

# Formulating waterborne coatings for corrosion protection

**Chi Him Lo**

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**Academic supervisors:**

Dr Lee Fielding and Prof Stuart Lyon

**Industrial supervisor:**

Dr Bob Luigjes

**SUSTICOAT coordinator:**

Dr Simon Gibbon

# Overview

- Introduction: Waterborne metal coatings and associated formulation challenges
- Part 1: Preparation and testing of model coating formulations using styrene-acrylic latices with varying  $T_g$
- Part 2: Effect of organosulfur surfactant on corrosion protection properties and microstructure development
- Conclusions



# Waterborne coatings for steel protection

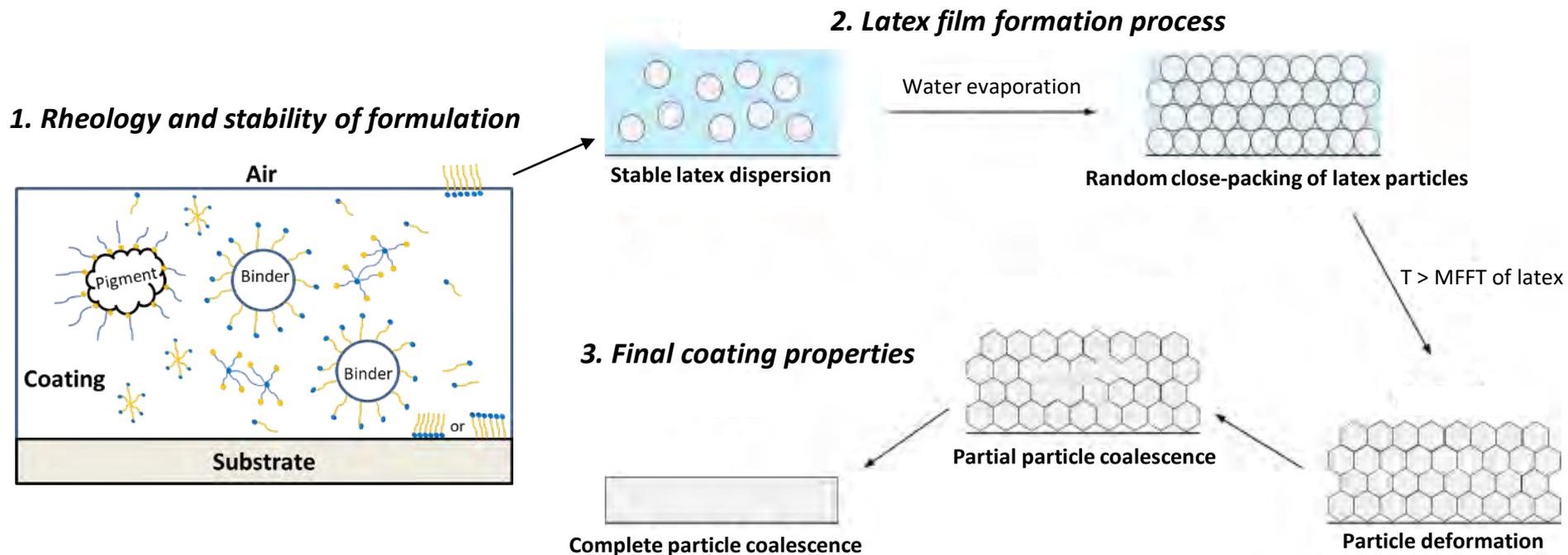
- Decorative metal coatings are gradually shifting from solventborne systems toward one component waterborne systems
- **Main advantages of waterborne coatings:**
  - ✓ Lower toxicity, odour, flammability and VOC emission
  - ✓ Water as the main dispersion medium -> easier to dilute and clean



- **Performance requirements:**
  - I. Adhere to steel during service time
  - II. Provide protection against atmospheric corrosion
  - III. Good aesthetic properties (e.g. low haze, high gloss and good hiding power)

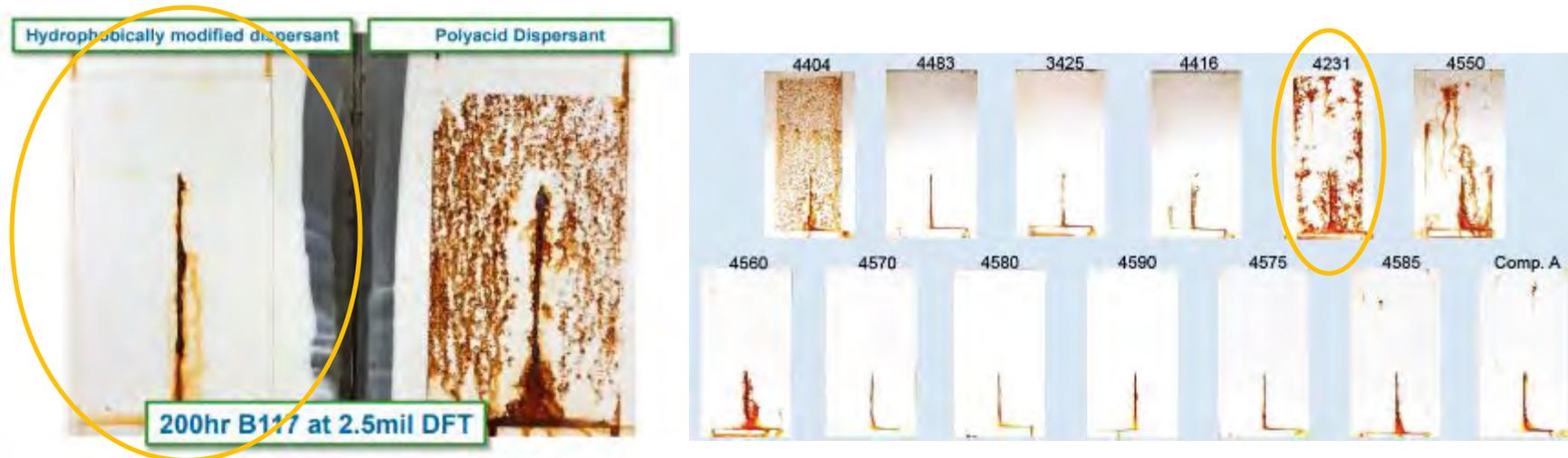
# Drying process and latex film formation

- Drying and film formation of aqueous colloidal dispersion is complex
- Attainment of a coherent and defect-free coating is essential for achieving good protective properties
- Surfactants and additives can influence formulation properties, film-forming properties and final coating properties



# Challenges in formulating waterborne metal coatings

- Change in one ingredient can have detrimental effect on corrosion protection properties



- Hydrophobic additives** are often claimed to reduce water sensitivity and good for corrosion protection – *but this is not always the case*
- Better understanding on how surfactant additives affect coating microstructure development and corrosion protection properties is required

C. LeFever, presented in part at the UL Prospector Webinar, online, August, 2018

R. Erhardt and S. Oestreich, presented in part at the European Coatings Show 2015, Nuremberg, April, 2015

# Formulating model waterborne coatings

- Emulsifier stabilised styrene-acrylic latices with similar compositions but varying  $T_g$  (measured  $T_g$  from DSC = 43, 59 and 71 °C) were used without purification
- Formulation additives are used to prevent common film defects:
  - I. Neutralising agent – adjust pH to 9 for processing and storage stability
  - II. Flash rust inhibitor – prevent flash rust of metal during coating application and curing
  - III. Defoamer – eliminate foaming to ensure continuous film formation
  - IV. Coalescing agent – lower the minimum film formation temperature to 10 °C
  - V. Thickener – improve flow and achieve sufficient film thickness
- Coatings with dry film thickness  $\sim 50 \mu\text{m}$  were applied and cured under ambient conditions for 7 days

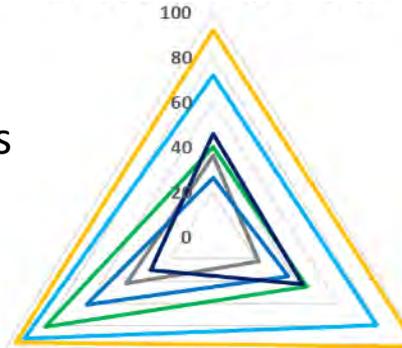


# Part 1: Preparation and testing of model coating formulations using styrene-acrylic latices with varying $T_g$

## Effects on surface properties

- No significant difference in gloss

Coating with  $T_g$ -43 latex



- Higher  $T_g$  coating has higher König hardness and water contact angle

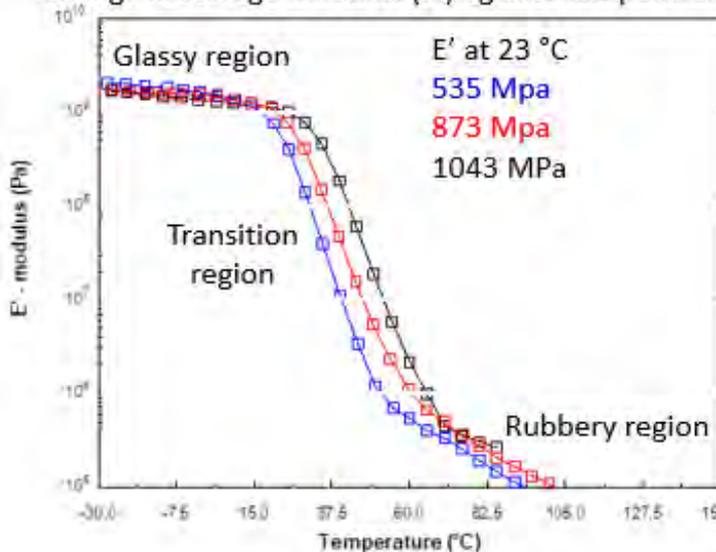
Coating with  $T_g$ -71 latex

Coating with  $T_g$ -58 latex

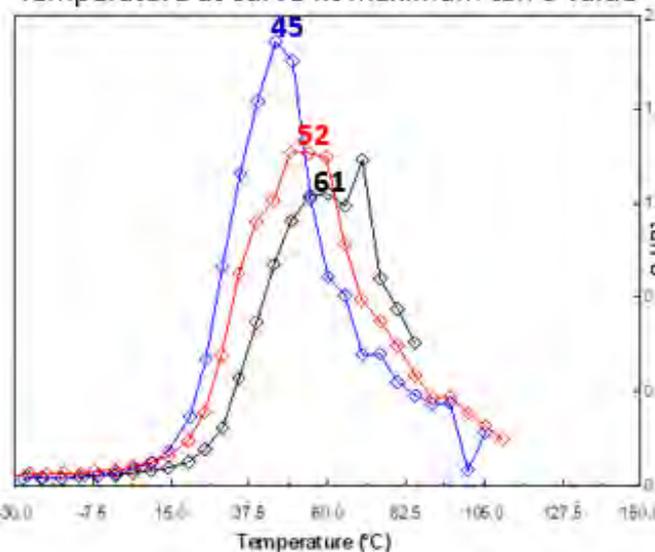
— Haze (HU) — Gloss (GU) — Pendulum hardness (s) —  $\theta_a$  (°) —  $\theta_r$  (°) — Hw (°)

## Effects on mechanical properties

Change in storage modulus ( $E'$ ) against temperature



Temperature at curve fit maximum  $\tan \delta$  value

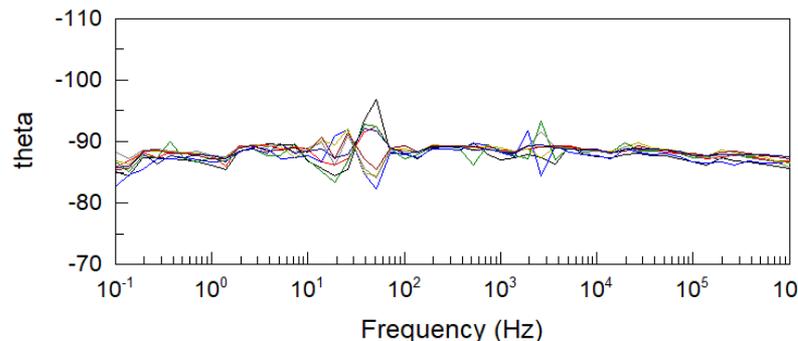
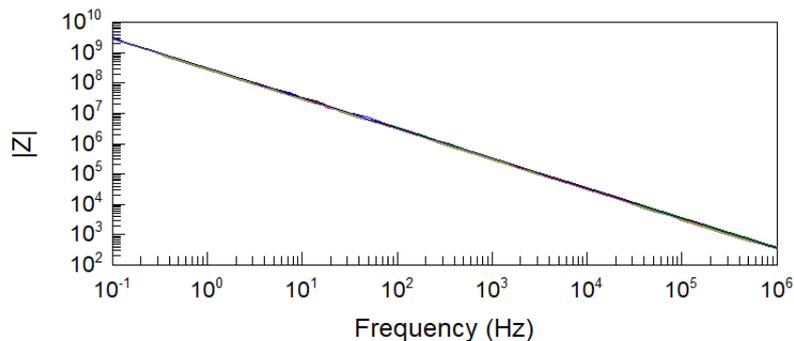


Storage modulus is related to the stiffness of the coating

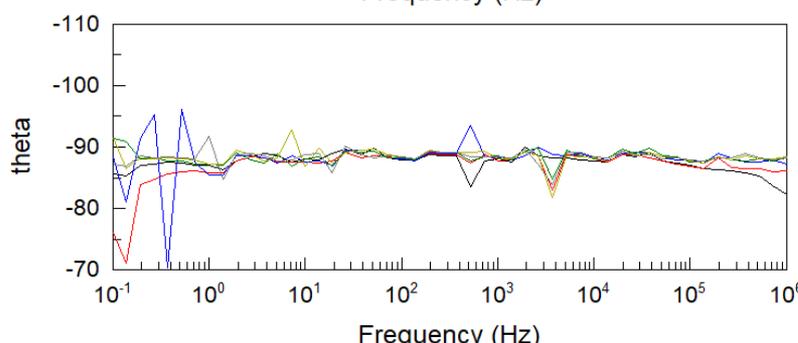
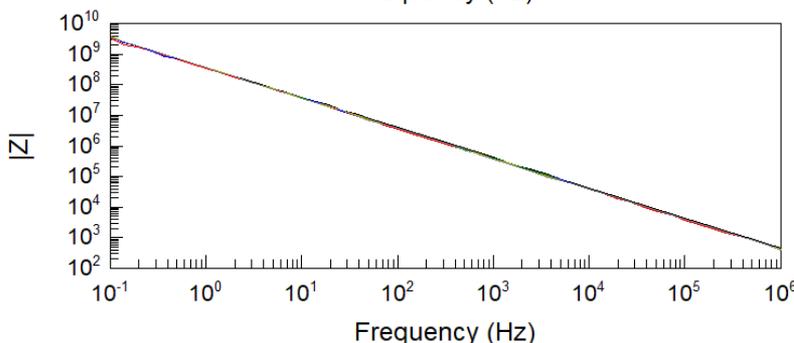
Tan  $\delta$  is the ratio of viscous to elastic response and an indication of the damping efficiency

# Effects on ionic barrier properties

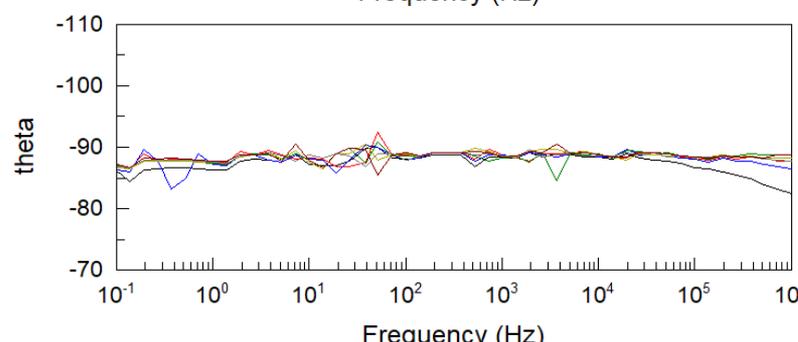
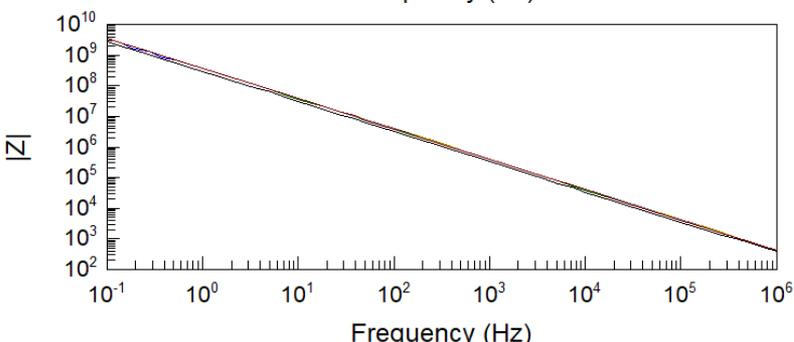
Electrochemical impedance spectroscopy (EIS) analysis of coated CRS panels immersed in 0.5M NaCl at RT for 7 days (exposed area = 3.14 cm<sup>2</sup>)



T<sub>g</sub>-43 coating



T<sub>g</sub>-58 coating



T<sub>g</sub>-71 coating

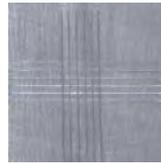
Good ionic barrier properties with impedance values over 10<sup>9</sup> Ω at 0.1 Hz

# Effects on adherence to steel and corrosion protection properties

- Cross-cut tests (ISO 2409) were performed before exposure to evaluate the separation resistance of coatings from cold rolled steel (CRS)

$T_g$ -43 and  $T_g$ -58 coatings:

GT0 after 1 day  
GT0 after 3 days  
GT0 after 7 days



GT0



GT5

$T_g$ -71 coating:

GT5 after 1 day  
GT4 after 3 days  
GT2 after 7 days

Higher  $T_g$  -> reduced adherence at RT

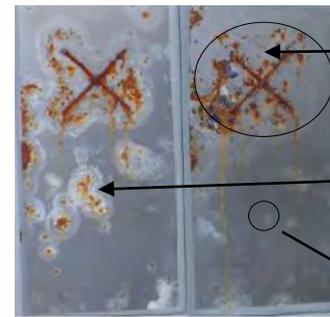
- Prohesion tests (ASTM G85 Annex A5) were performed and coatings were assessed after exposure for 750 hours



$T_g$ -43 coating



$T_g$ -58 coating



$T_g$ -71 coating

Severe corrosion propagation near scribed area

Corrosion in the coating body

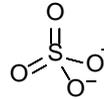
Small blistering

Higher  $T_g$  coating with good barrier properties  $\neq$  better in corrosion protection performance

# Part 2: Study with organosulfur surfactants

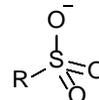
- Four surfactants with characteristic IR peaks in the 1000-1210  $\text{cm}^{-1}$  region were chosen:

I. Surfactant A with sulphate group



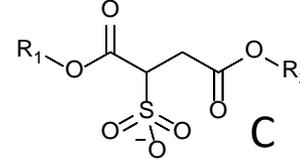
A

II. Surfactant B with sulphonate group



B

III. Surfactant C with sulphosuccinate group (more hydrophobic)



C

IV. Surfactant D: polymeric surfactant

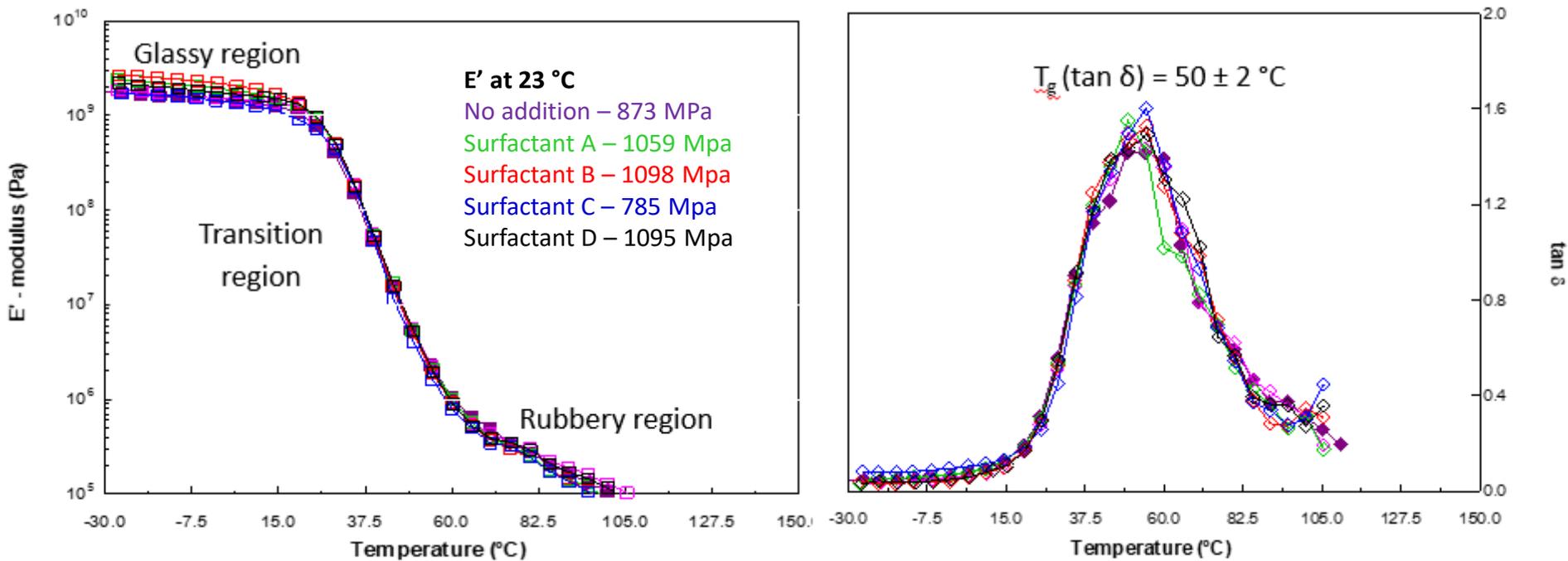
- Above 2.6 wt. % surfactant in the model coatings lead to discontinuous films with premature coating failures
- T<sub>g</sub>-58 coatings containing different organosulfur surfactants at 1.3 wt. % and 2.6 wt. % in dry films were assessed

Key questions to be answered:

1. How addition of organosulphur surfactant affects corrosion protection performance and microstructural development?
2. Is hydrophobic surfactant better for corrosion protection than hydrophilic surfactant?

# Influence of 1.3 wt % surfactant on performances of $T_g$ -58 coating

- Appearance: Minimal visible defects with  $20^\circ$  GU =  $98 \pm 1$  and haze =  $22 \pm 3$
- König hardness:  $40 \pm 5$  seconds
- All achieved GT0 in cross-cut tests before exposure



No significant change in surface properties, mechanical properties and adherence to steel

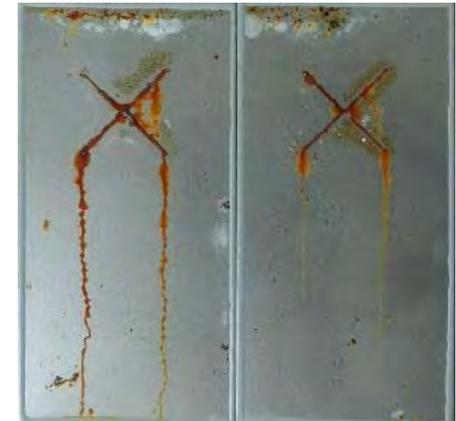
# Influence of 1.3 wt% surfactant on corrosion performance after 750 hours exposure



No surfactant addition



Surfactant D



Surfactant A

- Surfactant C is most hydrophobic based on hydrophobic-lipophilic balance (HLB) value
- But most severe performance deterioration with surfactant C



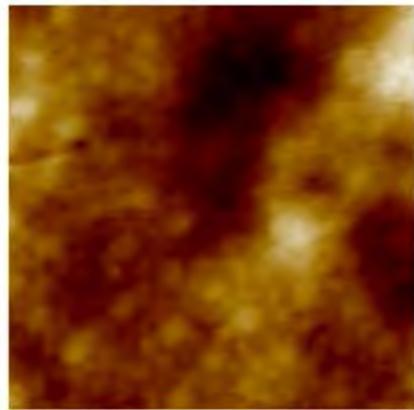
Surfactant B



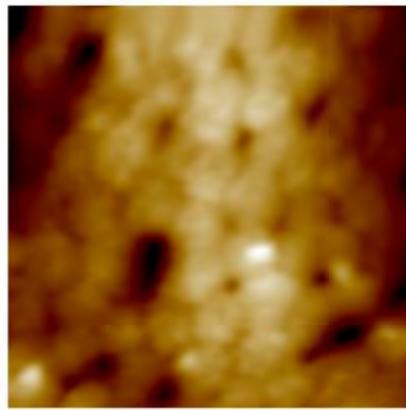
Surfactant C

# Influence of 1.3 wt. % surfactant on surface microstructure

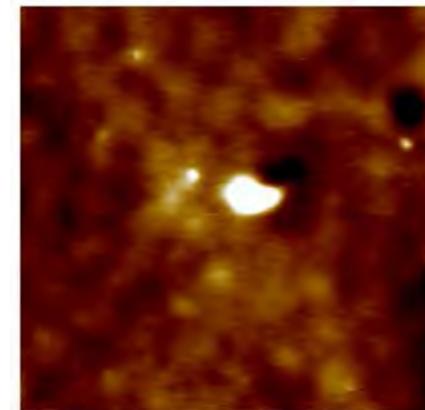
1  $\mu\text{m}$  x 1  $\mu\text{m}$  AFM height images before prohesion



Height 200.0 nm  
No surfactant addition

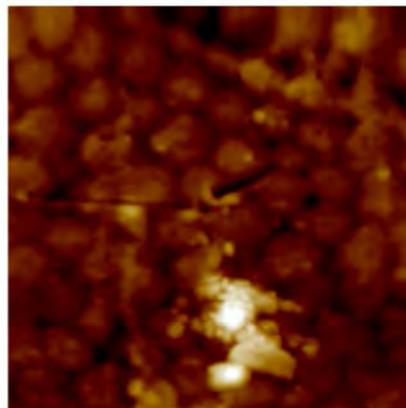


Height 200.0 nm  
Surfactant D

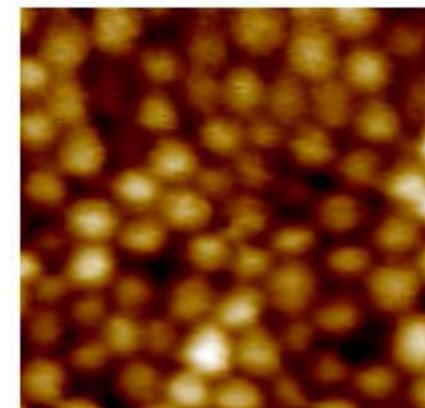


Height 200.0 nm  
Surfactant A

Deterioration in performance may be associated with surfactant suppressing particle coalescence

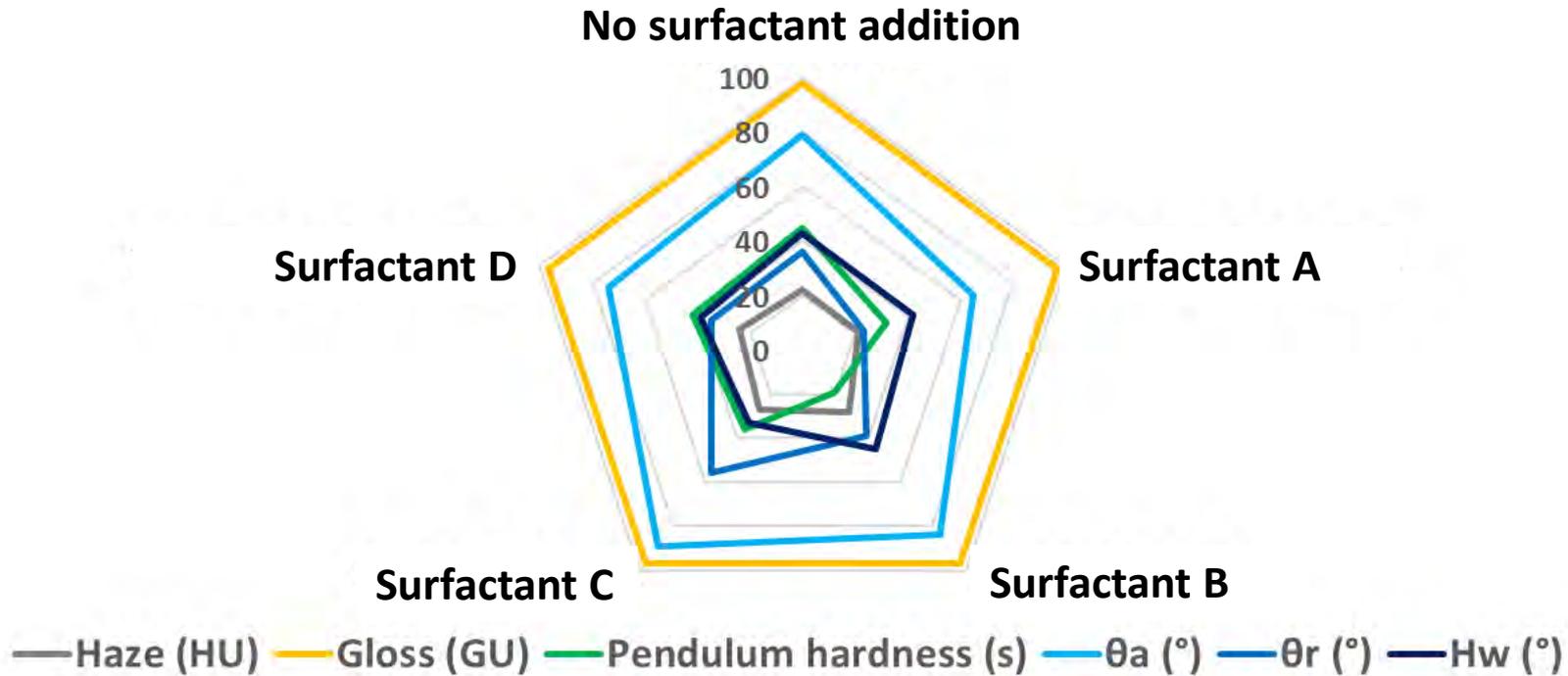


Height 200.0 nm  
Surfactant B



Height 200.0 nm  
Surfactant C

# Influence of 2.6 wt % surfactant on surface properties of T<sub>g</sub>-58 coating



No significant change in gloss and haze

Significant changes in surface hydrophobicity by adding different surfactants,

More hydrophilic surfactant -> lower contact angle

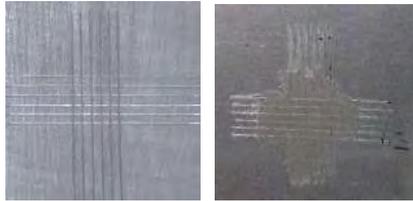
More hydrophobic surfactant -> higher contact angle

# Influence of 2.6 wt% additional surfactant on corrosion protection performances

Cross-cut test (ISO 2409)  
before prohesion

Good adherence – GT0

Good adherence – GT0



GT0

GT5



No surfactant addition  
after 750 hours



Surfactant D  
after 750 hours

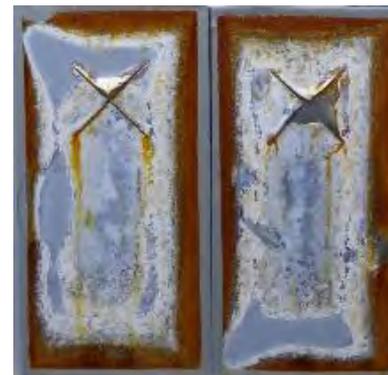
Images after  
prohesion  
exposure

Addition of excess  
surfactant can reduce  
adherence to steel and  
corrosion protection  
performance  
significantly

Poor adherence - GT5



Surfactant A  
after 70 hours



Surfactant B  
after 70 hours



Surfactant C  
after 260 hours

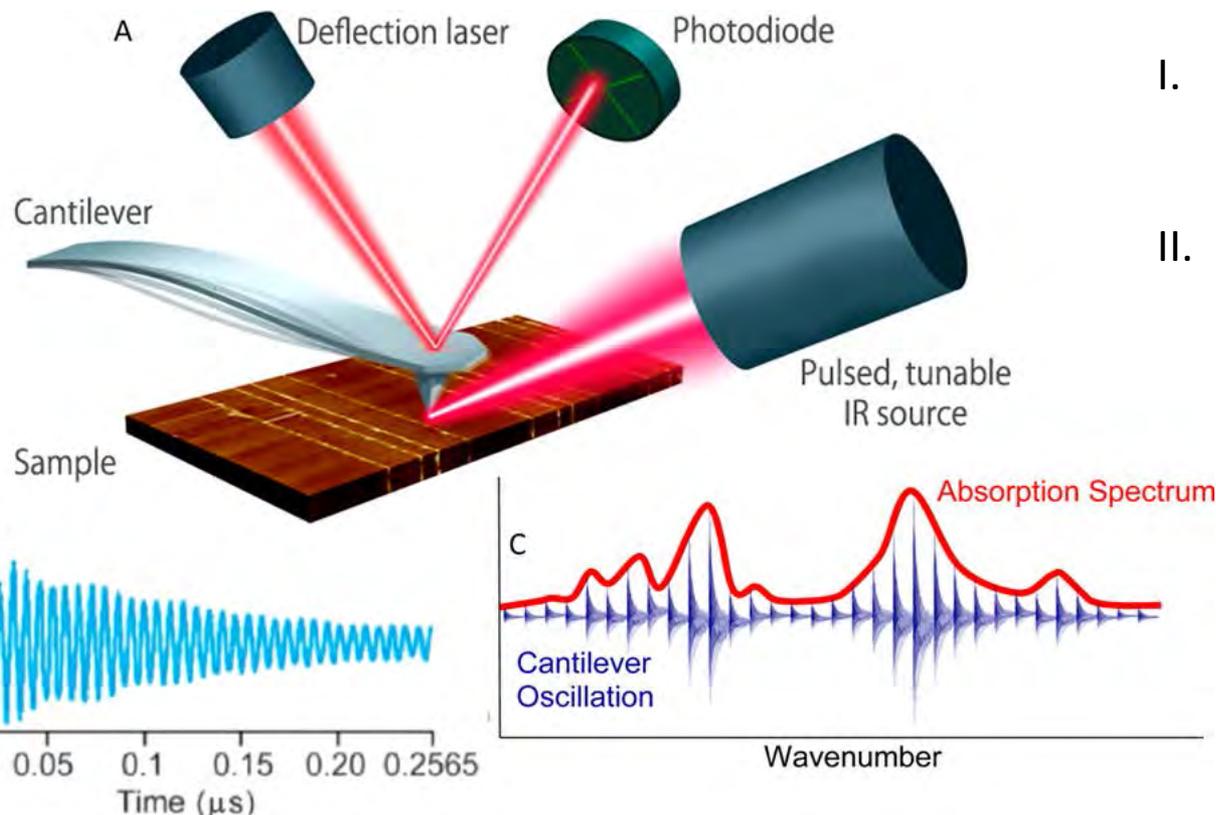
# Nanoscale structural and chemical analysis with AFM-IR spectroscopy

## Hybrid technique:

- I. Infrared spectroscopy and mapping for chemical analysis
- II. Imaging with spatial resolution of atomic force microscopy (nm scale)

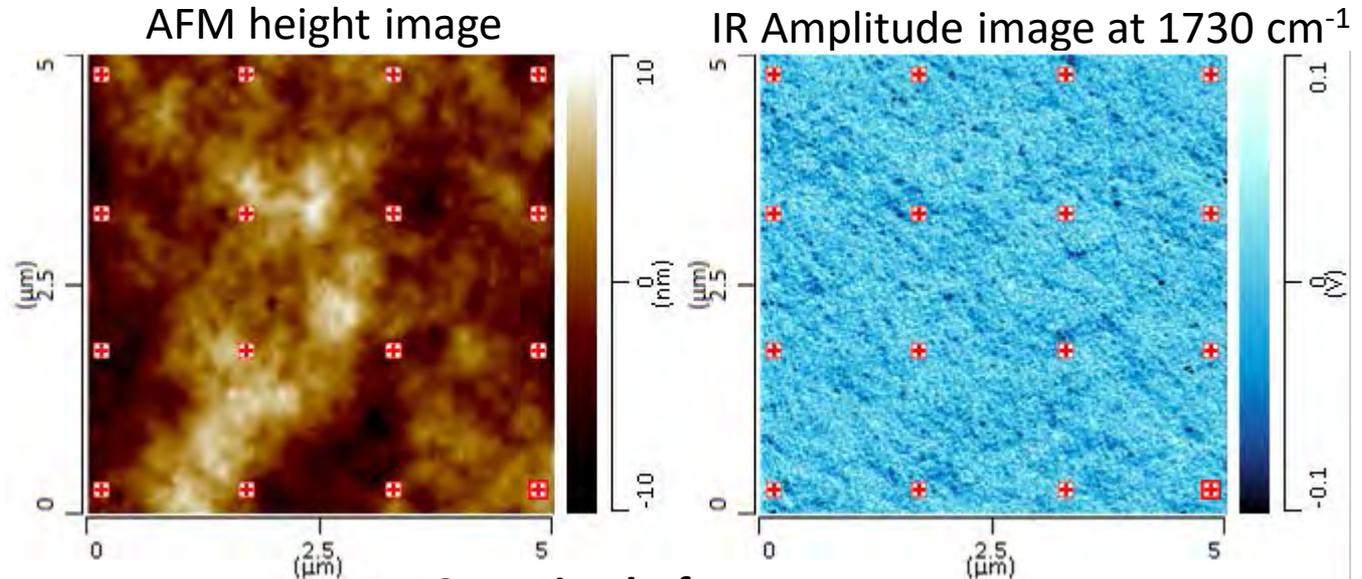
## Principle:

- Locally detect thermal expansion in a sample by infrared radiation using AFM probe



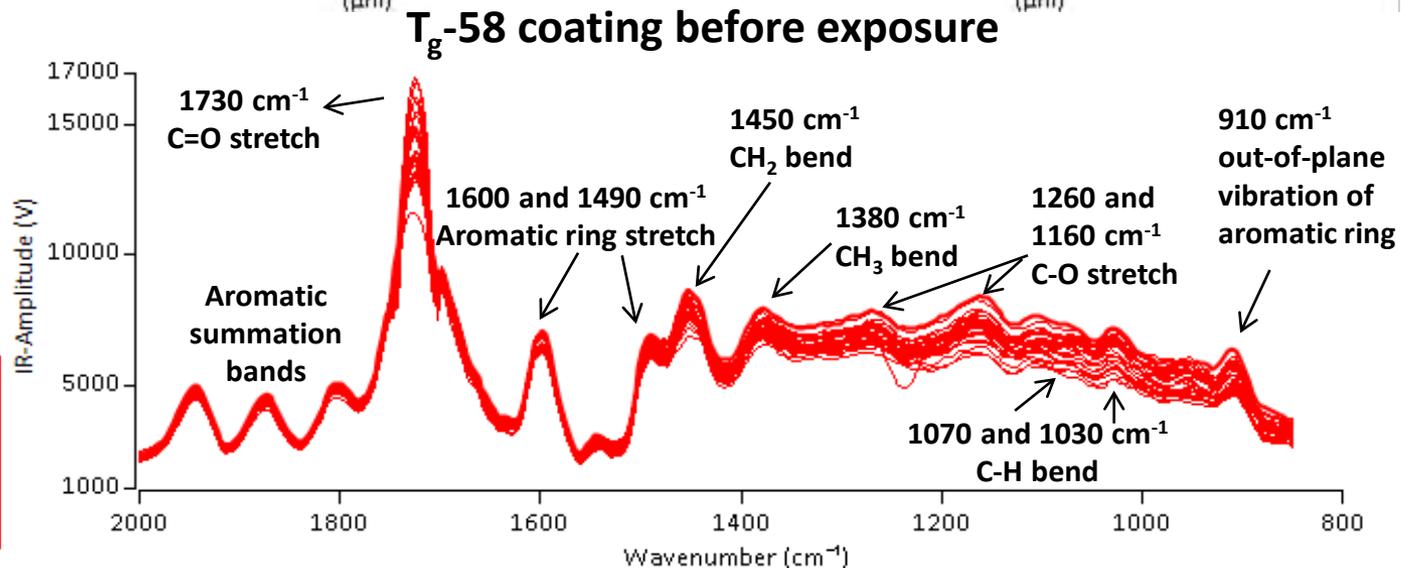
# Coating surface microstructure analysis by AFM-IR

Evidence of particle deformation and coalescence



Noisy but similar to ATR-FTIR spectra of latex

Can not be used to identify surfactant



# Influence of 2.6 wt. % surfactant on surface microstructure

1  $\mu\text{m}$  x 1  $\mu\text{m}$  images before prohesion

No post-addition

Surfactant B

Surfactant D

Height

1730  $\text{cm}^{-1}$

Height

1730  $\text{cm}^{-1}$

Height

1730  $\text{cm}^{-1}$

Acceptable particle coalescence

Surfactant suppressing particle coalescence

Surfactant accumulated at coating-air interface

1  $\mu\text{m}$  x 1  $\mu\text{m}$  images of non-corroded area after prohesion

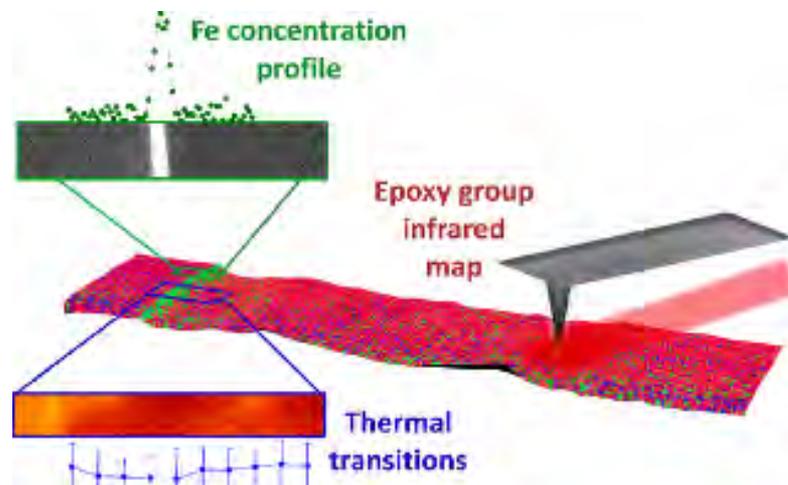
Swollen film

Nanoporous surface structure

*Cross-sectional study is needed!!*

# Cross section analysis with AFM-IR (1)

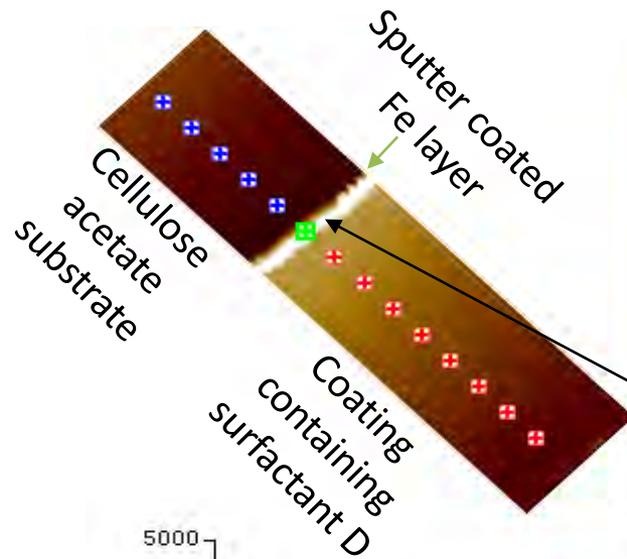
- Cross-section analysis can show differences between surface and bulk nanostructures
- Imaging nanoscale features of polymer coated steel by cross-section method is challenging
- Use of metal film substrate composed of 40 nm iron layer sputter coated onto cellulose acetate sheet
- 200 nm thick thin sections for AFM-IR imaging were prepared by ultramicrotomy



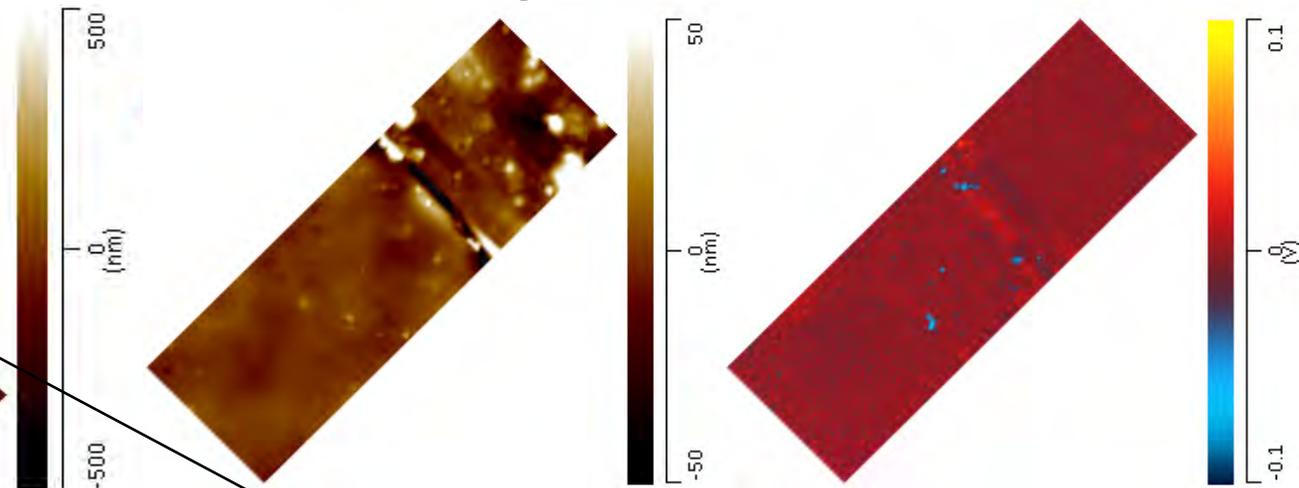
# Cross section analysis with AFM-IR (2)

T<sub>g</sub>-58 coating with 2.6 wt. % surfactant D

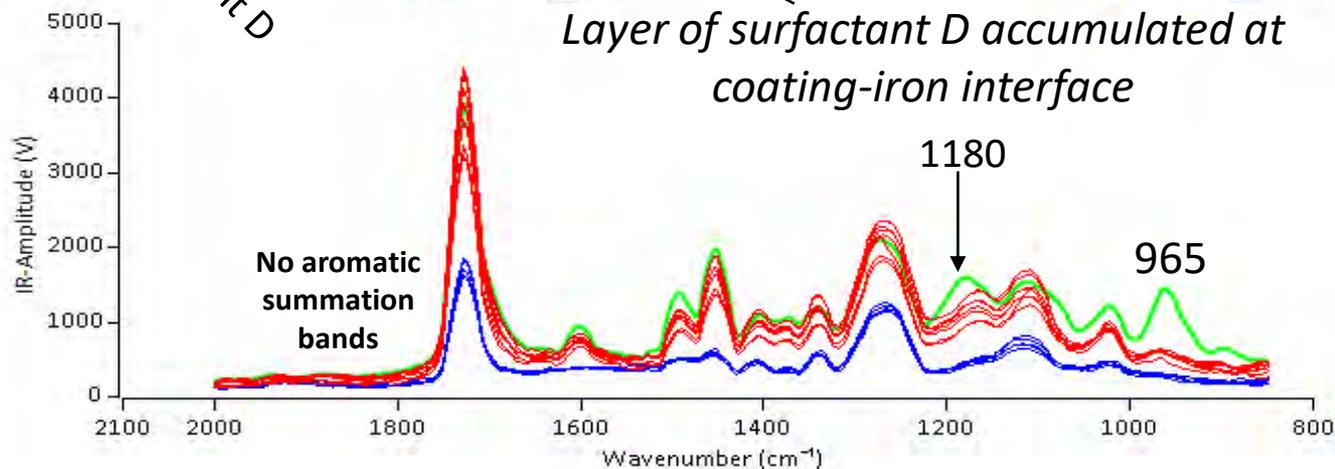
Height and 1730 cm<sup>-1</sup> maps (20 μm x 5 μm)



T<sub>g</sub>-58 coating (15 μm x 5 μm)



Layer of surfactant D accumulated at coating-iron interface

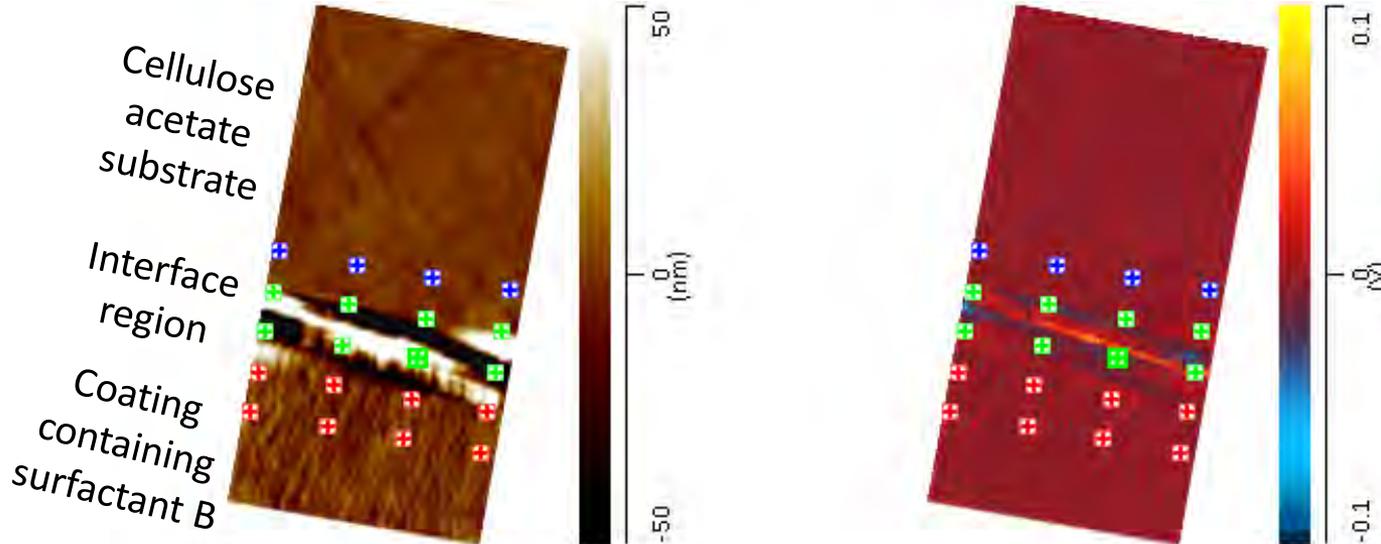


# Cross section analysis with AFM-IR (3)

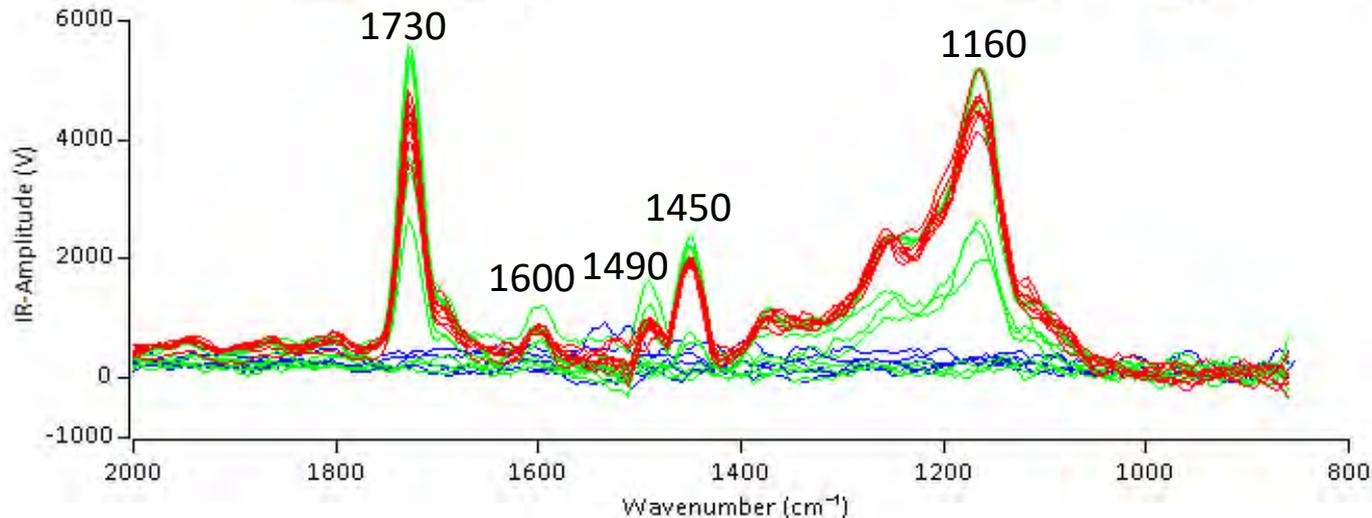
T<sub>g</sub>-58 coating with 2.6 wt. % surfactant B

5 x 10 μm Height

1730 cm<sup>-1</sup> IR amplitude map



Non-uniform/  
ruptured interface  
structure possibly  
due to the  
accumulation of  
surfactant B

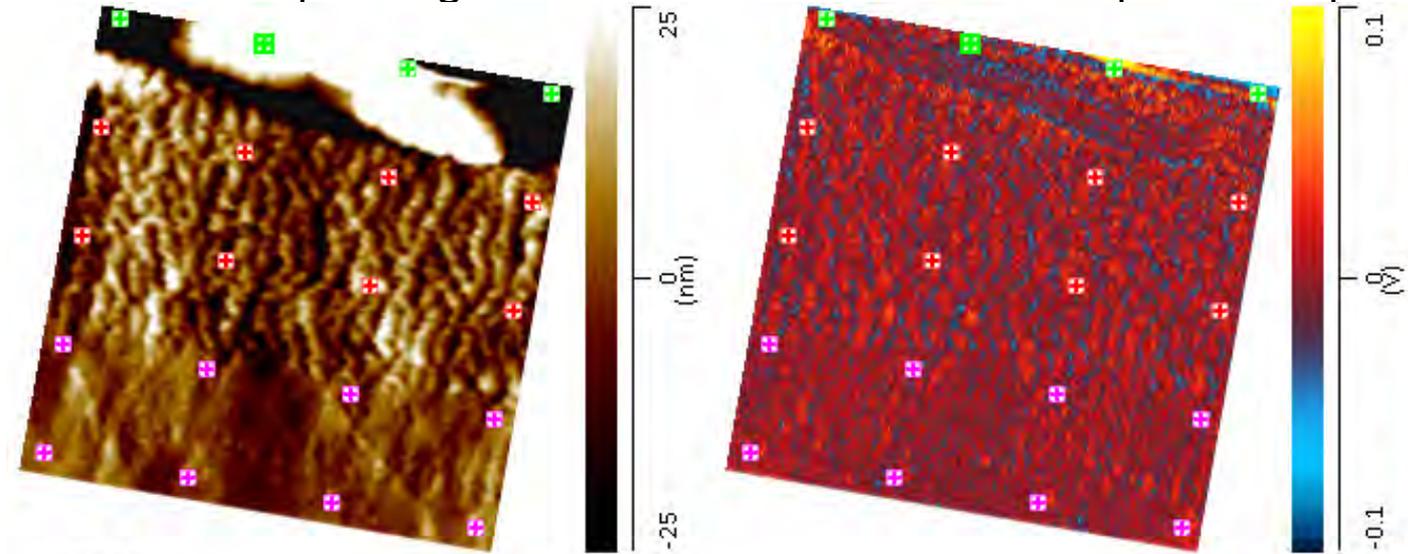


# Cross section analysis with AFM-IR (4)

$T_g$ -58 coating with 2.6 wt. % surfactant B

5 x 5  $\mu\text{m}$  Height

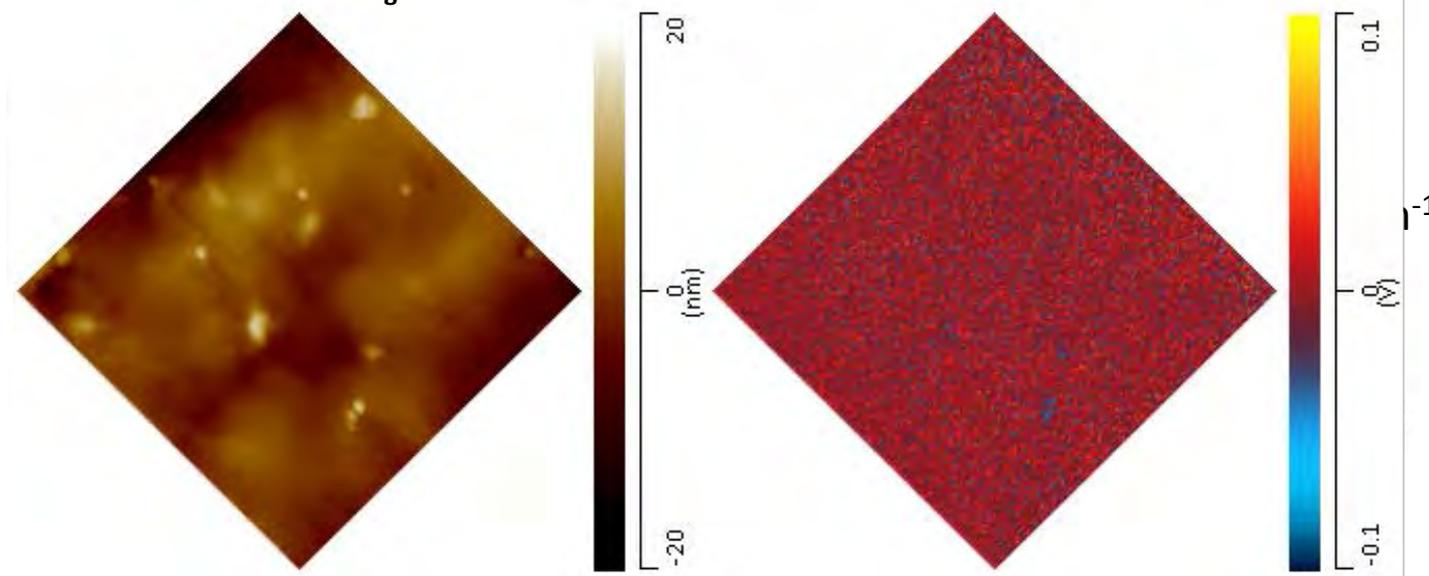
1730  $\text{cm}^{-1}$  IR amplitude map



Different level of particle coalescence across the coating

Sign of surfactant enrichment leading to poor particle coalescence at regions ( $\sim 2 \mu\text{m}$ ) near coating-iron interface

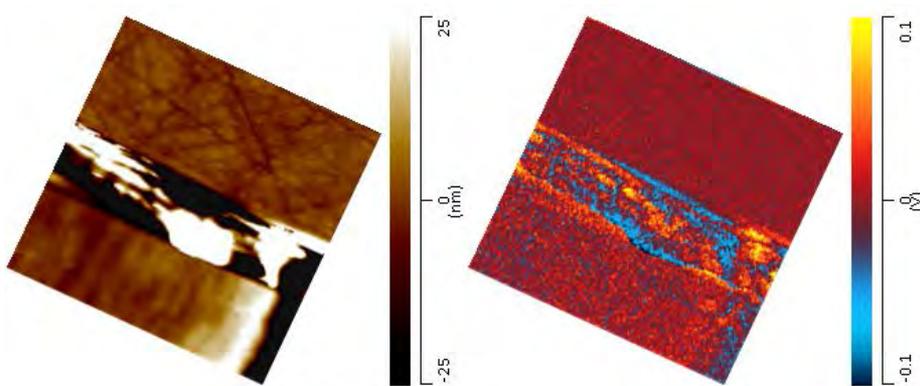
10000  $T_g$ -58 coating (5  $\mu\text{m}$  x 5  $\mu\text{m}$  maps)



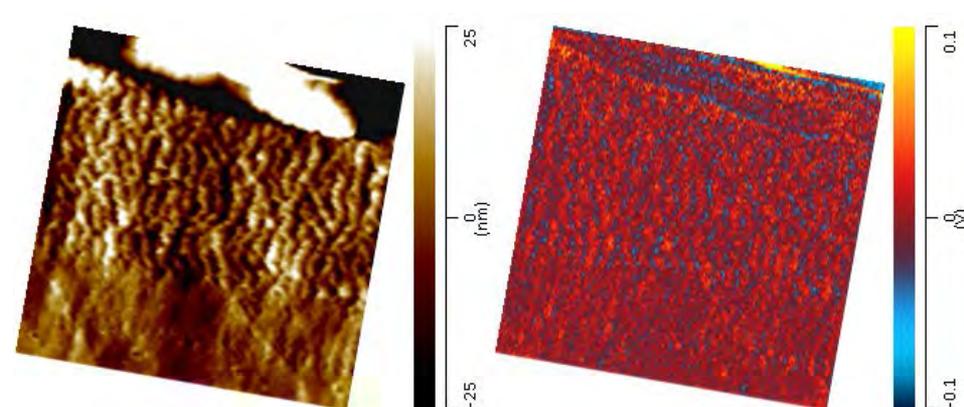
# Conclusions

- **Hydrophobic surfactants** are **not** always **better for corrosion protection** (need to consider distribution and adsorption behavior of surfactant)
- **Surfactants** can **suppress particle coalescence** during latex film formation, resulting in significant **deterioration of corrosion protection** properties
- Microstructural analysis on the **cross section** is required to **study the structure of the coating-metal interface**
- **Structure of the substrate-coating interface** can be **modified** depending on the chemical structure and concentration of surfactant used

Surfactant A (5  $\mu\text{m}$  x 5  $\mu\text{m}$  maps)



Surfactant B (5  $\mu\text{m}$  x 5  $\mu\text{m}$  maps)





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MANCHESTER  
1824

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## Thank you for your attention!