SM10: Characterising Micro- and Nano-Scale Interfaces in Advanced Composites

Polymers: Multiscale Properties

28 June 2007

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Aims and Rationale

The project aims to develop quantitative methods for characterising interfacial properties in dispersed and continuous filled polymeric materials, such as continuous and discontinuous fibre-reinforced polymers and nanocomposites.

Nanocomposites are a new emerging class of materials, with a predicted market of $1 billion by 2010, with claimed significant performance advantages over traditional materials

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Specific Objectives

- Develop methods to enable micro-scale strain mapping, stress transfer, adhesion strength and fracture toughness measurements at the interface between filler and matrix for continuous, discontinuous and nano-filled systems.

- Development of methodologies for using new physical/chemical measurement techniques (i.e. nanoindentation, nano-mechanical tester, scanning probe measurements (AFM, SECM), Raman) to measure the above properties.

Specific Objectives

- Develop capability to measure the properties of interphases in fibre-reinforced polymeric systems including surface coatings (i.e. fibre sizing) for optimising adhesion between the reinforcement and matrix.

- Evaluate predictive models for use with FEA to determine accuracy and applicability to continuous and dispersed filled systems.

- Demonstrate the use of the techniques developed within the project through the use of case studies on commercial materials.

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Deliverables

- **Critique of test methods and predictive analysis for characterising interfacial properties in filled systems (NPL Report) - completed.**
- **Case studies (micro- to nano-scale) on the application of interfacial characterisation methods to filled systems (scientific paper).**
- **Evaluation of predictive model(s) for characterising interfacial and interphase properties in filled systems (scientific paper).**

Work Programme

D2: Interfacial Characterisation Methods

- Develop and evaluate new measurement techniques identified in D1 (review) for characterising interfacial properties

- Case studies based on different reinforced systems ranging from micro- to nano-scale to assess techniques in terms of data generated, sensitivity and degree of resolution

D3: Predictive Models

- Evaluate model(s) for predicting interfacial properties in dispersed and continuous filled polymeric materials

- Predictive analysis will be compared with the results from the case studies to be carried out in D2 - models to include filler/matrix adhesion and dispersion for nanocomposites, stress transfer and interfacial failure criteria

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Case Study 1: GRP Pultruded Rods

- Fibre products: E-glass and ECR glass
- Resin: Vinylester
- Surface treatments: Organosilane
- Properties:
  - Flexure strength/stiffness
  - Glass transition temperature
  - Environmental durability/permeation
    - Alkaline solution/elevated temperature
    - Combinatorial analysis
- Suppliers:
  - Fibreforce Composites Ltd
  - Saint-Gobain Vetrotex

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GRP Pultruded Rods

- Fibre Volume Fraction (V_f)
  - Well bonded: 56.2 ± 0.7
  - Poorly bonded: 55.8 ± 0.8
- Glass Transition Temperature (T_g)
  - Well bonded: 118.2 °C
  - Poorly bonded: 122.2 °C

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GRP Pultruded Rods – Flexure Properties

Material	Moisture Content (%)	Flexural Modulus (GPa)	Flexural Strength (MPa)
Dried at 50 °C			
Well Bonded	0.00	33.8 ± 0.8	853 ± 39
Poorly Bonded	0.00	30.1 ± 1.1	371 ± 56
1 Month			
Well Bonded	0.16 ± 0.07	36.0 ± 1.1	871 ± 61
Poorly Bonded	0.27 ± 0.15	29.2 ± 0.8	281 ± 6
3 Months			
Well Bonded	0.27 ± 0.04	36.1 ± 1.4	866 ± 52
Poorly Bonded	0.83 ± 0.22	28.3 ± 1.9	298 ± 31

- Flexural stiffness and strength reduced due to poor fibre/matrix interfacial strength
- Poorly bonded systems tend to absorb higher levels of moisture

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Case Study 2: Glass Flakes

- Flake products: REFG302, REFG101 and REF600 or REF160N
- Resin: Polypropylene
- Surface treatments: None, aminosilane and titanate
- Mechanical properties:
  - Hardness
  - Impact (fracture toughness)
  - Flexure strength/stiffness
  - Thermal conductivity/thermal expansion
  - Permeation
- Supplier: NGF Europe

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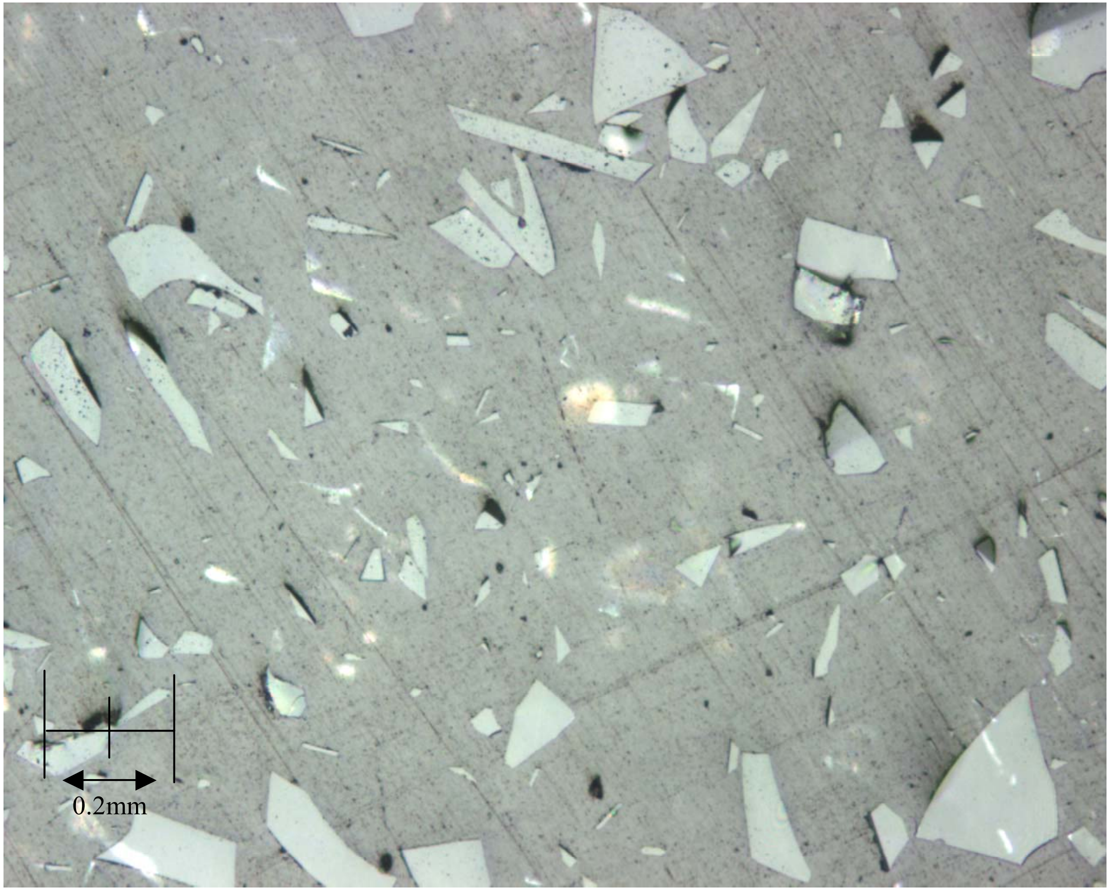
Glass-Flake/Polypropylene – Physical Properties

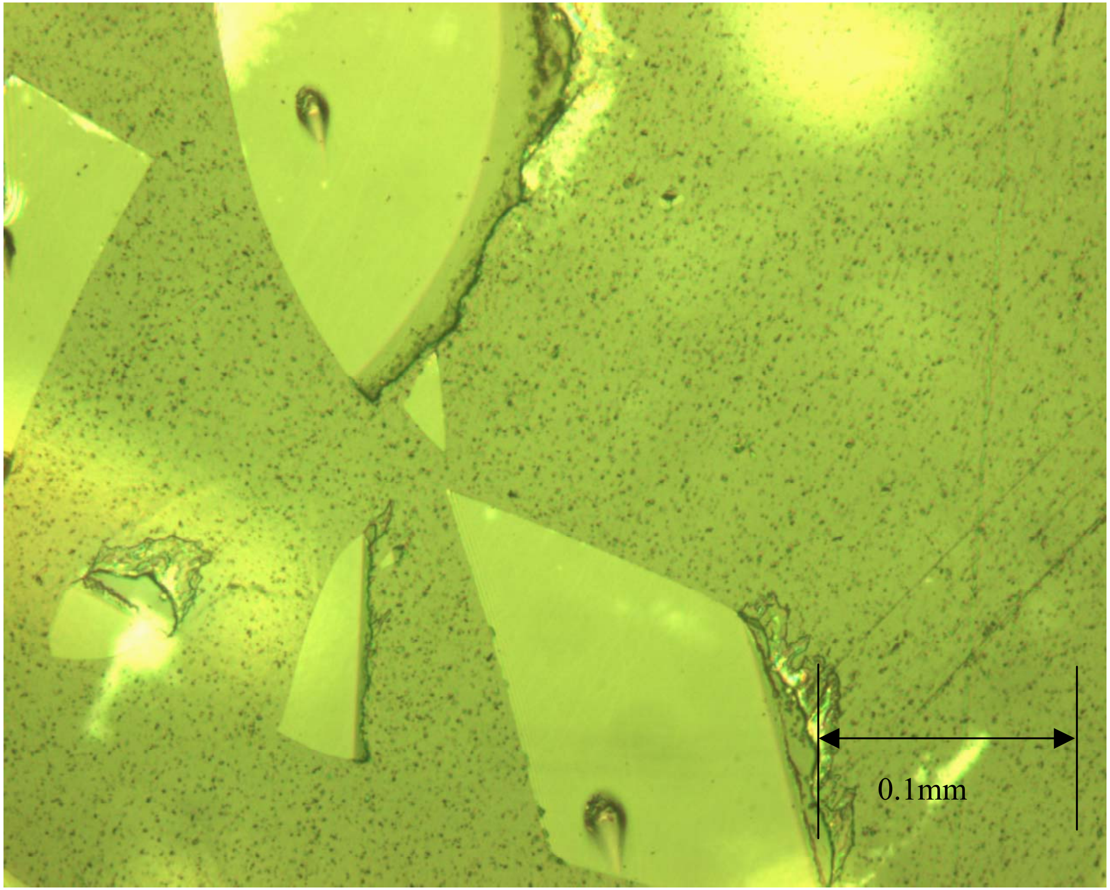
Material	Density (kg/m^3)	Volume Fraction (%)	Shore Hardness D
Polypropylene	905 ± 1	**N/A**	21.9 ± 0.1
Untreated Flake	1,126 ± 1	13.3 ± 0.1	22.0 ± 0.1
Titanate			
0.09%	1,115 ± 1	12.7 ± 0.1	21.9 ± 0.1
0.42%	1,121 ± 2	13.1 ± 0.1	22.0 ± 0.1
Aminosilane			
0.05%	1,129 ± 1	13.5 ± 0.1	22.0 ± 0.1
0.28%	1,117 ± 1	12.7 ± 0.1	22.0 ± 0.1

- Fibre volume fraction and density almost identical for the five composite materials
- Surface hardness independent of surface treatment and presence of glass flakes

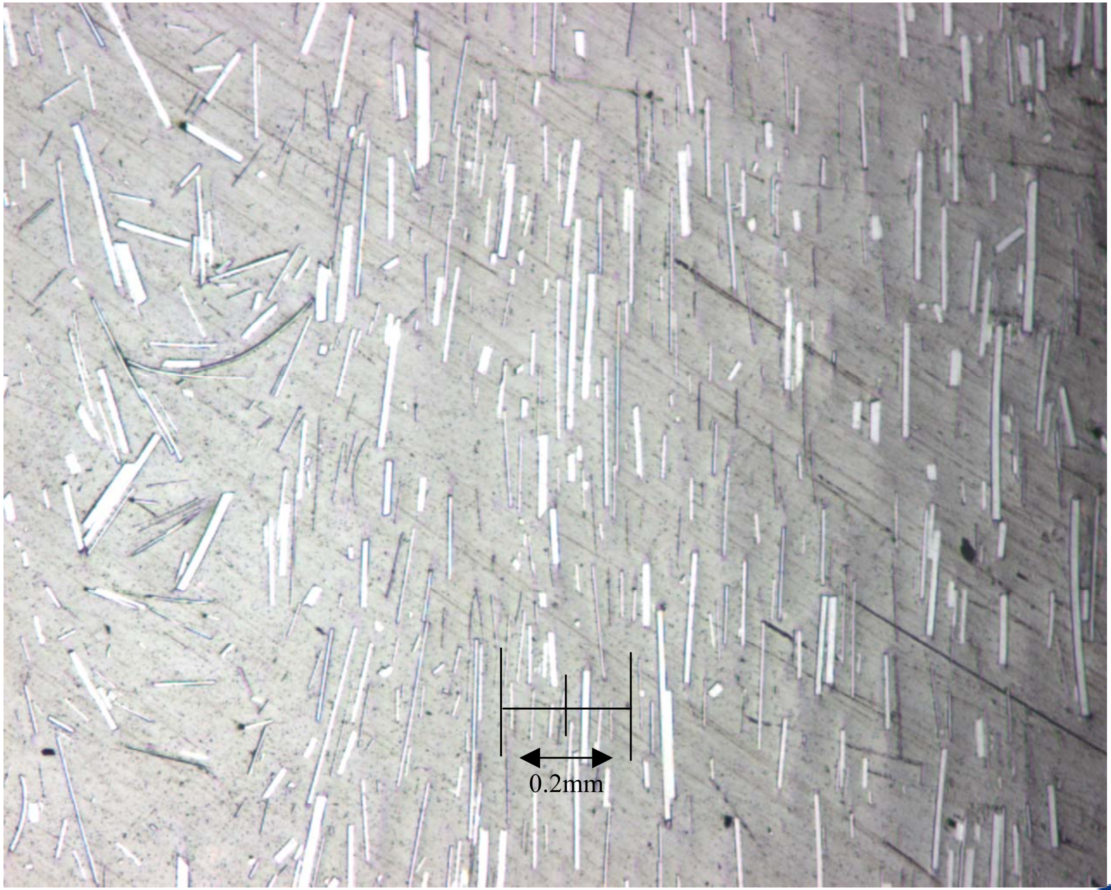
Glass-Flake/PP (Titanate 0.09%) – Plan View



Glass-Flake/PP (Titanate 0.42%) – Plan View



Glass-Flake/PP (Untreated) – Side View



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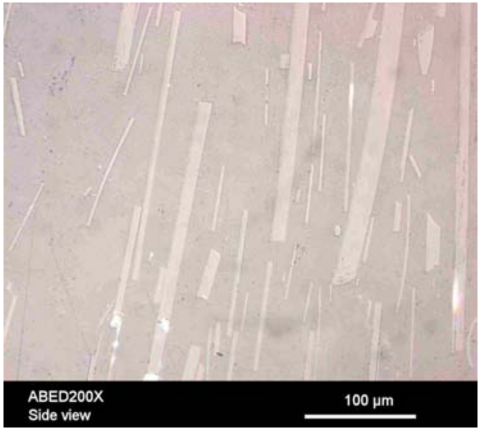
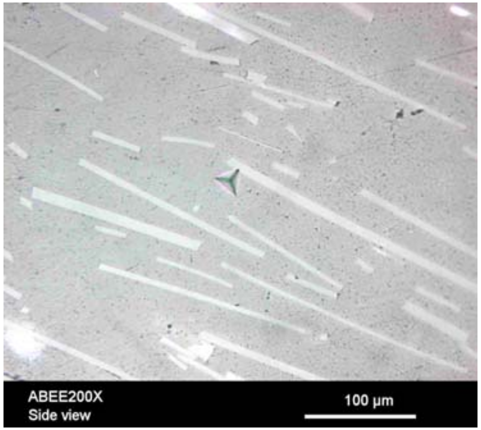
Glass-Flake/PP – Various Surface Treatments

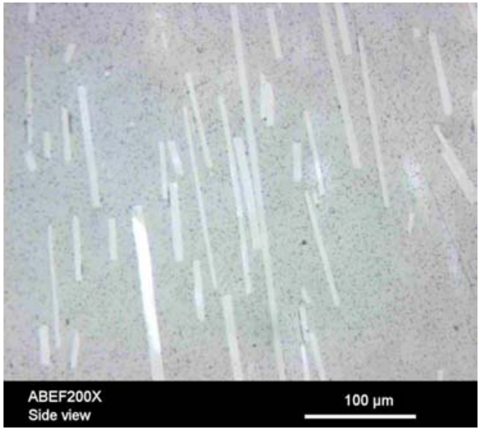
Untreated flakes



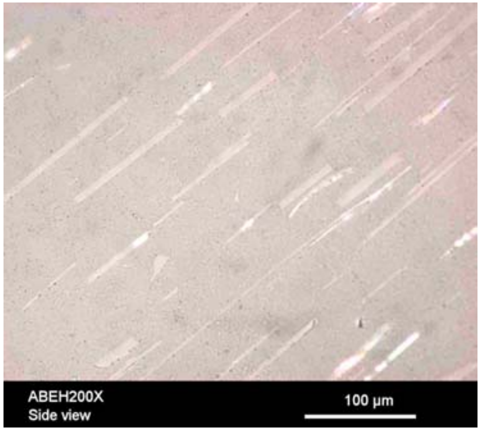
0.05% Aminosilane



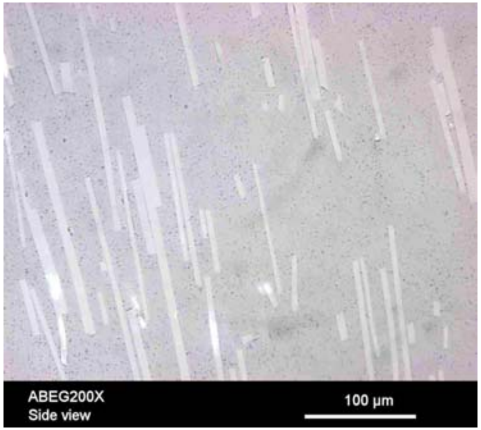
0.28% Aminosilane



0.09% Titanate



0.42% Titanate



200X magnification cross sectional photographs - normal to the thickness of the glass flakes

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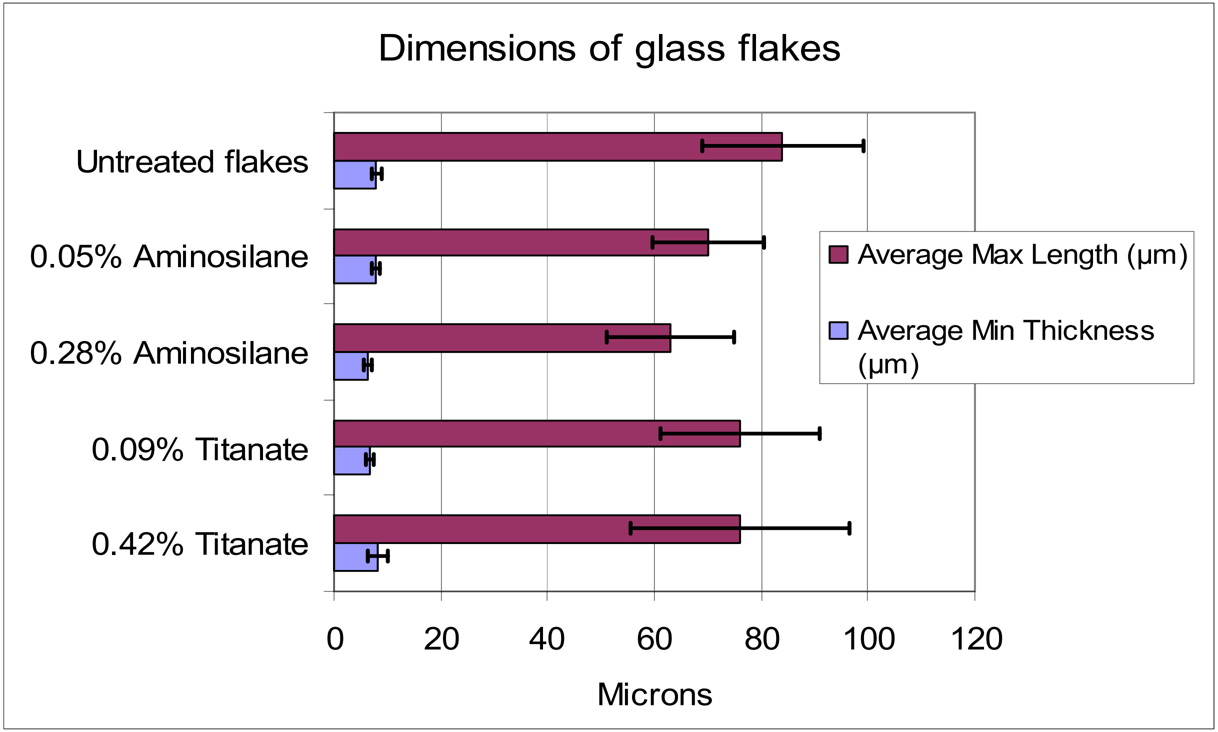
Glass Flake/Polypropylene



Dimensions taken from photographs at 100X taken normal to the thickness of the flakes

Known issues

- **Exact orientation of flakes difficult to ascertain**
- **Difficult to attain high contrast plan view photographs due to reflective nature of glass**

	Average Min Thickness (µm)	95% Certainty in average min thickness	Average Max Length (µm)	95% Certainty in average max length
Untreated flakes	7.9	1.0	84	15.0
0.05% Aminosilane	8.0	0.8	70	10.3
0.28% Aminosilane	6.3	0.9	63	12.0
0.09% Titanate	6.8	0.8	76	14.9
0.42% Titanate	8.1	1.9	76	20.5

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Glass-Flake/Polypropylene – Thermal Properties

Material	T_g (°C)	T_{melt} (°C)	Crystallinity (J/g)
Polypropylene	11.0	153.2	116.7
Untreated Flake	11.7	157.2	82.07
Titanate			
0.09%	12.3	152.7	80.20
0.42%	12.1	152.9	77.83
Aminosilane			
0.05%	11.3	153.5	69.94
0.28%	12.1	153.5	75.59

- T_g and T_{melt} independent of surface treatment and presence of fibres
- Crystallinity reduced with introduction of glass flakes
- Crystallinity decreases slightly with increasing filler/matrix interfacial strength

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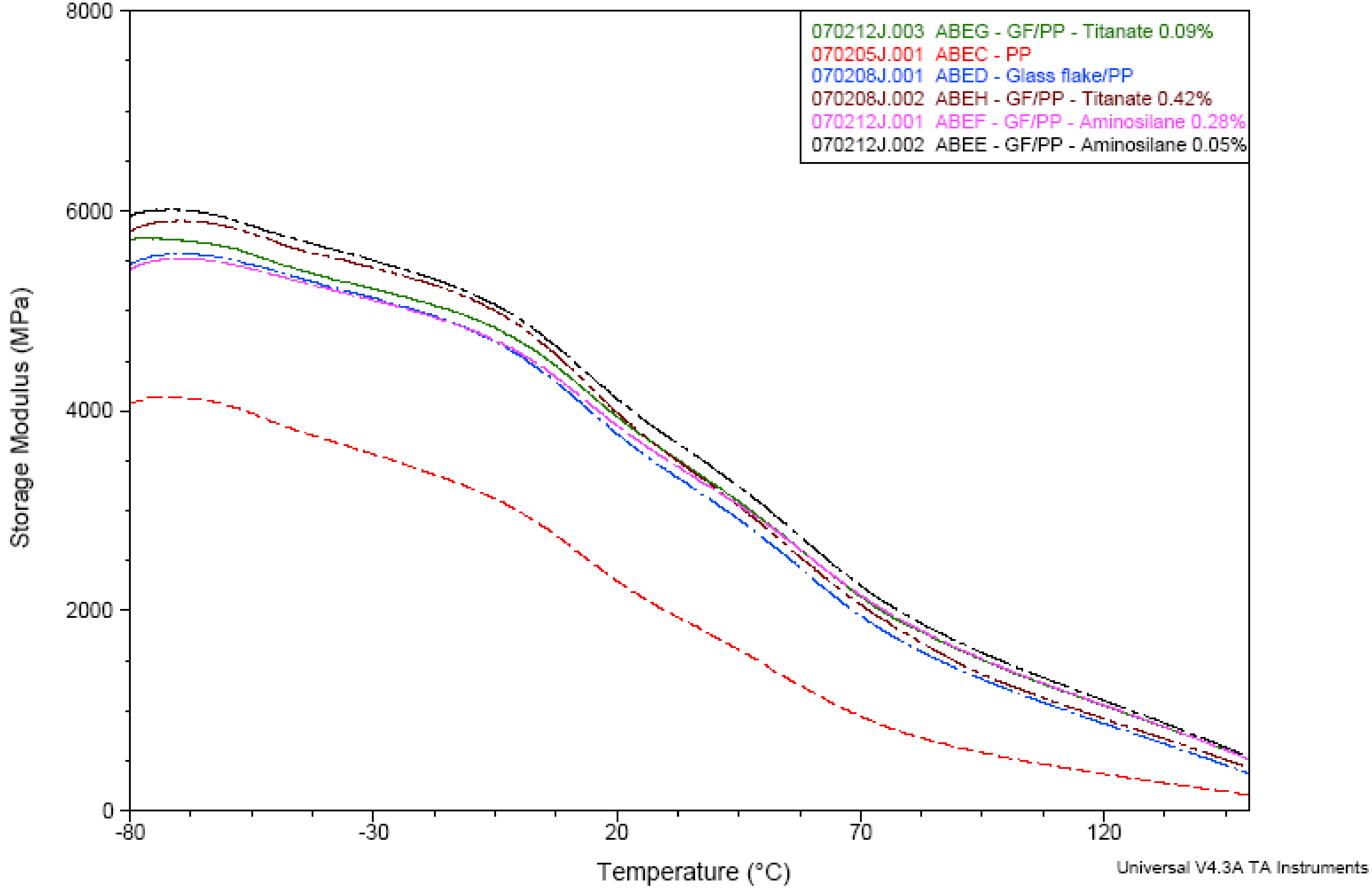
Glass-Flake/Polypropylene – Storage Modulus



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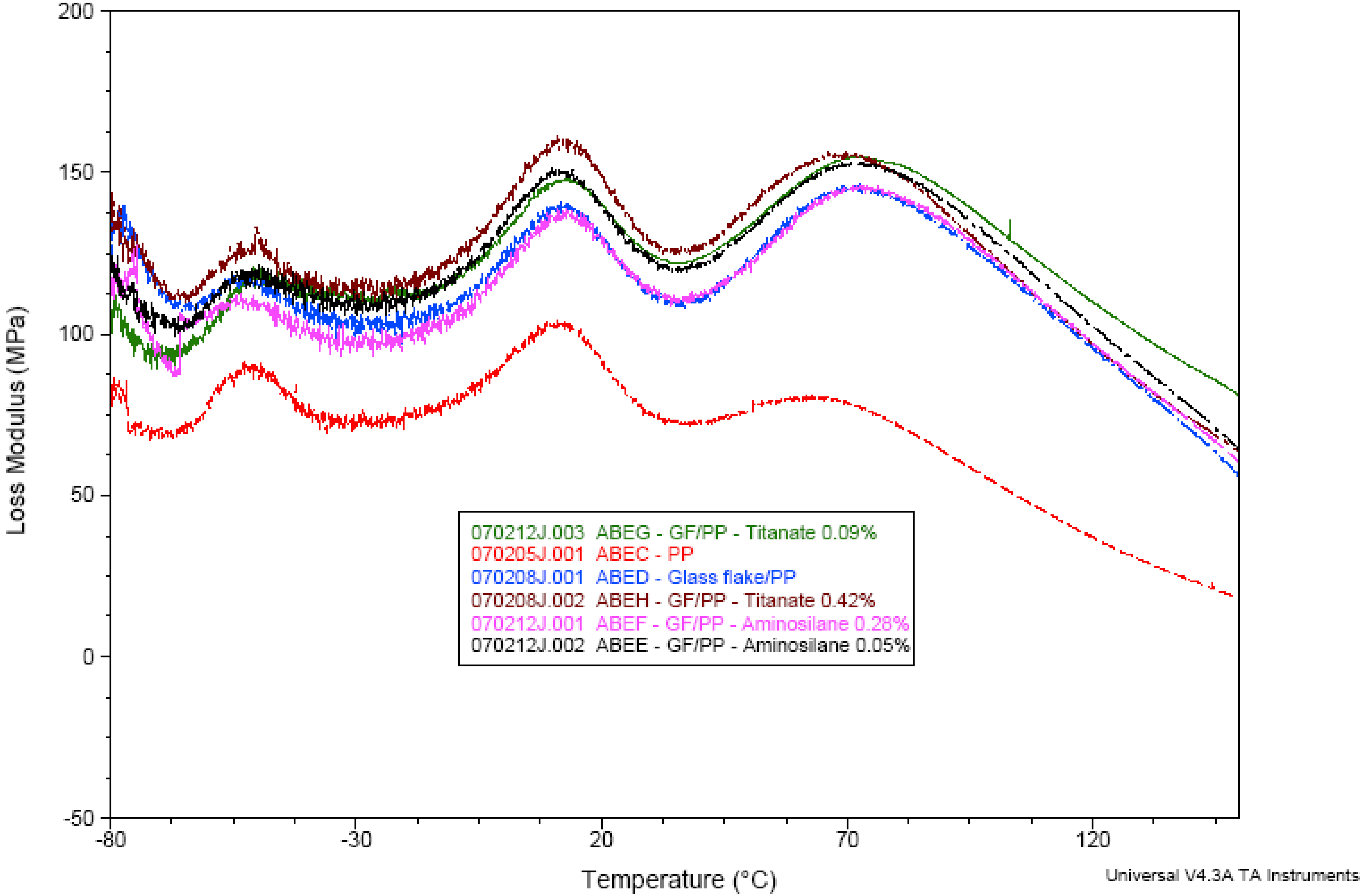
Glass-Flake/Polypropylene – Loss Modulus



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Glass-Flake/Polypropylene - Flexure Modulus (GPa)

Material	Longitudinal	Transverse
Polypropylene	1.91 ± 0.05	1.94 ± 0.07
Untreated Flake	3.39 ± 0.09	3.21 ± 0.06
Titanate		
0.09%	3.28 ± 0.09	3.27 ± 0.16
0.42%	3.04 ± 0.22	3.05 ± 0.11
Aminosilane		
0.05%	4.34 ± 0.17	4.13 ± 0.09
0.28%	4.30 ± 0.03	4.05 ± 0.16

- Flexural stiffness increases with increasing filler/matrix interfacial strength
- Poorly bonded systems tend to exhibit lower flexure stiffness

Glass-Flake/Polypropylene - Flexure Strength (MPa)

Material	Longitudinal	Transverse
Polypropylene	42.36 ± 0.28	44.84 ± 0.13
Untreated Flake	44.11 ± 0.20	43.32 ± 0.45
Titanate		
0.09%	44.47 ± 3.73	43.46 ± 0.59
0.42%	41.57 ± 0.62	40.51 ± 0.62
Aminosilane		
0.05%	55.31 ± 3.02	53.50 ± 0.31
0.28%	56.12 ± 1.03	53.91 ± 0.57

- **Flexural strength increases with increasing filler/matrix interfacial strength**
- **Poorly bonded systems tend to exhibit lower flexure strength**

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Glass-Flake/Polypropylene - Flexure Strain (%)

Material	Longitudinal	Transverse
Polypropylene	5.16 ± 0.04	5.16 ± 0.14
Untreated Flake	3.68 ± 0.02	3.82 ± 0.08
Titanate		
0.09%	3.73 ± 0.07	3.91 ± 0.13
0.42%	3.87 ± 0.08	4.03 ± 0.15
Aminosilane		
0.05%	3.02 ± 0.03	3.27 ± 0.08
0.28%	3.17 ± 0.07	3.43 ± 0.14

- **Strain-to-failure decreases with increasing filler/matrix interfacial strength**
- **Well bonded systems tend to be less ductile**

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Glass-Flake/Polypropylene – Elastic Properties

* Calculated

Material	Tension Test	Plate Twist Test	Predicted
<u>Elastic Modulus (GPa)</u>			
Polypropylene	1.89 ± 0.04	-	-
Glass Flake/PP (untreated)	4.20 ± 0.09	-	5.33
Glass Flake/PP (0.05% aminosilane)	4.77 ± 0.28	-	5.39
<u>Poisson's Ratio</u>			
Polypropylene	0.39 ± 0.02	-	-
Glass Flake/PP (untreated)	0.32 ± 0.02	-	0.45
Glass Flake/PP (0.05% aminosilane)	0.28 ± 0.01	-	0.45
<u>Shear Modulus (GPa)</u>			
Polypropylene	0.68*	0.57	-
Glass Flake/PP (untreated)	1.59*	1.66	1.84
Glass Flake/PP (0.05% aminosilane)	1.86*	1.90	1.86

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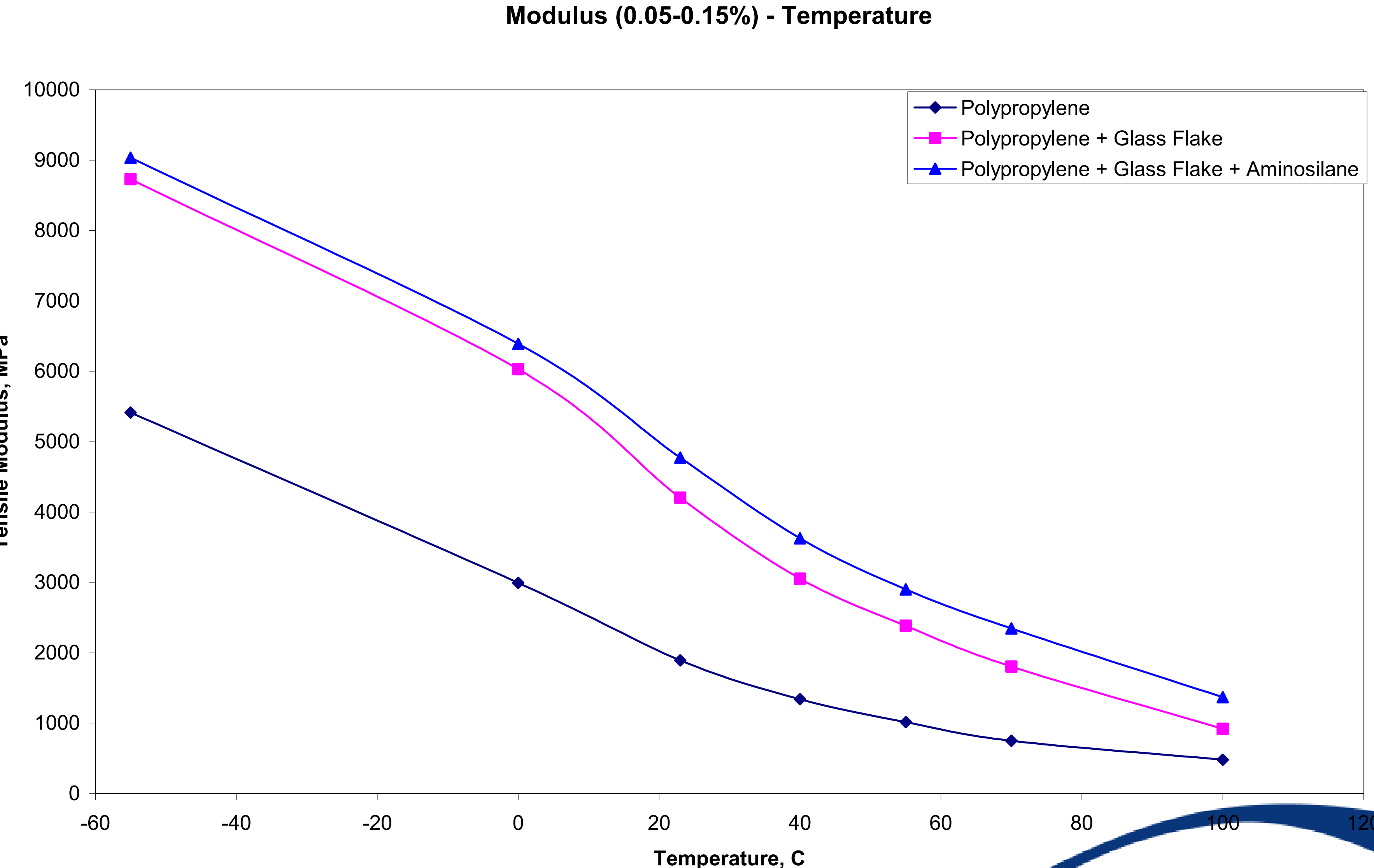
Glass-Flake/Polypropylene



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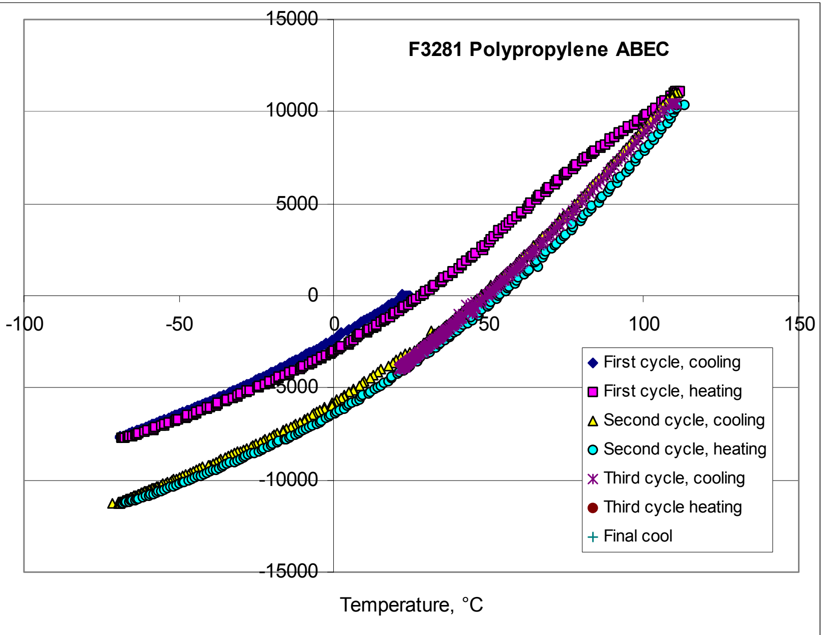
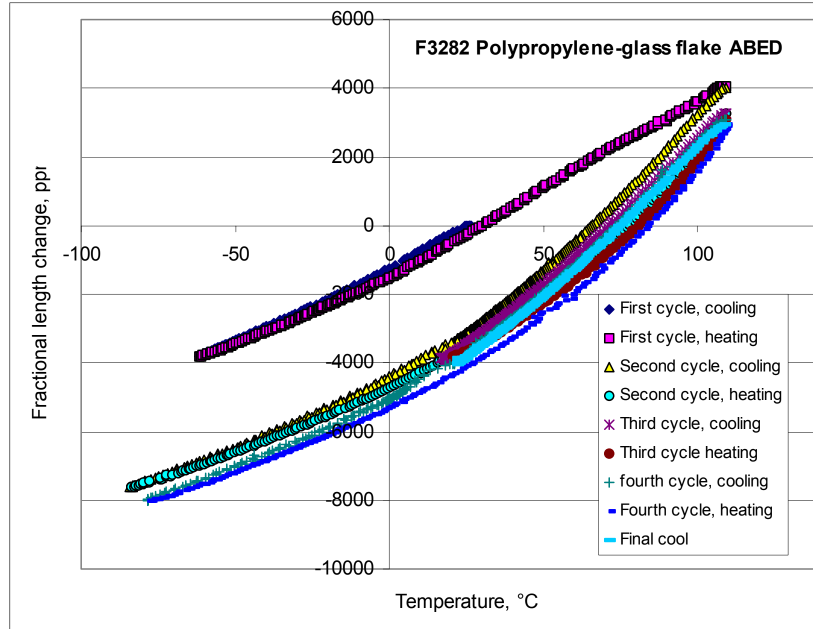
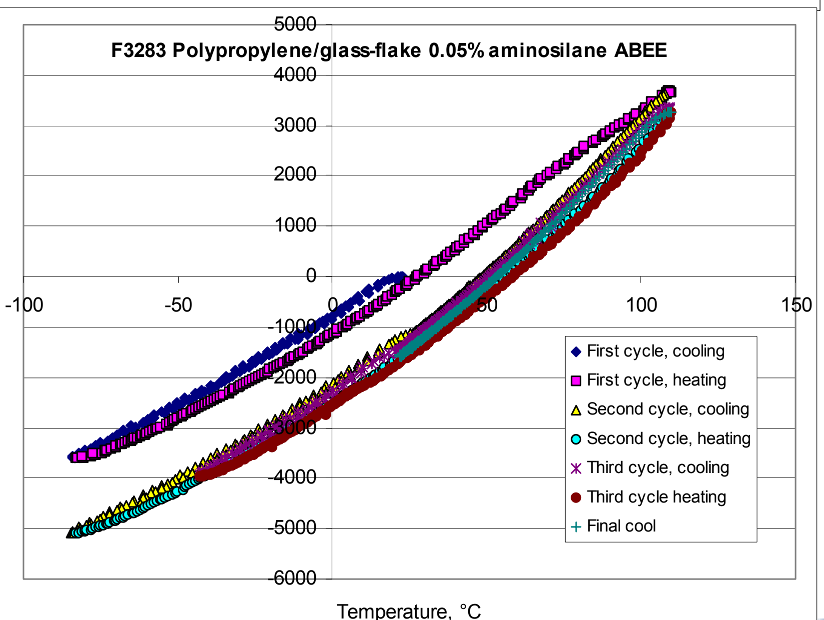
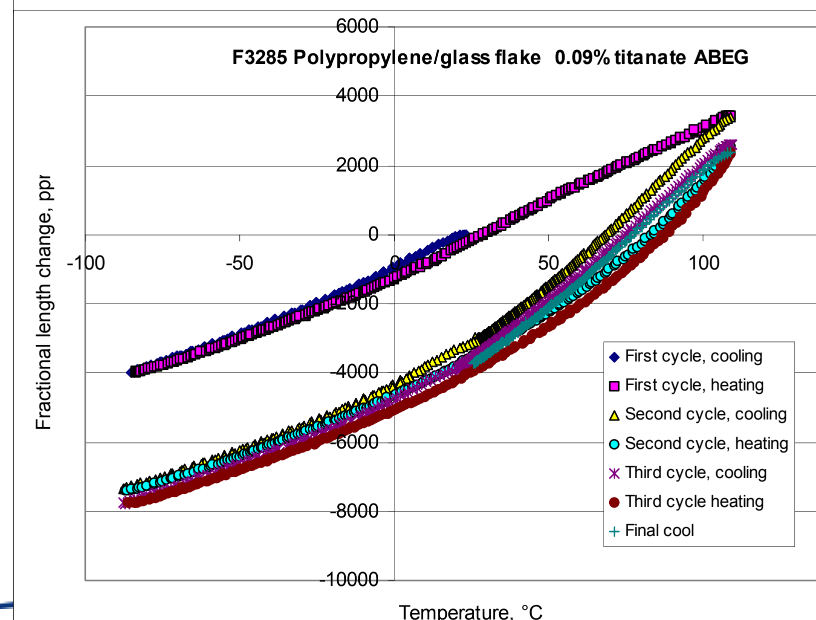
Glass-Flake/Polypropylene - CTE









Glass-Flake/Polypropylene – Residual Strain

Material	Residual Strain (%)
Polypropylene	0.31
Untreated	0.35
Titanate **0.09%** **0.42%**	 0.32 0.25
Aminosilane **0.05%** **0.28%**	 0.11 0.14

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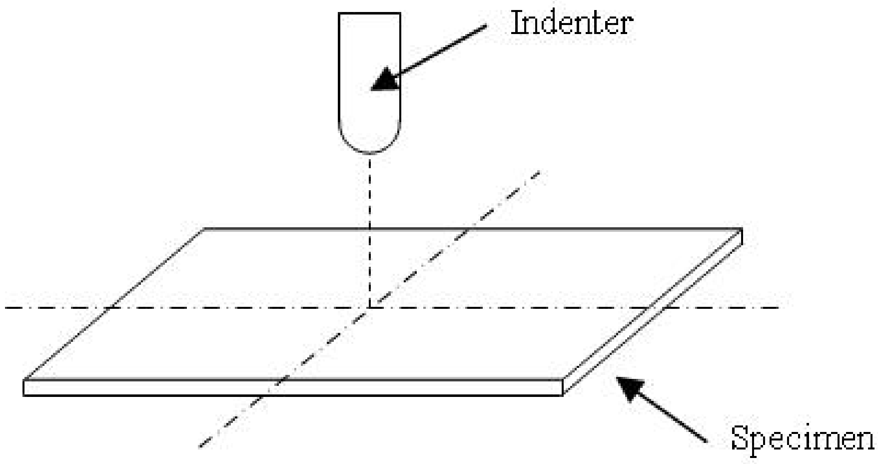
Glass-Flake/Polypropylene - Impact Resistance

- Total weight (g): 2069.1
  - Carrier weight (1721.1 g) + 20 mm diameter indenter (348 g) - calibrated with 12.49 kg weight
- Drop height (m): 0.25
- Impact velocity (m/s): 2.22
- Drop energy (J): 5.11
- Load cell: 2 kN



Glass-Flake/Polypropylene - Impact Resistance

Material	Peak Energy (Joules)	End Energy (Joules)	Peak Force (N)
Untreated Flake	0.73 ± 0.15	3.08 ± 0.29	265 ± 35
Titanate			
0.09%	0.81 ± 0.11	3.06 ± 0.31	304 ± 11
0.42%	0.75 ± 0.10	2.86 ± 0.44	257 ± 58
Aminosilane			
0.05%	0.74 ± 0.15	2.52 ± 0.53	296 ± 24
0.28%	0.60 ± 0.07	2.51 ± 0.13	263 ± 22

- Absorbed energy decreases with increasing filler/matrix interfacial strength
- Poorly bonded systems exhibit higher impact resistance

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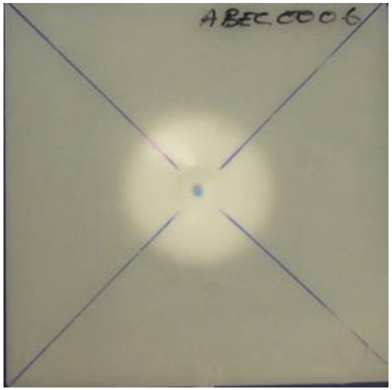
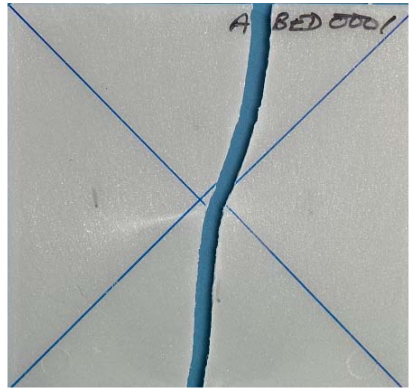
Glass-Flake/Polypropylene - Impact Resistance

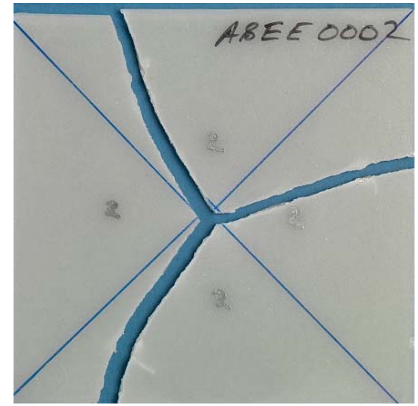
Polypropylene



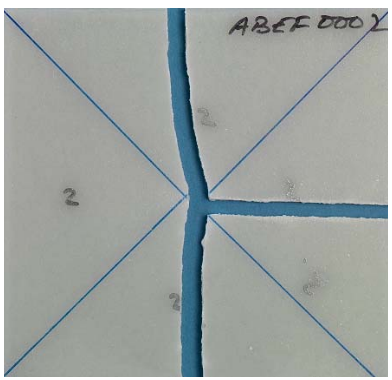
Untreated flakes



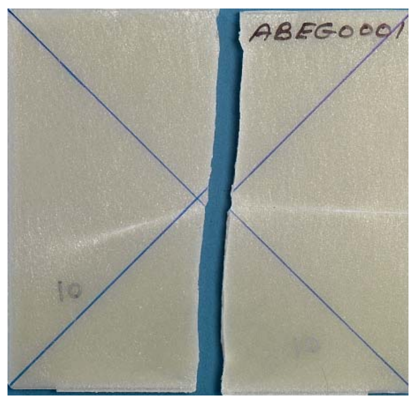
0.05% Aminosilane



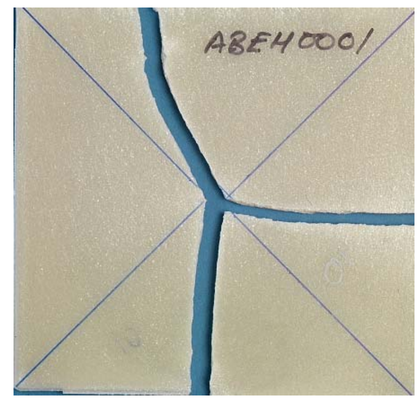
0.28% Aminosilane



0.09% Titanate



0.42% Titanate



Case Study 3: Nanocomposite

- PNCs: Nanoparticle reinforced PMMA composites
- Weight additional levels (wt %)
- Mechanical properties:
  - Fracture toughness (impact resistance)
  - Tensile properties
  - Creep rupture (environmental effects)
    - Solvent craze resistance
  - Permeation
- Supplier: Lucite International UK Ltd

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Any Questions?

Website

http://www.npl.co.uk/materials/programmes/characterisation

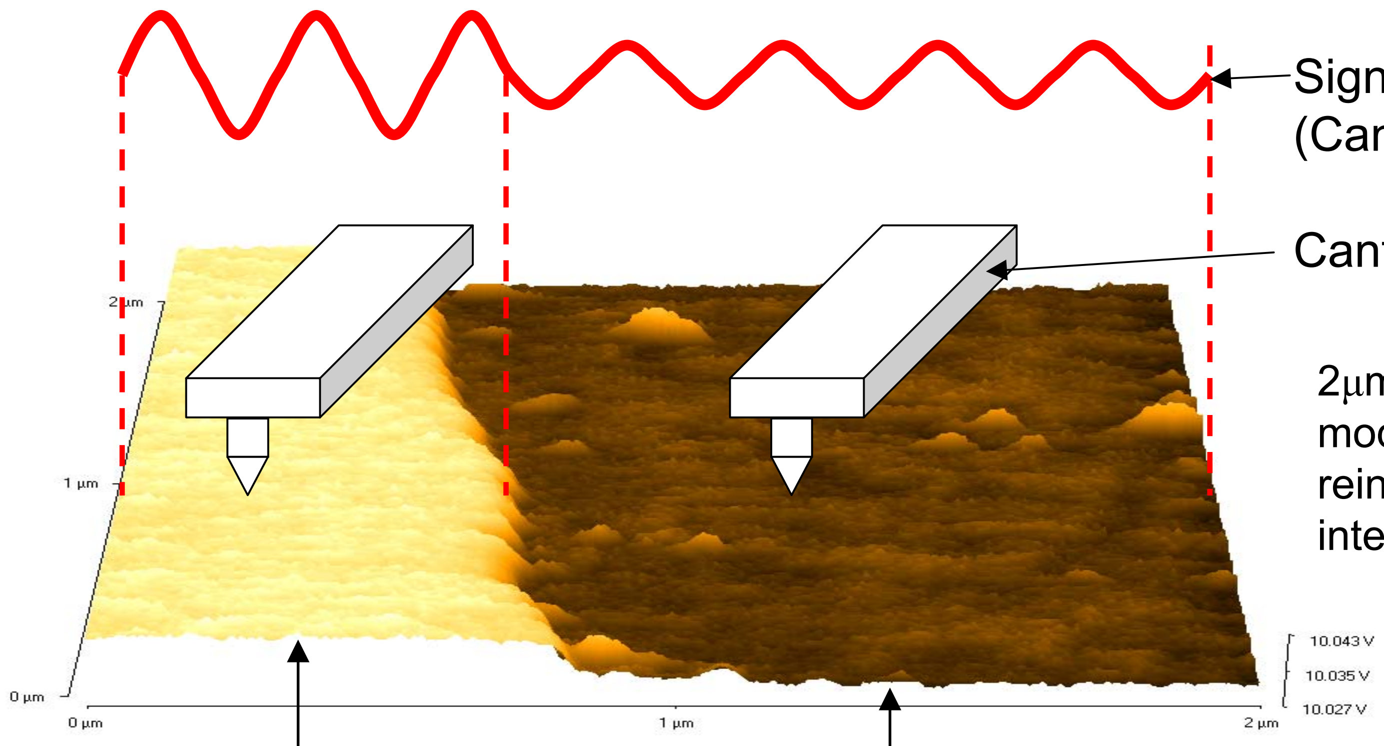
User Name: multiscale
Password: iagmember

Force Modulation AFM (FM-AFM)

The contact force on sample is modulated

The cantilever deflects as the surface resists oscillation

High elastic modulus samples cause greater deflection of cantilever



2µm Scan in FM-AFM mode of a Glass Flake reinforced PP over the interface

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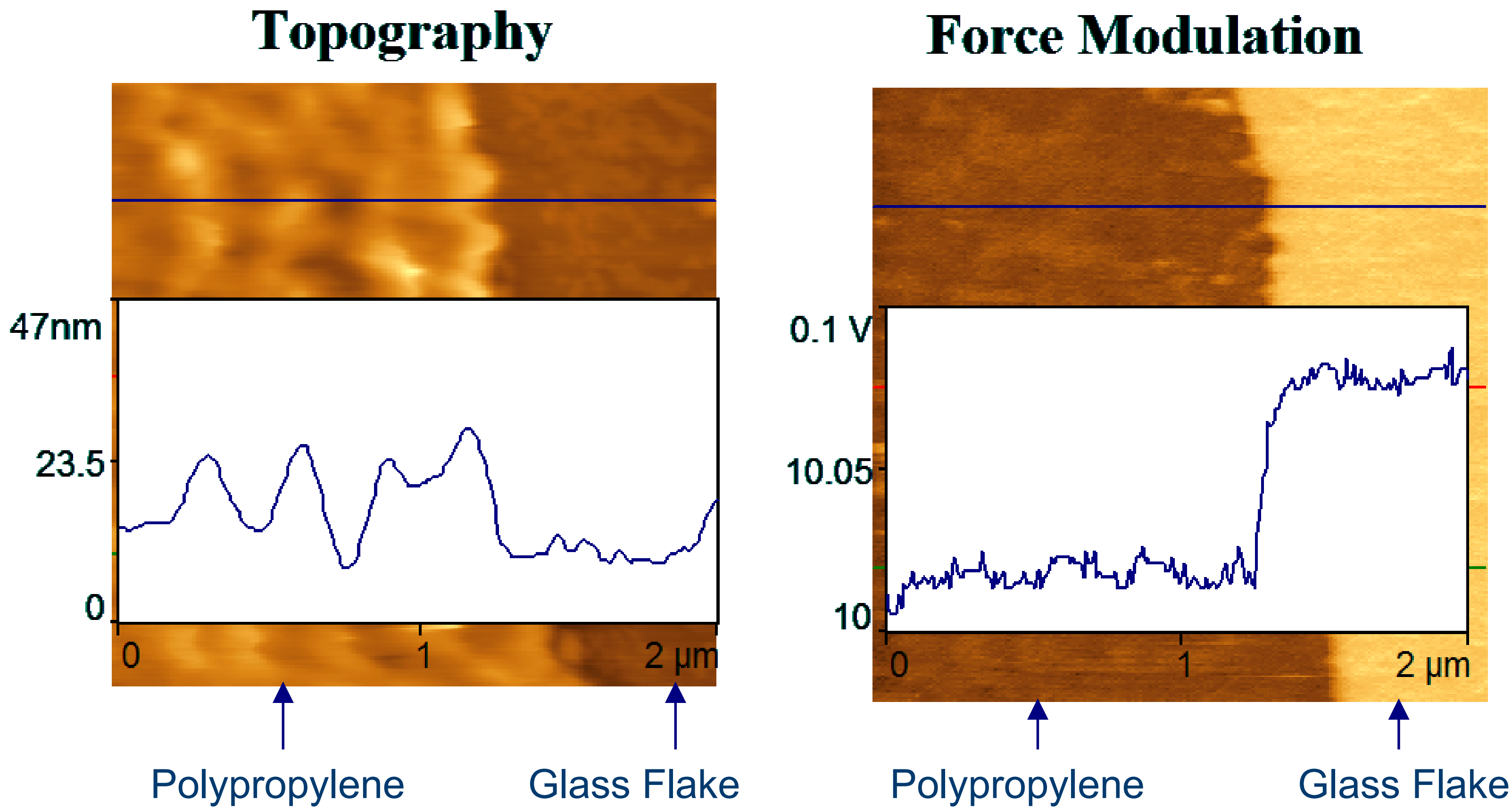
Independence to Topography

Large amplitude = High surface elastic modulus

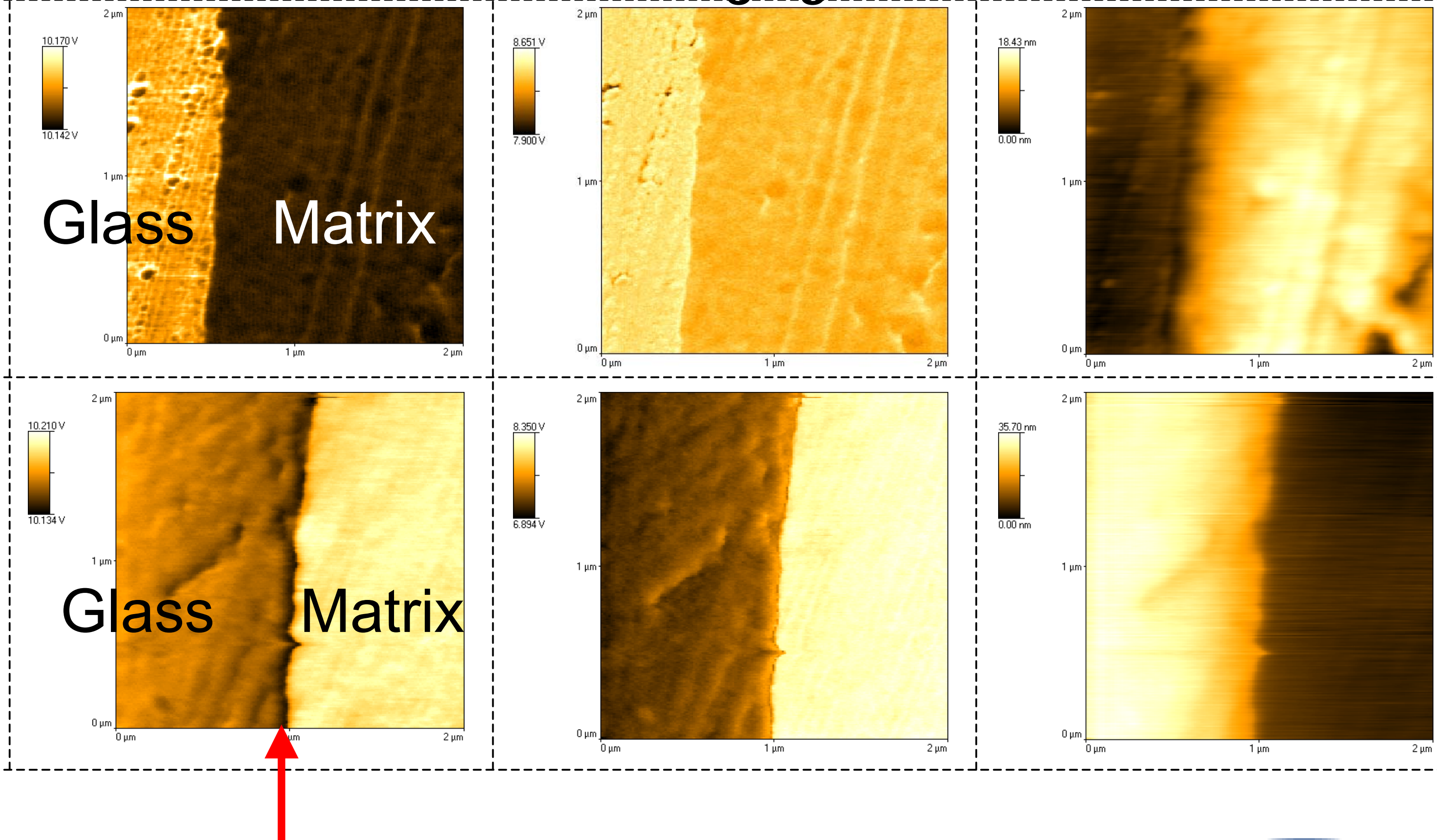
Small amplitude = Low surface elastic modulus



2µm Scan in FM-AFM of Glass flake reinforced PP with 0.09% Titanate coating

2µm FM-AFM scan of GFRP with poor and good interfacial bonding

	Force modulation	Phase Imaging	Topography
Good Interface			
Poor Interface			



Clear band of different tip-surface interaction for the poor interface sample

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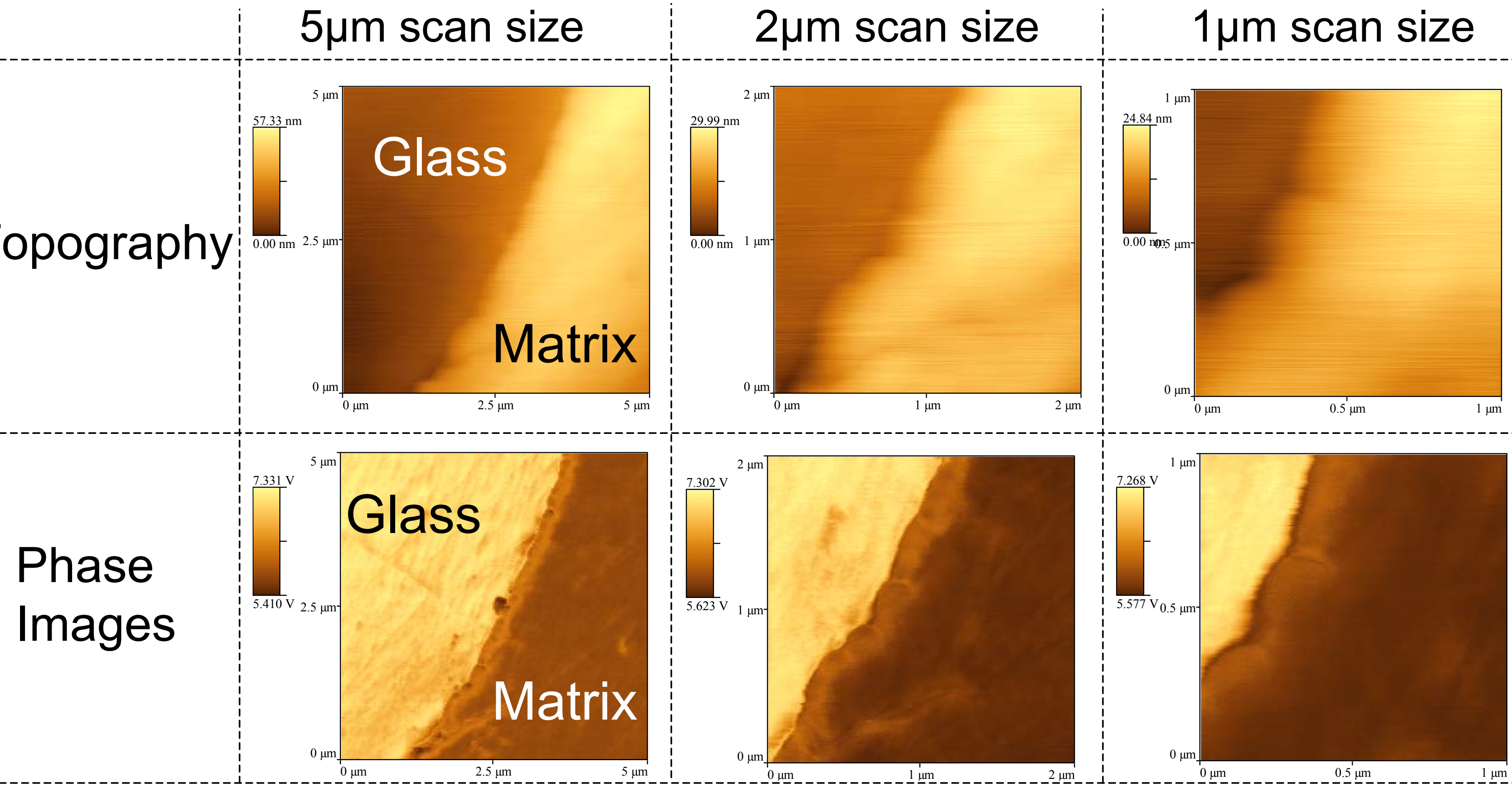
Phase Image of interface region for poorly bonded sample



5,2 and 1µm Phase Images of a portion of a unidirectional GFRP specimen with poor interfacial bonding

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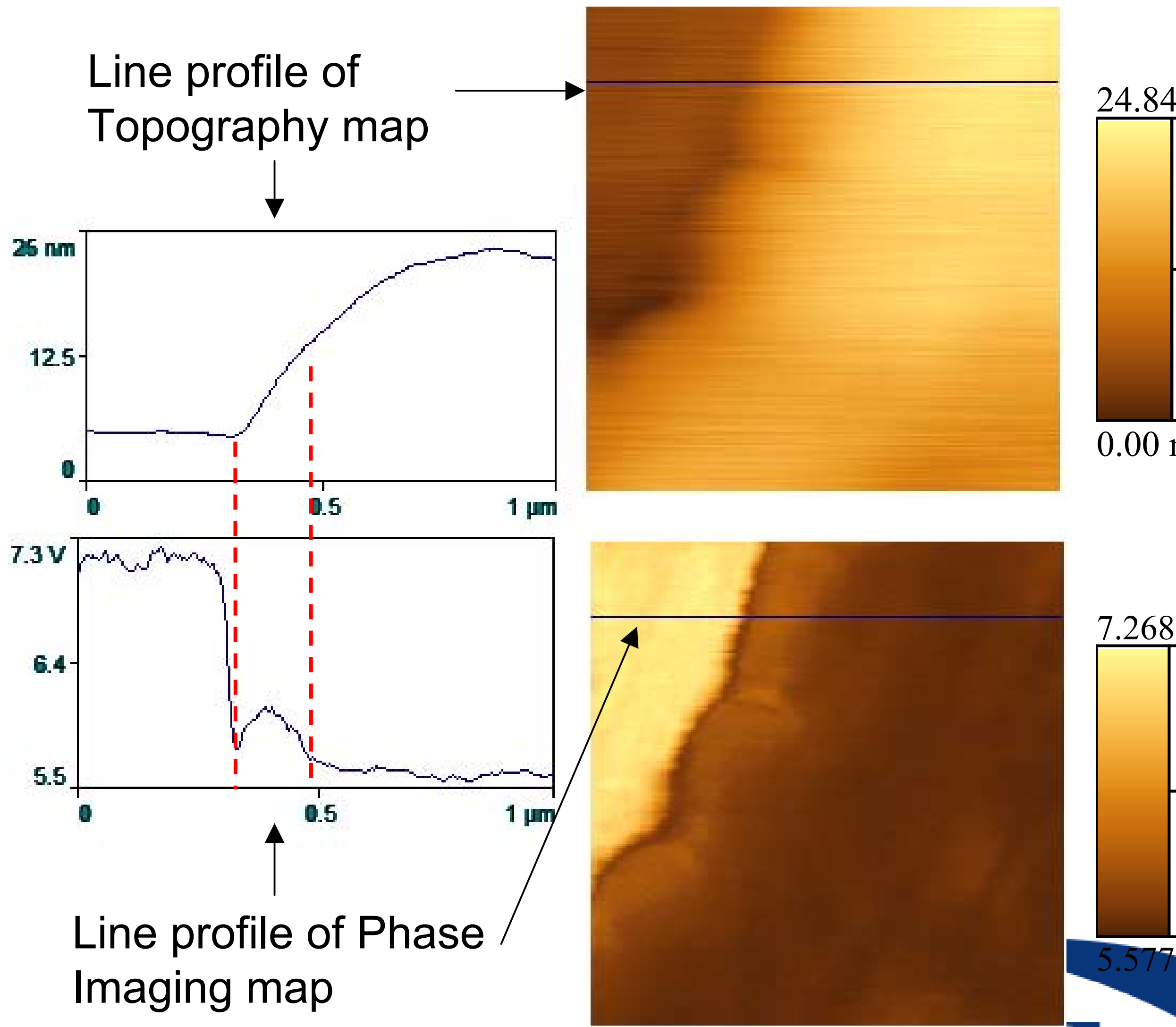
Analysis of phase diagram in locating the interphase

- Region of 50 to 300nm found with different phase & FM response
- Key issues need to be addressed including
    - Calibration methods
        - Tip validation
    - Reproducibility
    - Creep behaviour
    - Surface preparation
    - Relating FM and Phase to elastic modulus values



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Summary

- Clear differences between fibre and matrix shown by
- Currently unable to find an interphase for glass flake samples
- Differences between good and poor bonding visualised

Future work

With specific attention taken to the GFRP with good and poor bonding

- Calibration methods
- Depth of tip penetration (to find creep within the matrix)
- Non contact phase imaging
- Intermittent contact methods
- Nano indentation using diamond AFM tip

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