intrinsic sources of silicone: peel ply

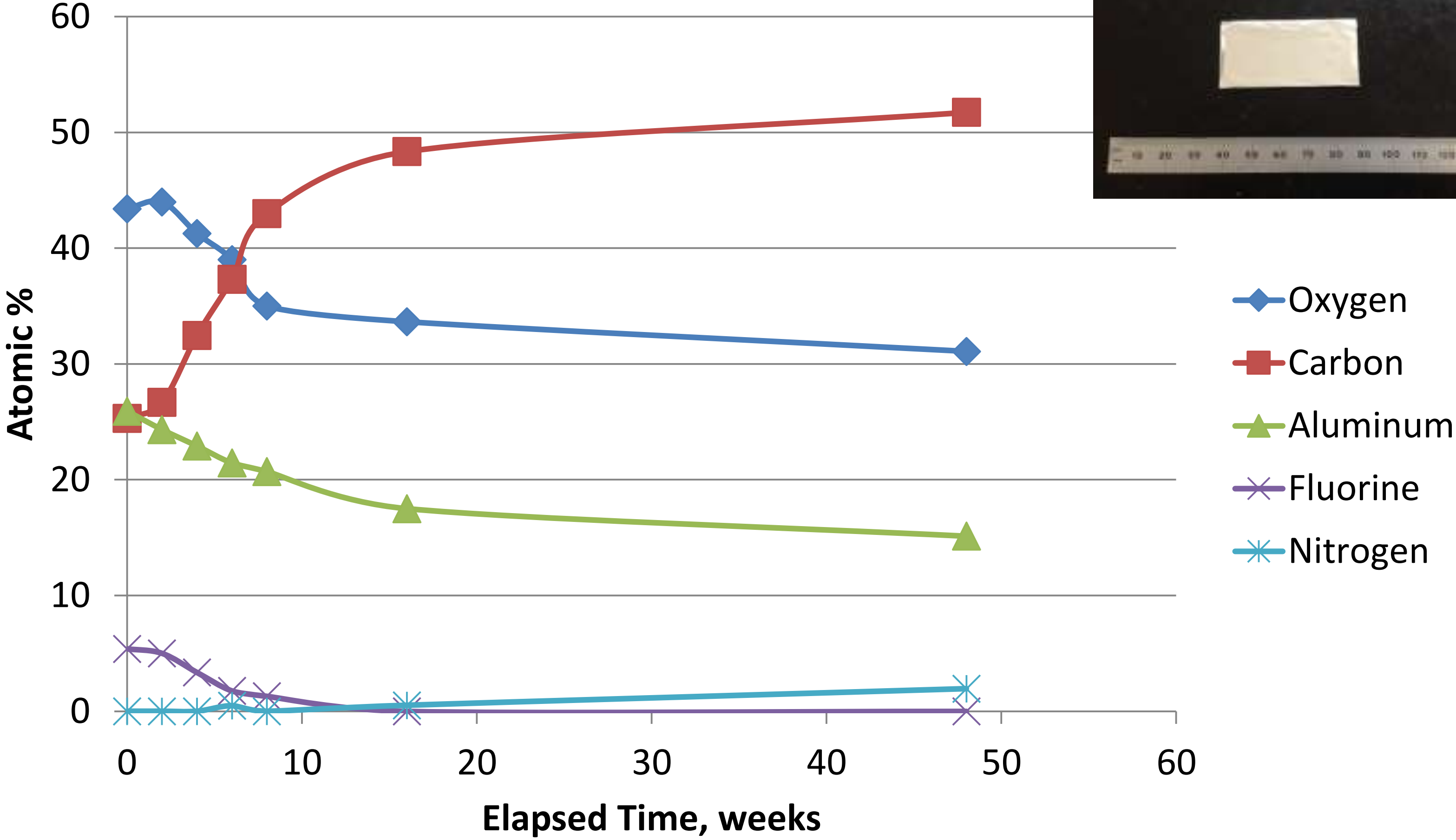


“Quantitative detection of peel ply derived contaminants via wettability measurements”, R.G. Dillingham, B.R.Oakley, P.J. Van Voast, P.H. Shelley, R.L. Blakley, C.B. Smith, J Adh Sci Tech. 26 1563–1571 (2012).

Extrinsic sources of silicone: shop supplies, PPE



Extrinsic sources of silicone: aerosol



Airborne contaminants: Mfg Area 1

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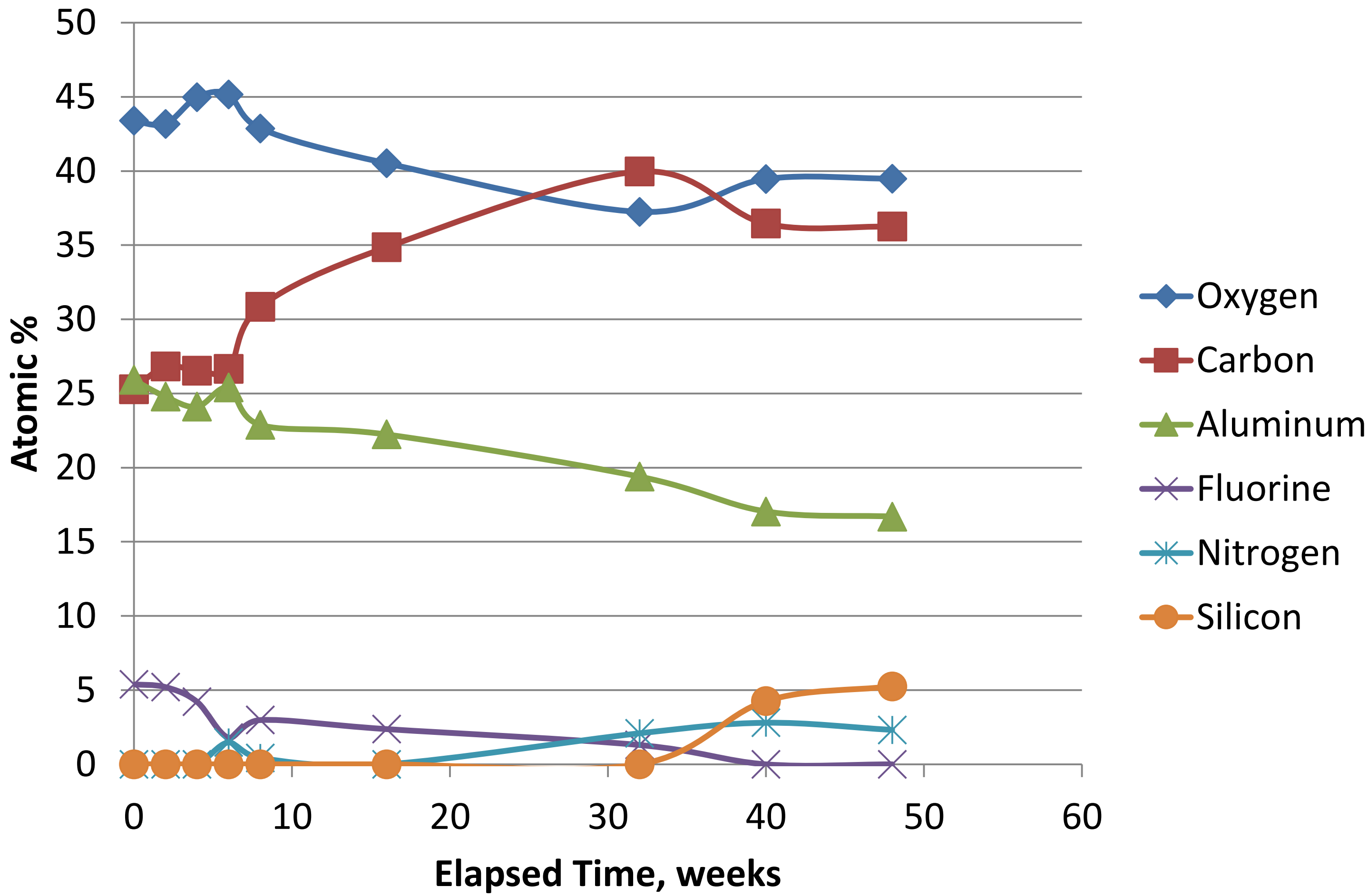
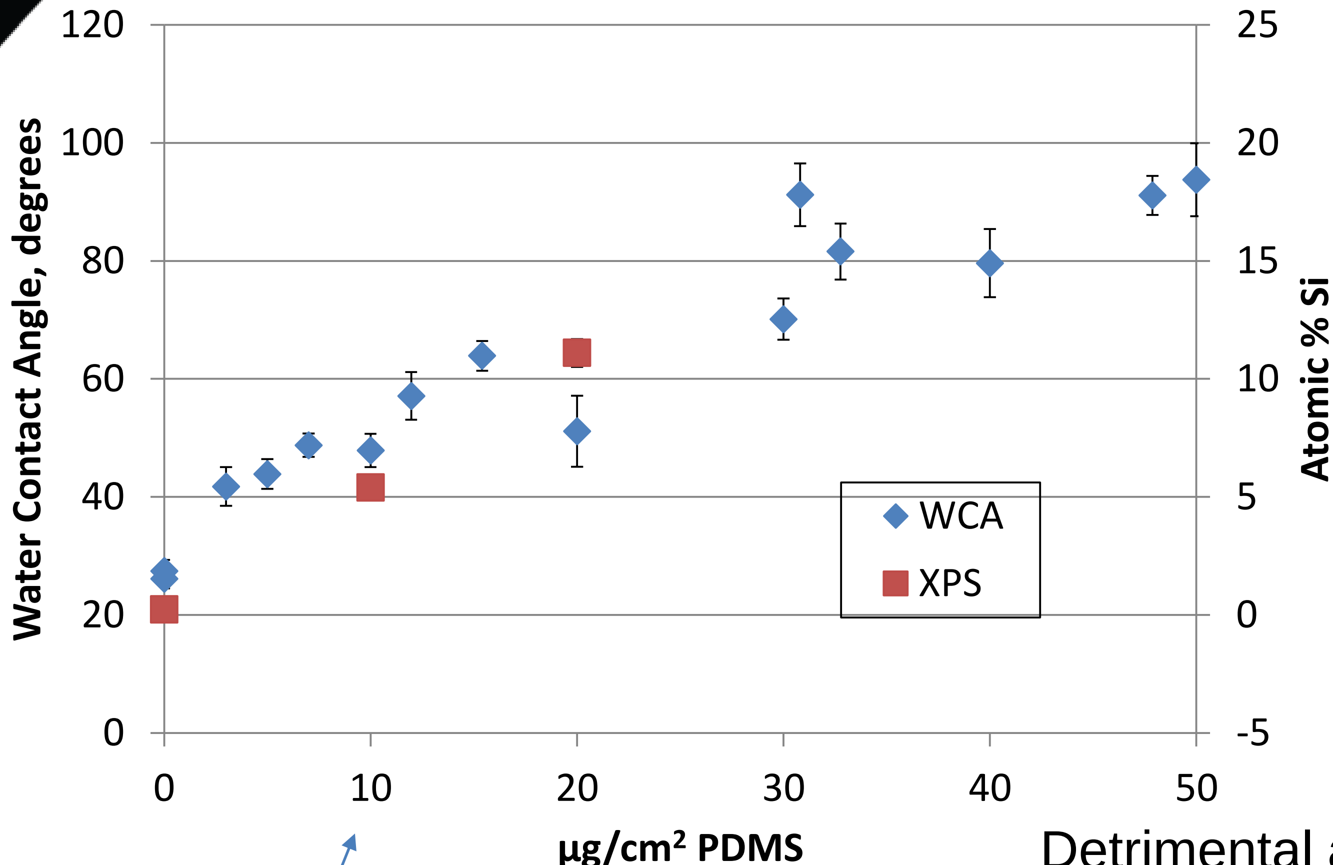
Extrinsic sources of silicone: aerosol



Airborne contaminants: Mfg area 2

Tramp silicone contamination is a reality, even in controlled environments

Quantifying Siloxane on Bond Surface

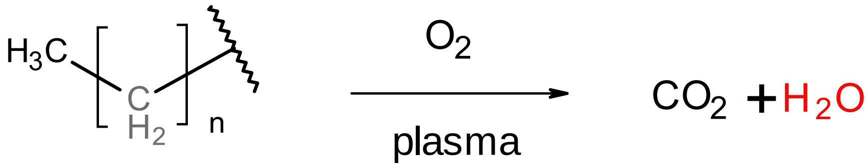


1-2 molecular layers (10µg/cm²)

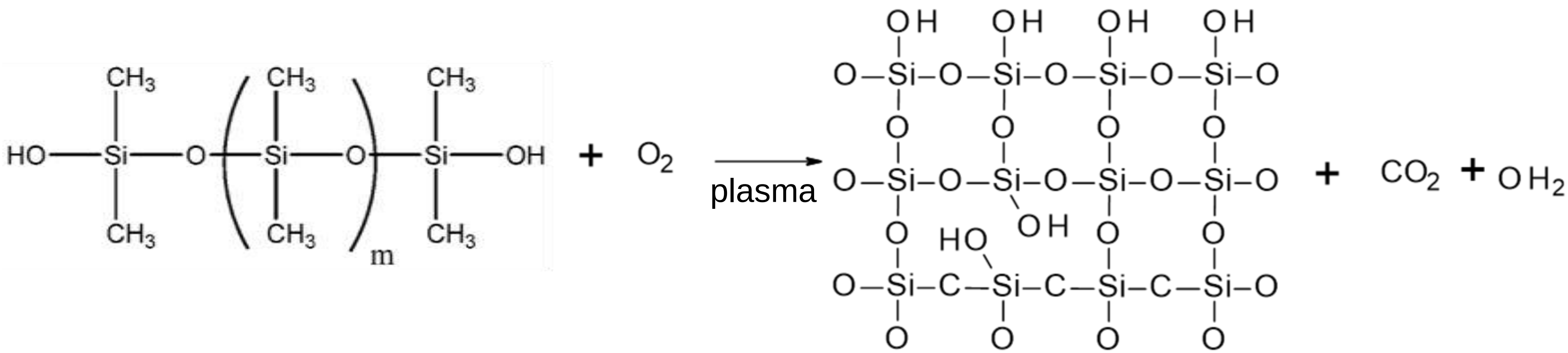
Detrimental amounts are detectable via:

- XPS
- LIBS
- Water contact angle

General contaminant response to plasma

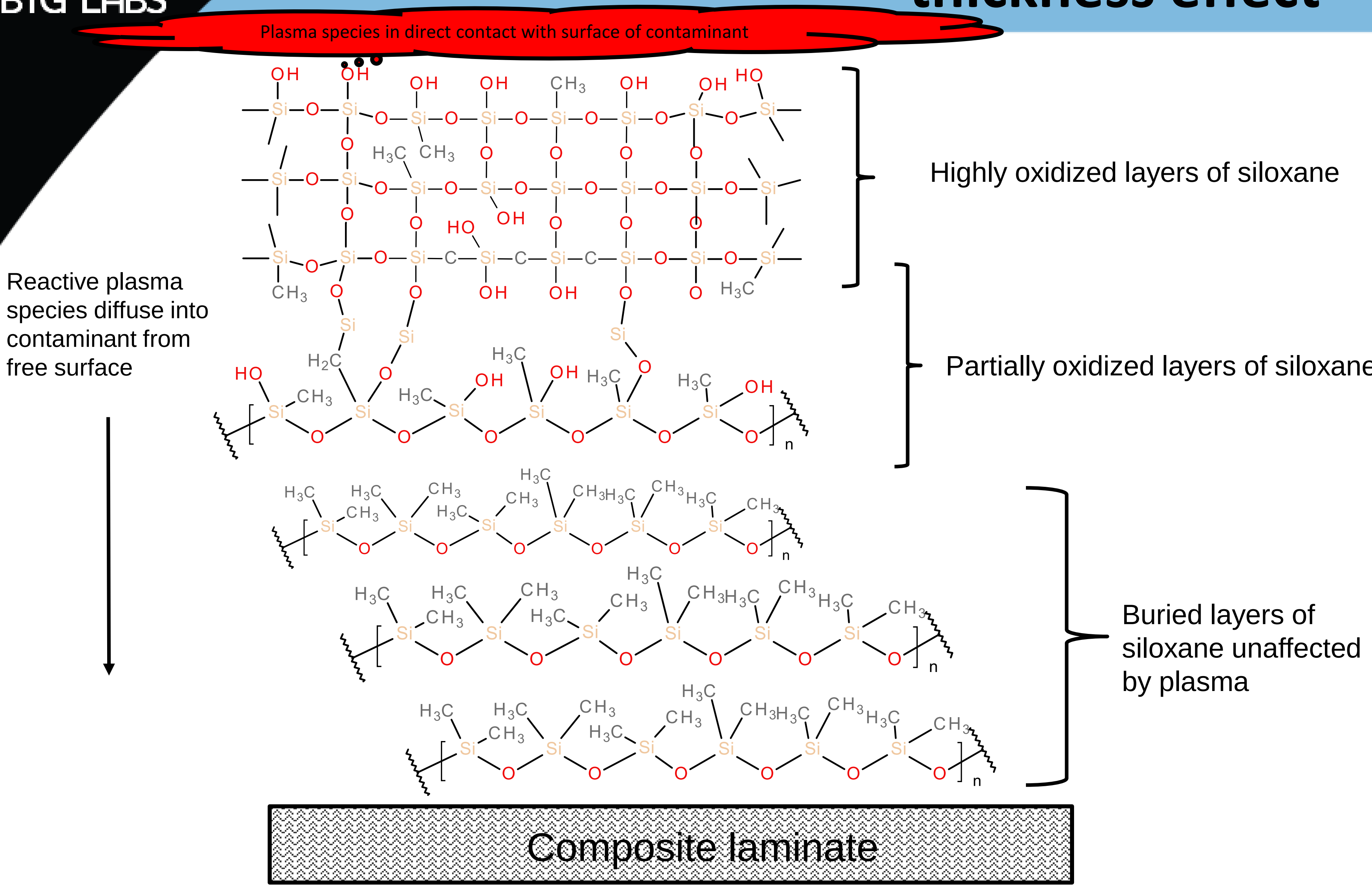


- Hydrocarbons oxidize to volatile species
- Rate of volatilization is independent of film thickness



- Siloxanes oxidize to silica + gases
  - silica can promote adhesion (sol-gel; silanes)
- Reaction proceeds from surface→interior
  - Rate is controlled by diffusion of gas phase species into and out of silica film
  - Rate rapidly diminishes to zero as reaction proceeds

Siloxane response to plasma: thickness effect



Remediation of silicone contaminated surfaces

- Silicones are the most detrimental contaminant identified
- Contamination of bond surfaces by silicones is a real possibility in manufacturing environments
- Existing inspection techniques can identify the presence of detrimental amounts on bond surfaces

- An effective composite treatment process must be able to accommodate the possibility of varying amounts of silicone contamination
  - How much silicone can be effectively inactivated via a particular atmospheric pressure plasma treatment?
  - If a surface is contaminated above this threshold, can it be remediated via
    - More plasma residence time, power, distance
    - Additional precleaning prior to plasma

Plasma treatment of silicone contaminated surfaces

Threshold level: 10 µg/cm² silicone + plasma treatment

2X threshold: 20 µg/cm² silicone + plasma treatment

- Small amounts of siloxane can be successfully remediated by atmospheric pressure plasma without resorting to process parameter adjustment
- What about larger amounts of silicone?

Essentially 100% cohesive failure

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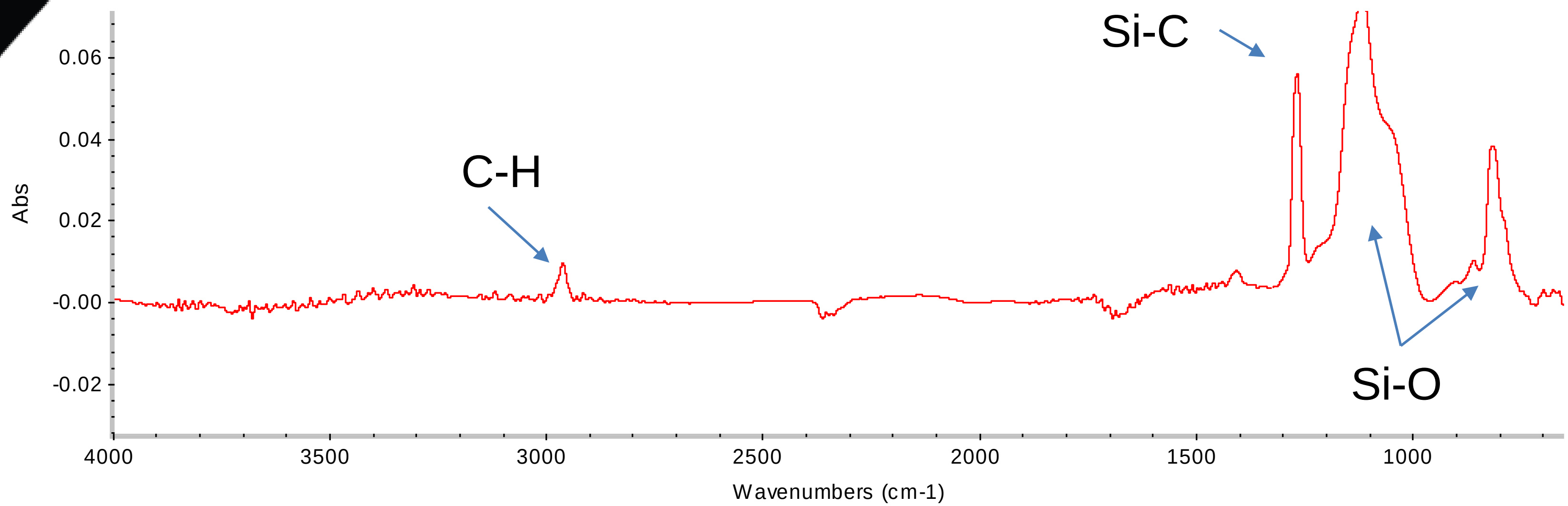
Remediation of siloxane contamination via plasma processes

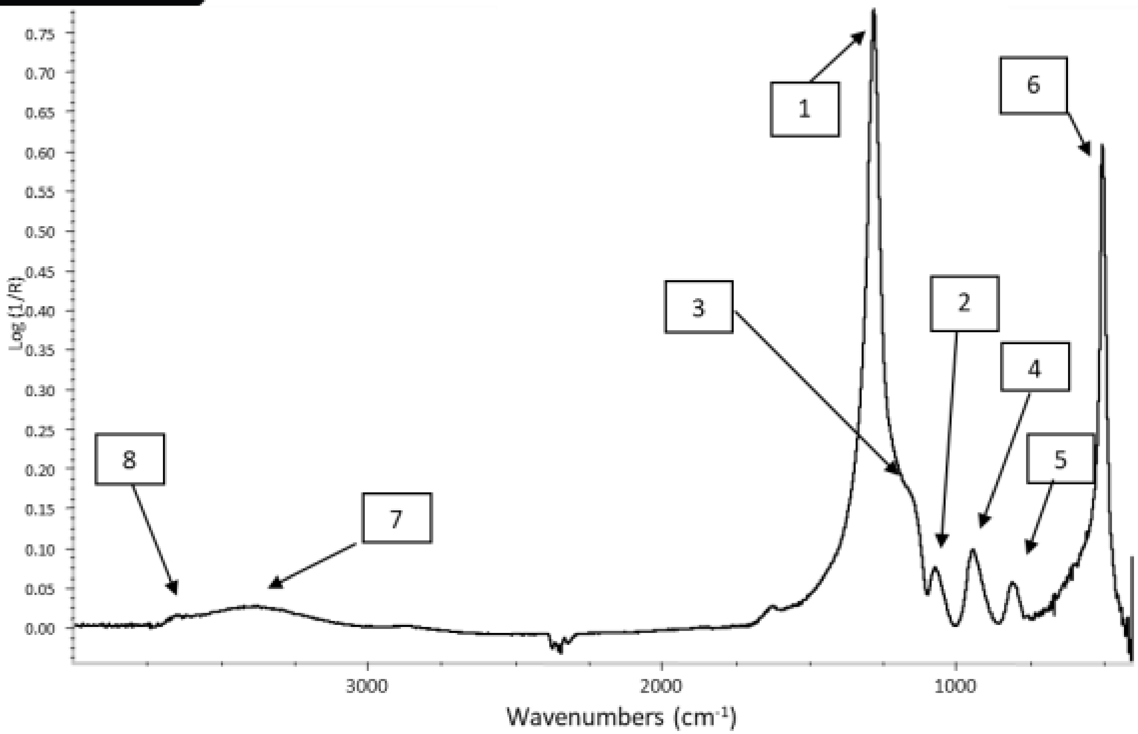
- Silicone mold release applied to chrome-plated steel coupons (ferrotype plate) for grazing angle reflection FTIR and water contact angle analysis
  - Absorbance proportional to film thickness
  - Spectral features provide chemical structural information
- Precleaning via solvent wiping
  - Pre-moistened IPA wipes
  - Bioact 105: aliphatic hydrocarbons + alcohol + citrus terpenes
- Effect of plasma on as-applied films
- Effect of plasma on precleaned surfaces
- Strategies for effective process monitoring

Grazing angle FTIR of silicone



- Relatively simple FTIR spectrum
- 1275 cm^{-1} Si-C mode is diagnostic of organosilicone
- Grazing angle technique approaches monolayer sensitivity

Grazing angle FTIR of plasma polymerized silica

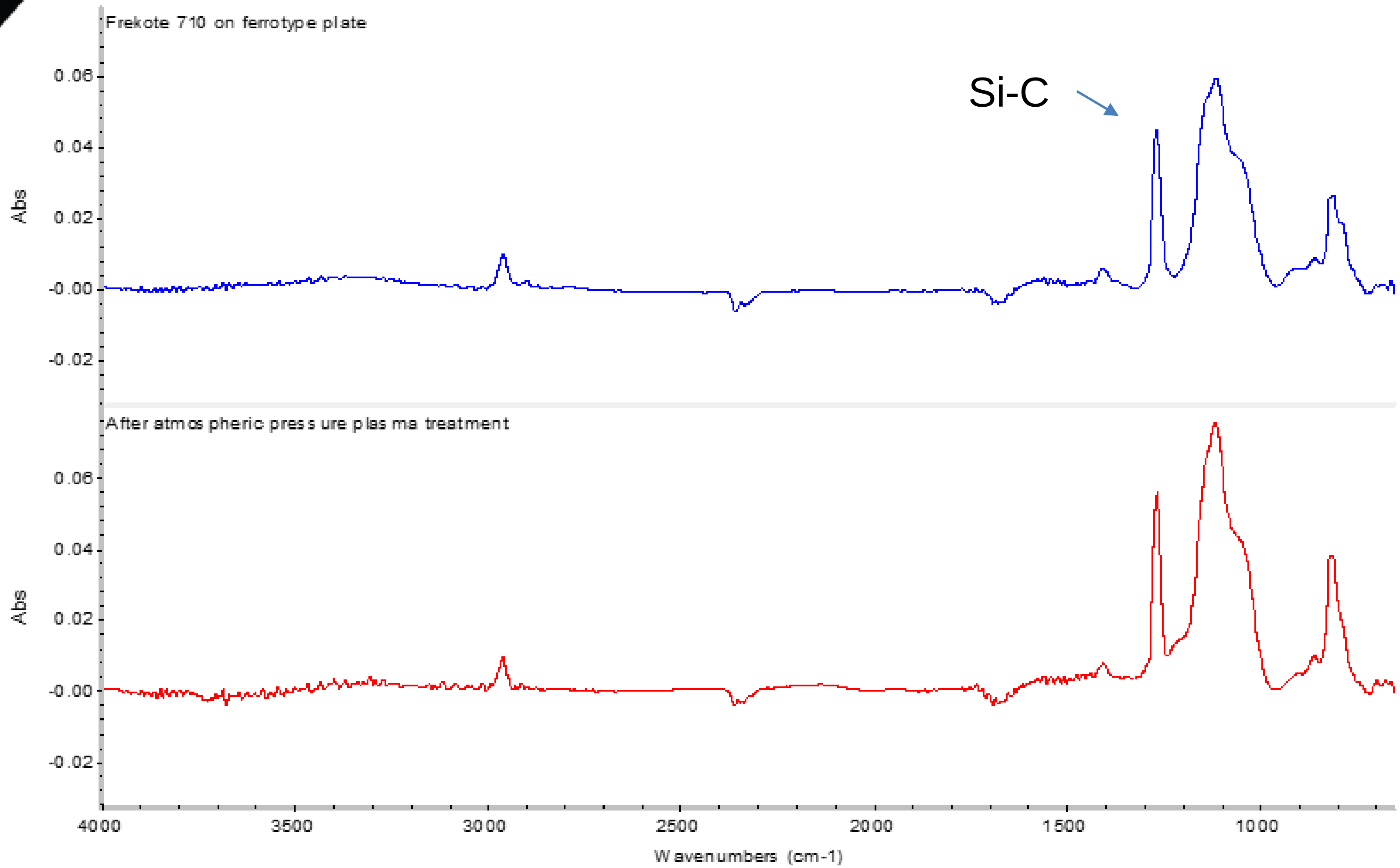


Band ID	cm^{-1}	Assignment
1	1250	Si-O-Si asymmetric stretch (AS1), LO mode
2	1075	Si-O-Si asymmetric stretch (AS1), TO mode
3	1180	Si-O-Si asymmetric stretch (AS2), TO + LO modes
4	945	Si-O stretch, non-bridging oxygen
5	502	Si-O-Si rocking
6	810	Si-O-Si symmetric stretch
7	3350	O-H stretching, adjacent H-bonded
8	3600	O-H stretching, isolated

- Complex FTIR spectrum due to vibrational modes associated with network formation (TO, LO vibrations) and network defects
- Conversion of silicone to silica via plasma is readily and quantifiably detectable via FTIR

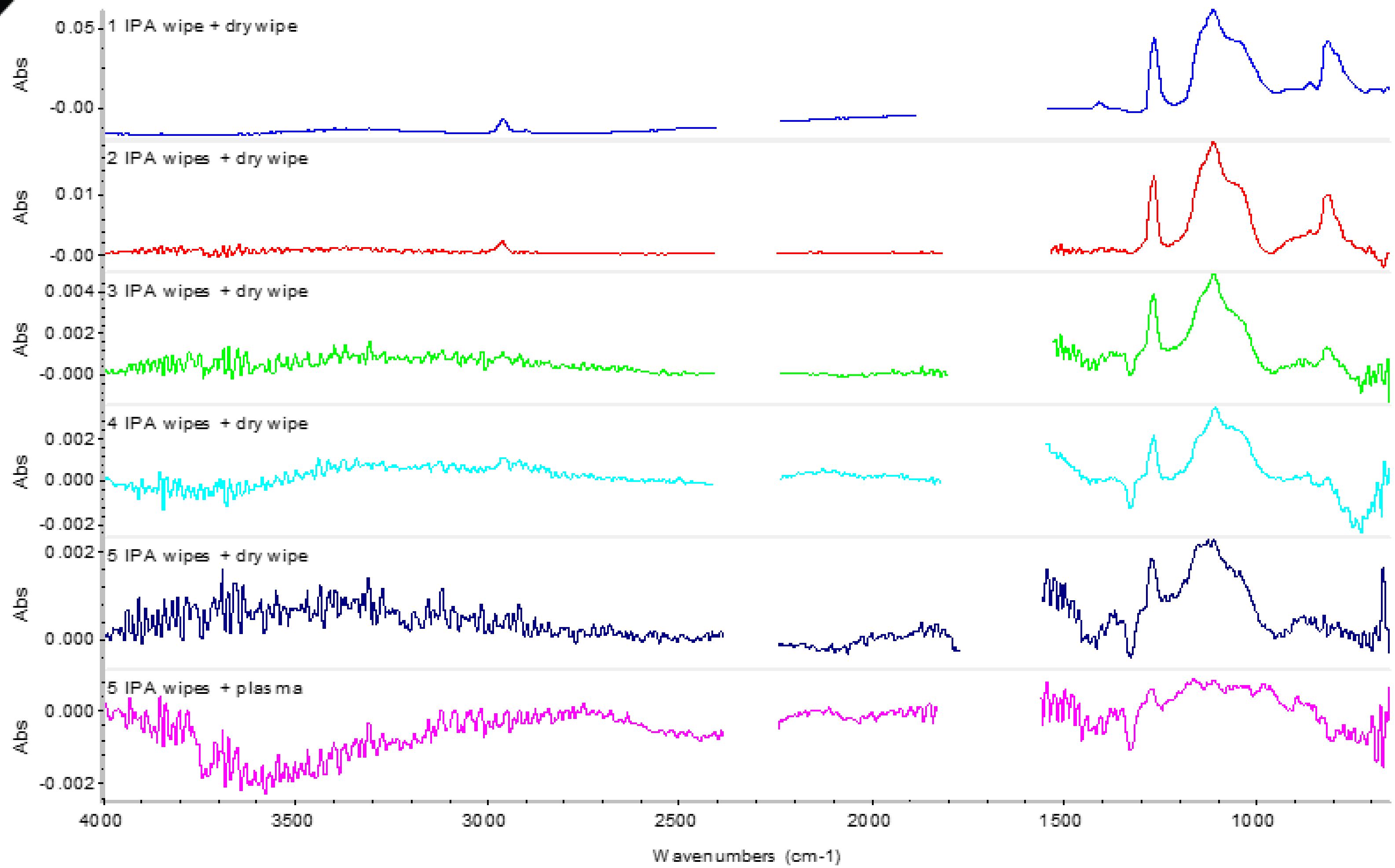
“Effect of Deposition Conditions on Structure and Properties of Plasma-polymerized Silica Primers”, R.G. Dillingham, Journal of Adhesion 84 (8) 702-724 (2008).

Plasma treatment of thick siloxane film



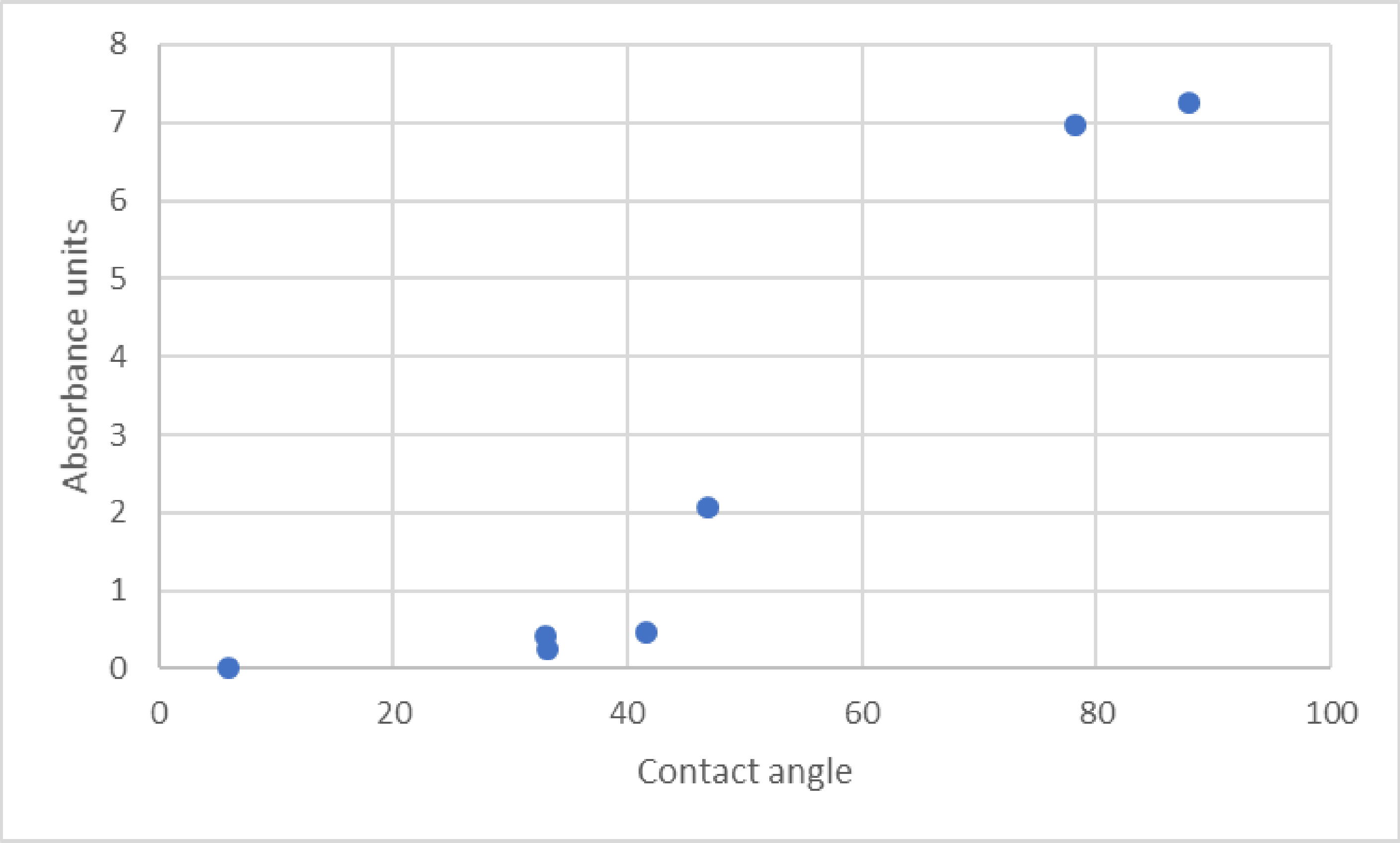
No discernible effect on spectrum

Effect of solvent precleaning



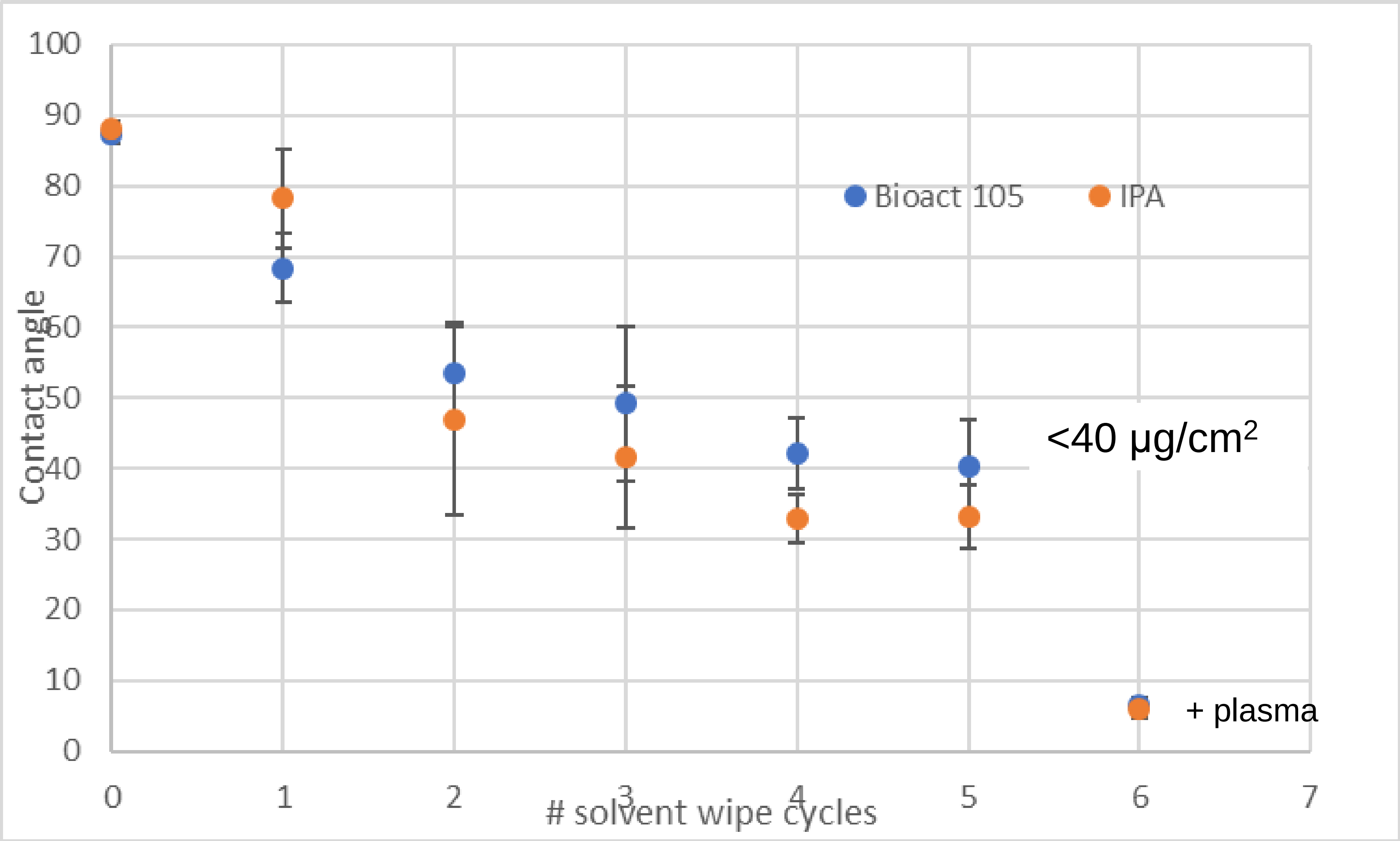
~25X reduction in film thickness due to solvent cleaning; plasma appears to be effective on precleaned surface

Monitoring precleaning process via water contact angle measurement



- Rapid contact angle measurements quantify amount of silicone on surface prior to plasma treatment

Monitoring precleaning process via water contact angle measurement



Solvent precleaning appears to have removed sufficient contaminant to allow successful plasma treatment

Conclusions

- Atmospheric pressure plasma treatment is a viable option for composite material surface preparation
- Due to the potential for variability in the surface of material entering the process zone, simply ensuring consistent process parameters may not be sufficient to ensure product quality
- Process control needs to account for the variable state of material entering the process zone
- Monitoring and controlling pre-plasma surface properties needs to be an integral part of process specification