Microstructure identification in BPANI food can-coating systems

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Microstructure identification in BPANI food can-coating systems

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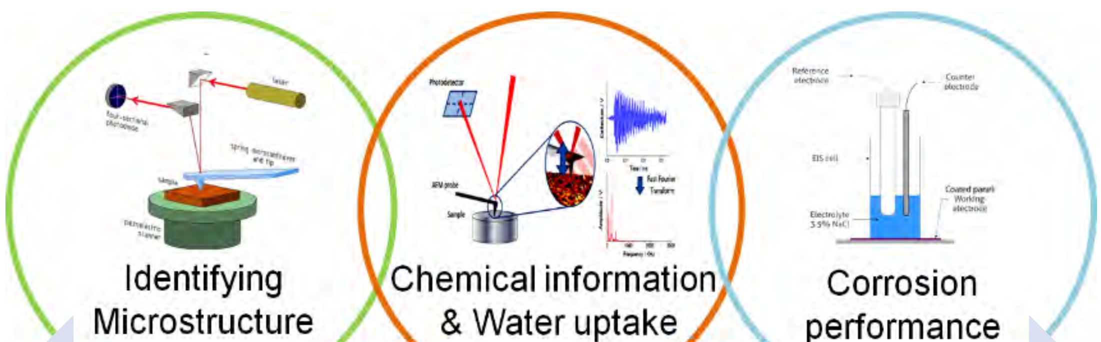
- ***Motivation:*** Bisphenol A non-intended (BPAni) coating system for food cans offer sustainable replacement over epoxy based coatings but comprise on the shelf life.

- ***Objective:*** To use the current understanding of organic coating at the UoM and their expertise in advance characterization techniques in studying industrial grade complex formulation BPAni food can coating,

- ***Microstructural guidance approach:*** As polymer system show high structure-to-property correlation, a good understanding of coating microstructure can be leverage to improve coating performance



Good understanding of microstructure can be leveraged to improve coating performance

BPANI Coatings Systems

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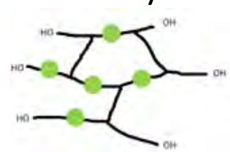
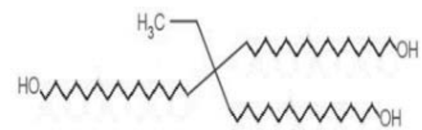
Vitalure® BPANI Coatings		
Variants	Chemical Resistant Type (CRT Coating)	Flexible Type (FT Coating)
Uses	Internal can coatings - 3 piece cans (standard ends and bodies)	Internal can coatings - 3 piece cans (standard ends and bodies, easy open ends)
Binder	CRT Polyester 	FT Polyester 
Formulation	solvent-based Crosslinkers- phenolic resin, benzoguanamine resin	solvent-based Crosslinkers- phenolic resin, benzoguanamine resin, isocyanate crosslinker (blocked IPDI)
Substrate	Electrolytic tinplated steel (ETP Steel)	Electrolytic tinplated steel (ETP Steel)
Cure Condition	200° C for 10 min at PMT (peak metal temperature)	200° C for 10 min at PMT (peak metal temperature)
Chemical resistant	Suitable for all types of food very acidic – very alkaline food	Suitable for mild acidic – alkaline food
Flexibility	Not suitable for easy open ends	Suitable for easy open end

Preliminary microstructural analysis by Atomic Force Microscopy (AFM)

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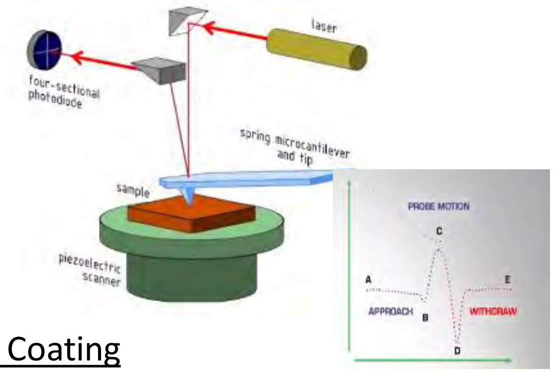
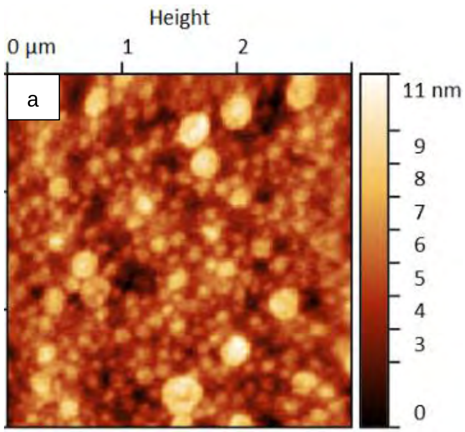
- Microstructure identification using AFM PeakForce QNM (Quantitative Nano-Mechanical) tapping mode



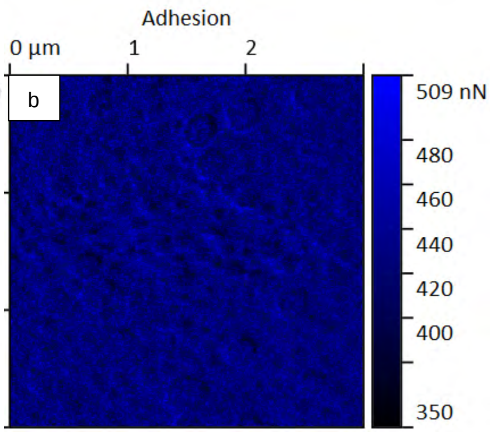
- Height images show two distinct morphology in CRT and FT coatings; "bead-like" in CRT and "island-like" in FT

CRT Coating

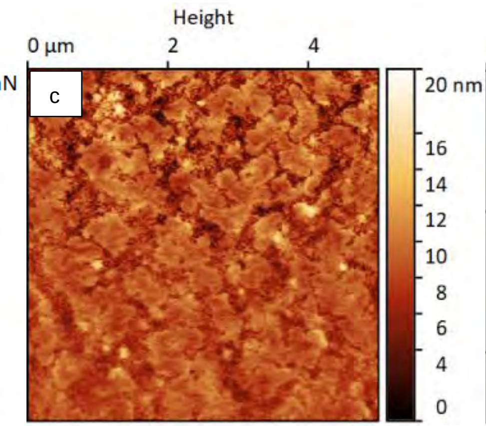
FT Coating



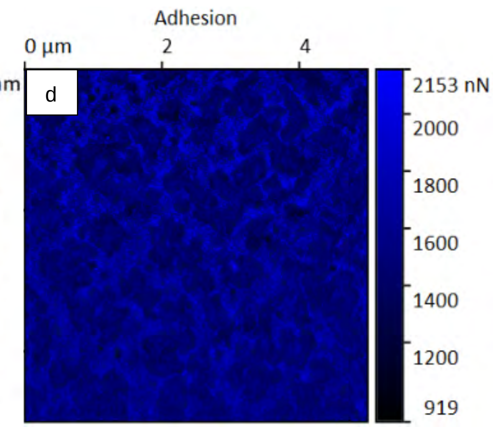
a. CRT Height image 10 µm x 10 µm



b. CRT Adhesion image 10 µm x 10 µm



c. FT Height image 5 µm x 5 µm



d. FT Adhesion image 5 µm x 5 µm

- Adhesion image: Force of adhesion is a quantity directly measured from the force-distance curves. Gives a indication of local mechanical properties – local hardness.

  Higher adhesion → Soft surface

  Lower adhesion → Hard surface

Preliminary microstructural analysis by Atomic Force Microscopy (AFM)

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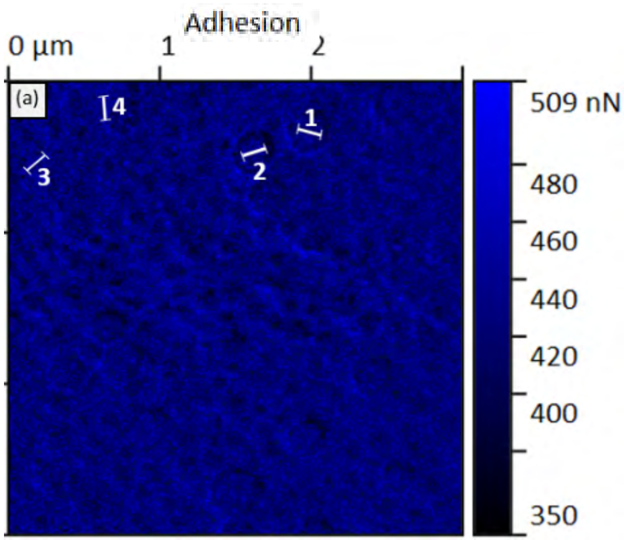
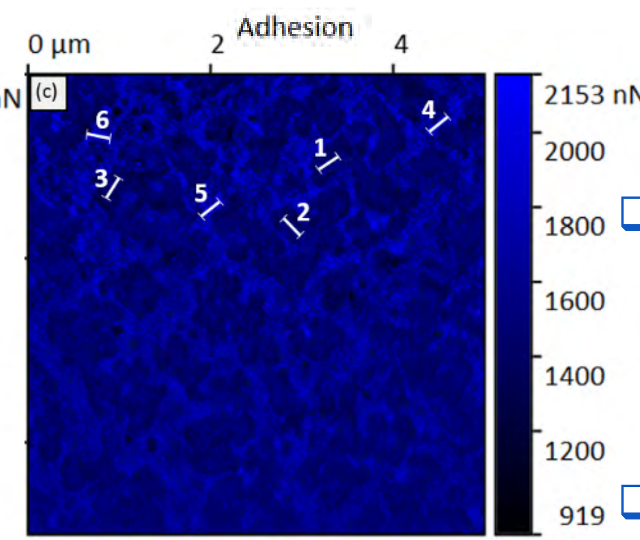
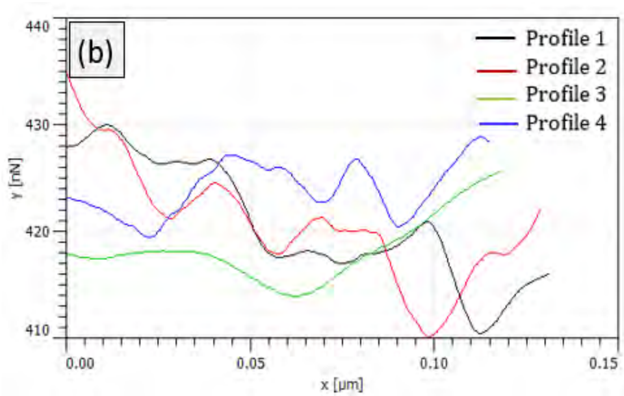
- Adhesion image profile analysis

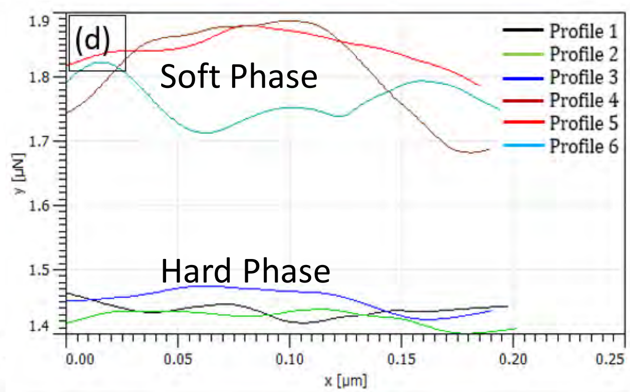


CRT Coating Adhesion image



FT Coating Adhesion image

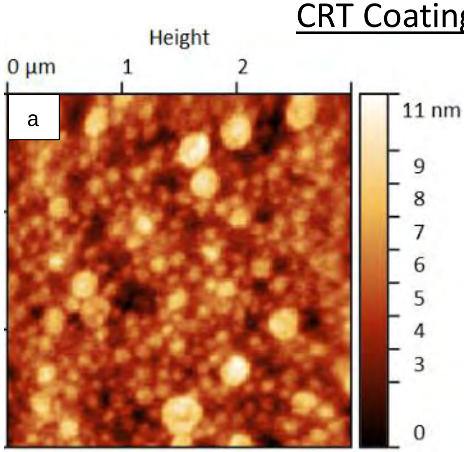




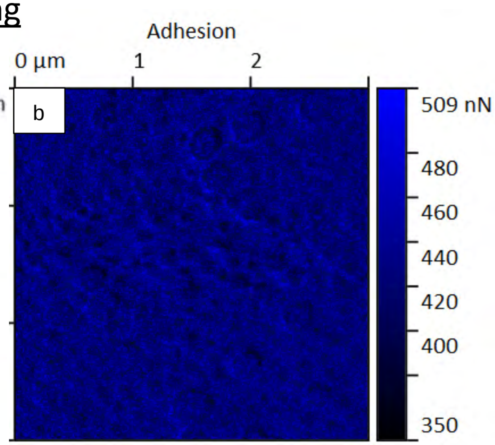
- In CRT coating, adhesion values average around a single value inside the bead or outside the bead.
- In FT coating, adhesion values average around two different values, each corresponding a “hard phase” and a “soft phase”

Thermal analysis supporting microstructure analysis

CRT Coating

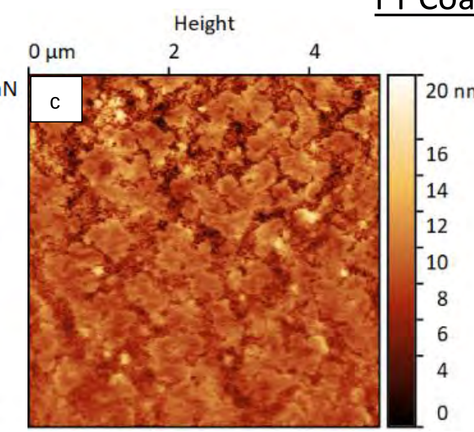


a. CRT Height image 10 µm x 10 µm

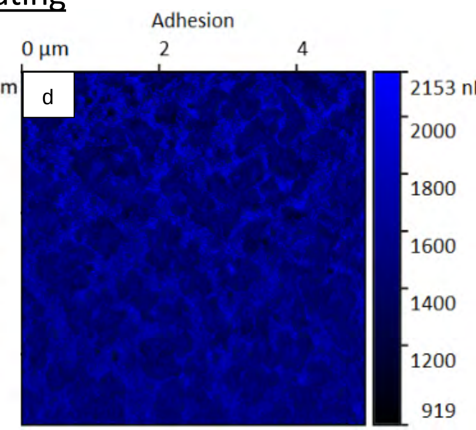


b. CRT Adhesion image 10 µm x 10 µm

FT Coating



c. FT Height image 5 µm x 5 µm



d. FT Adhesion image 5 µm x 5 µm

DSC

No.	**Sample name**	**Tg (°C)**
1	CRT	107

DSC

No.	**Sample name**	**Tg(1) (°C)**	**Tg (2) (°C)**
1	FT	8	40

DMA

No.	**Sample name**	**Tg(tan δ) (°C)**
1	CRT	105.5

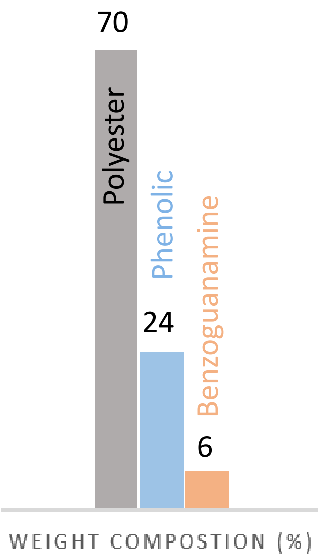
DMA

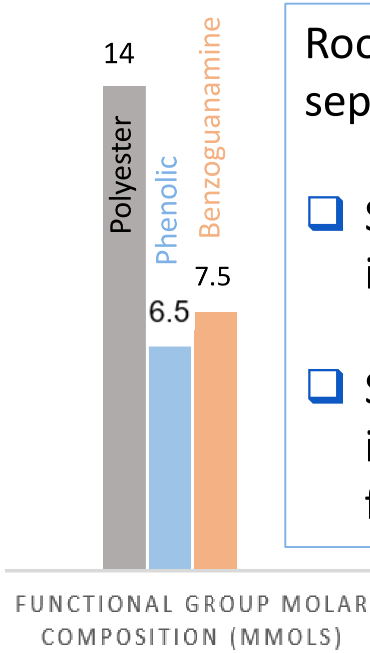
No.	**Sample name**	**Tg(tan δ) (°C)**	**Tg (E”) (°C)**
1	FT	5	38

- Thermal analysis support microscopy findings i.e. CRT coatings are homogeneous and FT coatings show two phases

Root cause of phase separation

Chemical resistant type (CRT) Coating

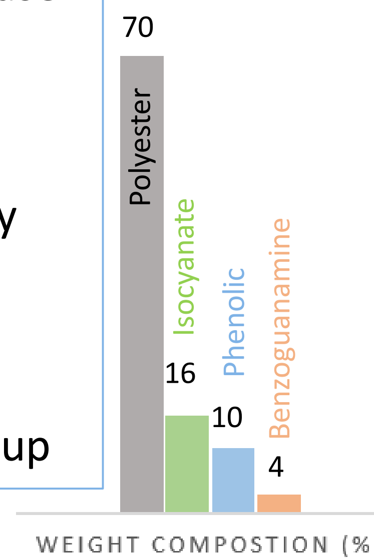


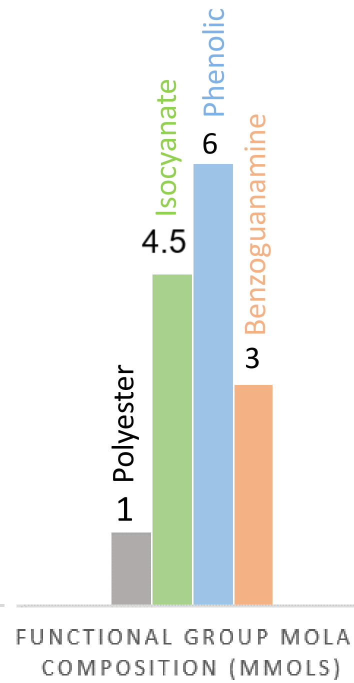


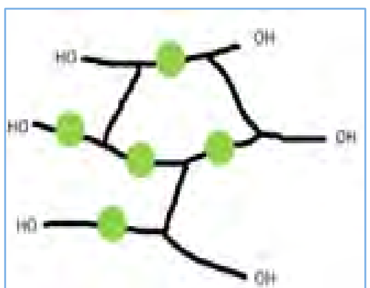
Root cause of phase separation

- ❑ Structural incompatibility
- ❑ Stoichiometry imbalance of functional group

Flexible type (FT) Coating



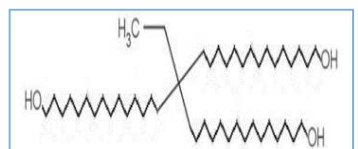




CRT polyester

– high hydroxyl, low molecular weight, high branching

– high aromatics and cycloaliphatic in the backbone



FT polyester

– low hydroxyl, high molecular weight, low branching

– linear hydrocarbon chains

Understanding phase separation in FT coting using Model Systems

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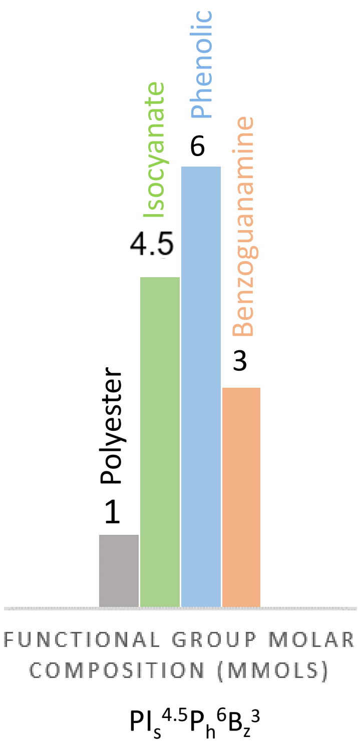
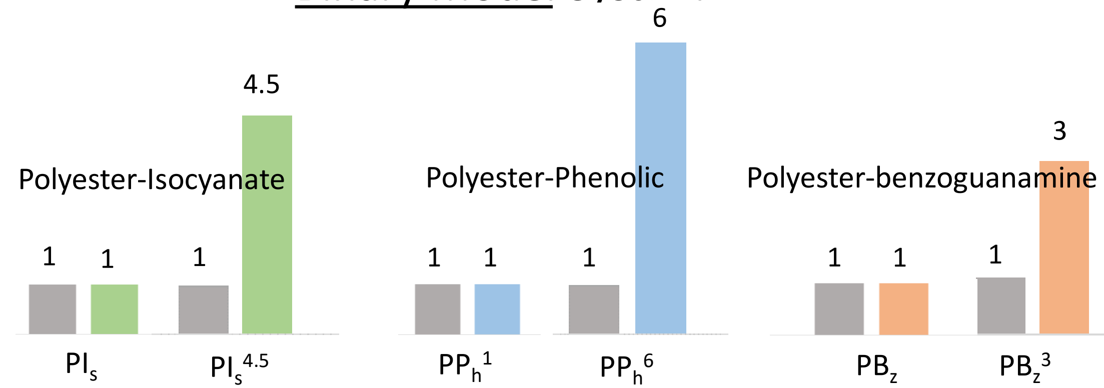
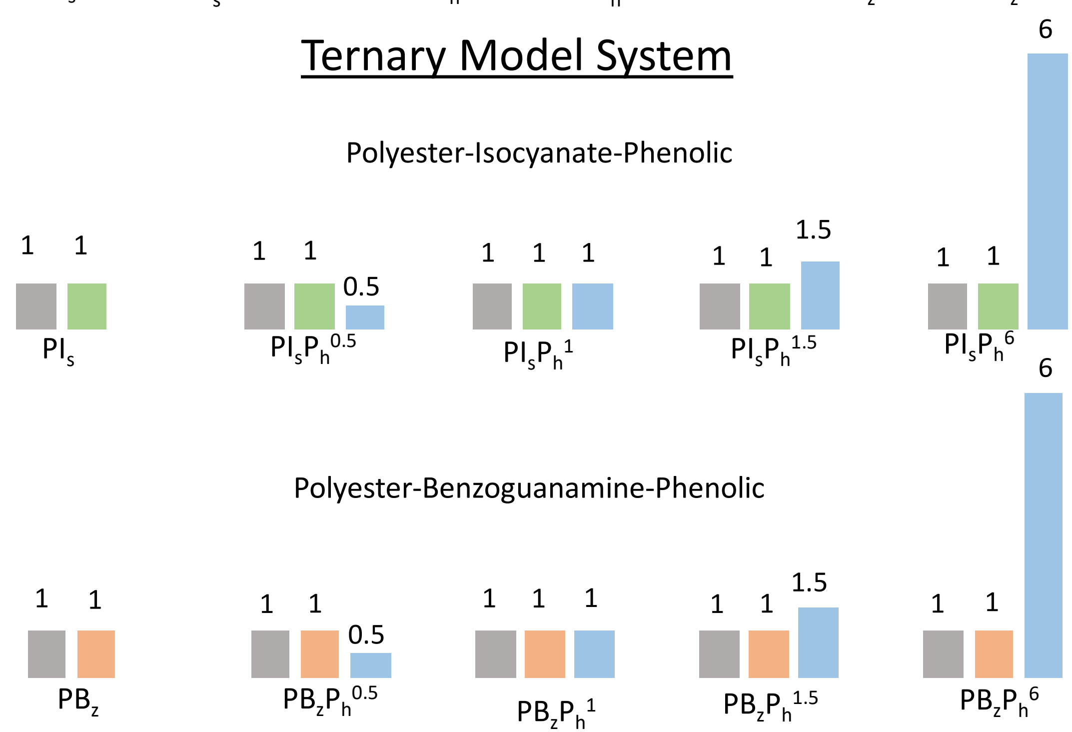
Polyester - P
Isocyanate - I_s
Phenolic - P_h
Benzoguanamine - B_z



Binary Model System

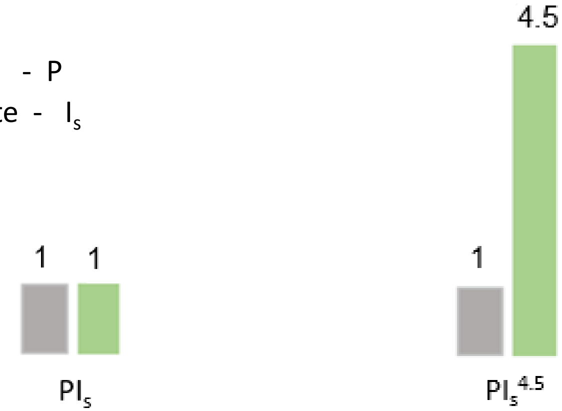


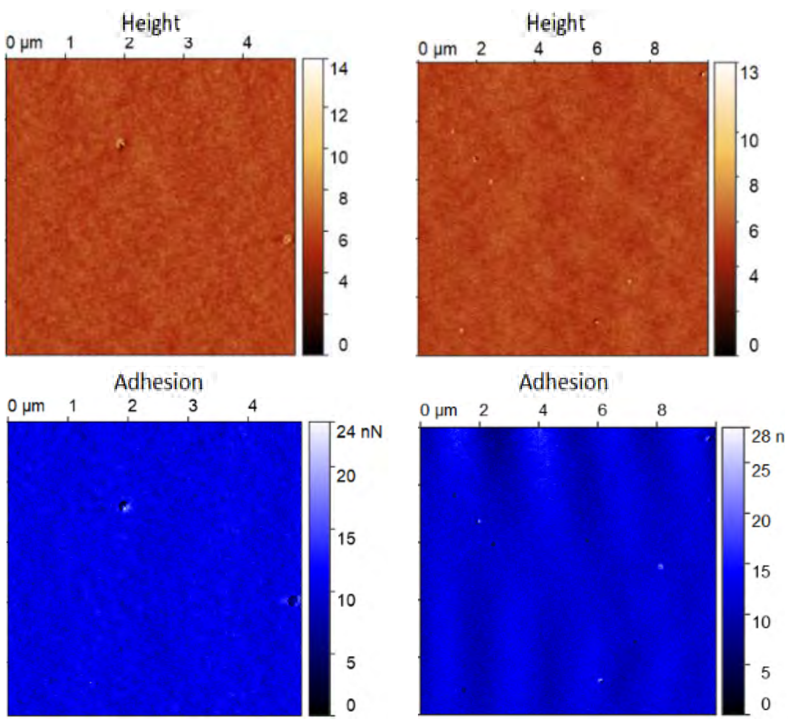
Ternary Model System

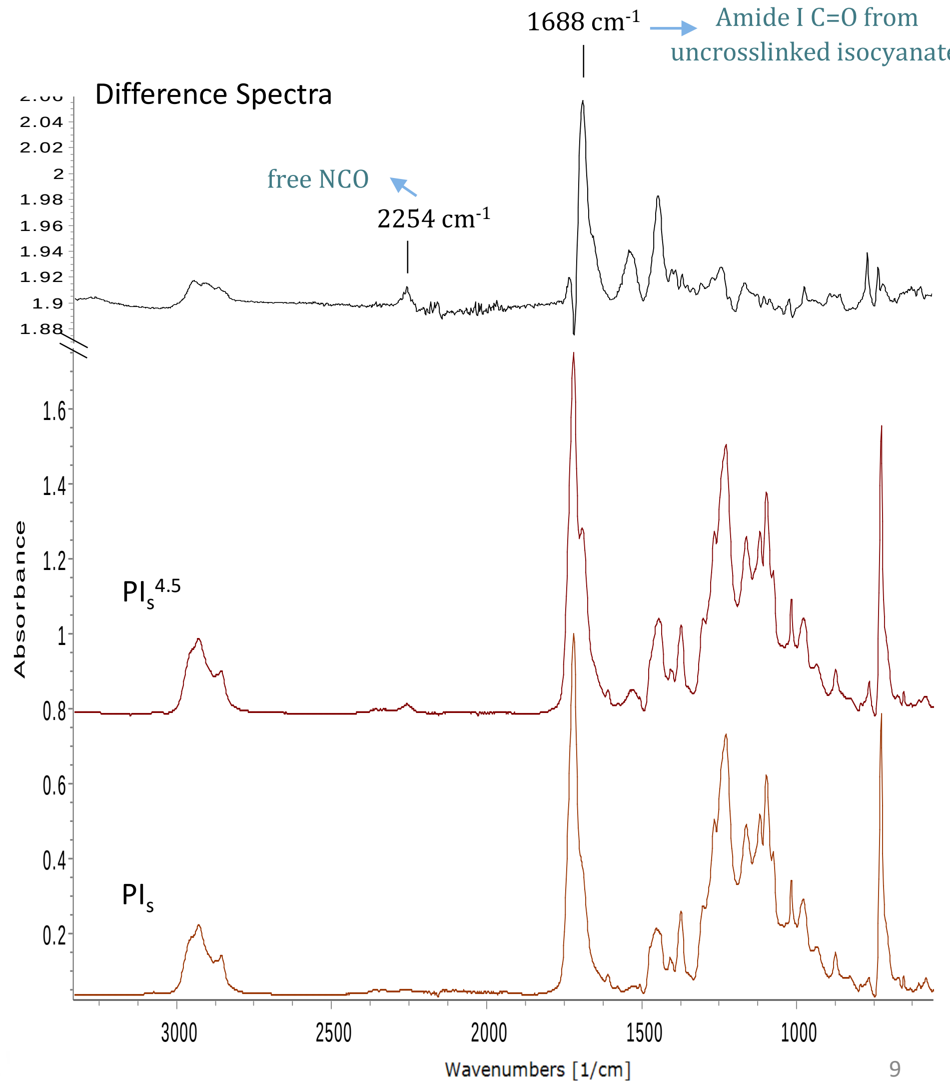


Binary Model System for Polyester-Isocyanate

Polyester - P
Isocyanate - I_s







Binary Model System for Polyester-Isocyanate

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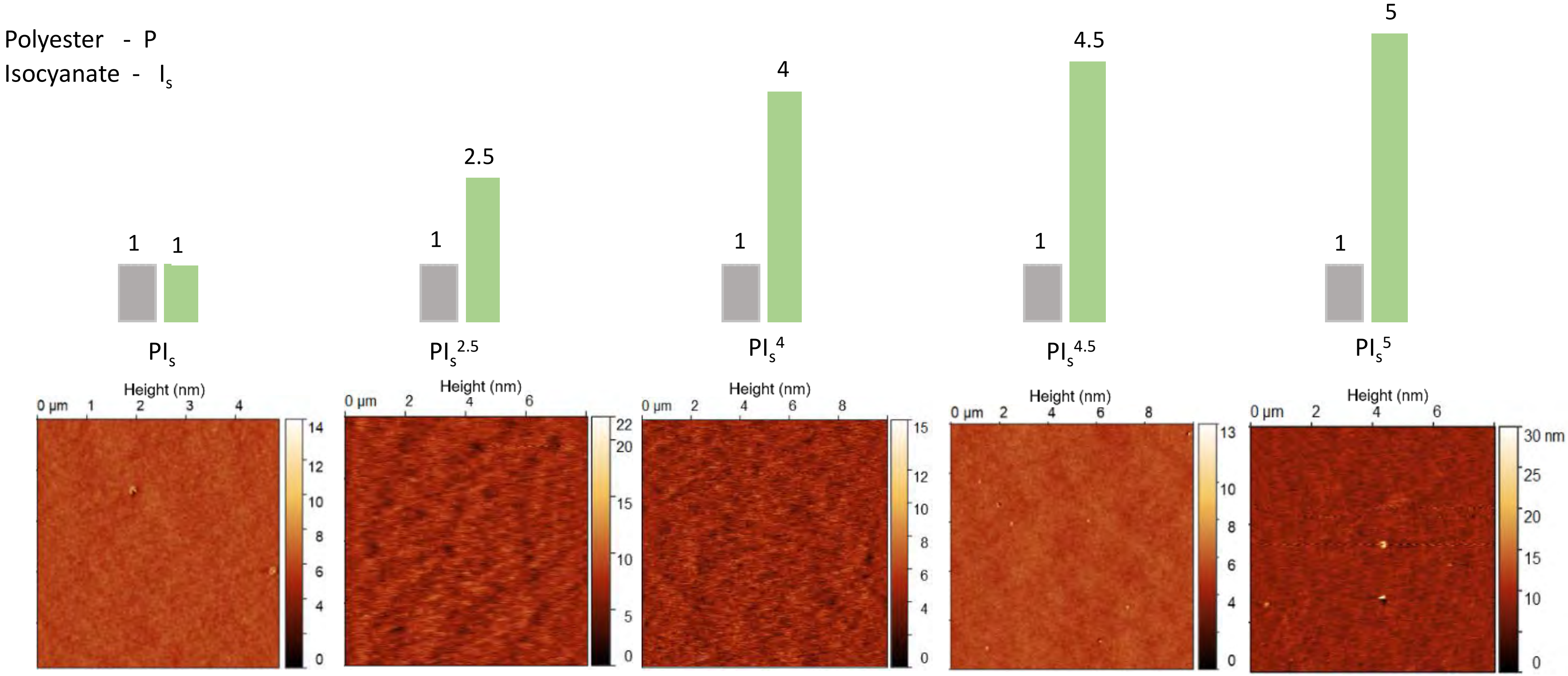

- Polyester-Isocyanate make homogenous coatings
- Isocyanate and polyester are compatible, unreacted isocyanate remains souble in polyester

Binary Model System for Polyester-Phenolic Polyester-Benzoguanamine

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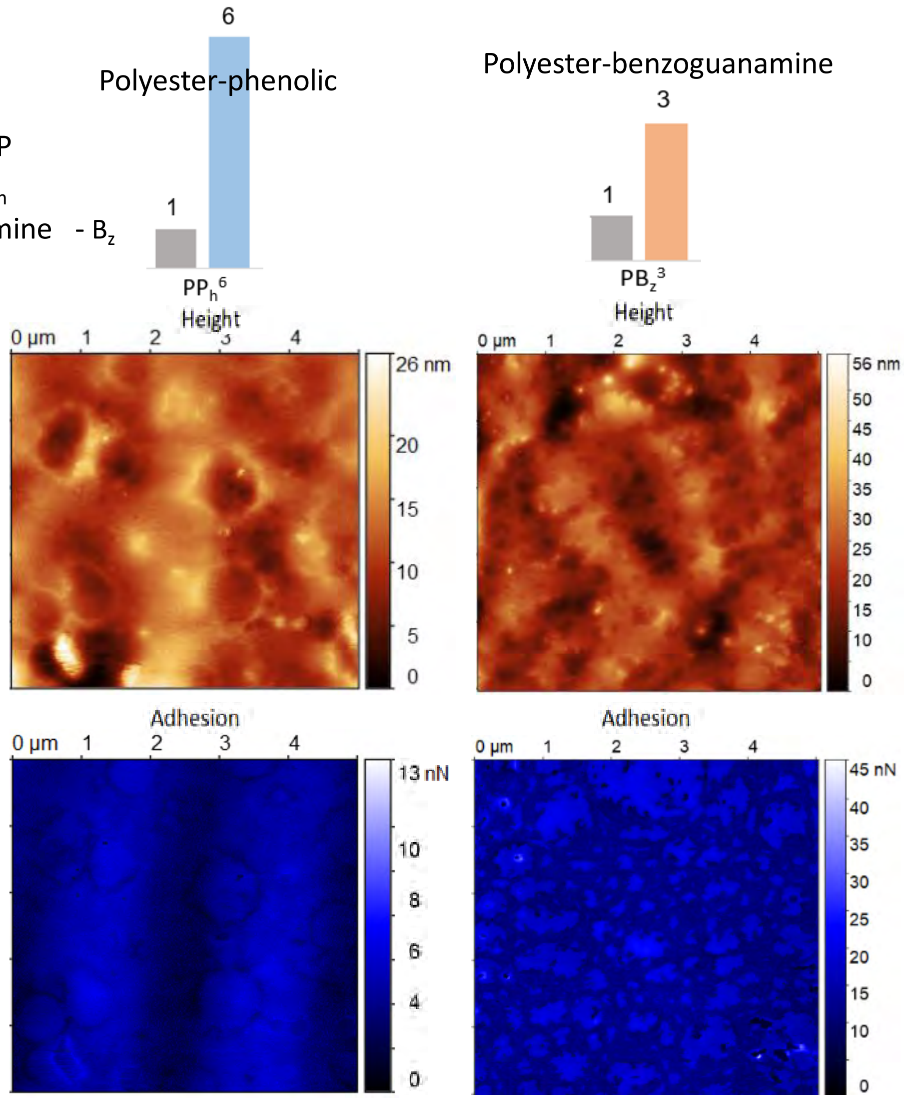
Polyester - P
Phenolic - P_h
Benzoguanamine - B_z

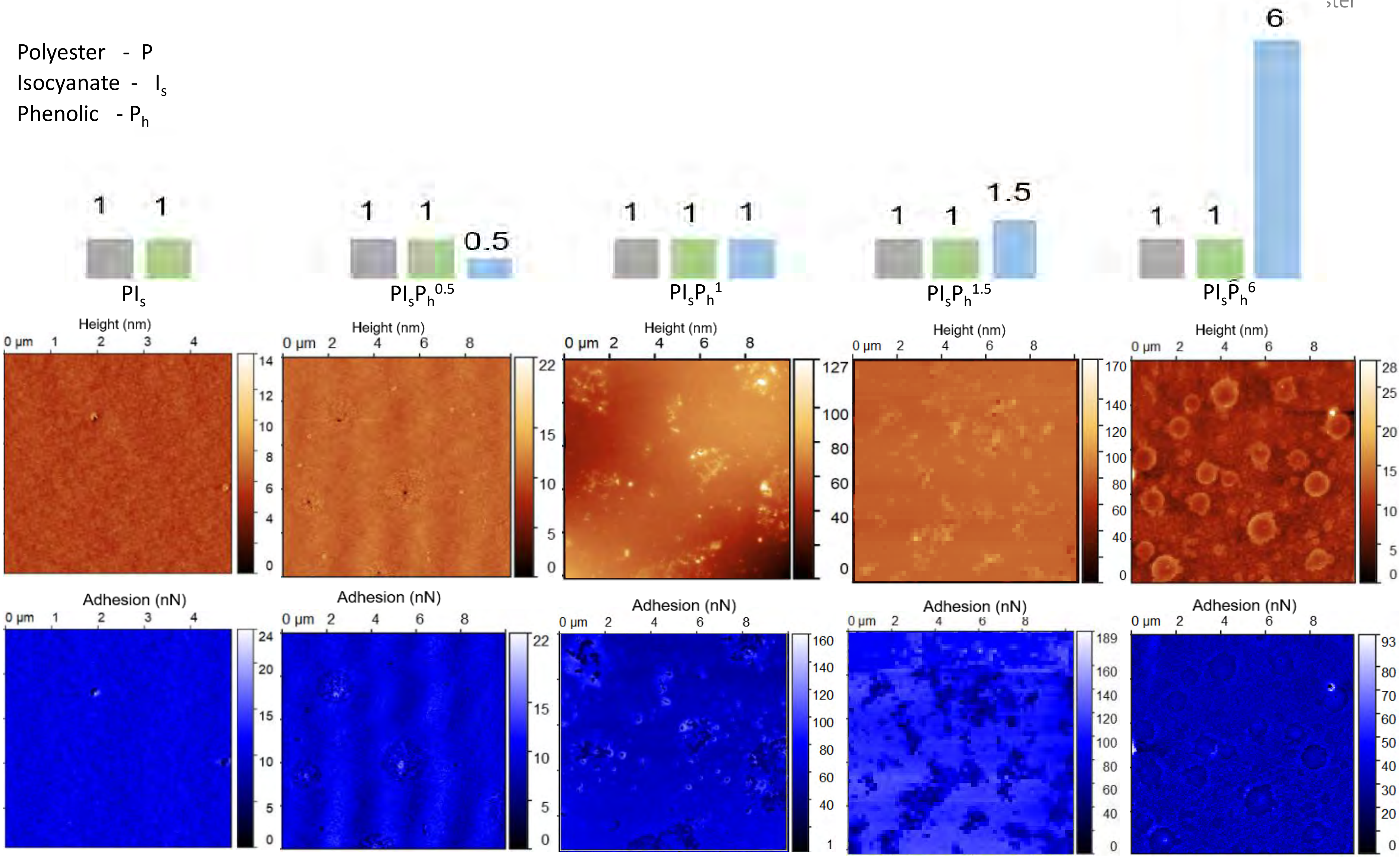


For binary system with stoichiometric excess

- Polyester-phenolic shows globular phase
- Polyester- benzoguanamine show two-phase morphology
- Phenolic/benzoguanamine incompatible with polyester

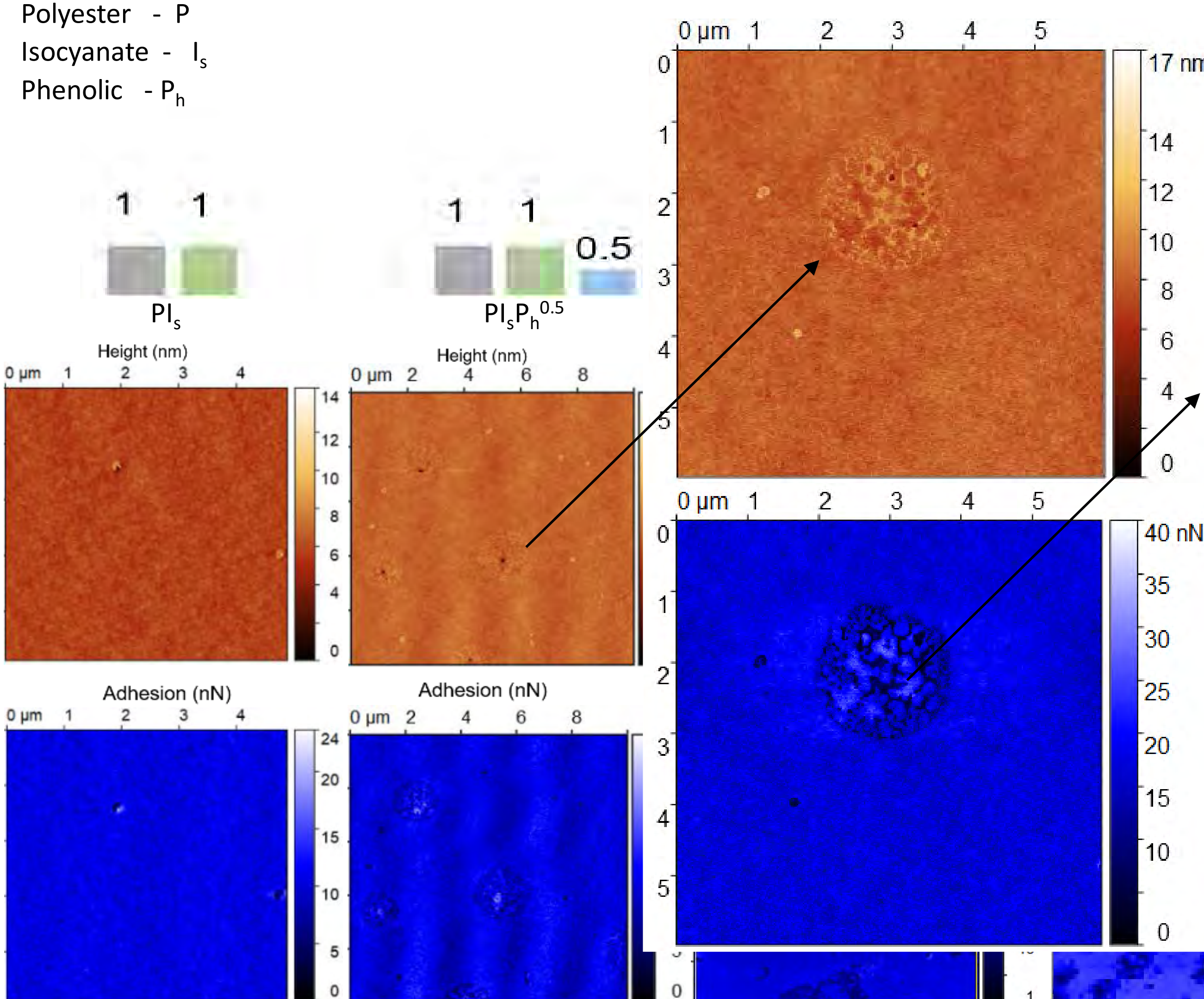
Ternary Model System for Polyester-Isocyanate-Phenolic

Polyester - P
Isocyanate - I_s
Phenolic - P_h



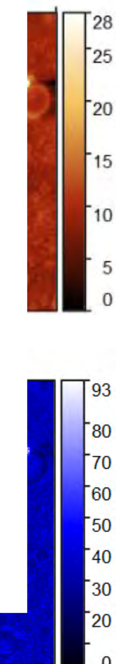
Ternary Model System for Polyester-Isocyanate-Phenolic

Polyester - P
Isocyanate - I_s
Phenolic - P_h



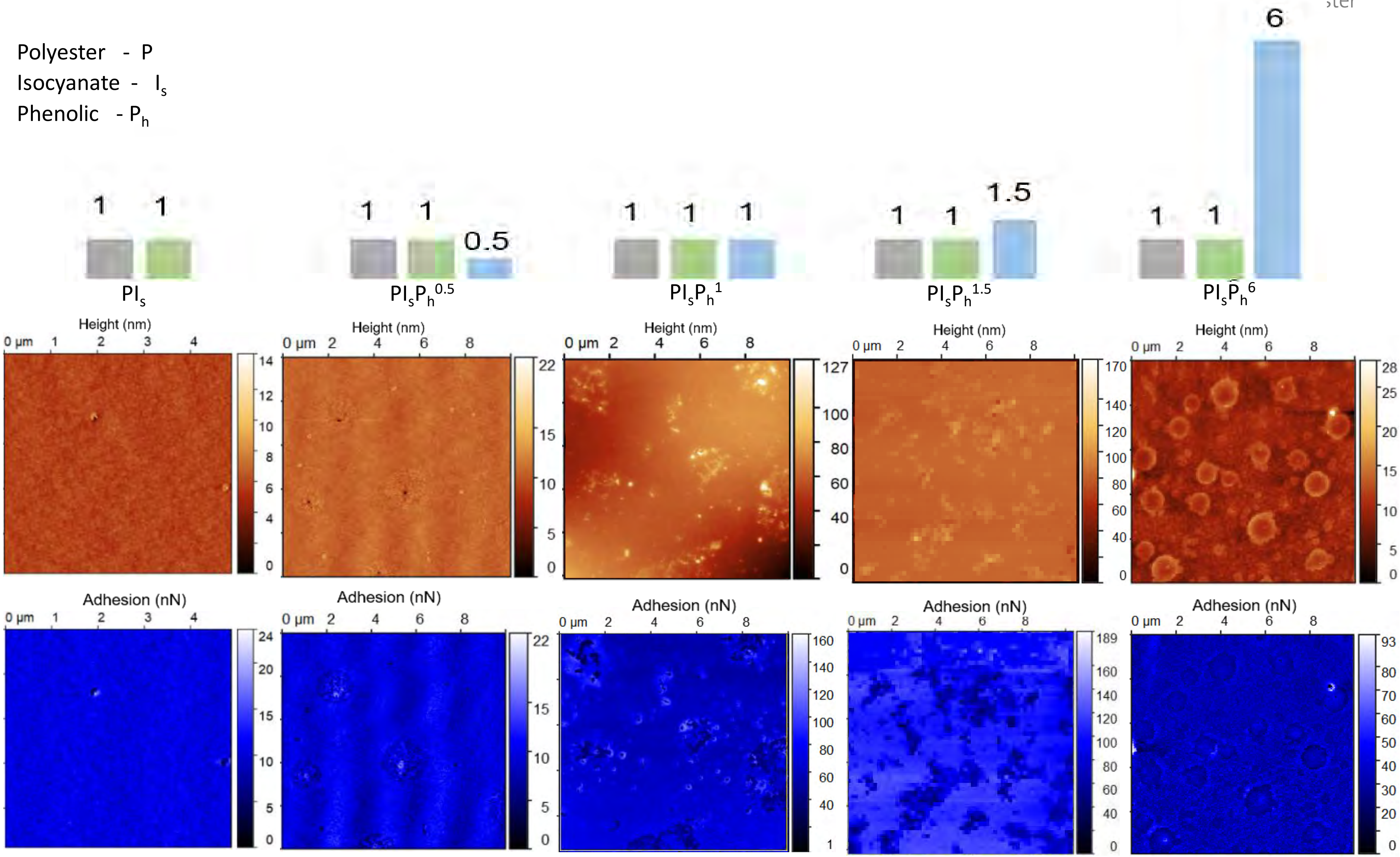
Clusters of co-continuous nodular domains

- Characteristic two phased structures
- "hard" nodular structures in "soft" bulk phase



Ternary Model System for Polyester-Isocyanate-Phenolic

Polyester - P
Isocyanate - I_s
Phenolic - P_h

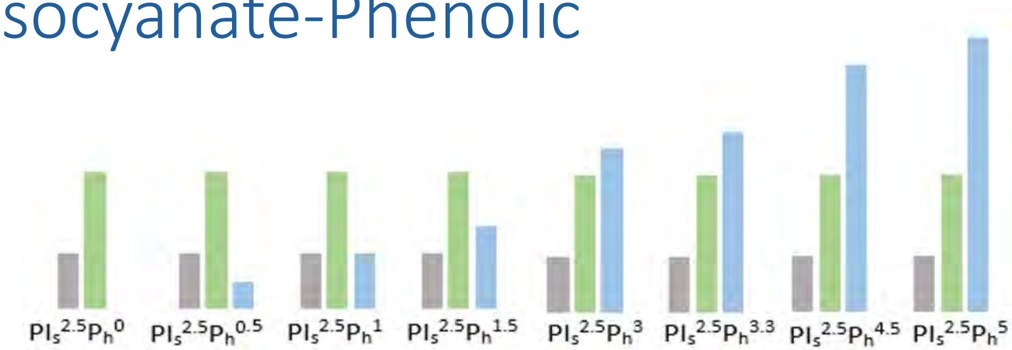


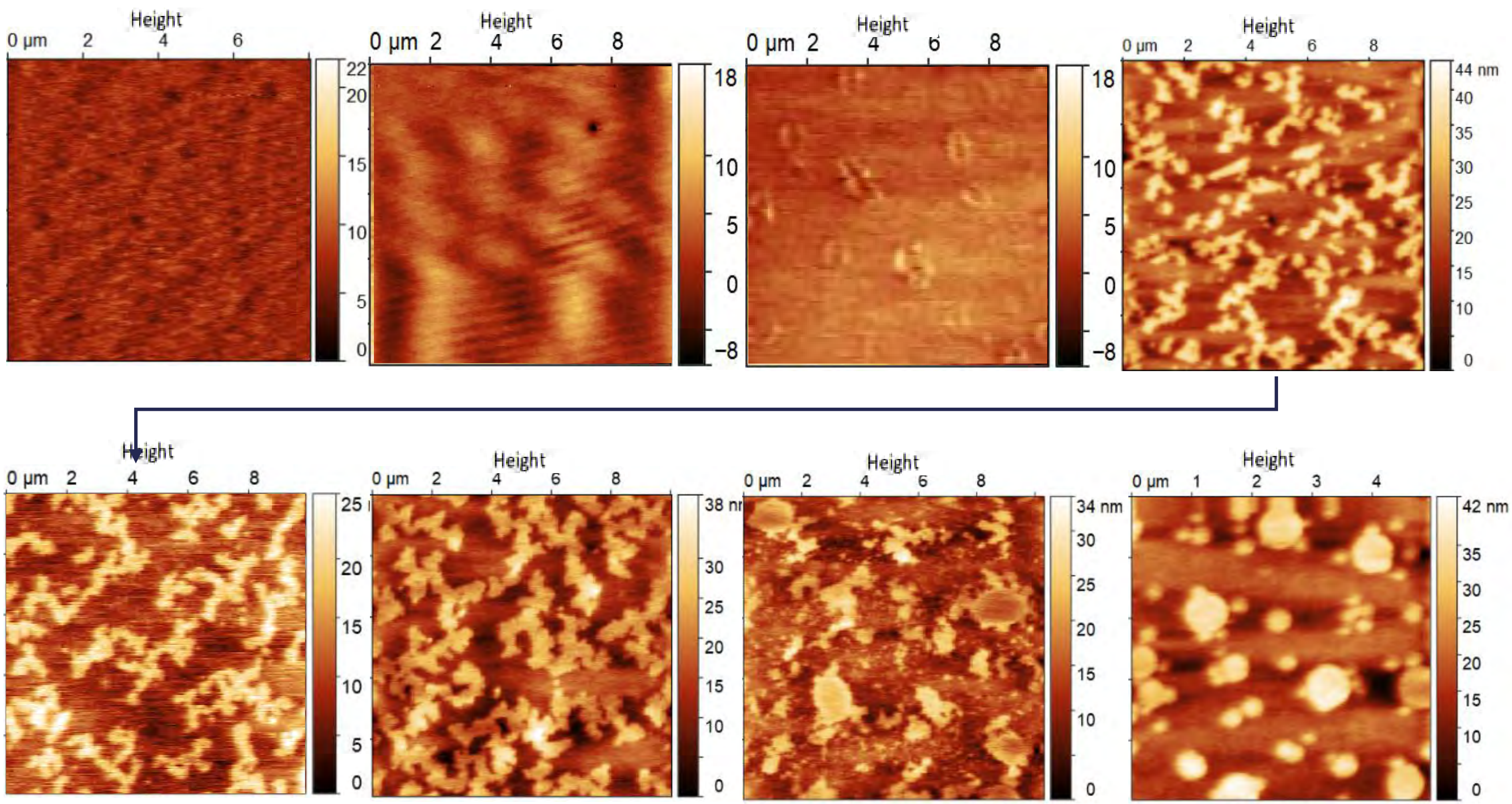
Ternary Model System for Polyester-Isocyanate-Phenolic

Polyester - P

Isocyanate - I_s

Phenolic - P_h





Nodular phase/Globular phase -mechanical properties (AFM PeakForce QNM)

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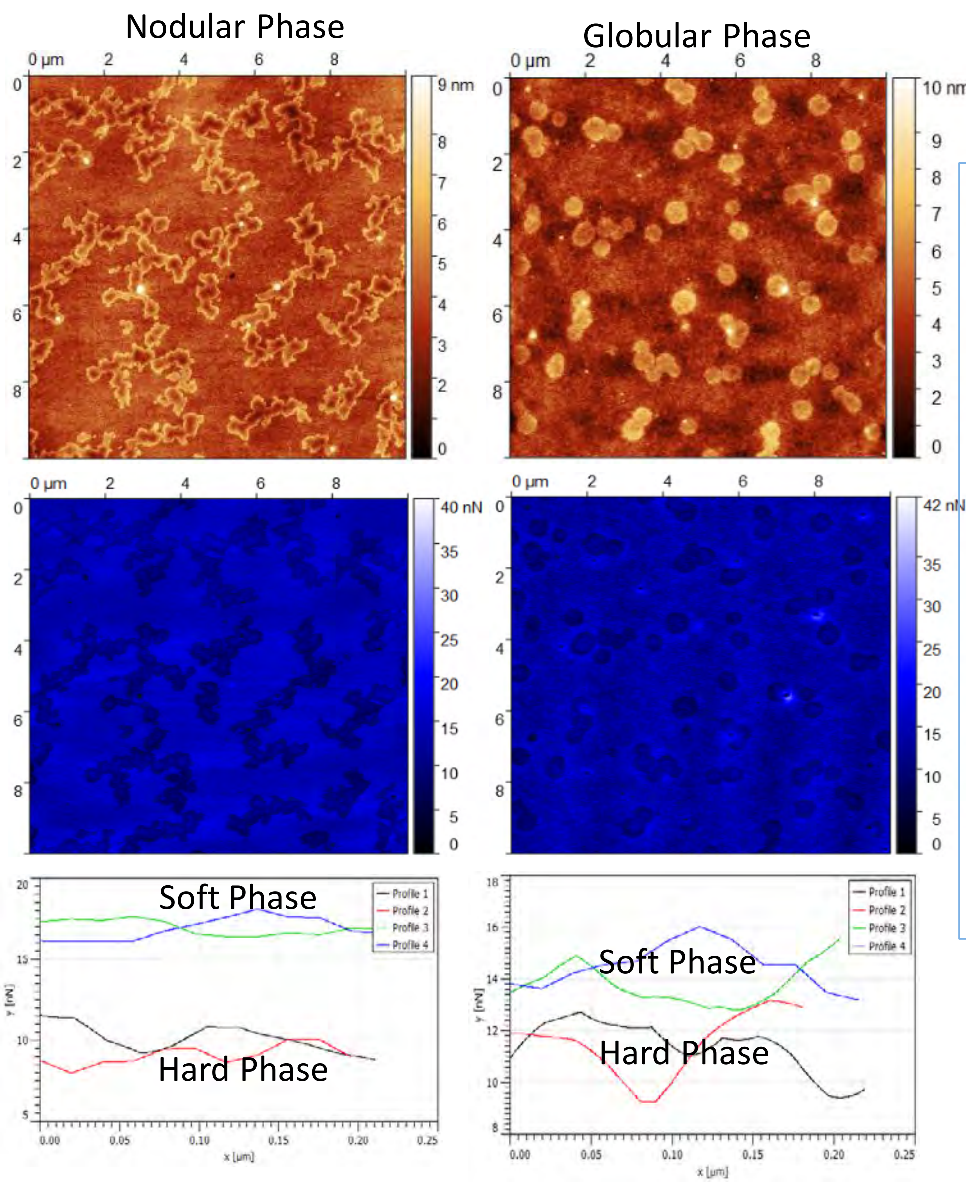

Two type morphologies based on amount of phenolic

- moderate amount → nodular morphology
- higher amount → globular morphology
- Physical differences (stiffness) between the two morphologies
  - nodular phase (higher stiffness)
  - globular phase (lower stiffness)

Nodular phase/Globular phase - chemical properties (bulk FTIR)

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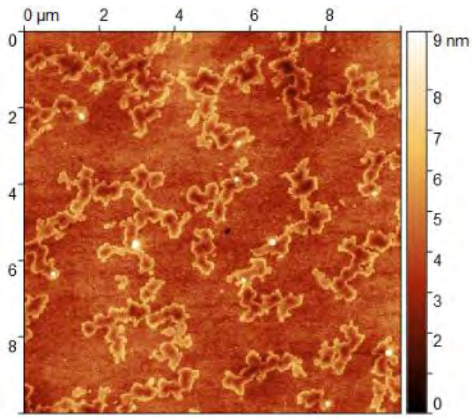
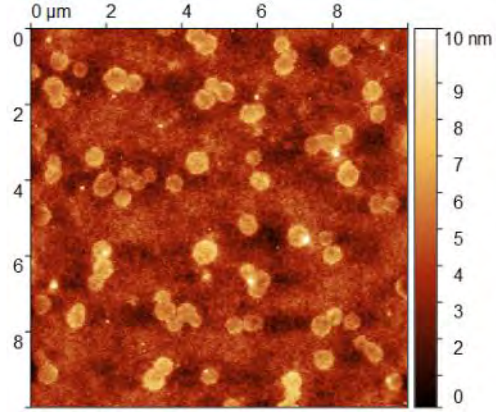
Nodular Phase



Globular Phase

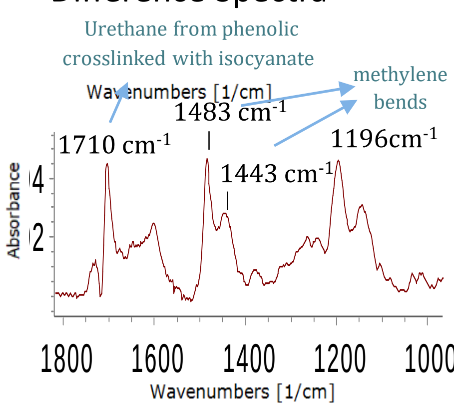


Difference Spectra obtained from bulk FTIR spectra

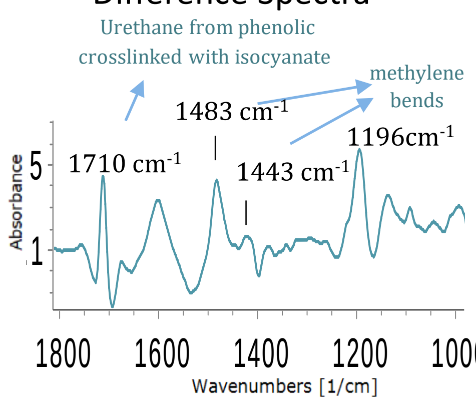
$PI_s^{2.5}P_h^{3.3}$ - $PI_s^{2.5}$
(Nodular Phase) (homogenous coating) same P:I_s ratio

$PI_s^{2.5}P_h^{3.3}$ - $PI_s^{2.5}$
(Globular Phase) (homogenous coating) same P:I_s ratio

Difference Spectra



Difference Spectra



Two type morphologies based on amount of phenolic

- moderate amount → nodular morphology
- higher amount → globular morphology
- Bulk FTIR shows subtle difference that cannot be resolved for chemical difference

Phase Diagram
Polyester-Isocyanate-Phenolic

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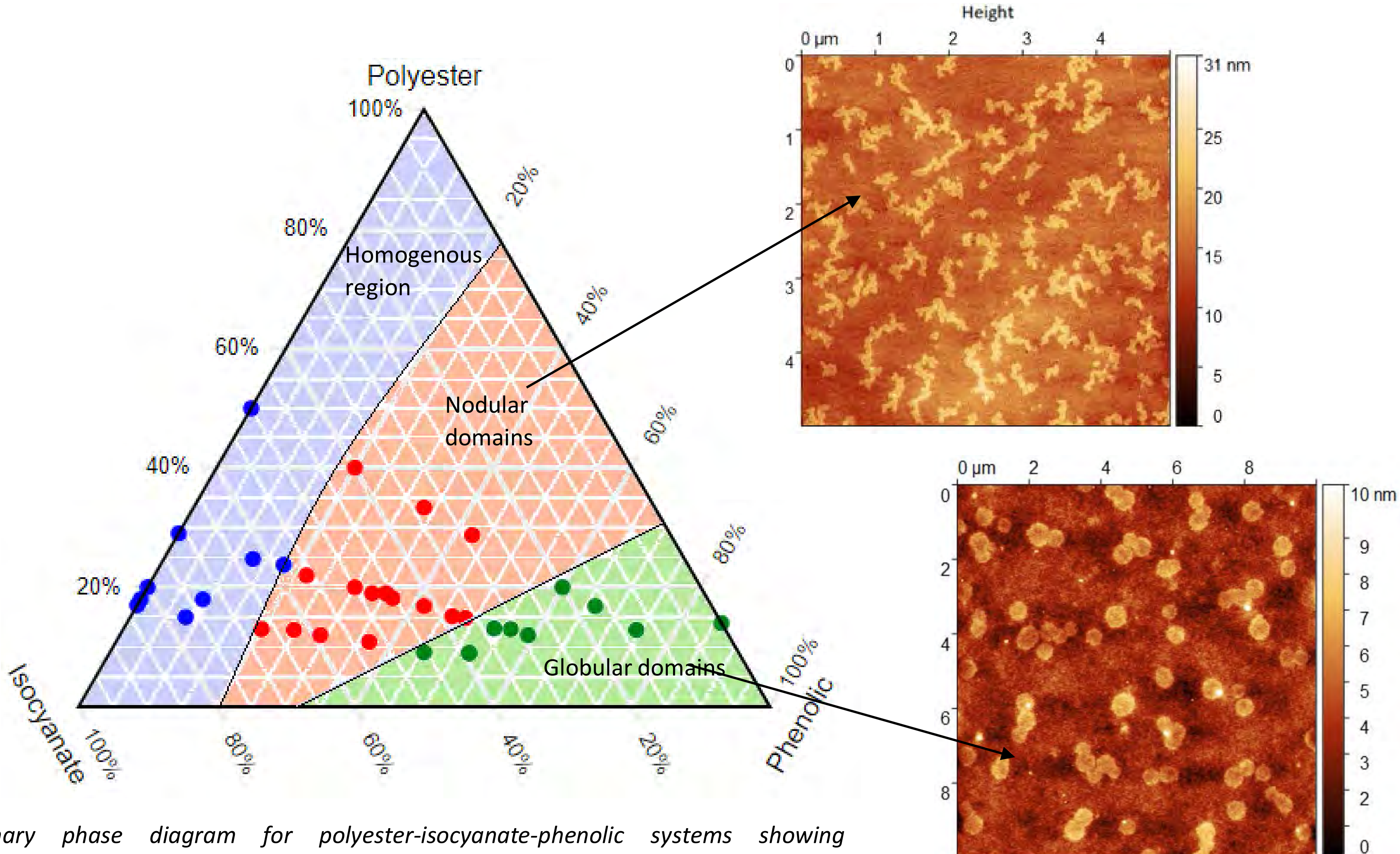

Ternary phase diagram for polyester-isocyanate-phenolic systems showing homogenous region (blue), nodular region (red) and globular region (green)

Nodular phase/Globular phase chemical properties - *AFM-IR Technique*

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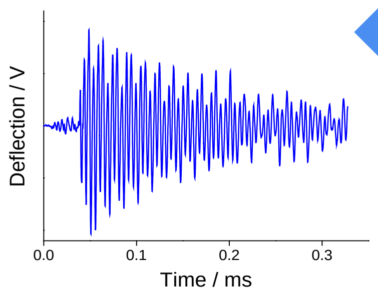
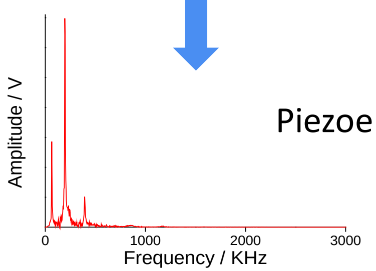




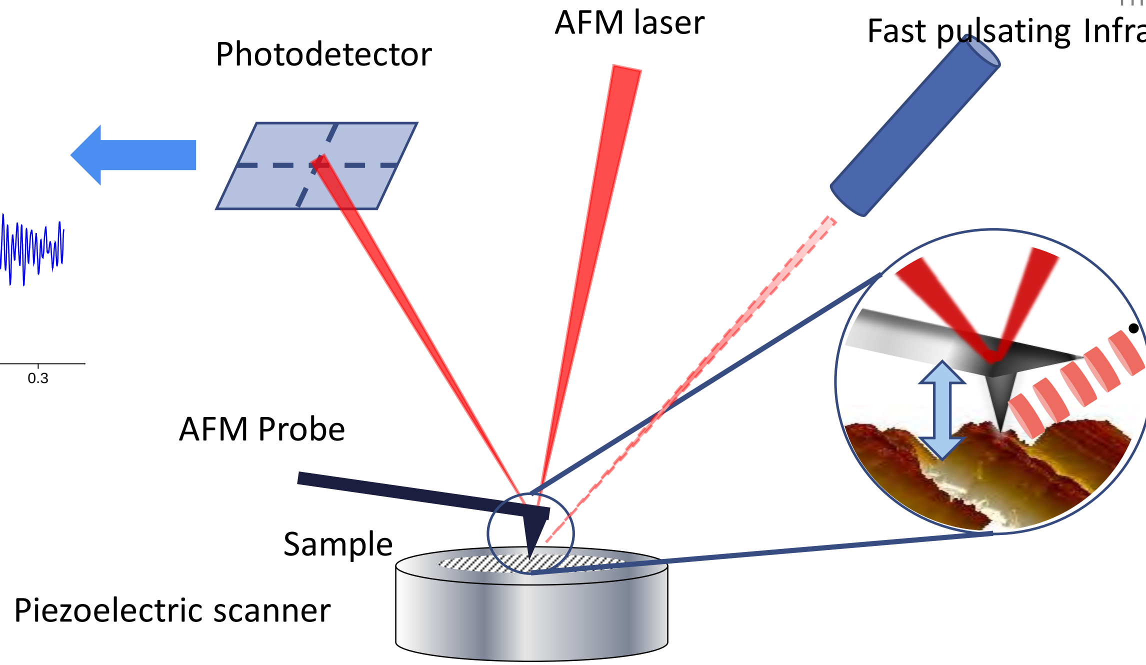


Photo thermally induced resonance (PTIR) AFM-IR

- AFM operating in contact mode, illuminated by a pulsed infrared source (OPO, 10 ns pulses, 1 KHz repeat rate).

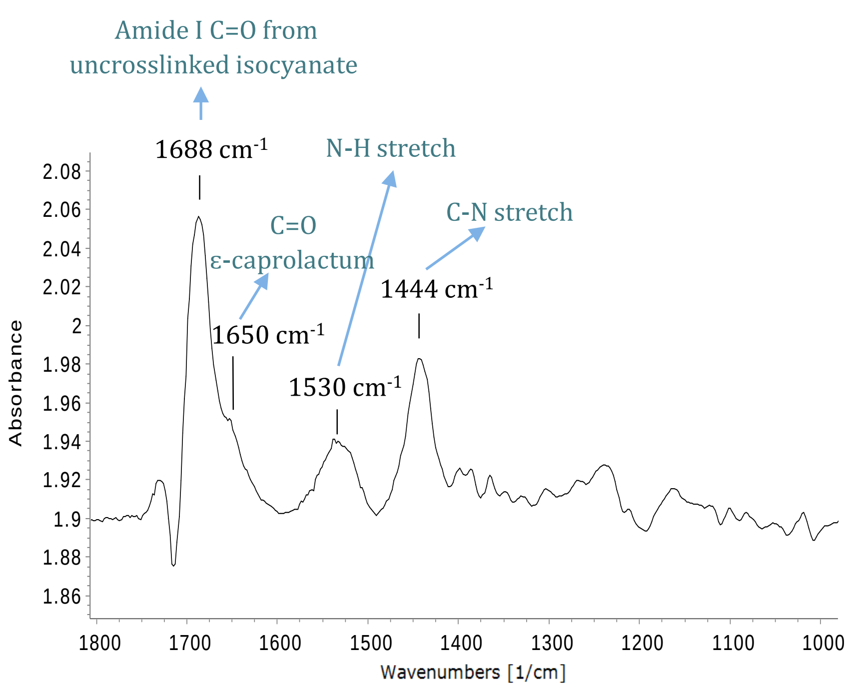
- The transient thermal expansion and relaxation occur at a rate faster than the feedback loop of the AFM measurement
- Contact mode AFM topographical information can be extracted simultaneously

- Thermal expansion of the sample in response to IR absorbance causes the cantilever to oscillate at it’s resonance frequency
- The oscillation amplitude of the cantilever is directly proportional to the amount of light absorbed and this in turn is directly proportional to the absorption coefficient.

Nodular phase/Globular phase chemical properties - Peak assignment

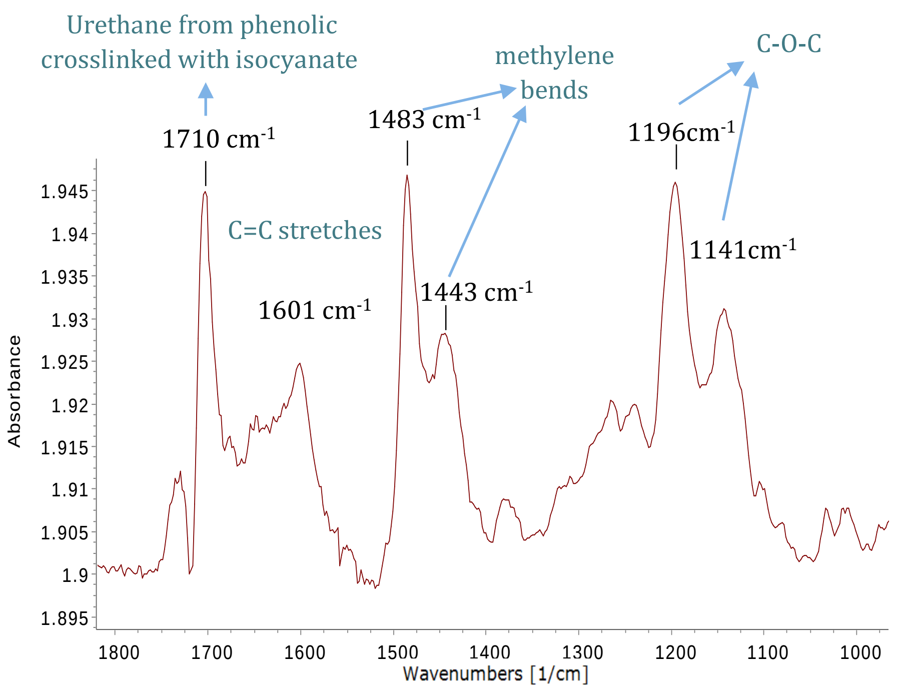
Peak assignment for of Isocyanate from FTIR bulk Spectra

Difference Spectra with Polyester Spectra subtracted from Polyester-Isocyanate



Peak assignment for of Phenolic from FTIR bulk Spectra

Difference Spectra with Polyester & Isocyanate Spectra subtracted from Polyester-Isocyanate-Phenolic



Homogeneous sample chemical properties - AFM-IR results: Local spectra beyond diffraction limit

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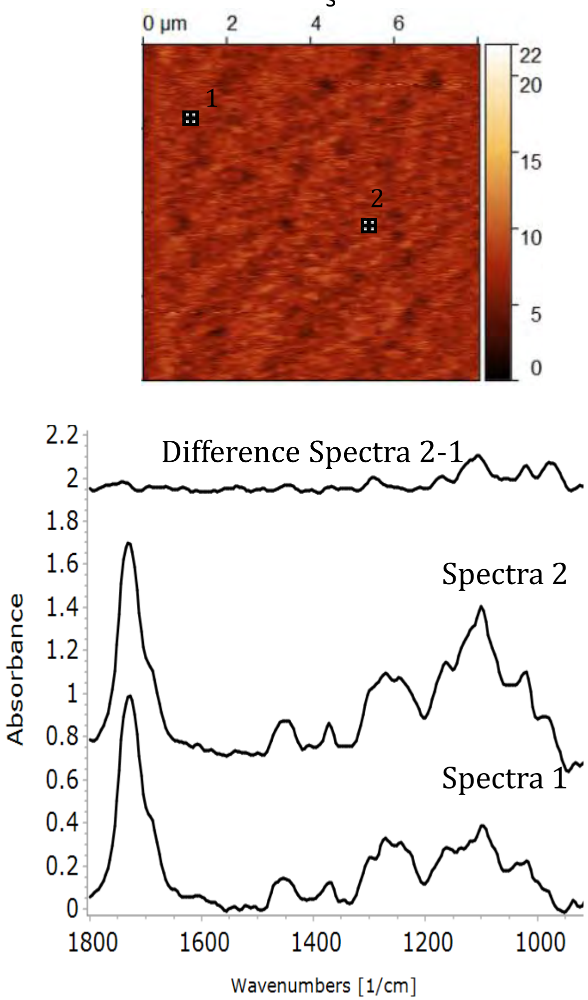
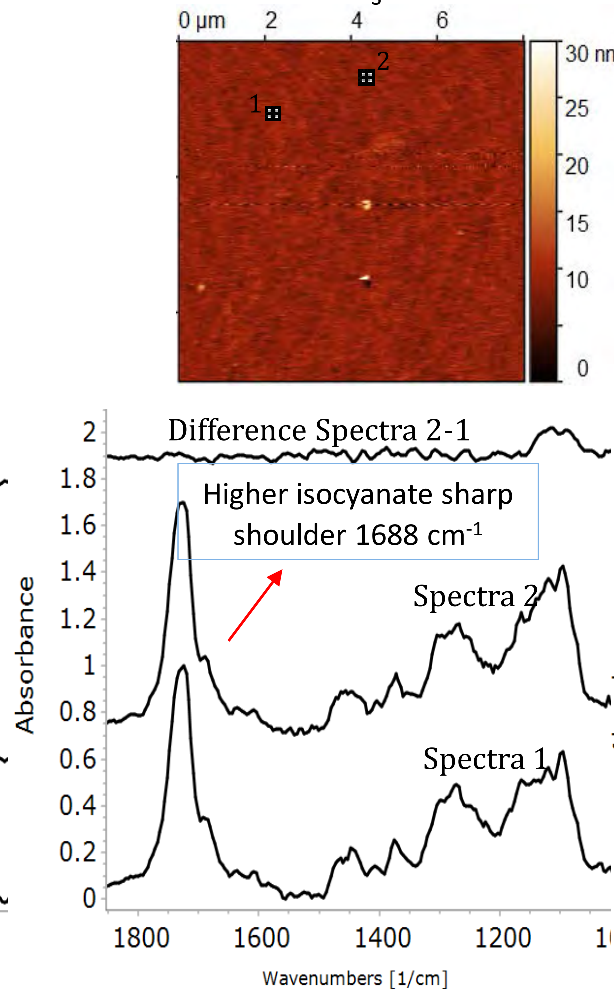
Polyester-isocyanate

$PI_s^{2.5}$

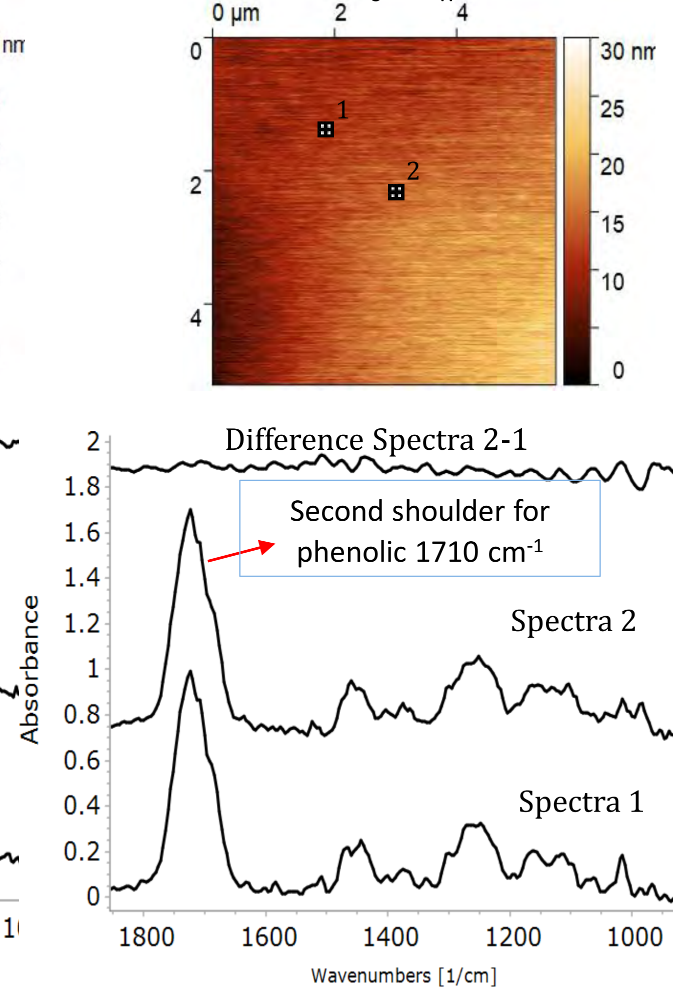


PI_s^5

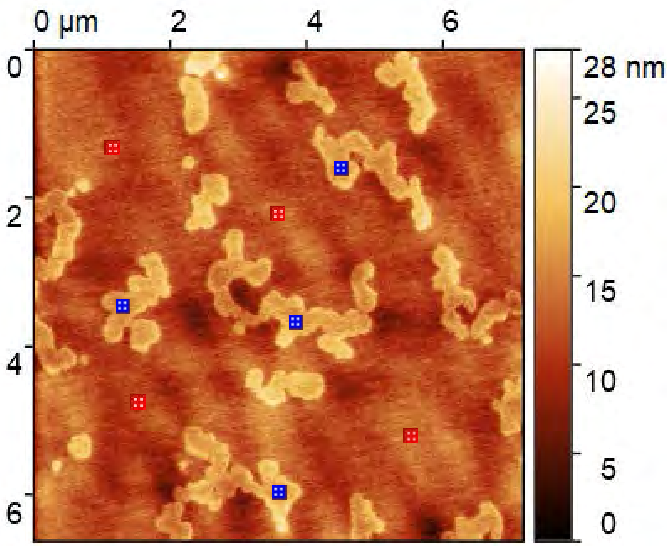


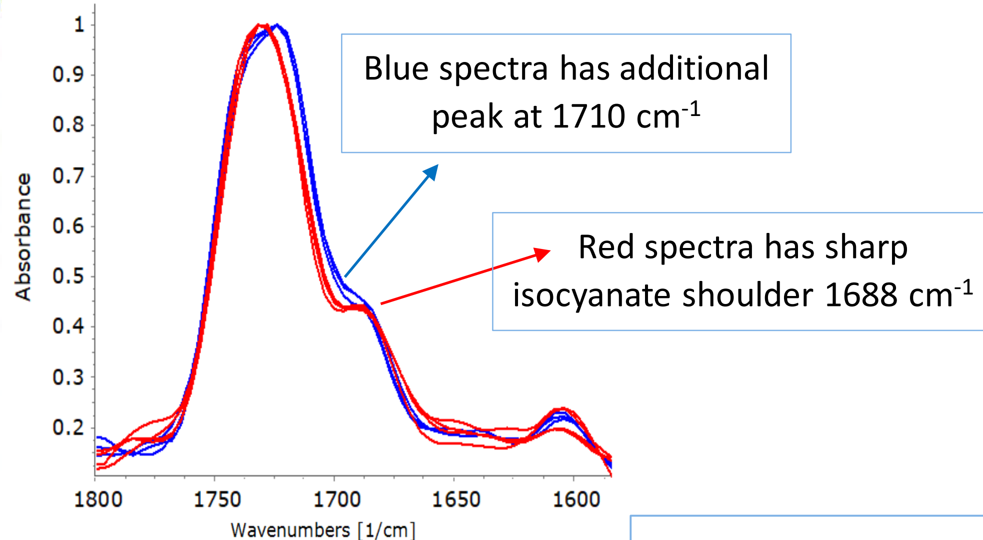
Polyester-isocyanate-polyester

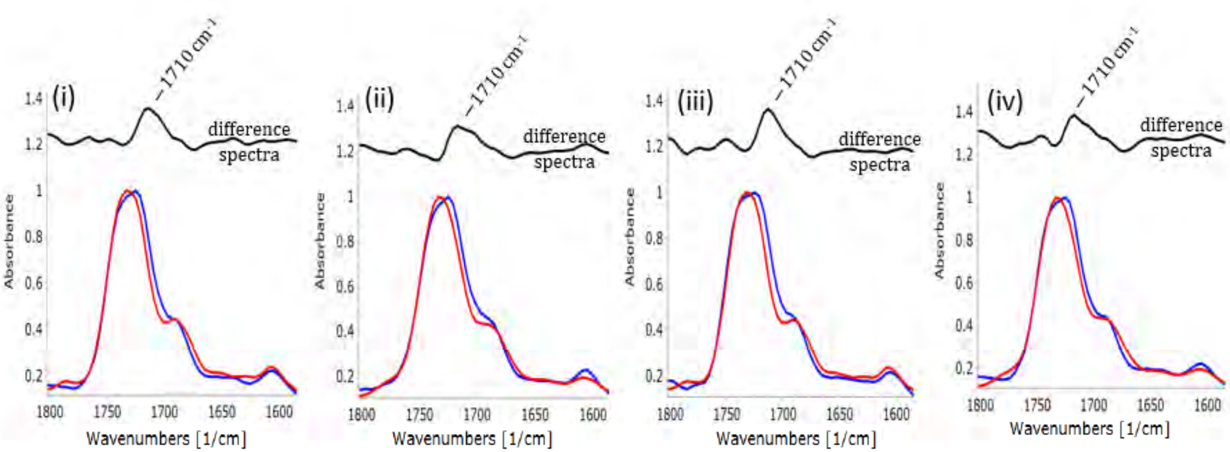
$PI_s^{2.5}P_h^{0.5}$



Nodular phase chemical properties - AFM-IR
Local spectra beyond diffraction limit







- The nodules show higher peak at 1710 cm^{-1}
- 1710 cm^{-1} characterised by presence phenolic crosslinked with isocyanate

Nodular phase chemical properties - AFM-IR
Local spectra beyond diffraction limit

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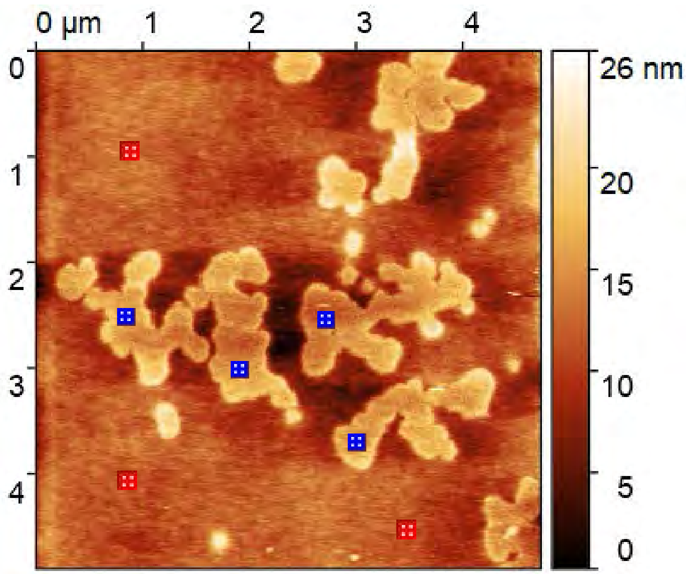
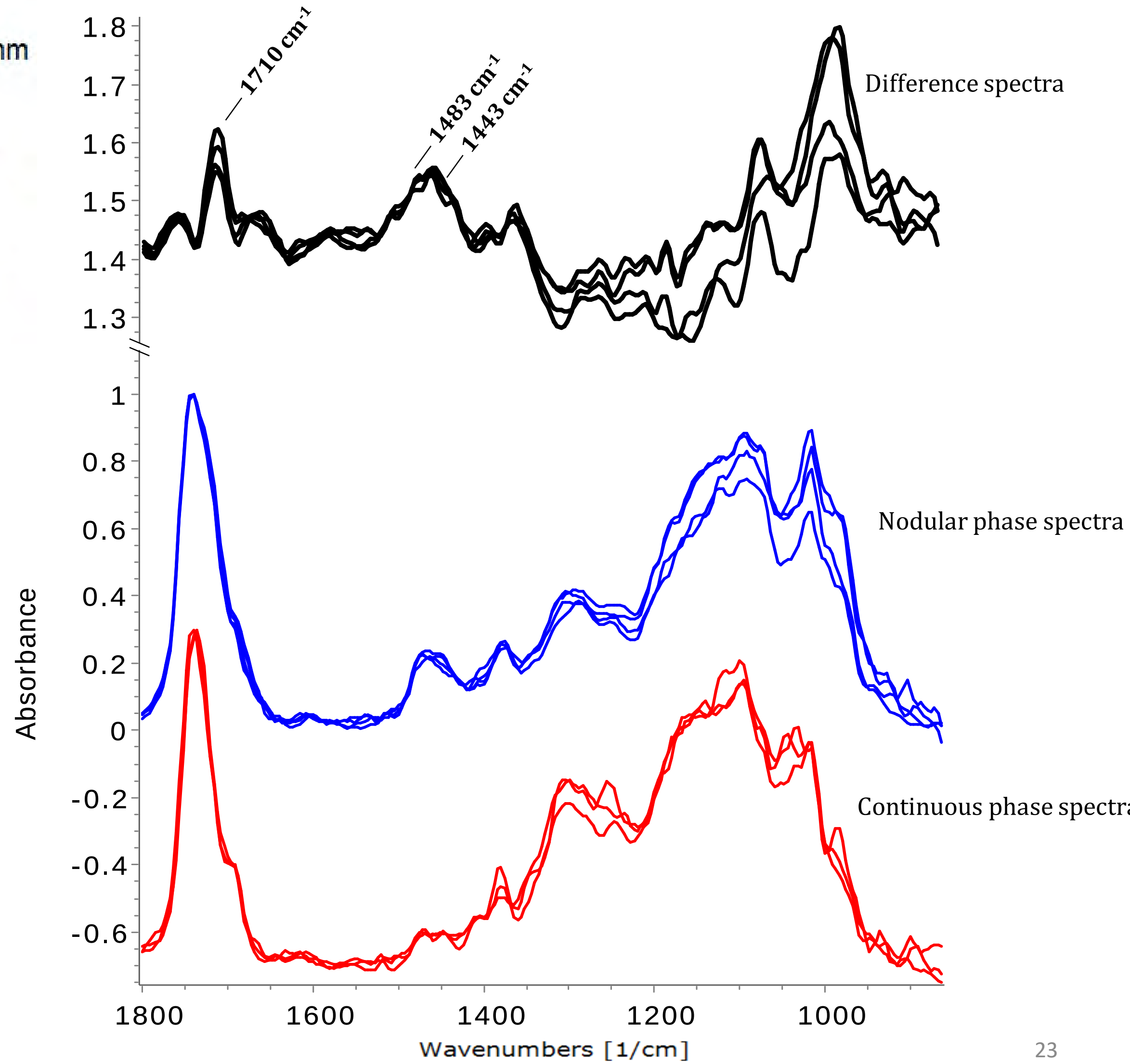


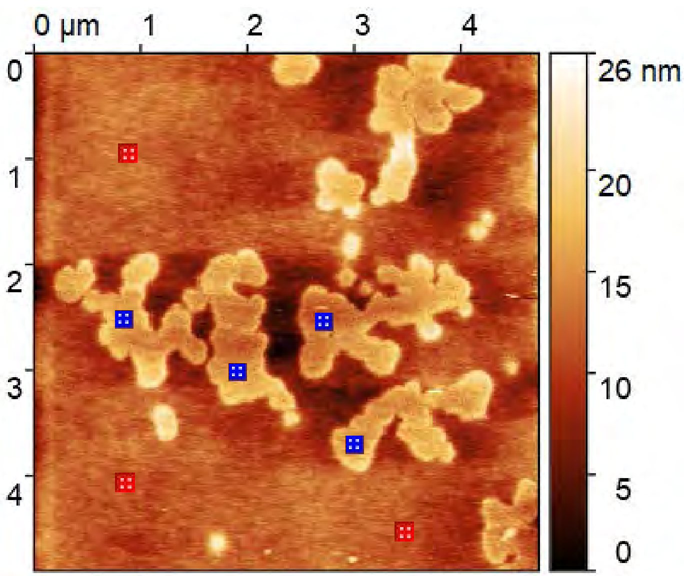


- The nodules shows all the characteristic peak of phenolic & isocyanate

- 1710 cm^{-1} (C=O from phenolic crosslinked with isocyanate)

- 1483 cm^{-1} & 1443 cm^{-1} (methylene from phenolic and C-N stretches from isocyanate

Nodular phase chemical properties - AFM-IR
Local spectra beyond diffraction limit



- This indicate that nodules are formed from phenolic-crosslinked-with-isocyanate rich-phase that phase separate as the hard phase from the soft continuous phase.

- Comparable to segmented PUs where

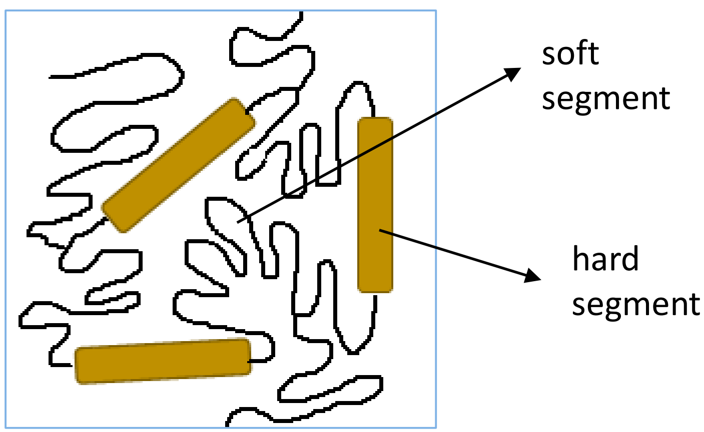
soft segment → linear/long-chained polyester

hard segment → chain-extenders (short chained polyols) crosslinked with isocyanate

- The nodules shows all the characteristic peak of phenolic & isocyanate

- 1710 cm^{-1} (C=O from phenolic crosslinked with isocyanate)

- 1483 cm^{-1} & 1443 cm^{-1} (methylene from phenolic and C-N stretches from isocyanate



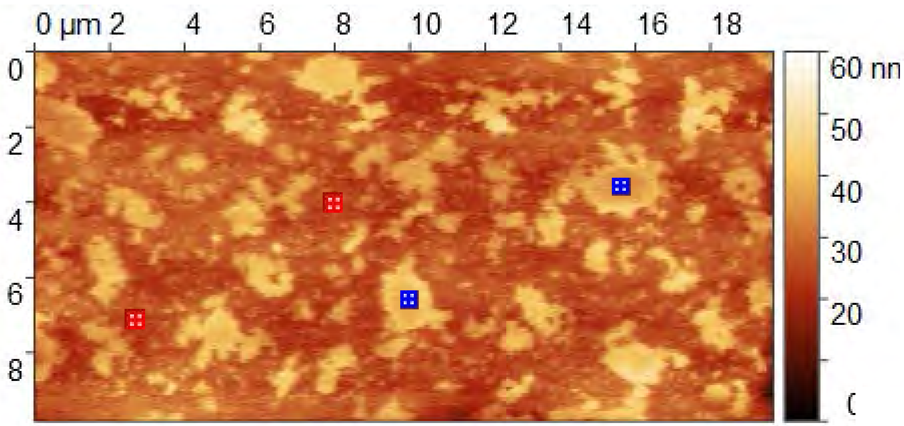
Segmented Polyurethanes

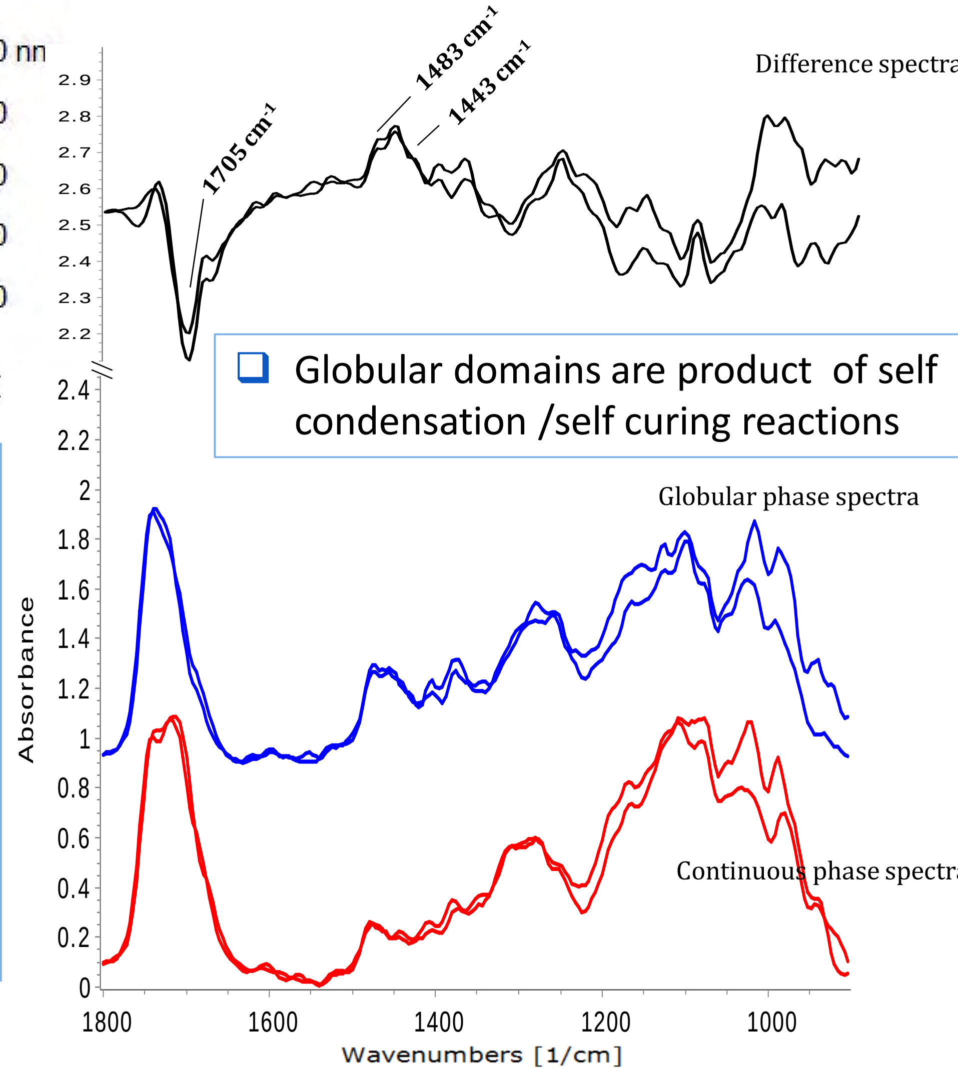
Globular phase chemical properties - AFM-IR Local spectra beyond diffraction limit

AkzoNobel

MANCHESTER 1824

The University of Manchester





- ❑ Globular domains are product of self condensation /self curing reactions

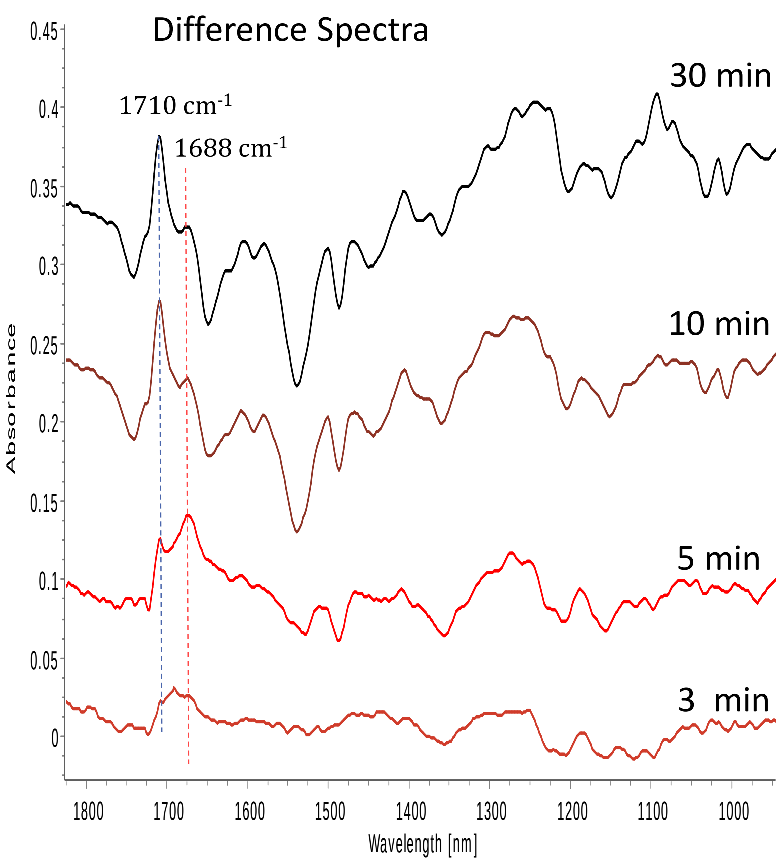
❑ Globular domains shows the characteristic peak

- Lack of 1705 cm^{-1} (C=O from phenolic crosslinked with isocyanate) from the continuous phase

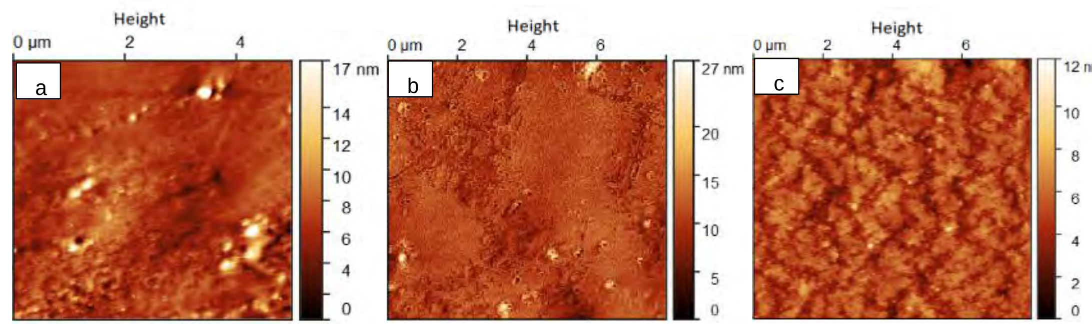
- Higher in 1483 cm^{-1} & 1443 cm^{-1} (characteristic of phenolic methylene from phenolic)

Understanding Phase separation in full formulation FT coatings

- Difference Spectra from bulk FTIR and coating shows gradual increase in peak at 1710 cm^{-1} and decrease in 1688 cm^{-1} at full cure.



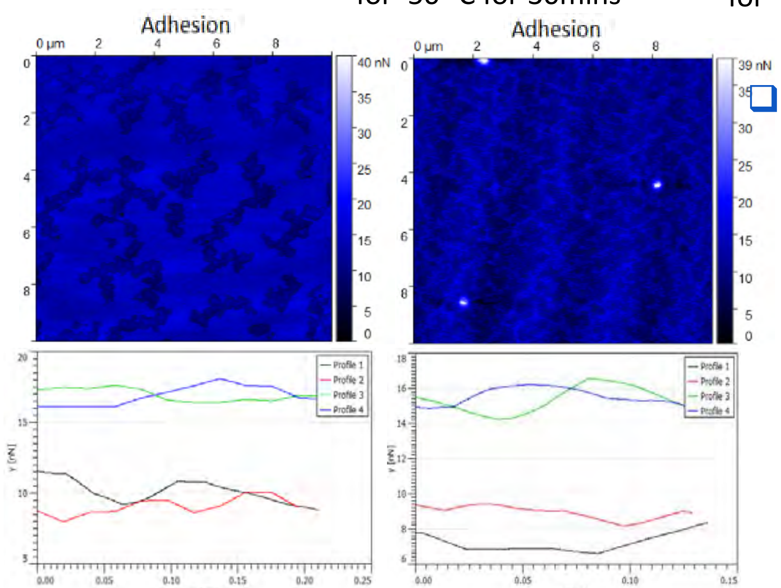
- Two phased morphology observed only when cured above deblocking temperature of IPDI



air-dried at RT for 48 hrs

air-dried at RT for 48 hrs for 50° C for 30mins

air-dried at RT for 48 hrs for 200° C for 10mins



- Stiffness map between nodular phase model system and FT coating quite comparable

Conclusions of microstructural identification

- In FT coating the phase separation stems from incompatibility between linear polyester and aromatic rich branched phenolic/benzoguanamine and also from stoichiometric imbalance

- In binary system of polyester-isocyanate, isocyanate does not cause phase separation, any stoichiometric excess of isocyanate remains dissolved in the bulk.

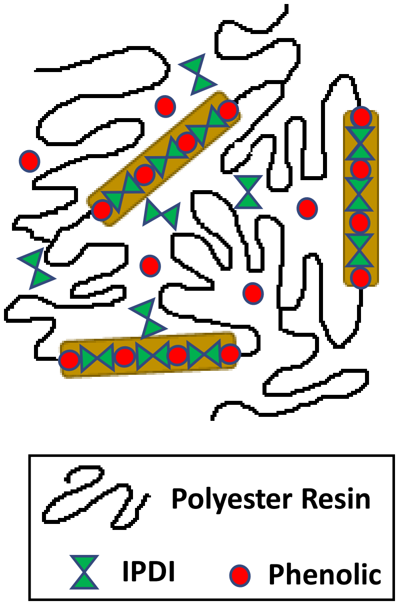
- In ternary system of polyester-isocyanate-phenolic, low stoichiometry of phenolic make homogenous coating

- In ternary system of polyester-isocyanate-phenolic, moderate stoichiometry of phenolic (above a certain threshold concentration) produces nodular phases which also make up “hard phase” phase separating from the “soft bulk phase”

- The chemical identification using AFM-IR technique shows nodular phase are phenolic crosslinked with isocyanate rich phase.

- The properties of nodular morphology shows good correlation with two phase morphology in FT coatings.

- A higher stoichiometry of phenolic will produce globular domains that are product of self-condensation between phenolic. This phase is less stiffer than the nodular phase.



Thank you for your attention!

Questions?

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