Studying Microstructure of Coatings to Understand Formulation Effects on Function

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Plan

- What SUSTICOAT is
- What is a Paint
- Description of approach taken
- Application to direct to metal waterborne paint
- Application to BPAni packaging coating
- Insights

SUSTICOAT

SUSTICOAT – SUSTainably Improved COATings

EU Marie Sklodowska-Curie European Industrial Doctorates

Enable more sustainable coatings

Remove formulation blockers

Focus on corrosion protection

5 Early stage researchers – spend 50% AkzoNobel / 50% UoM

Paints are complex systems

Formulation well understood with current ingredients

Improved sustainability requires new materials / processes

Understanding of impact of formulation on microstructure provides new guidance to choose more sustainable approaches

Definition of a Paint

A material

used for decorating and/or protecting a surface

in a thin surface film,

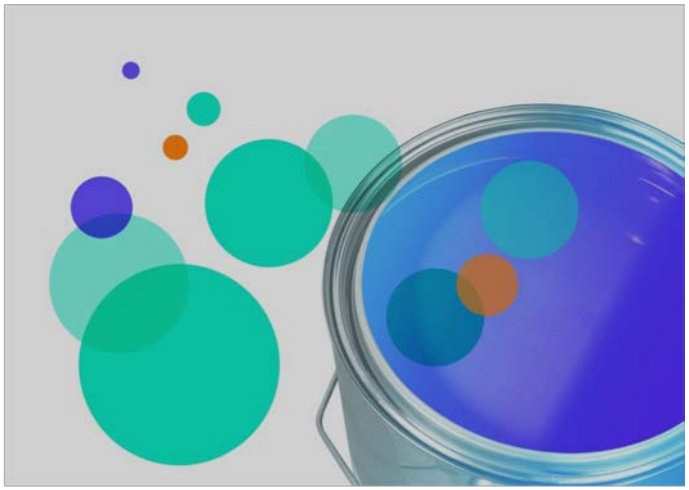
originating from a mixture

consisting of a solid pigment

suspended in a liquid

that when applied to a surface dries

to form a hard coating



Paint – The Mixture

Resin or binder is the material that holds the dry paint film together and provides adhesion, water resistance, chemical resistance etc..

Pigments provides aesthetics and may provide function – anti-microbial, …

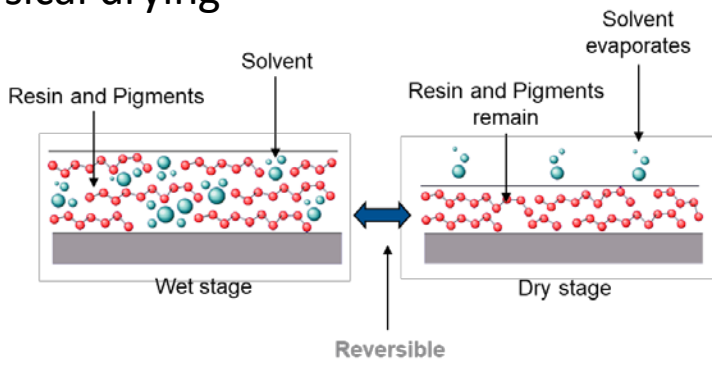
Suspension medium allows painting – solventborne / waterborne

Transition from liquid to solid – “drying”:

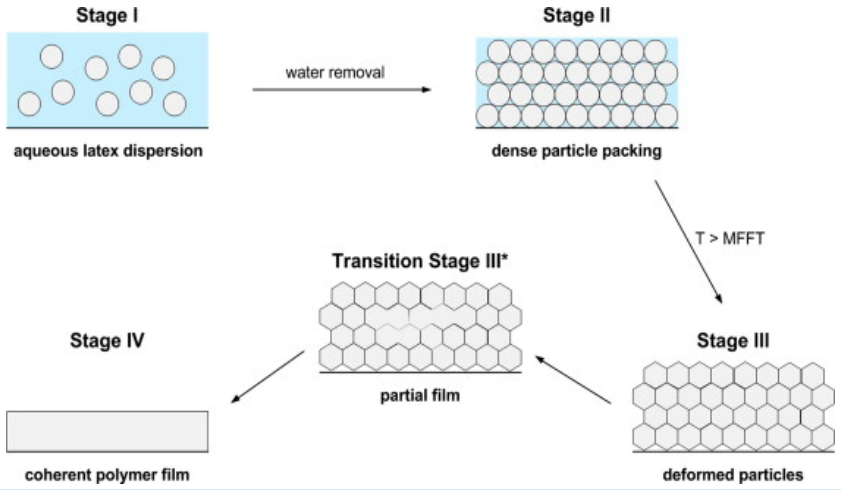
- Physical drying
- Chemical curing
- Coalescence

Drying

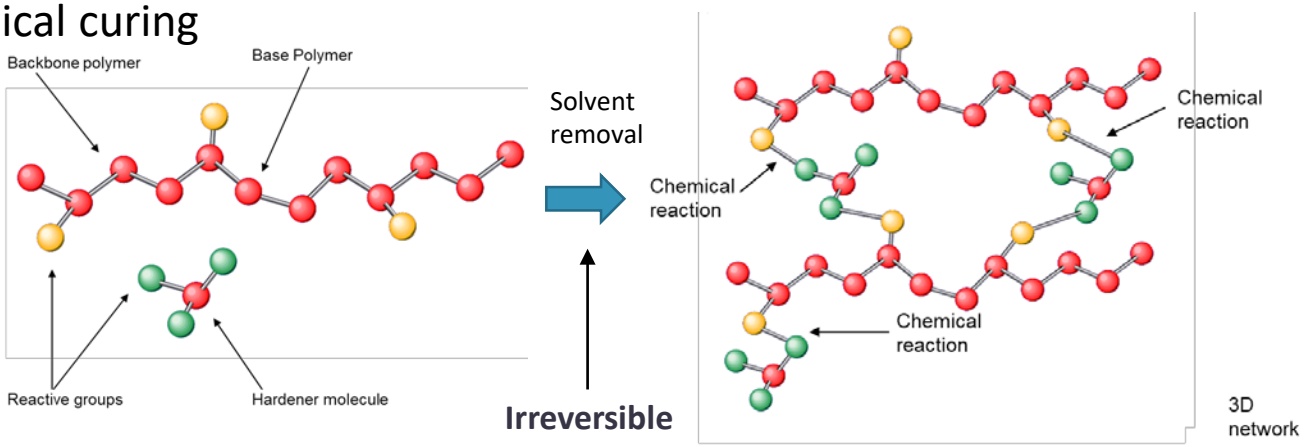
Physical drying



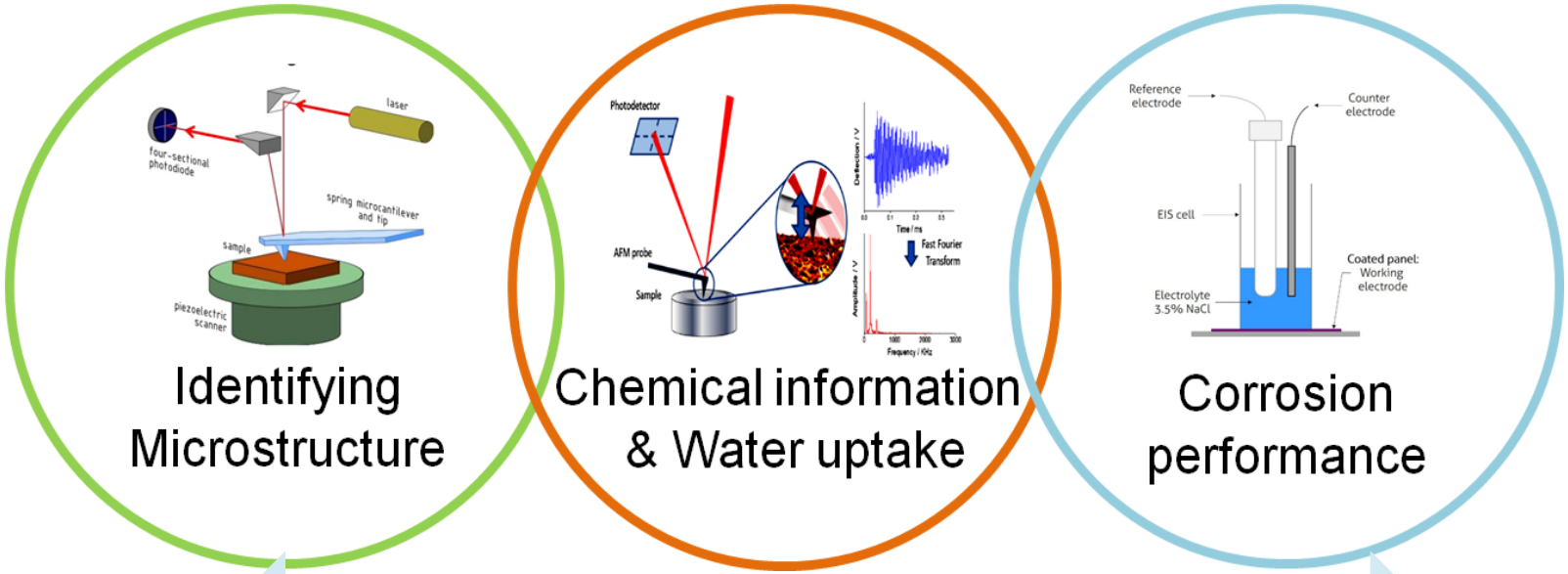
Waterborne paint – resin as latex



Chemical curing



Approach



Good understanding of microstructure can be leveraged to improve coating performance

Characterisation – Structure & Chemistry

IR Spectroscopy

Pro: IR absorptions act as "fingerprints" of chemical composition

Con: Diffraction limit of light limits spatial resolution (few µm)

+

Atomic Force Microscopy (AFM)

Pro: Uses a scanning probe interaction with sample, very high resolution

Con: Surface topography

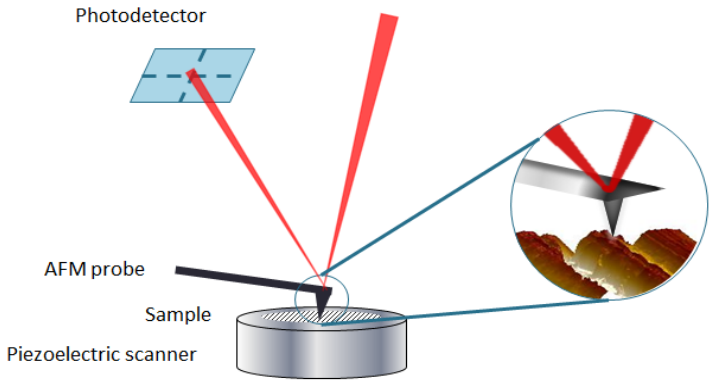
→

AFM – IR

Hybrid Technique

- AFM-IR allows organic functional groups to be detected under ambient conditions with nanoscale resolution.

Photo thermally induced resonance (PTIR) AFM-IR



AFM-IR

AkzoNobel

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The University of Manchester

Introducing nanoIR2™
now with top side illumination

DTM Waterborne Coatings

Waterborne coatings on metal

- Main advantages:

✓Better for HSE with lower toxicity, odour, flammability and VOC emission

✓Water as main solvent - easier cleaning and thinning

- Direct to metal (DTM) coatings provide additional cost and time benefits

- Challenges:

I. Optimum formulation to avoid early failures and provide long term corrosion protection

II. Binder with good barrier properties and adhesion to the metal surface

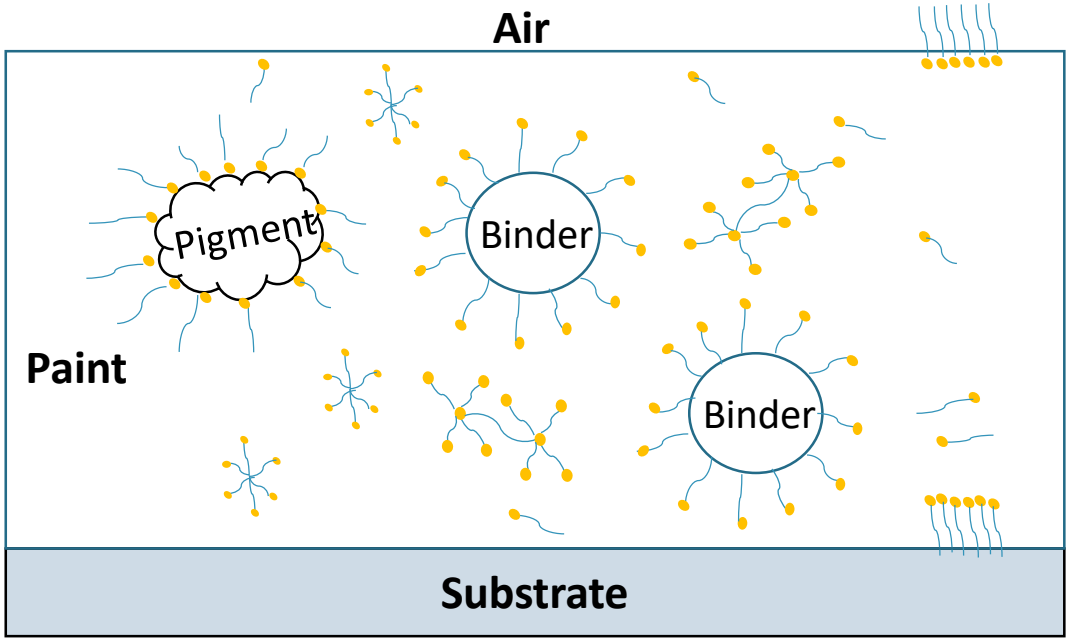
III. Suitable for the specific service environment

DTM Waterborne Coatings

Role of surfactant

Surfactants are amphiphilic molecules which can:

I. Provide kinetic stability
II. Prevent film defects
III. Improve performance and appearance



Examples:

- Pigment dispersant
- Wetting agent
- Defoamer
- Binder emulsifier
- Associative thickeners

Known problems associated:

- Appearance and aesthetic qualities
- Adhesion and mechanical properties
- Barrier and protective properties

Keddie, J. and A. F. Routh (2010). Fundamentals of Latex Film Formation: Processes and Properties, Springer Netherlands.

DTM Waterborne Coatings

Problems when formulating

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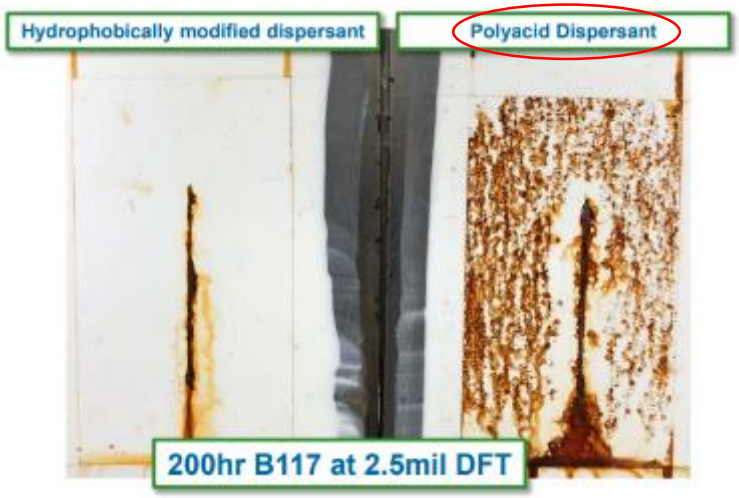
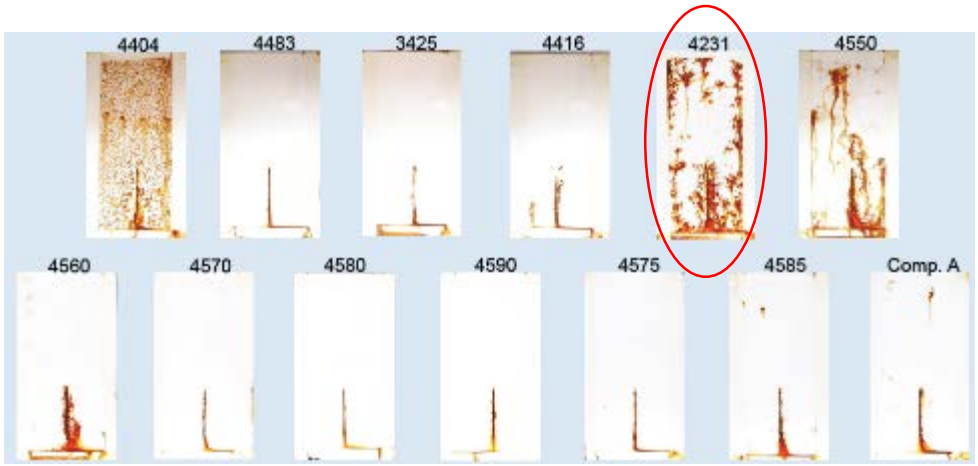
Additive can have detrimental effect on corrosion protection





4231 is hydrophobic polycarboxylate copolymer

- Discrepancies in corrosion protection performance with hydrophobic surfactants
- Better understandings required to select and develop optimum additives to improve the performance

DTM Waterborne Coatings

AFM-IR of model DTM before prohesion

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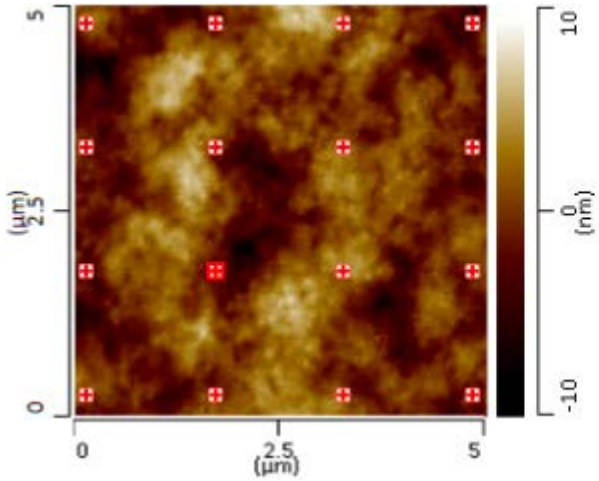
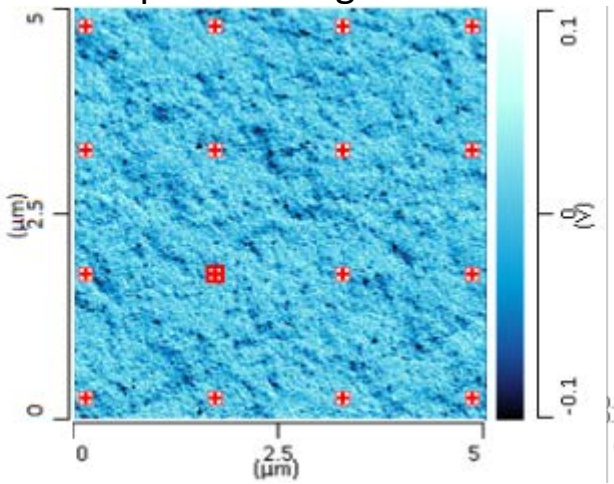
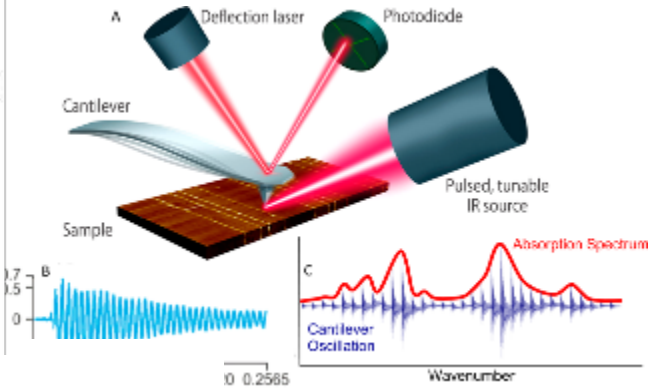
AFM height image

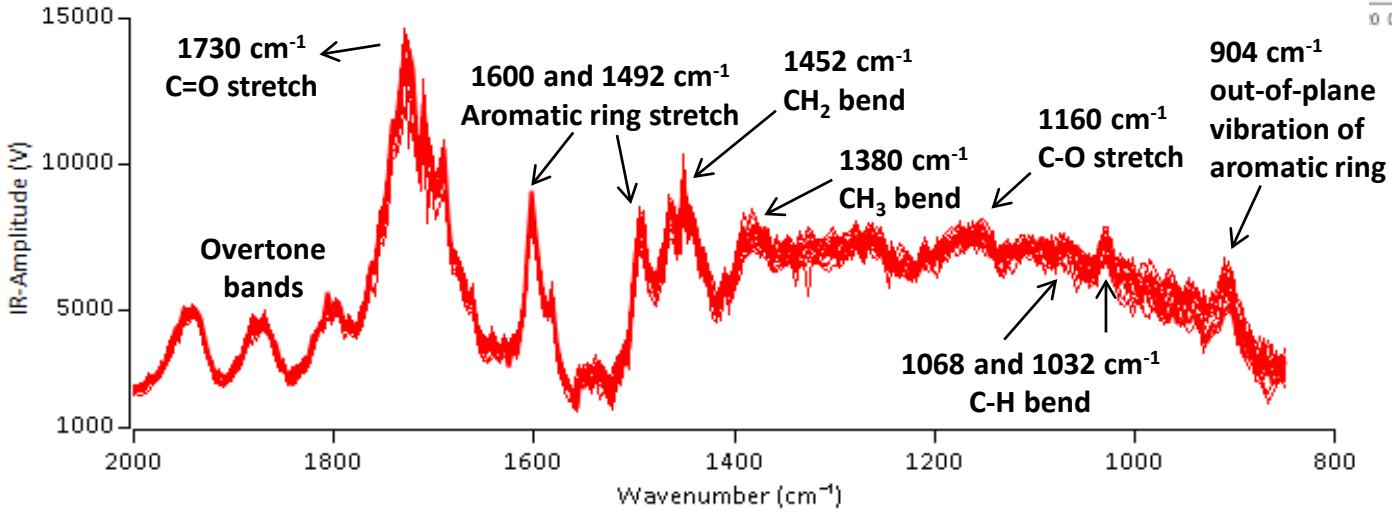


IR Amplitude image at 1730 cm^{-1}



Working principle:





Noisy but similar to ATR-FTIR spectra

DTM Waterborne Coatings

Sulfur-containing surfactants

- Surfactant A with sulphate group, surfactant B with sulfonate group, surfactant C with sulfosuccinate group (more hydrophobic based on HLB) and polymeric surfactant D have been post-added to the model DTM formulation for the study
- All surfactants have two characteristic IR peaks in the 1020-1210 cm^{-1} region
- Post-adding above 1 wt. % can cause severe foaming, de-wetting, cratering and inadequate viscosity, leading to discontinuous films (i.e. premature coating failures)
- Formulations containing 0.5 wt.% and 1 wt.% (i.e. dry films containing 1.3 wt.% and 2.6 wt. %) of various surfactants were analysed

No post-addition

0.5 wt.%

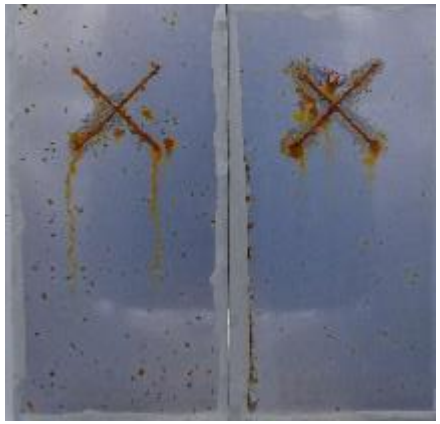
1.0 wt.%

No significant differences in appearance

DTM Waterborne Coatings

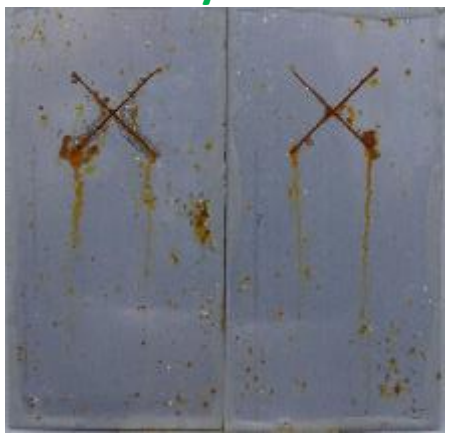
Prohesion test with 1% surfactant samples

Good dry adhesion



No post-addition
after 500 hours

Good dry adhesion



Polymeric surfactant D
after 500 hours

Poor dry adhesion

Surfactant A after 72 hours

Poor dry adhesion

Surfactant B after 72 hours

Poor dry adhesion

Surfactant C after 261 hours

DTM Waterborne Coatings

Surface analysis of 1 wt. % surfactant addition

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No post-addition

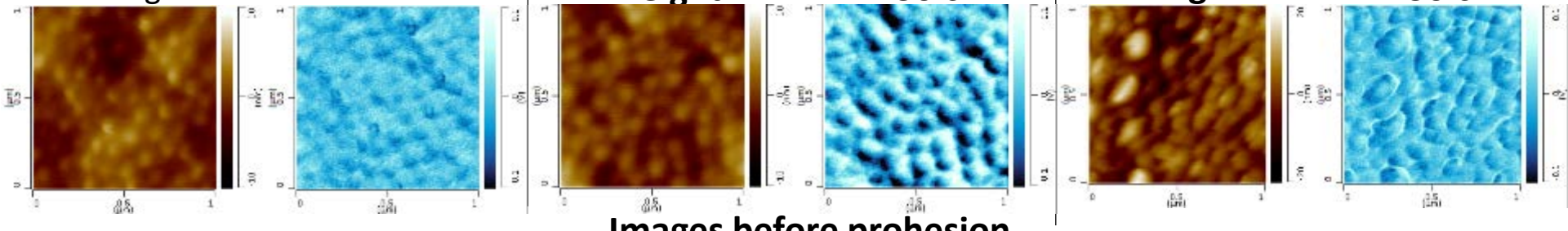
Height 1730 cm^{-1}

Surfactant B

Height **1730 cm^{-1}**

Polymeric surfactant D

Height **1730 cm^{-1}**



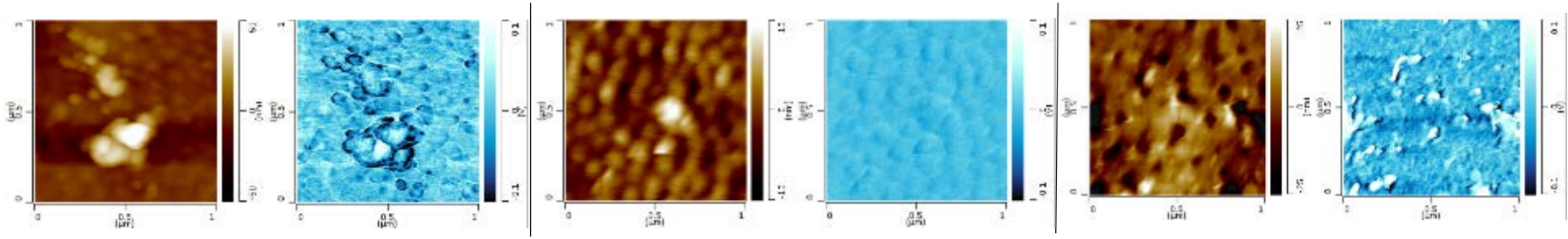
Images before prohesion

Incomplete particle coalescence

Surfactant hindering particle coalescence

Surfactant accumulated at coating-air interface

Clearly this is not the complete story!!



Images of non-corroded area after prohesion

DTM Waterborne Coatings

Summary

AFM-IR

Allows direct study of degree of film formation

Identification of localisation of surfactants

Polymeric surfactant gives

Good corrosion performance

Good adhesion

AFM-IR shows this is due to good film formation

Bisphenol A non intent (BPANI)

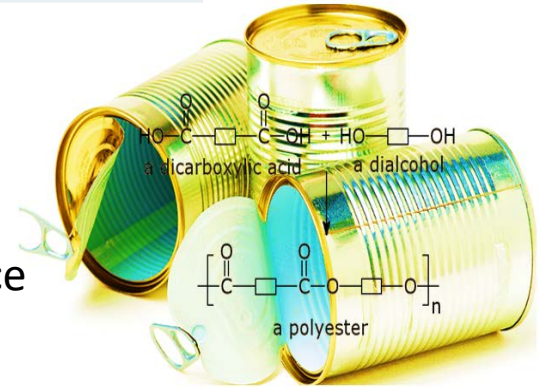
- Important class of food can coating - Bisphenol A non intended (BPANI) based on polyester

- AkzoNobel developed two types polyester based food can coating:

Coating type	Binder	Co-Binder	Cross linkers	Property
Coating A	Polyester	Phenolic	Benzoguanamine, Isocyanate	Flexible & moderate chemical resistant
Coating B	Polyester	Phenolic	Benzoguanamine	Stiff & high chemical resistant

- Complex chemistries

- Objective: To study practical coating system and efficiently characterize them in order to understand their performance



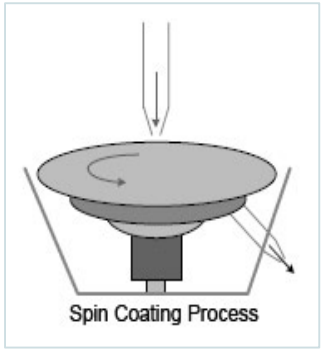
BPANI

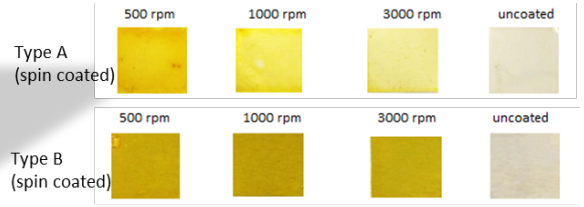
Coating system & sample preparation

- Two BPANI coating system (solvent based) with distinct properties were chosen
- Formulation chemistry is complex, due to complex monomers and crosslinkers.
- Sample preparation: Bar coated/ Spin coated on to tin plated steel substrates
  Temperature: ~200 °C , 10 min at PMT

Coating A

- Binders: Polyester, Phenolics
- Crosslinkers: Benzoguanamine, Isocyanate
- Properties: Flexible & moderate chemical resistant





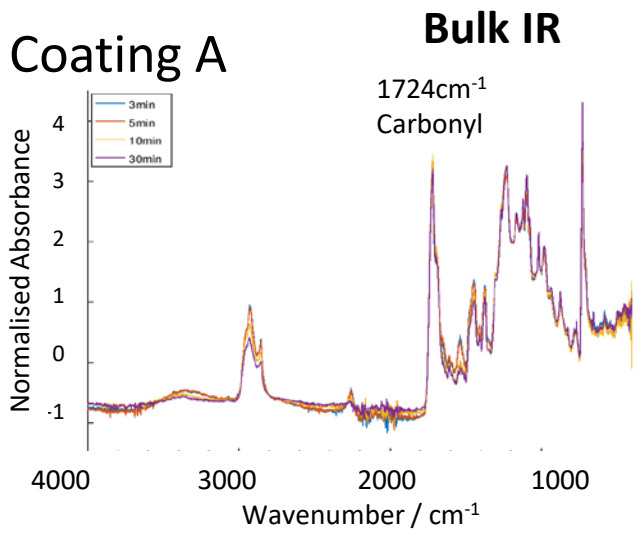
Coating B

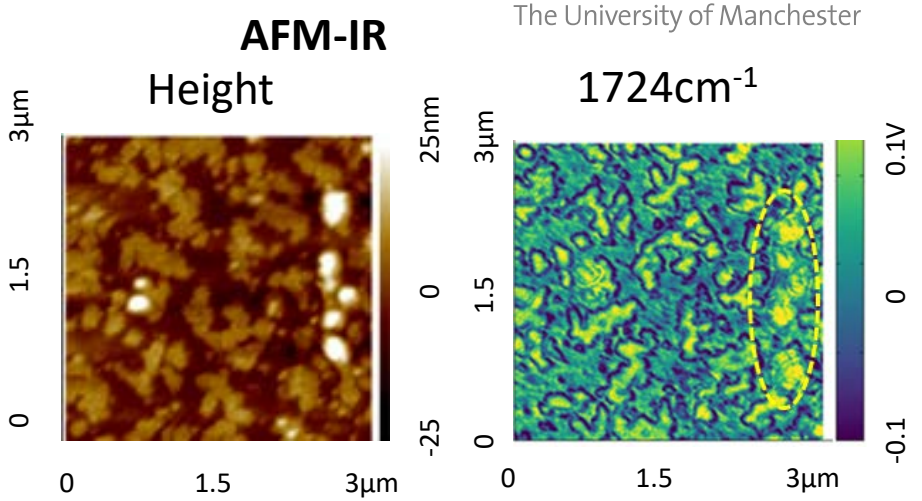
- Binders: Polyester, Phenolics
- Crosslinker: Benzoguanamine
- Properties: Stiff & high chemical resistant

BPAni

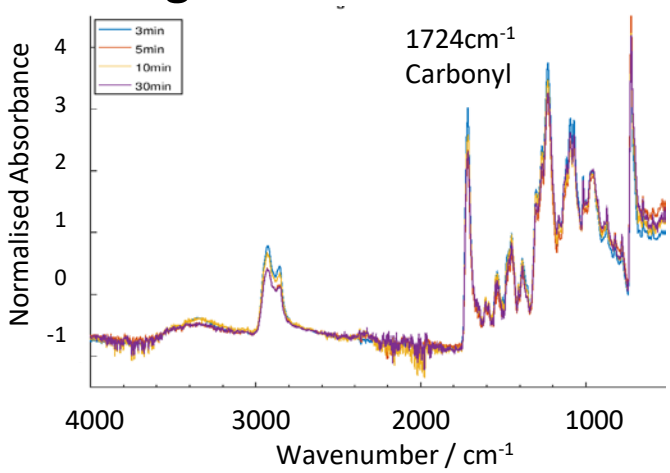
Microstructure

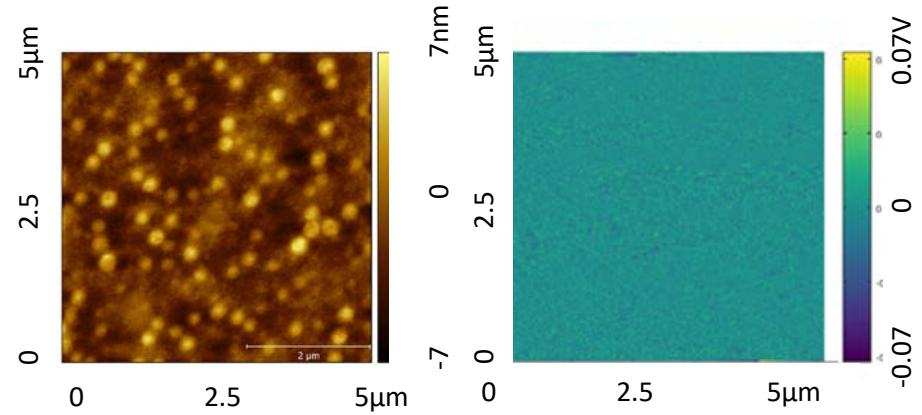
- Coating A





- Coating B





BPAni

Coating B - Water uptake

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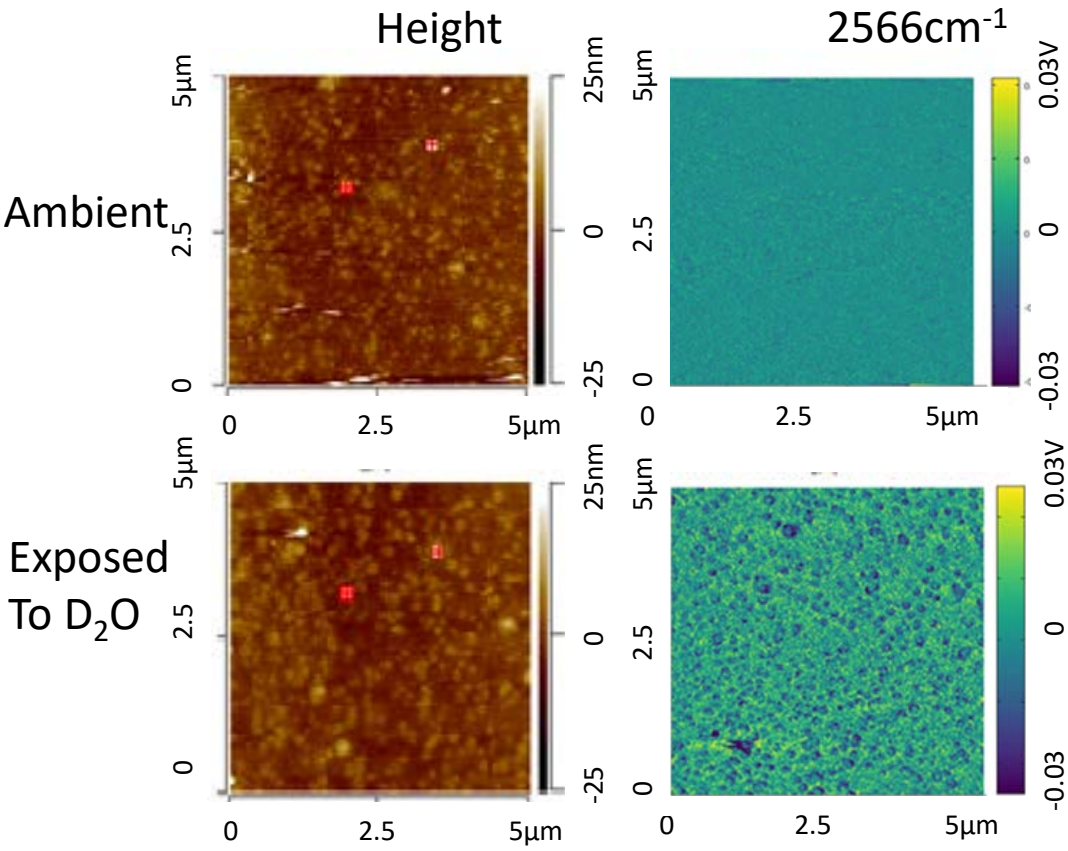
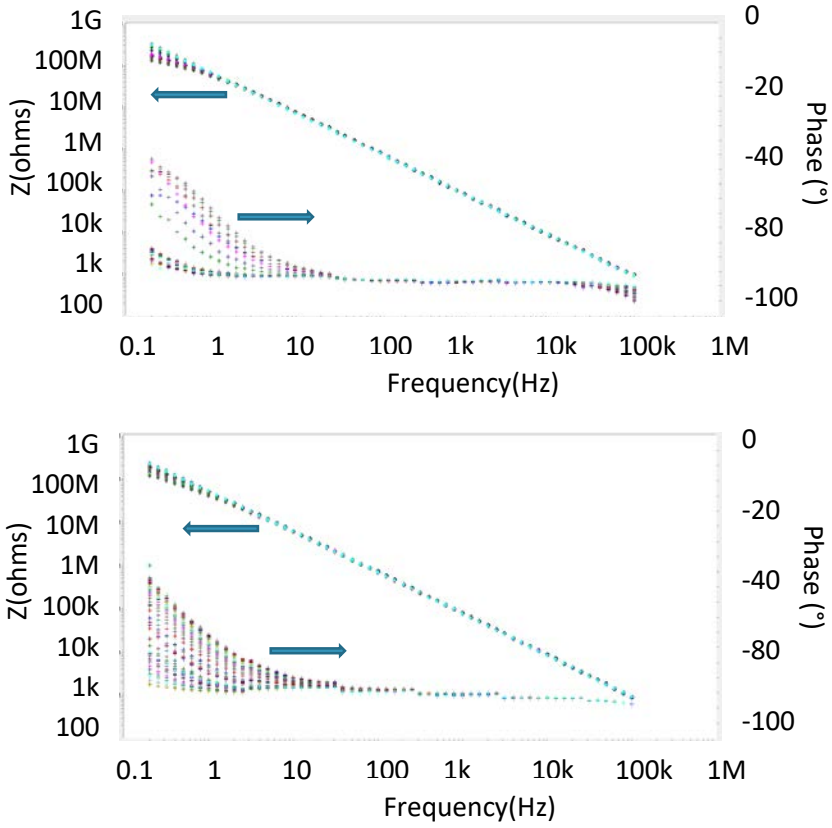


Electrochemical Impedance Spectroscopy



BPAni

Summary -

AFM-IR

Able to identify heterogeneous micro-structures

Able to study dynamic process of water uptake within polymer

Corrosion Protection

Increased water uptake does not mean increased corrosion

Transport of ions required for corrosion not just presence

Acknowledgments

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