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Mapping the Transport Channels in an Epoxy Coating with AFM-IR

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Acknowledgements

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Stuart Smith

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EPSRC

Engineering and Physical Sciences
Research Council

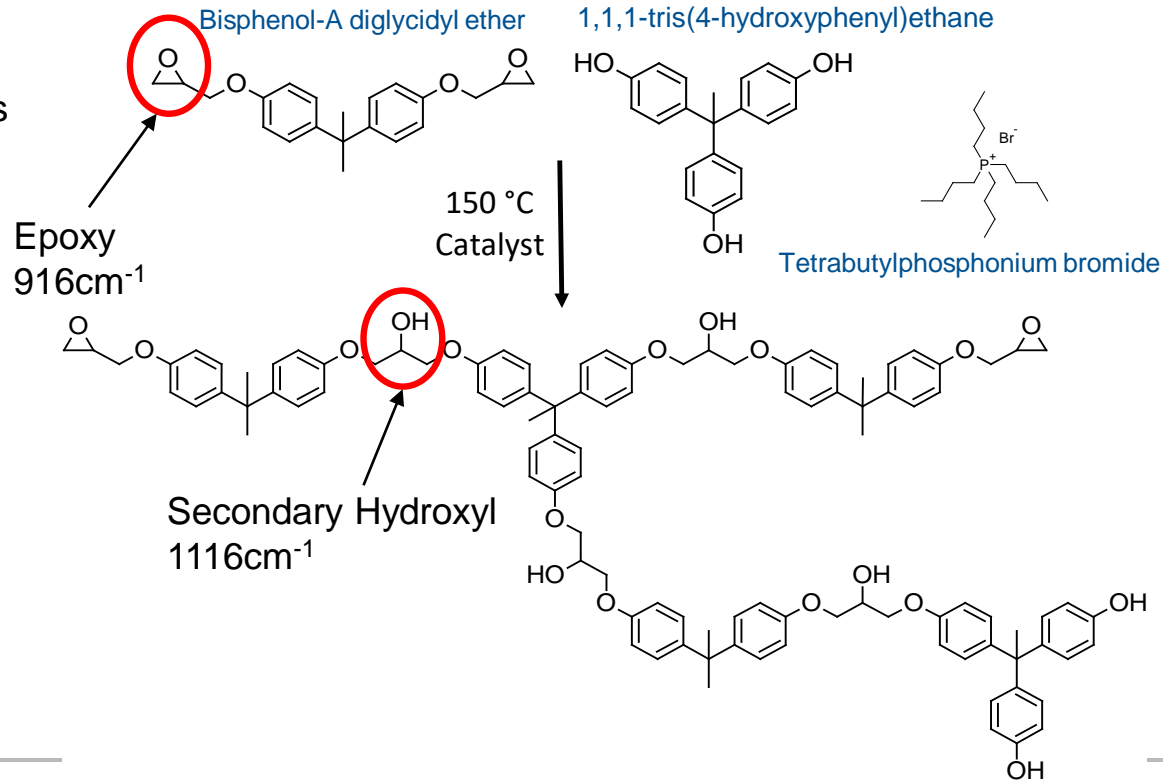
Background

- ↗ Clear epoxy based can coating
- ↗ Why does an apparently homogeneous coating fail in the absence of a visible defect?
- ↗ Thermoset crosslinked polymer
- ↗ Phenomenology – Commercial system epoxy-phenolic
- ↗ Deeper understanding - Model systems
- ↗ Characteristic infrared vibrations



Background

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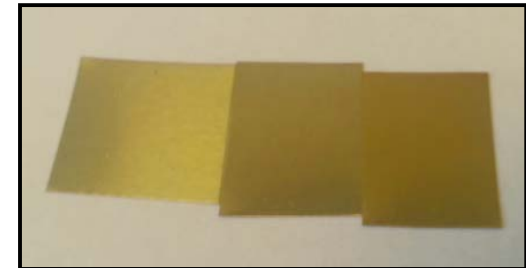


Corrosion Protection Failures

Why does an apparently homogeneous fail in the absence of a visible defect?

Can Coatings: Why do we see failure of unpigmented, nominally homogeneous epoxy phenolic coatings at seemingly random points, in the absence of a defect?

- ↗ Funke: Protection by barrier properties, active pigments, adhesion.
- ↗ Mayne: Failure linked to ionic resistance – identified D and I areas.
- ↗ Taylor: Interfacial water, aggressive species and connection between electrolyte and substrate required for corrosion.
- ↗ **Nguyen's Model: Water ingress occurs through interconnected regions of low molecular weight or low cross-linking density, these then widen to form conducting pathways through the coating.**



E.M. Kinsella, J.F.O. Mayne, British Polymer Journal 1, 173-176,1969

S.R. Taylor, IEEE Transactions on Electrical Insulation 24, 5, 787-806, 1989

W. Funke, in R.A. Dickie, F.L. Floyd, Polymeric Materials for Corrosion Control, ACS Symposium Series 322, 222-228, 1985

T. Nguyen, J.B. Hubbard, J.M. Pommersheim, Journal of Coatings Technology 68, No855, 45-56,1996

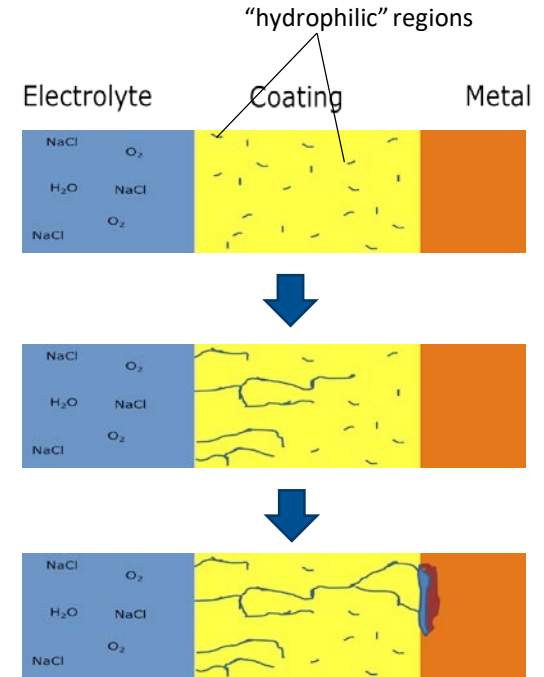
Concluding Hypothesis

- Nominally homogeneous epoxy coatings are actually heterogeneously cross-linked at the nanoscale.
- Diffusion of water occurs preferentially through less-dense regions.
- Plasticisation of the polymer by absorbed water and internal stresses generated by its heterogeneous distribution then leads to deformation of the coating and clustering of water, ultimately yielding hydrophilic nano-voids in the coating.
- Hydrophilic pores eventually form a percolating pathway through the coating, permitting rapid ion transport (corrosion!).
- However, it appears that the nanostructure is only one factor in controlling water uptake and ion transport through resins, where cross-linking density (limiting the rearrangement step) is more important.

Degradation of Clear Coatings

Nguyen's Model

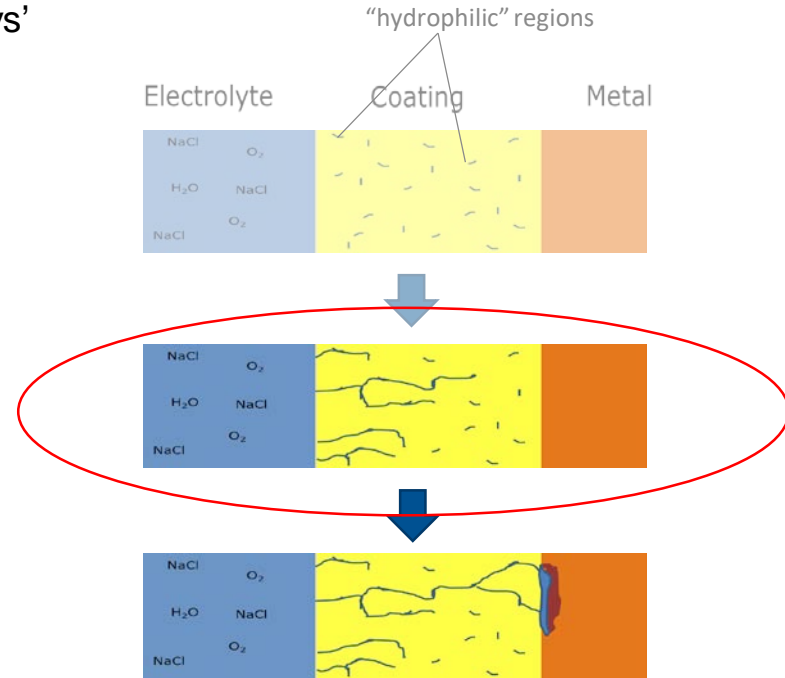
- Water uptake is thought to be the first stage of coating degradation.
- Ion transport channels then develop from 'hydrophilic pathways' through coatings.
- This process is **not** understood:
 - Does a pore structure form during water uptake?
 - Is it related to the coating constituents and nanostructure?



Degradation of Clear Coatings

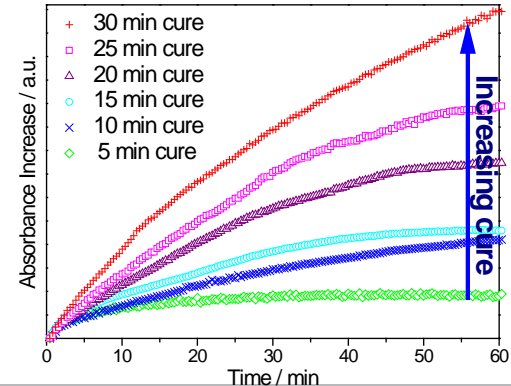
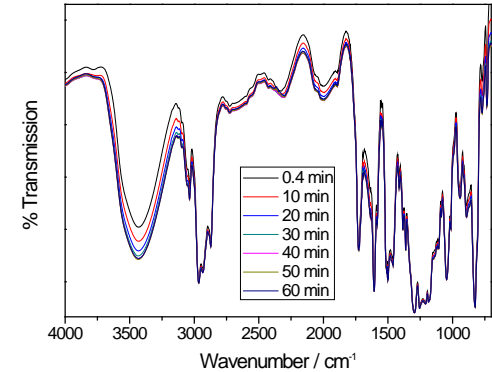
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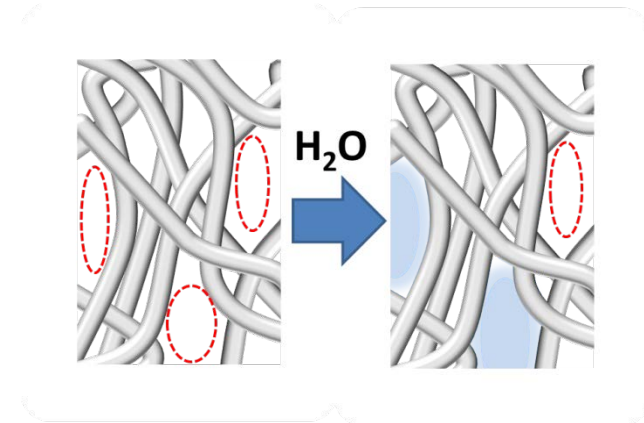
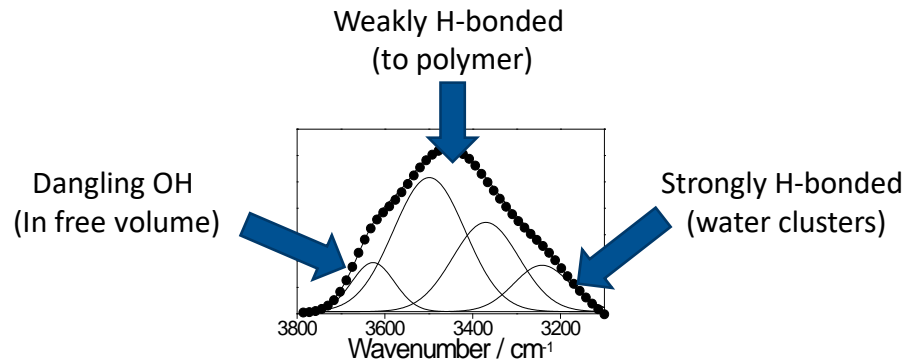
Water Uptake vs. Cure Time

- Short-term water uptake under humid conditions.
 - Longer cure = increase water uptake
- Same degree of hydrogen bonding for all samples
 - similar environment
- Comparable results for a model epoxy-phenolic resin.



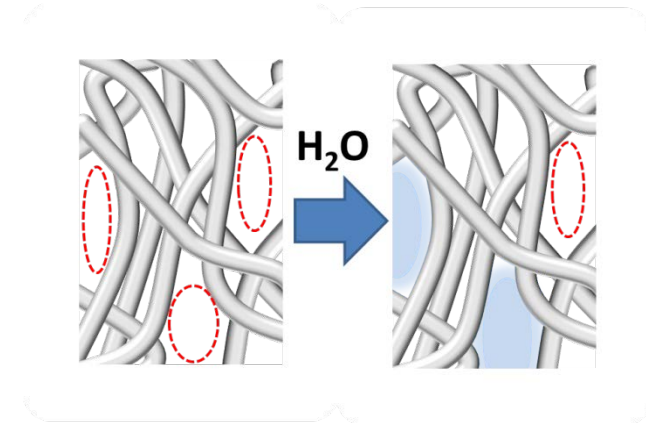
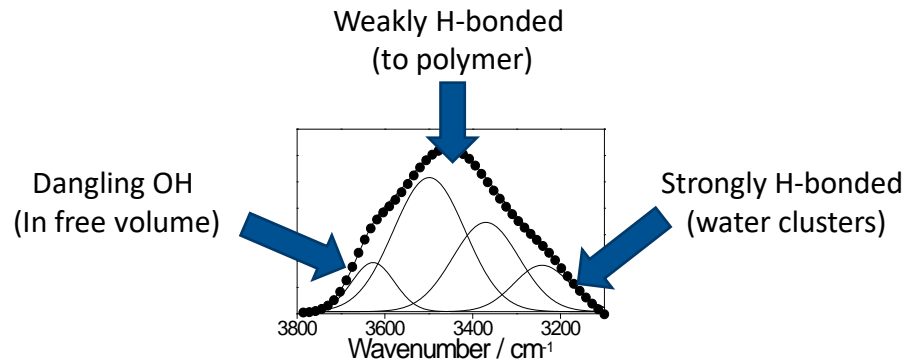
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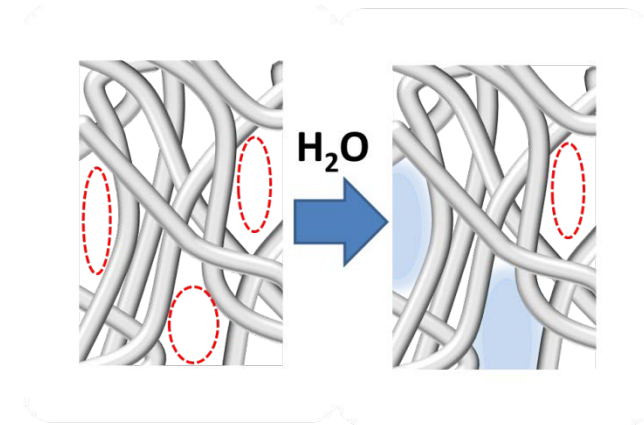
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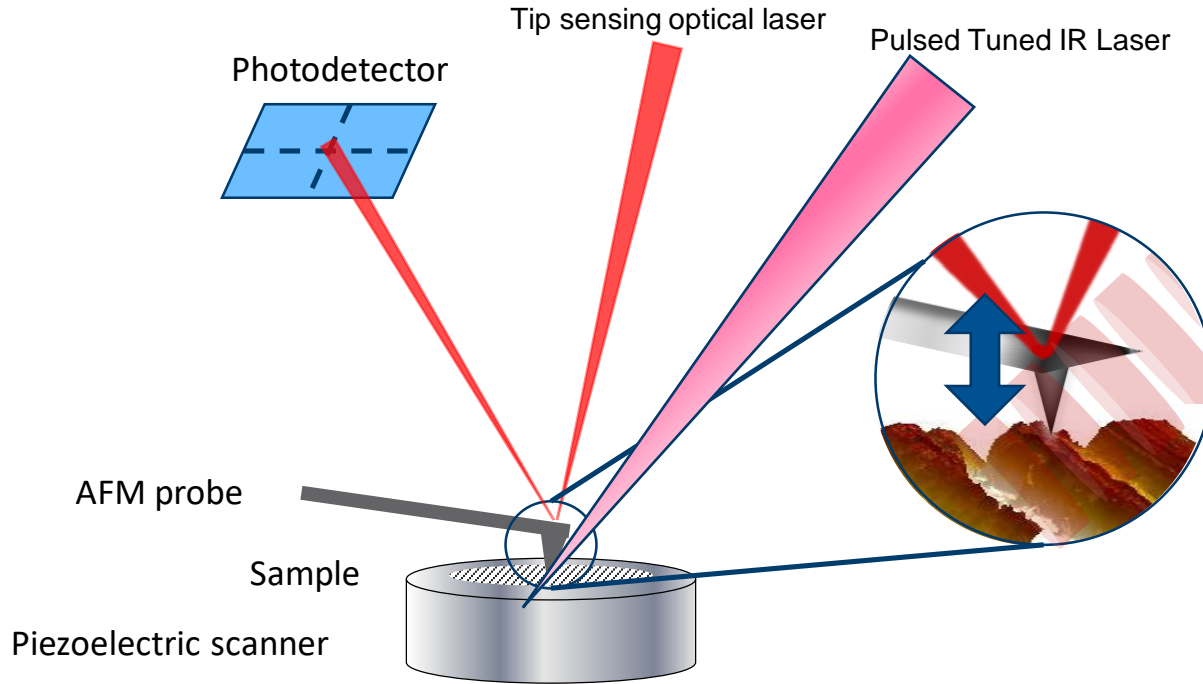
INCREASED
WATER UPTAKE
DUE TO FREE
VOLUME NOT
POLARITY

Dang
(In free

ended
ers)



The AFM-IR Technique



- AFM imaging allows nanoscale topographic measurement of samples.
- AFM-IR also measures local infrared absorbance at this scale.

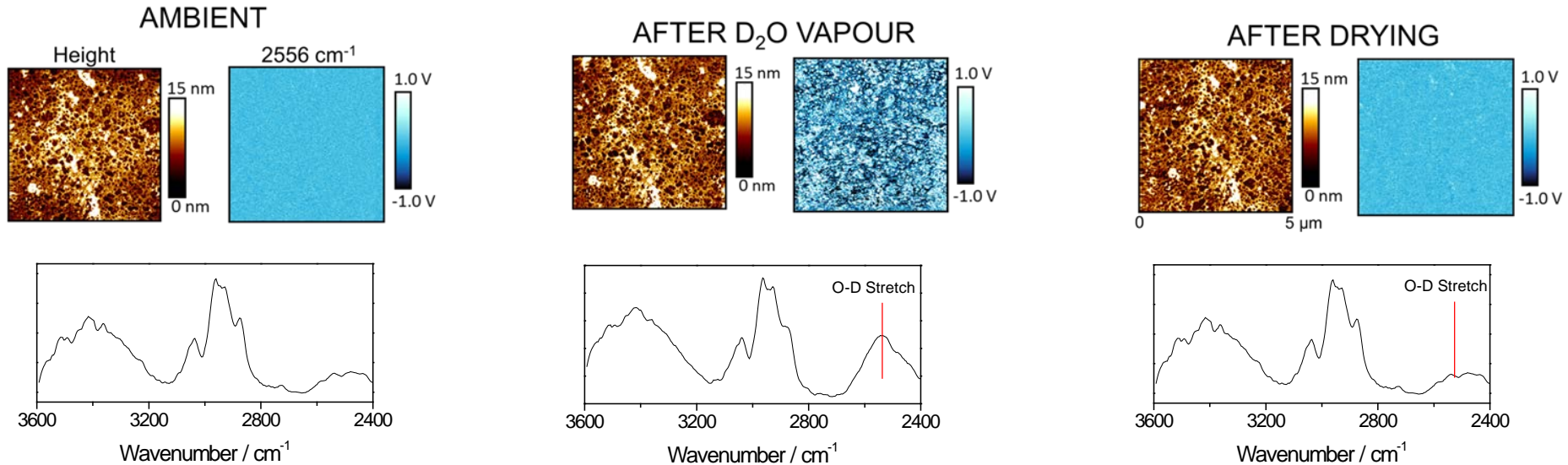


Extreme Water Uptake by AFM-IR

Correlation between the coating porosity and water uptake

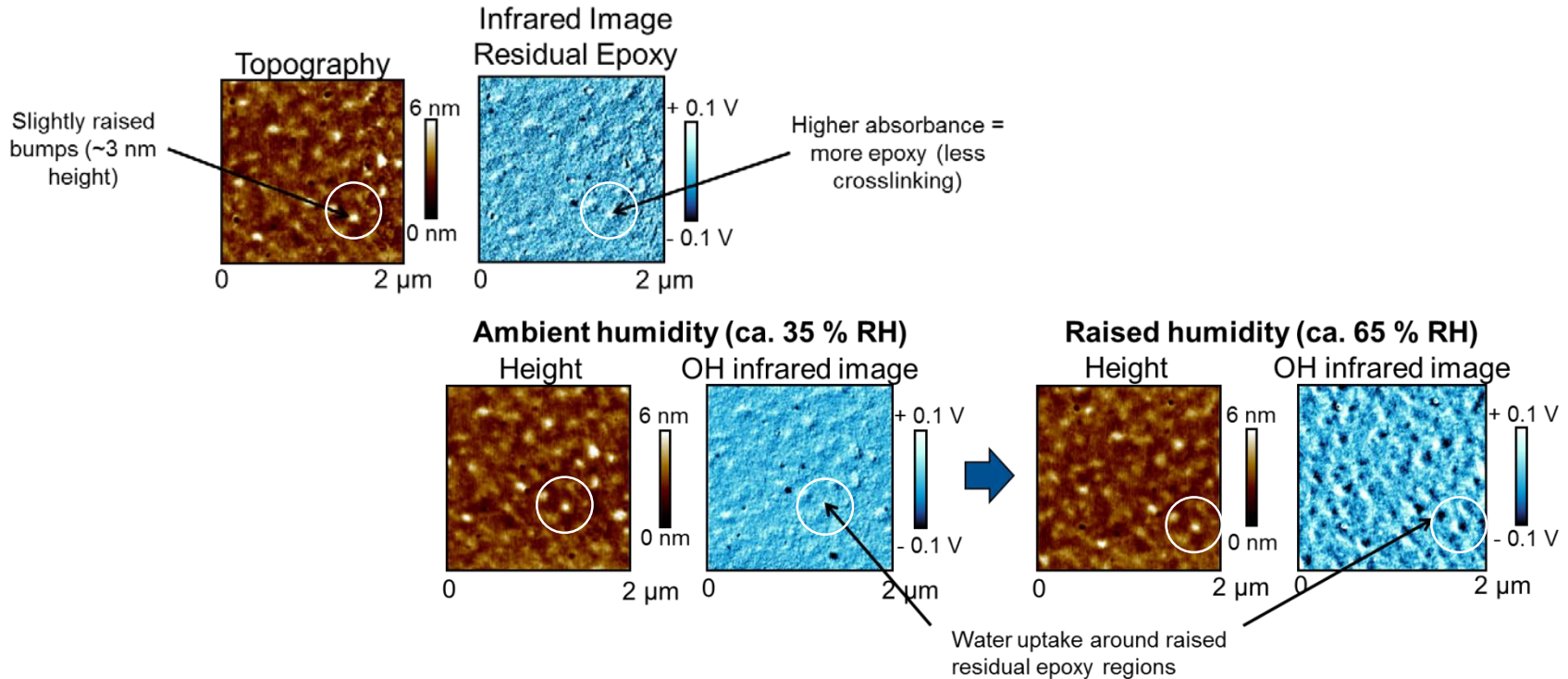
- After 3 days immersion in water or electrolyte, a nano-porous structure develops.
- Measurement of D₂O vapour absorption using AFM-IR shows that these pores are relatively hygroscopic.

=> REARRANGMENT



Water Uptake by AFM-IR

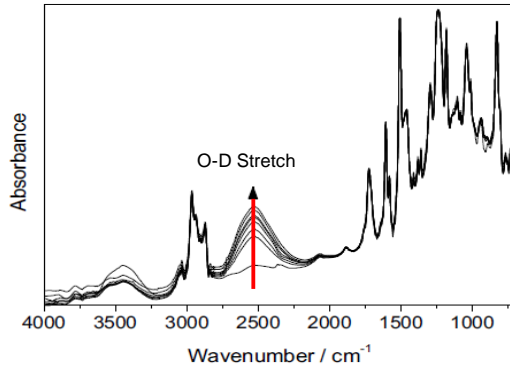
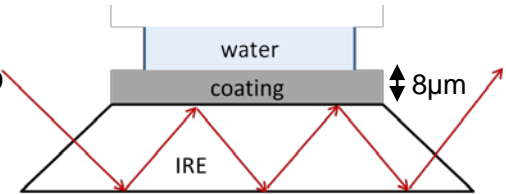
Is water uptake heterogeneous across coatings?



Water Uptake by ATR-IR

Does the coating really saturate rapidly?

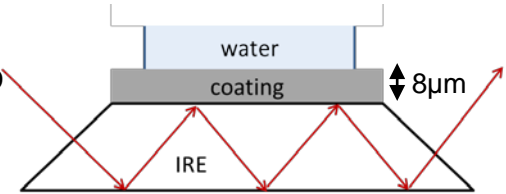
- ↗ ATR FTIR with a fluid cell allows long-term water sorption to be monitored.
- ↗ Sorption can be plotted by integration of the O-D band during exposure to D₂O.
- ↗ Short term experiments show that water penetrates 8 μm coating (to within the ca. 500 nm sampling depth with a Ge IRE) within 6 min sampling time.
- ↗ Long-term water uptake then slowly continues.



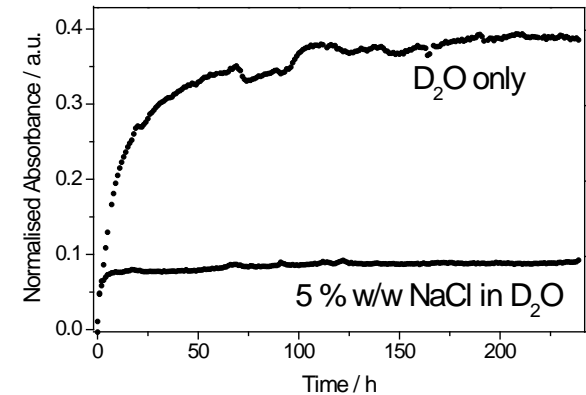
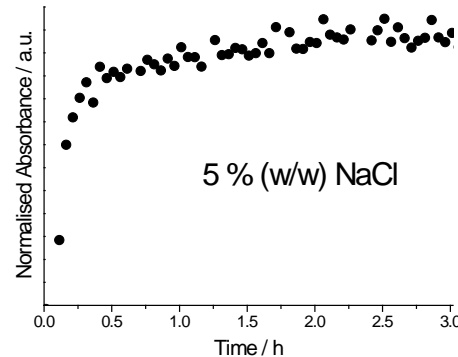
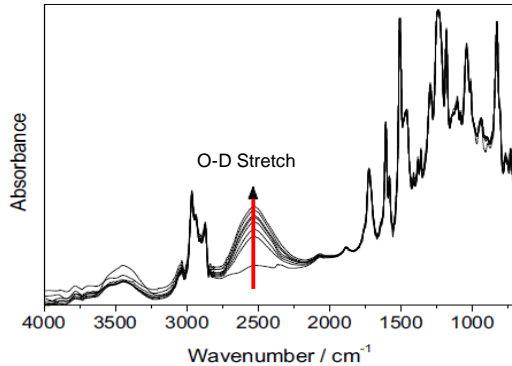
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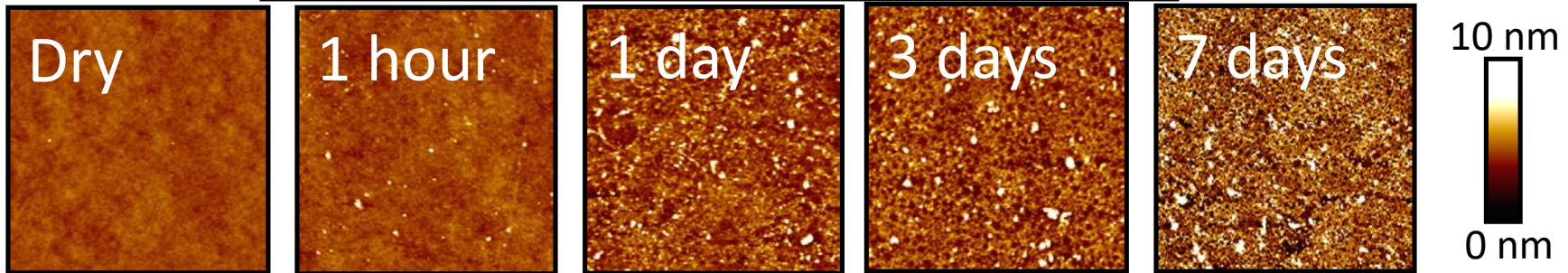


Physical Properties After Immersion

The mechanism of long-term water uptake

Decreased T_g (plasticisation) leads to long-term deformation of the samples. Lower CA and surface structure indicate long-range rearrangements of the network structure in the presence of absorbed water.

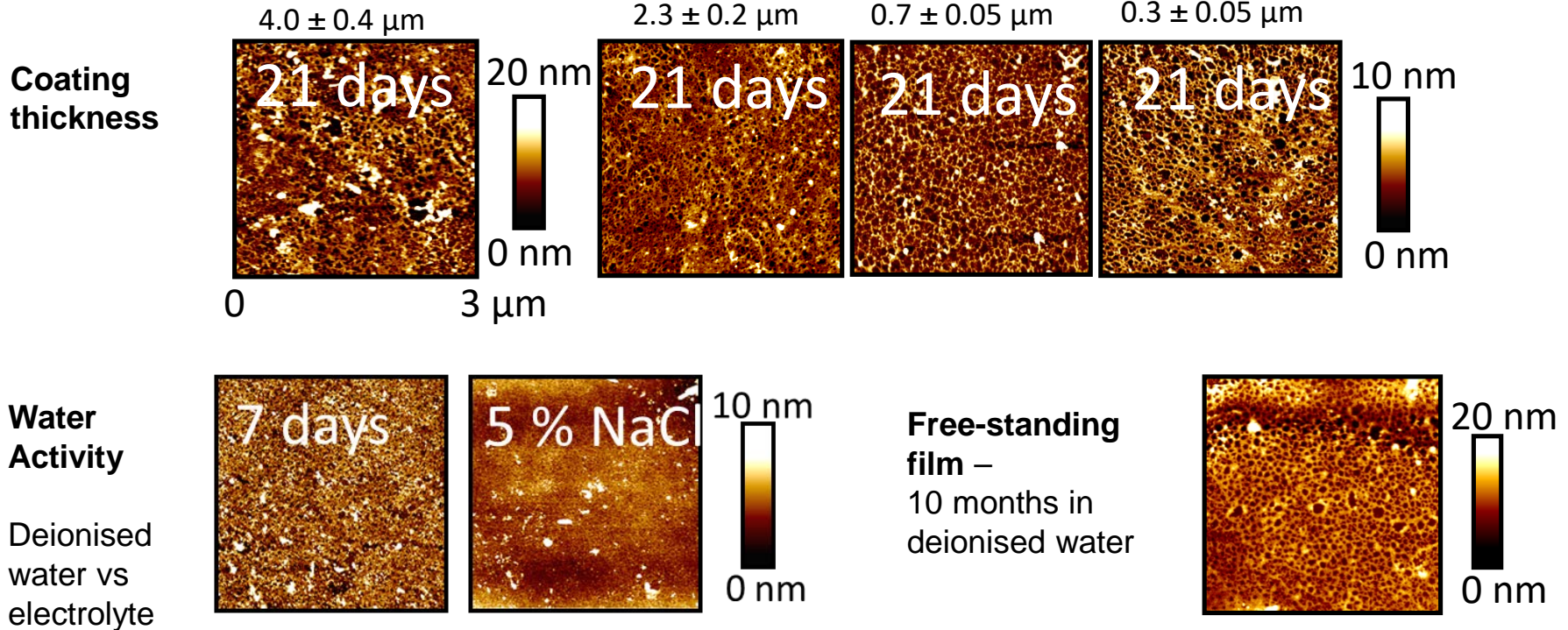
Sample	T_g	Contact Angle
Dry (as deposited)	89.3 °C	90 ± 1 °
1 hour immersed in H ₂ O	90.5 °C	89 ± 2 °
1 day immersed in H ₂ O	88.1 °C	87 ± 2 °
3 days immersed in H ₂ O	87.7 °C	83 ± 1 °
7 days immersed in H ₂ O	84.7 °C	83 ± 1 °



4 μm x 4 μm peakforce tapping mode AFM images

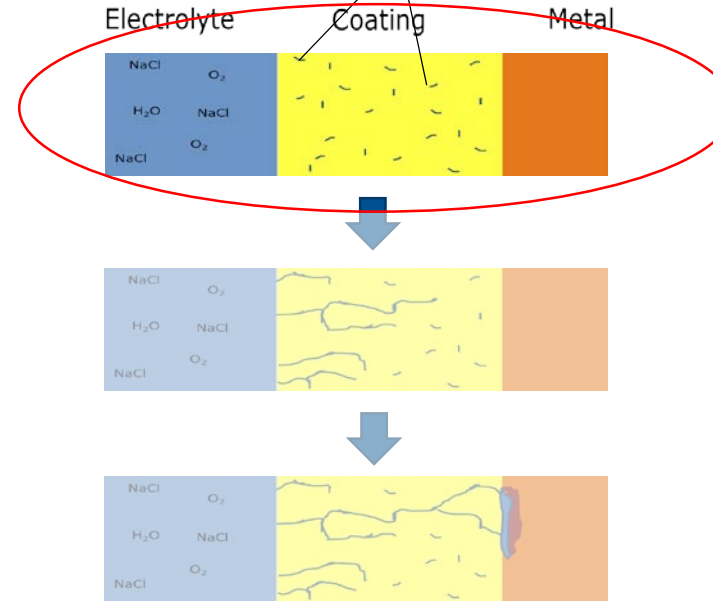
AFM Analysis after Immersion in Water

The development of coating porosity



Degradation of Clear Coatings

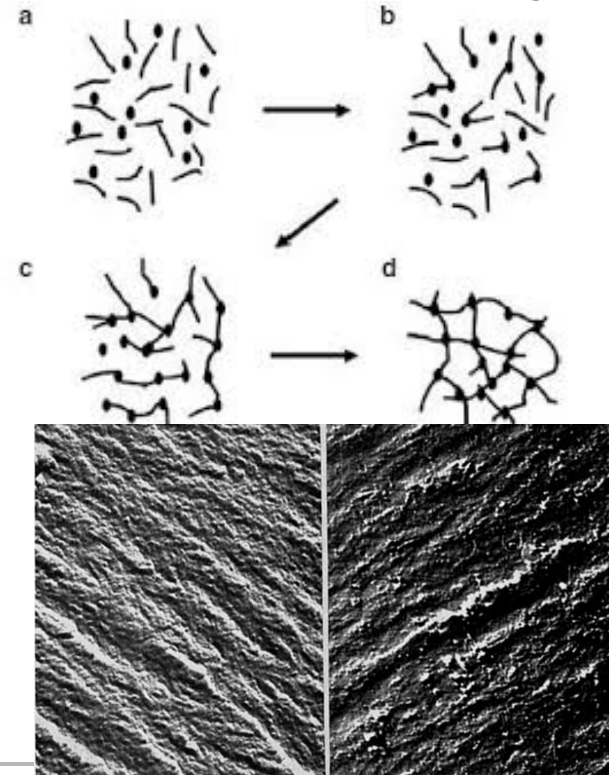
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Corrosion Protection Failures

Why does an apparently homogeneous coating fail in the absence of a visible defect?

- Statistical models predicting homogeneous network development match the gel point well.
- Electron microscopy reports dating back to 1950's show that fracture interfaces seem to display 'nodular' heterogeneous structure.
- But controversial and disputed in the literature, e.g., Karl Dušek, *Die Angew. Makromol. Chemie* 1996, 240, 1–15: lack of two distinct thermal transition points, densities etc. Proposed to be imaging artefacts.

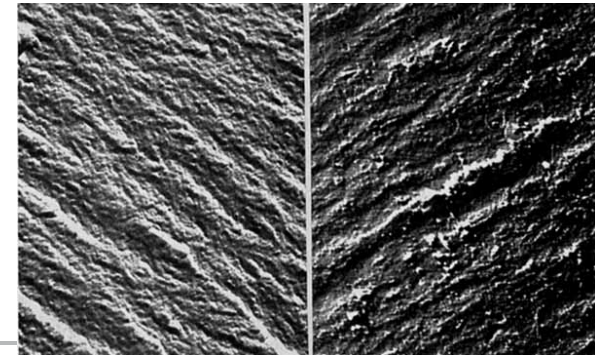
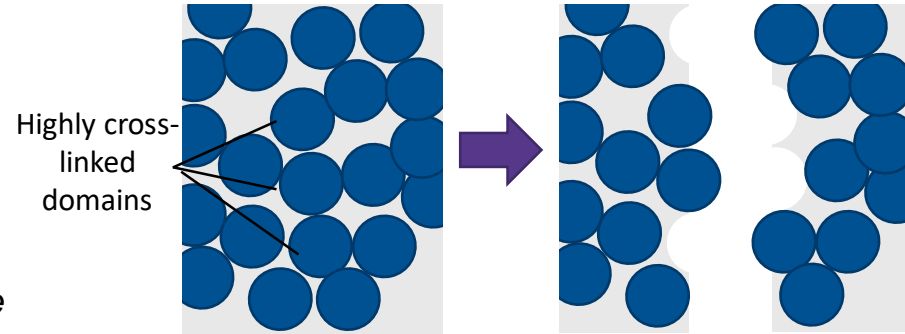


Occurrence of Globular Formations in Thermosetting Networks,
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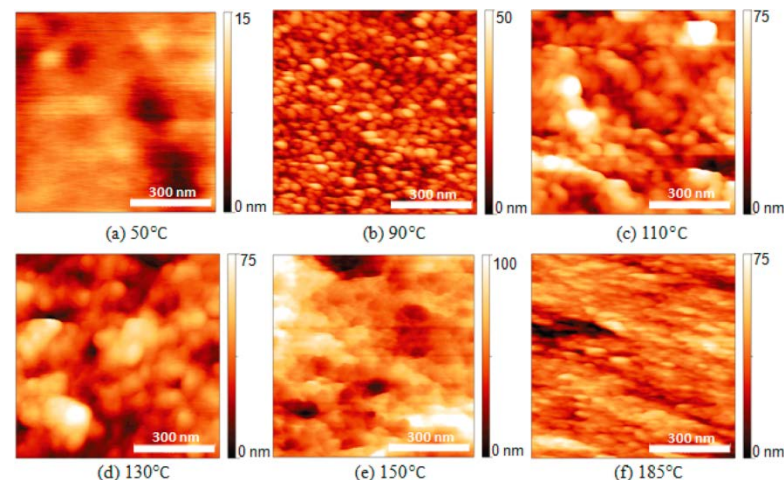
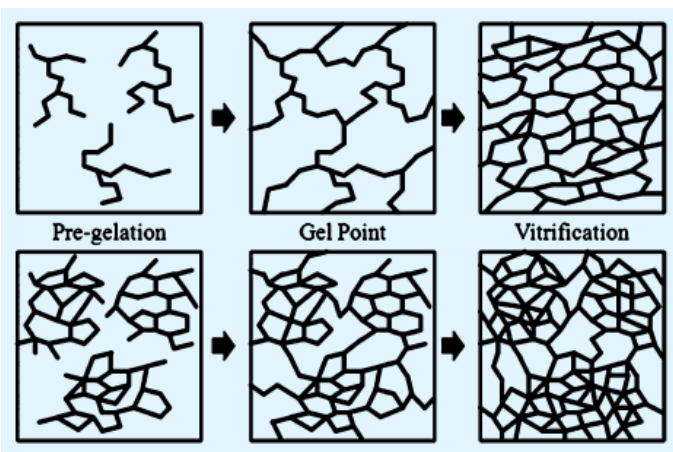
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Heterogeneous Nanostructure in Thermosetting Resins

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- But, remains controversial, at this length scale tip artefacts are proposed as an explanation (Duchet, J.; Pascault, J. Do Epoxy–Amine Networks Become Inhomogeneous at the Nanometric Scale? *J. Polym. Sci. Part B: Polym. Phys.* 2003, 41, 2422–2432.).



Thermal Control of Nanostructure and Molecular Network Development in Epoxy-Amine Thermosets Sahagun, C.; Morgan, S. *ACS Appl. Mater. Interfaces* **2012**, 4, 564–572.

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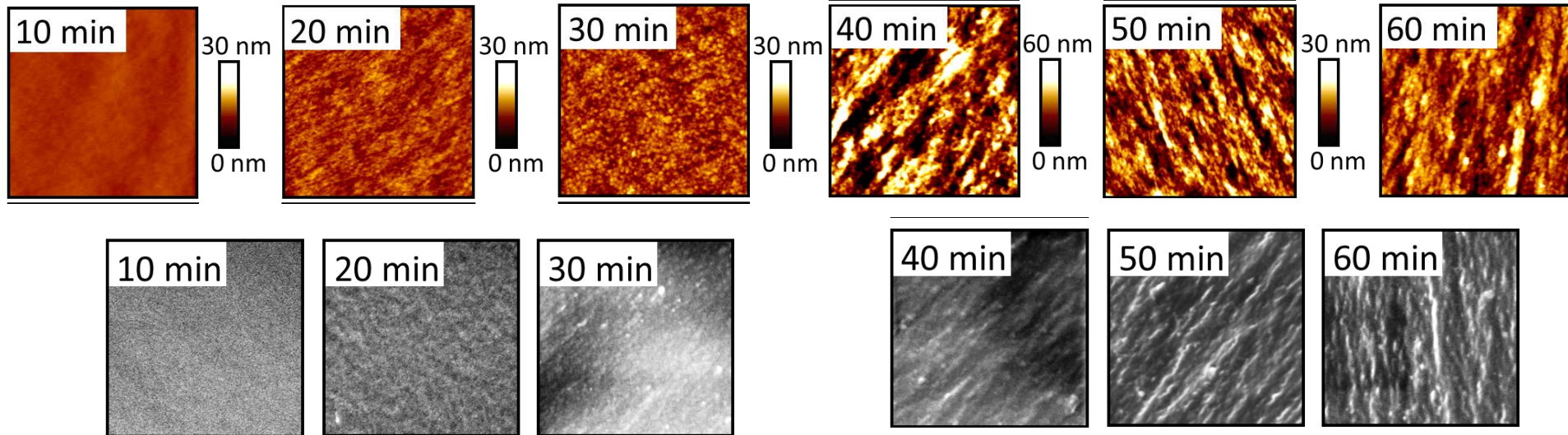
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Nanostructure of the Epoxy-Phenolic Resins

- Slowing the cure reaction (lowering the catalytic content to 0.1 %) allowed us to observe the development of a nodular internal morphology.
- Since artefacts in SEM and AFM have different origins, and 10 minute cure samples appear homogeneous, it seems likely this represents a real internal structure.



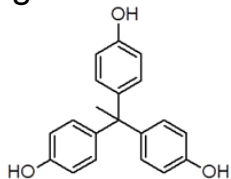
2 μm x 2 μm peakforce tapping mode AFM and SEM images

Controlling the Nanostructure

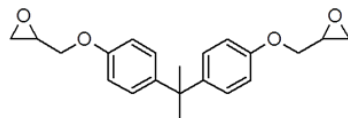
Mono-functional Additives

Various temperatures, high/low functionality precursors, catalyst content and epoxy amine resin nanostructures have been investigated.

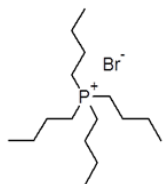
The addition of 4-benzylphenol to the epoxy-phenolic resin was shown to result in homogeneous internal nanostructures.



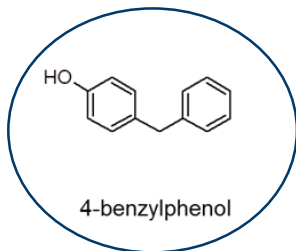
1,1,1-tris(4-hydroxyphenyl)ethane



Bisphenol-A diglycidyl ether

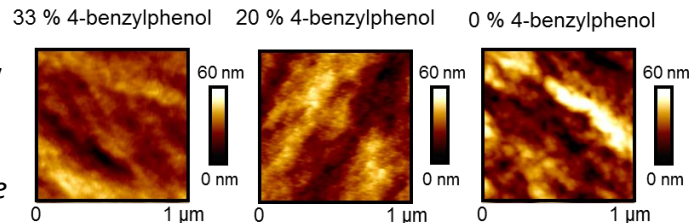


Tetrabutylphosphonium bromide

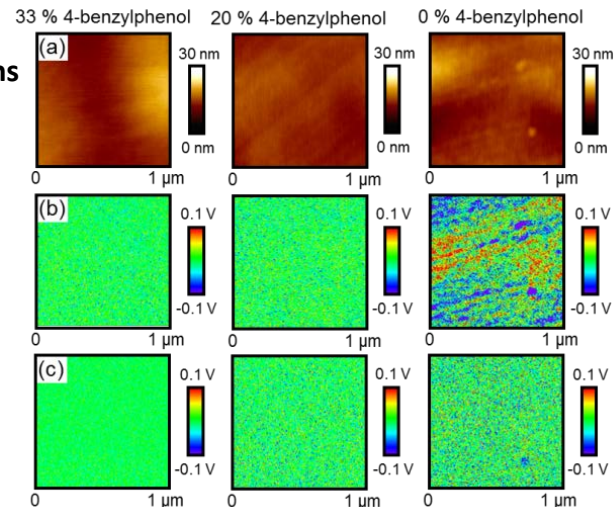


4-benzylphenol

Cryogenically fractured
– peak force tapping mode



Microtomed cross-sections
– contact mode Height



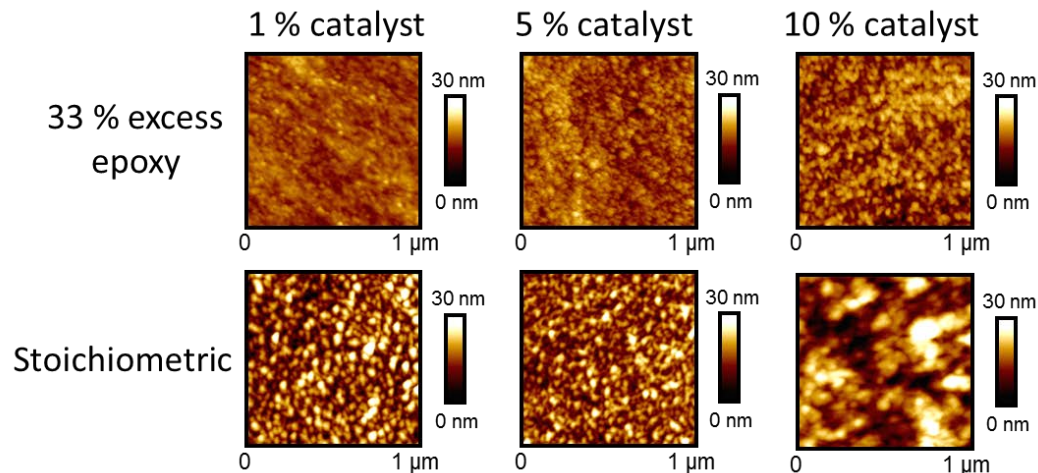
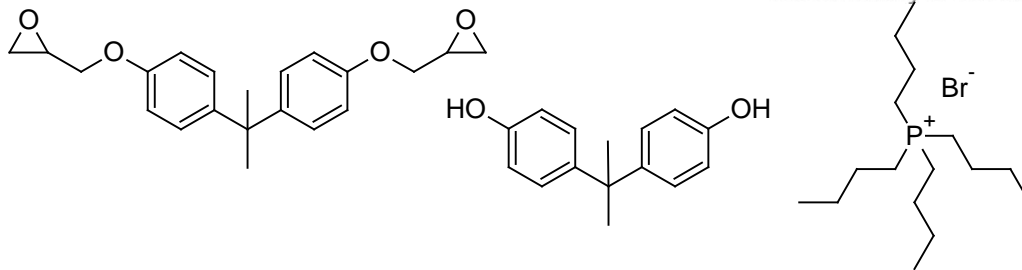
1116 cm^{-1}
Secondary hydroxyls – proxy for cure

1504 cm^{-1}
Aromatic groups – unchanging on cure

Controlling the Nanostructure

Stoichiometry and Catalyst Selectivity

- Using 2 + 2 system: DGEBA and BPA to explore the effects of reaction selectivity (epoxy reaction with the phenolic vs. secondary OH groups)
- Reaction through secondary OH results in cross-linking and resin formation.
- Excess epoxy results in more homogeneous resins, which become increasingly nodular as catalyst content increases.

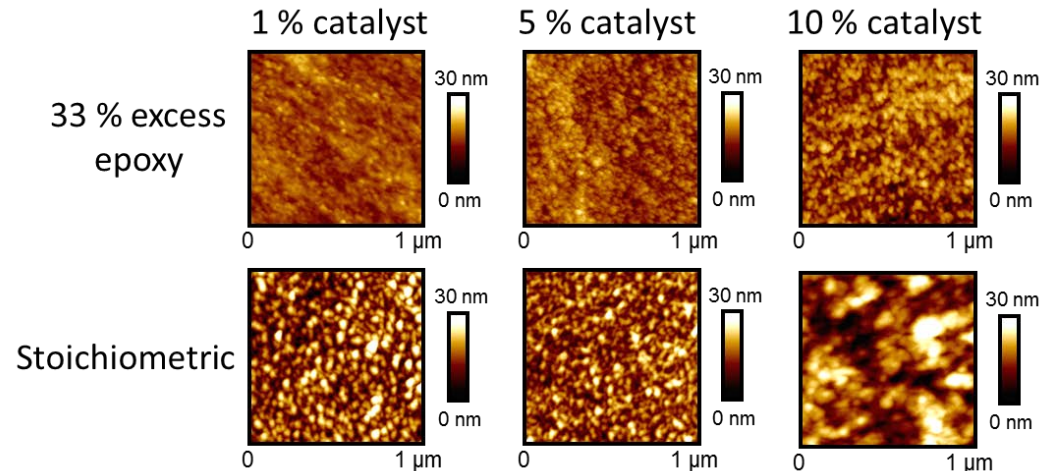
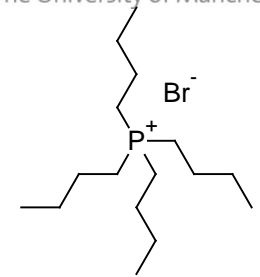


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Catalyst affects
network
formation..?



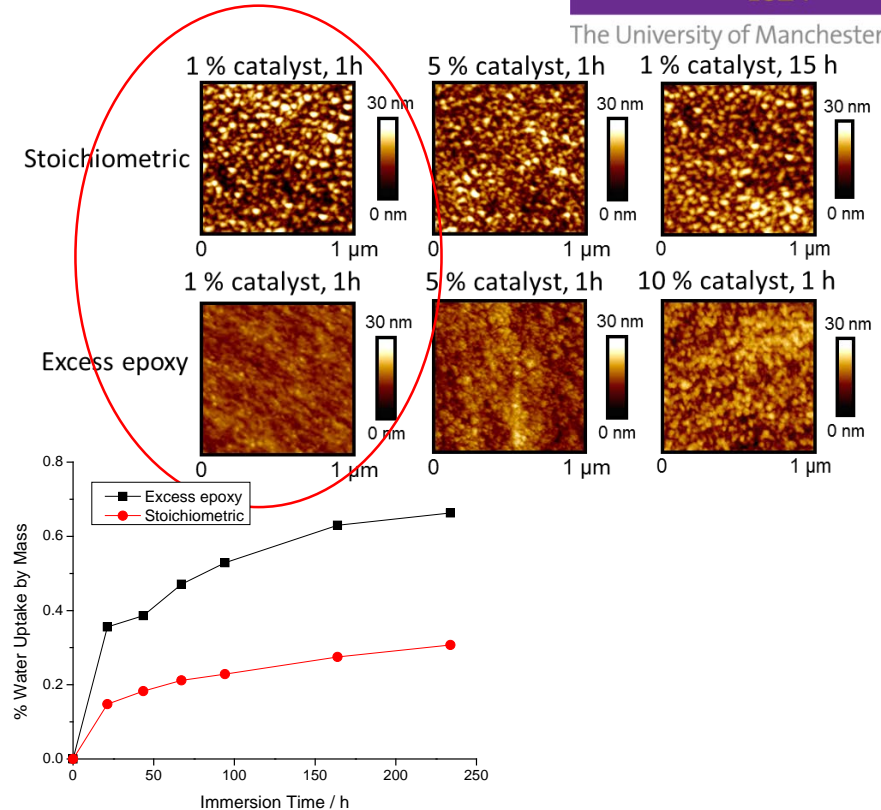
Controlling Small Molecule Transport..?

Nanostructure and water uptake

- Nanothermal analysis showed that catalyst plasticises the resins.
- To examine the effects of nanostructure resins prepared using 1 % catalyst compared.
- Gravimetric analysis was performed over a 10 day period by immersion in deionised water (pH 5).

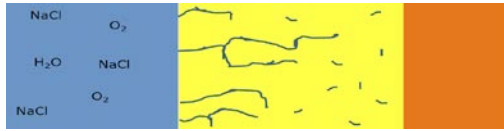
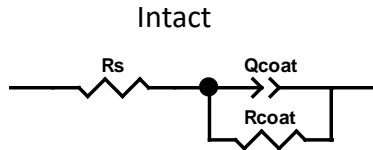
➤ *More homogeneously structured (and less polar!) excess epoxy resins were less resistant to water uptake.*

Catalyst Content	Thermal Transition Temperature	
	Stoichiometric epoxy	Excess
1 %	90.1 ± 0.9 °C	83.4 ± 0.4 °C
5 %	88.4 ± 0.4 °C	79.3 ± 0.3 °C
10 %	83.9 ± 0.7 °C	77.9 ± 0.3 °C

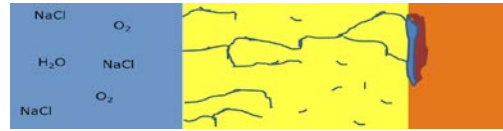
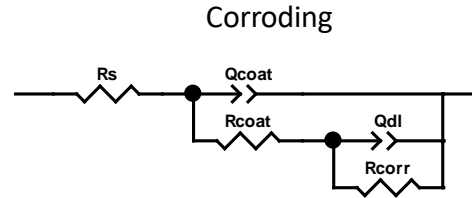


Controlling Small Molecule Transport..?

Electrochemical impedance spectroscopy (EIS): Nanostructure and ion transport



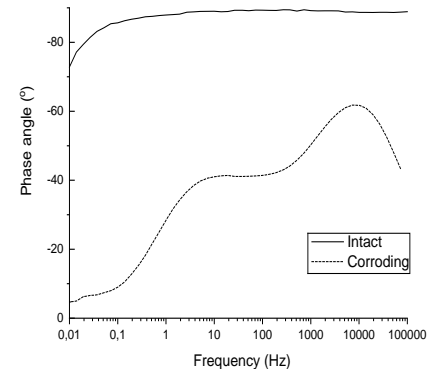
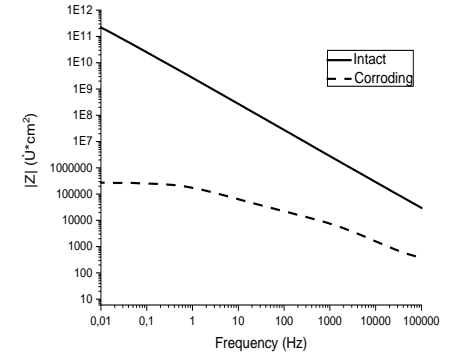
No ion transport pathway



With an ion transport pathway

- **50 %** of the excess epoxy samples **failed** (two time constant behaviour) immediately. All fail within the tested immersion time (4 days).
- Stoichiometric formulations survived longer (i.e., prevented ion transport between the electrolyte and metal) and 66 % showed no signs of corrosion after 4 days.

➤ *Nanostructure is not the controlling factor!*



Current Hypothesis

- ↯ Nominally homogeneous epoxy-phenolic coatings are actually heterogeneously cross-linked at the nanoscale.
- ↯ Diffusion of water occurs preferentially through less-dense regions.
- ↯ Plasticisation of the polymer by absorbed water and internal stresses generated by its heterogeneous distribution then lead to deformation of the coating and clustering of water, ultimately yielding hydrophilic nano-voids in the coating.
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SUSTICOAT



The SUSTICOAT project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 721451

MOOC – On Course to Corrode

<http://www.couresera.org/manchester>



ACPOC 2021 – EFC Event 451

Advances in corrosion protection by organic coatings

Christ's College, Cambridge, 5th - 9th September 2021

Sunday reception 5th September

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Then 4 days of coatings and corrosion – Gordon Conference Style

Sustainable coatings and formulations

Smart and functional coatings

Film formation and degradation

Under-film corrosion

Conversion layers

Other related areas

Pigments, inhibitors and smart coatings

Mechanisms of protection

Adhesion and its enhancement

Surface preparation

Test methods

Organised by Stuart, University of Manchester and Geraint Williams, University of Swansea

Further details to follow – <https://acpocconference.org/>

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Thank You for Your Attention

Stay Safe