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

Polymers: Multiscale Properties

22 April 2008

Deliverables

- **D1: Critique of test methods and predictive analysis for characterising interfacial properties in filled systems**

  NPL Report - completed

- **D2: Develop and evaluate new measurement techniques identified in D1 for characterising interfacial properties. Case studies (micro- to nano-scale) on the application of interfacial characterisation methods to filled systems**

  Scientific paper (March 2009)

- **D3: Evaluation of predictive model(s) for characterising interfacial and interphase properties in filled systems**

  Scientific paper (March 2009)

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Recap

- AFM has been demonstrated to be a suitable method for qualitative imaging of surface elasticity and quantitative surface elastic modulus measurements
- SEM is suitable for qualitative comparison with AFM measurements
- Methodology is being investigated for preparing TEM specimens and subsequent analysis of composite interfaces

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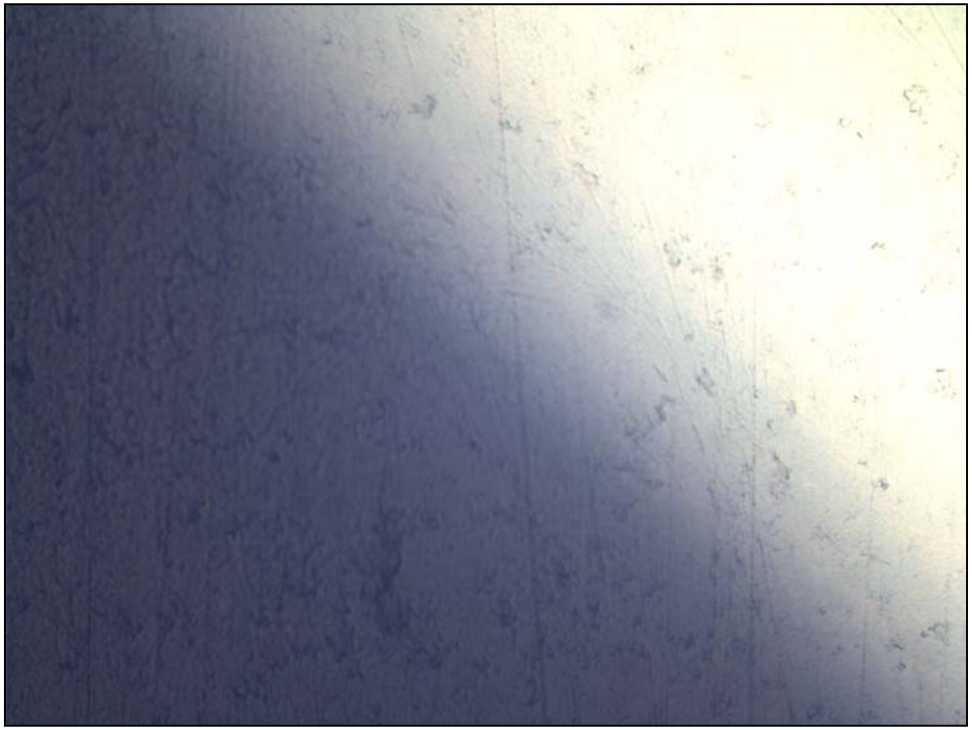
Recap

- Calibration of measurements and relation to elastic modulus, as well as issues of repeatability and sensitivity of measurements will influence the effectiveness of any industrial AFM method.

- Primary research activities:
  - Manufacture and assessment of reference samples for AFM measurements (calibration)
  - Relating AFM measurements to surface elastic modulus
  - TEM specimen preparation and analysis

Reference Samples

- Single phase reference samples developed elsewhere
- Two phase reference sample

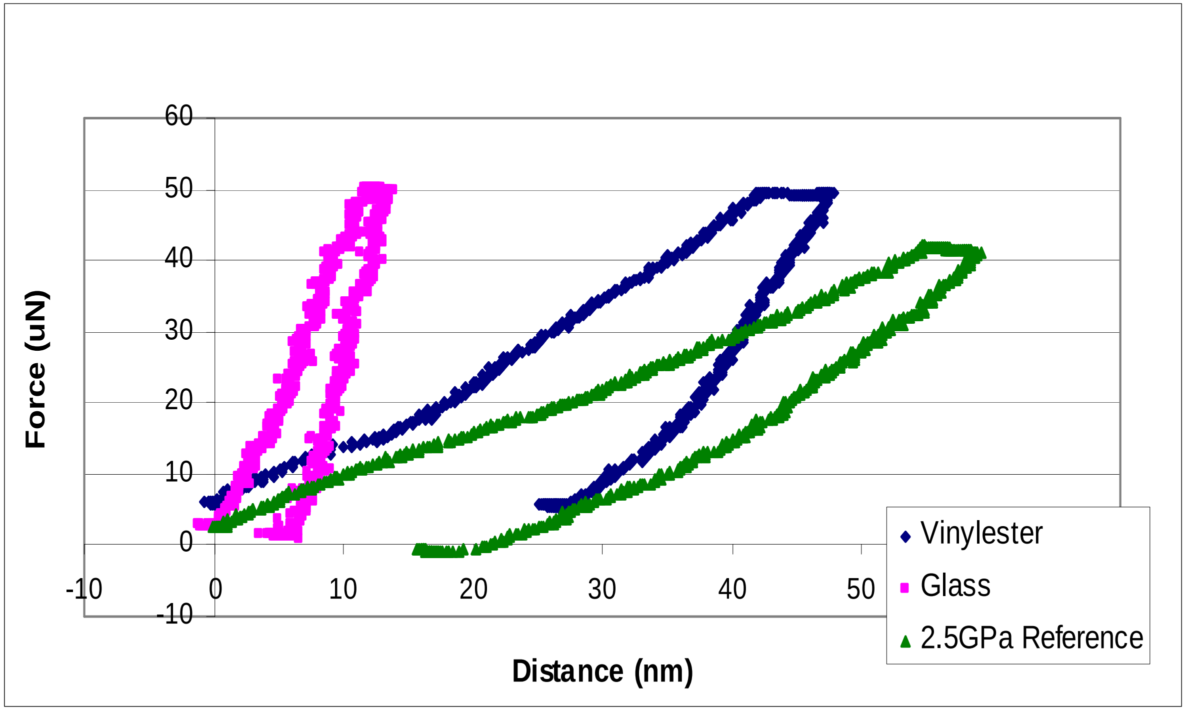


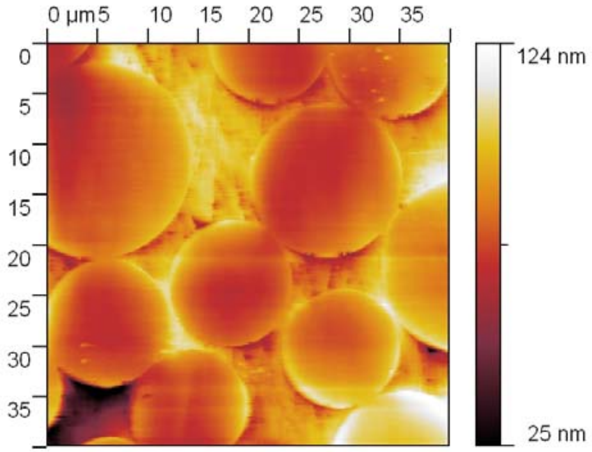
Optical photograph in transmission mode of two phase (prototype) reference sample.

Indentation

Indentation tip size will limit resolution available for measuring interphase

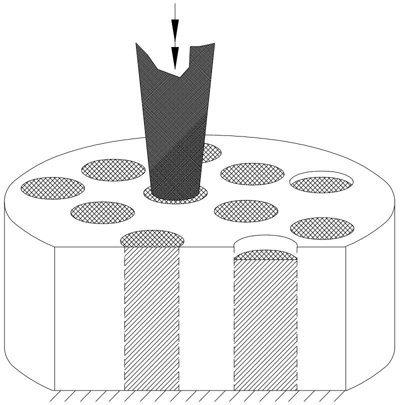
Topographic Image of GRP interface taken using AFM indenter tip before indentation



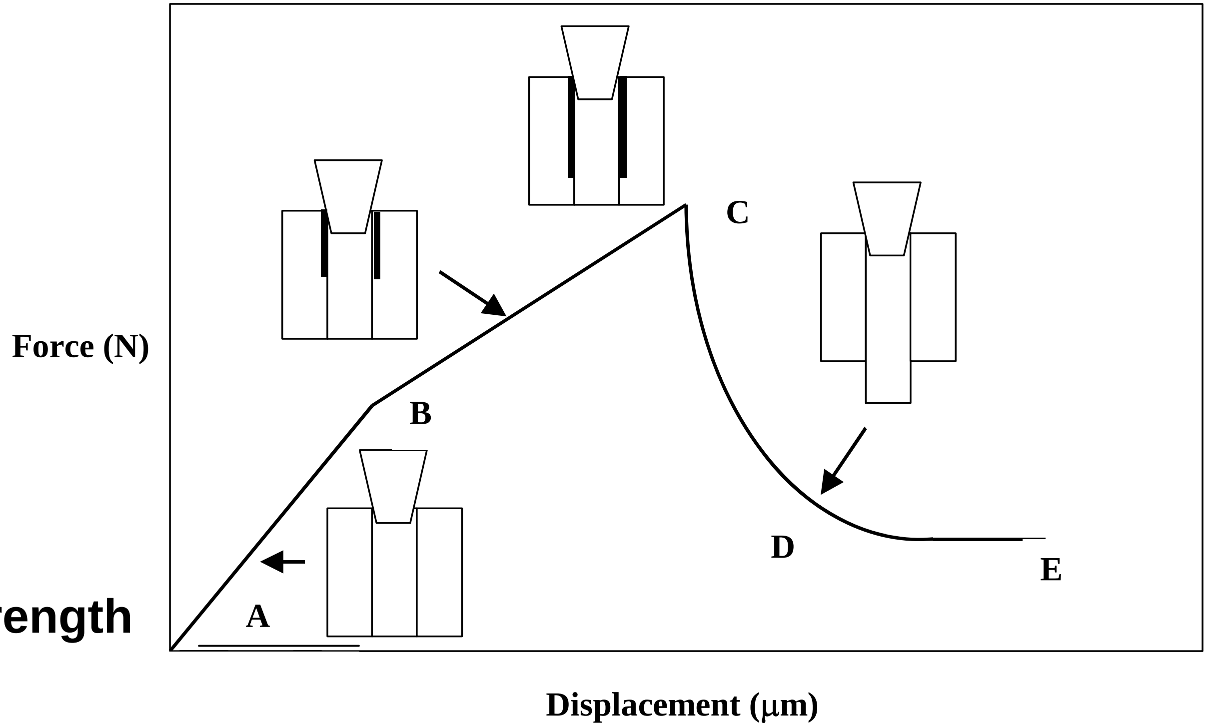


Indentation curves obtained for glass fibre, vinylester matrix and reference sample

Microindentation (Push-out) Test



$$\tau_i = \frac{nF}{2\pi r^2}$$



τ_i, = interfacial shear strength
F = debonding force
r = fibre radius
n = volume fraction + fibre/matrix stiffness parameter

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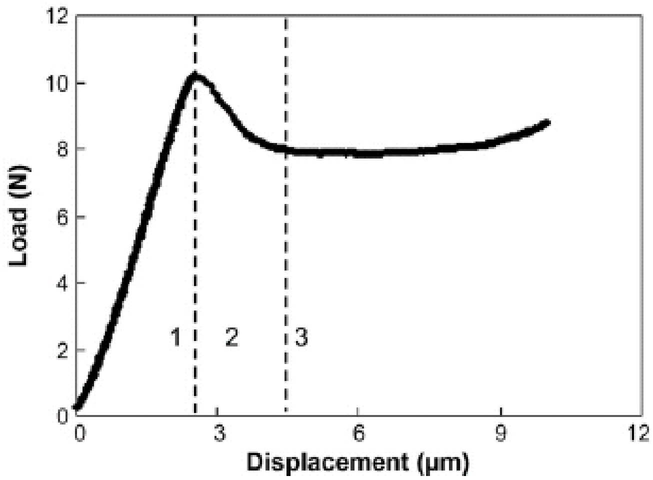
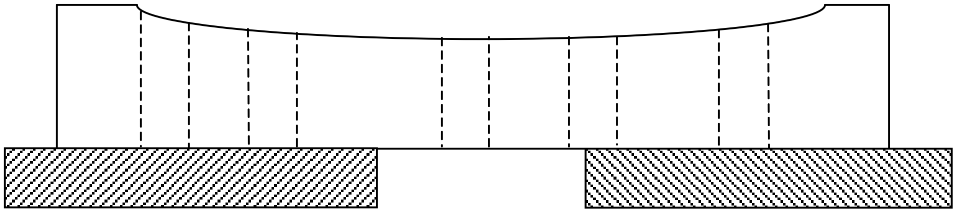
Fracture Testing



Typical load-displacement curve for a single fibre push-out test. Reproduced from finite element analysis of single-fibre push-out tests of continuous Al_2O_3 fibre-reinforced NiAl composites (Y Chen, W Hu and Y Zhong, Materials Science and Engineering A 460-461, 2007).

- **Fibre push-out test**
  - **Limited to GRP rod samples**
  - **Sample preparation key**
    - **<300 µm**
  - **Minimise bending during indentation**



TEM polishing equipment can produce 1 mm diameter sections to required thickness

Lateral Force Method (LFM)

H. Zhang et al. / Acta Materialia 52 (2004) 2037–2046

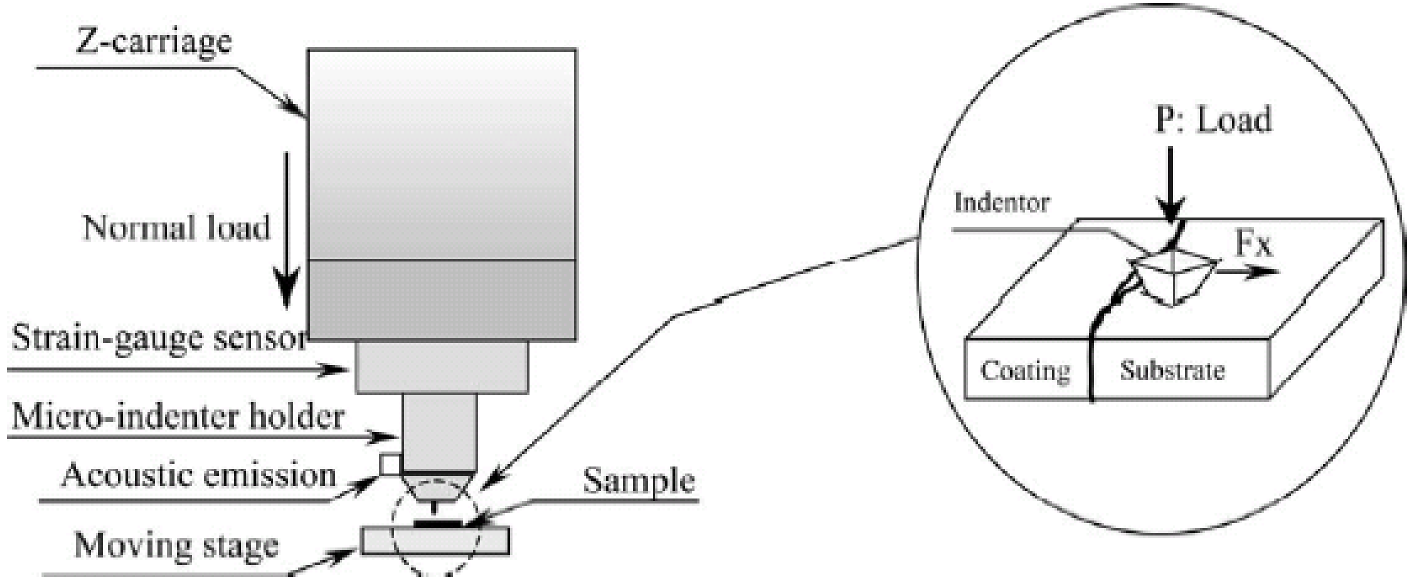


Fig. 1. A schematic diagram of the setup for indentation measurement.

- Method proposed for thin films

Lateral Force Method (LFM)

- Indent in vicinity of fibre
- Monitor load-displacement and lateral forces
- Lateral forces change on initiation of interfacial failure

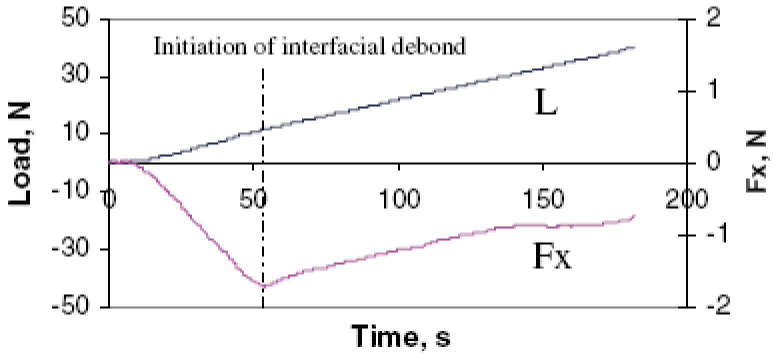


Fig. 2. Load–time and lateral force Fx–time curves of an Al_2O_3/Al 6061 bond.

H. Zhang et al. / Acta Materialia 52 (2004) 2037–2046

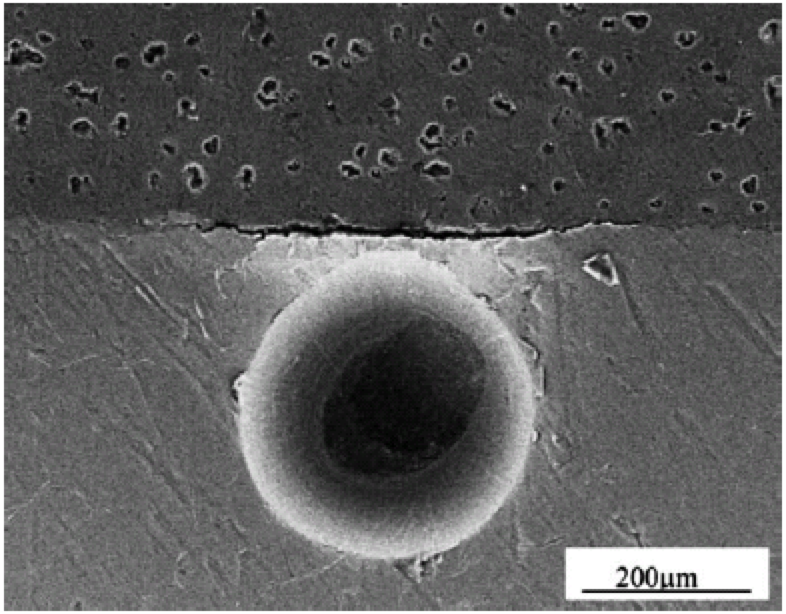
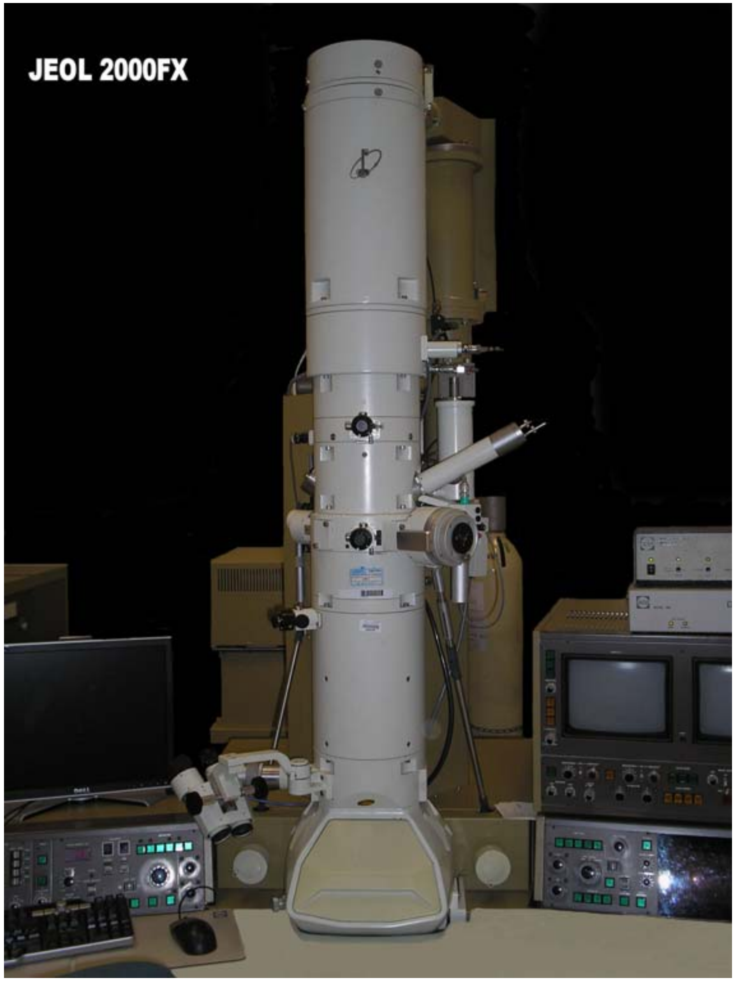


Fig. 3. Debond at an Al_2O_3/Al 6061 interface caused by indentation.

Limitations

- Current system tested for brittle interfaces using microindentation (200 μm indentation)
- Adaptation of existing equipment required to monitor lateral force during indentation
- Combination of plastic and elastic deformation prior to interfacial failure

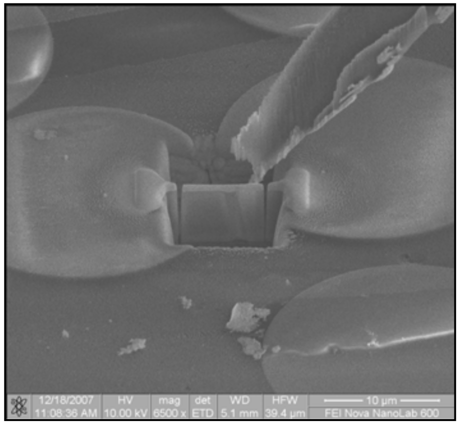
Transmission Electron Microscopy (TEM)

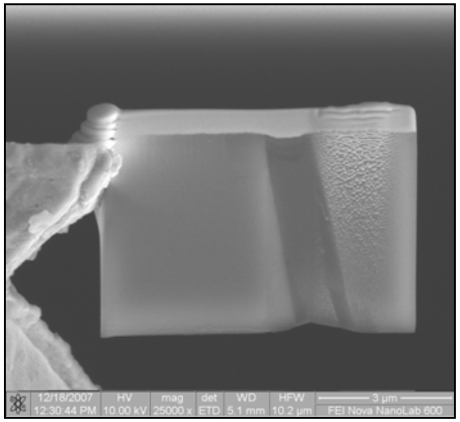


JEOL 2000FX TEM at NPL

FIB preparation of the ultrathin specimens for TEM analysis (right)

10 μm x 5 μm ultrathin section across the interface (right)





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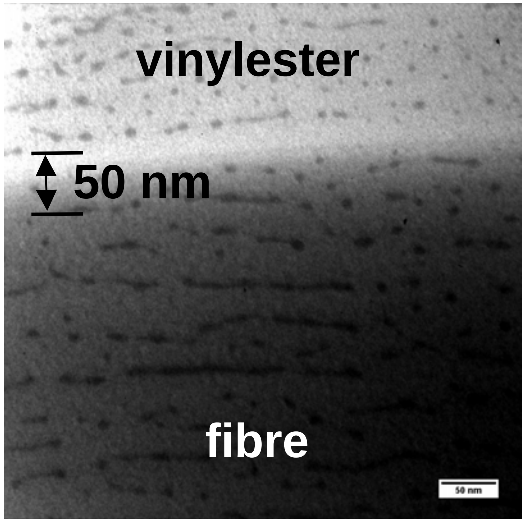
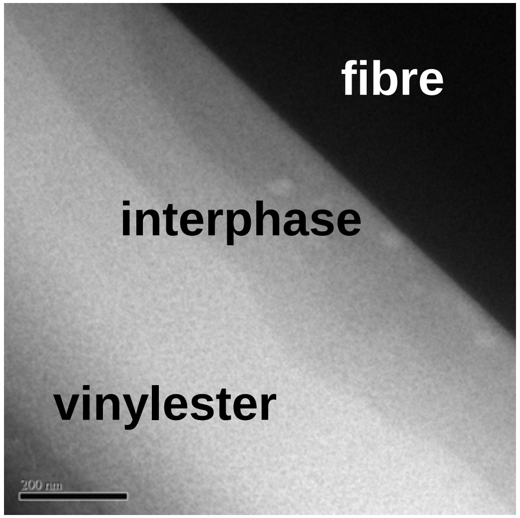
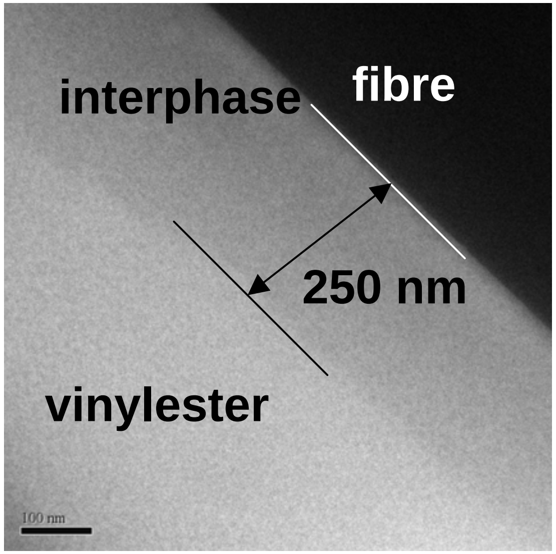
Transmission Electron Microscopy (TEM)

TEM micrograph of interface of well bonded GRP pultruded rod (left and right)





TEM micrograph of interface of poorly bonded GRP pultruded rod (left and right)



Transmission Electron Microscopy (TEM)

- Interphase of GRP pultruded rods
  - < 50 nm for well-bonded system
  - 100 to 350 nm for poorly bonded system
- Total evaluated interface length only 10 μm for each fibre
- Further sections to be prepared and evaluated

Future Work

- **Primary research activities in progress**
  - **Reference samples for AFM measurements**
  - **Relating AFM measurements to surface elastic modulus**
  - **TEM sample preparation and analysis**
  - **FEA modelling**
    - **Prediction of interfacial strength**
    - **Compare with concentric cylinder models**

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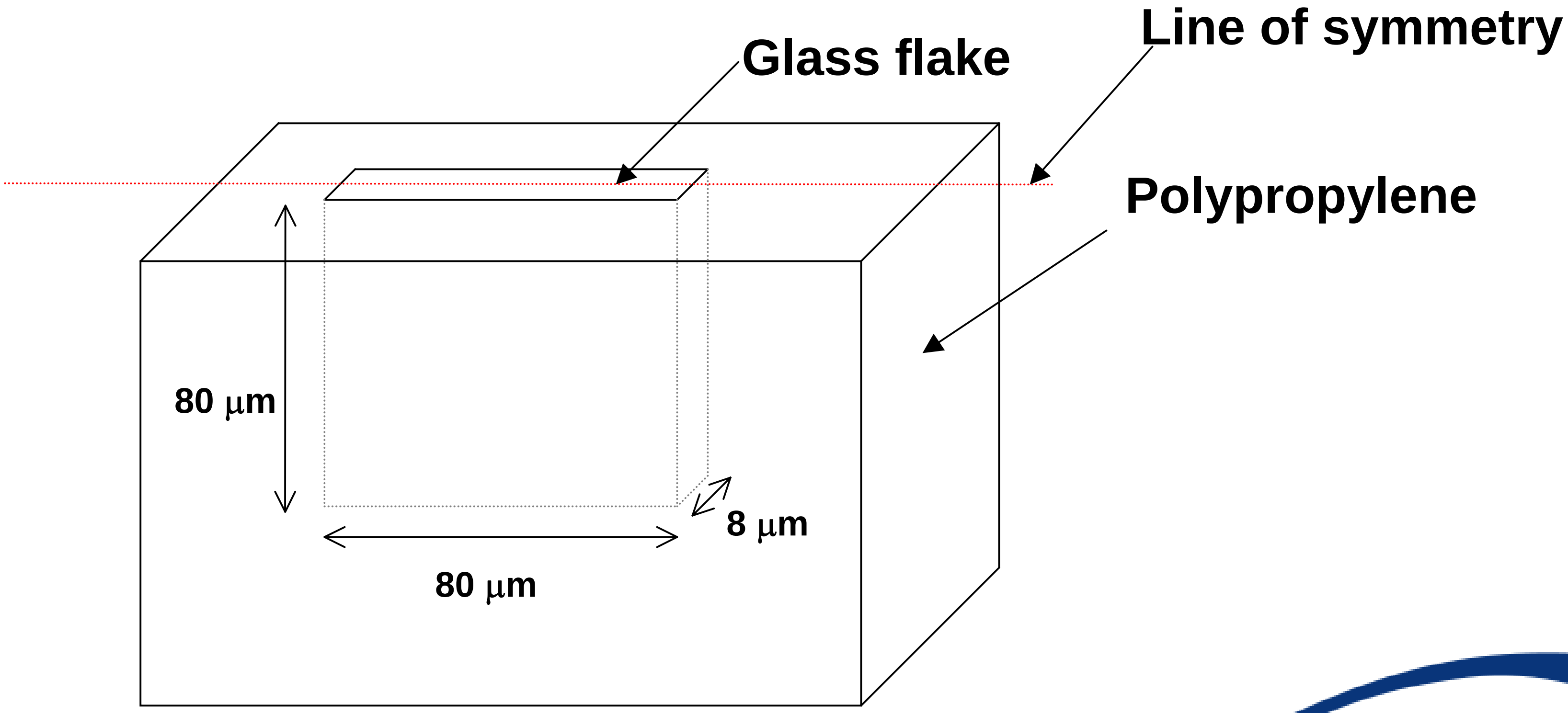
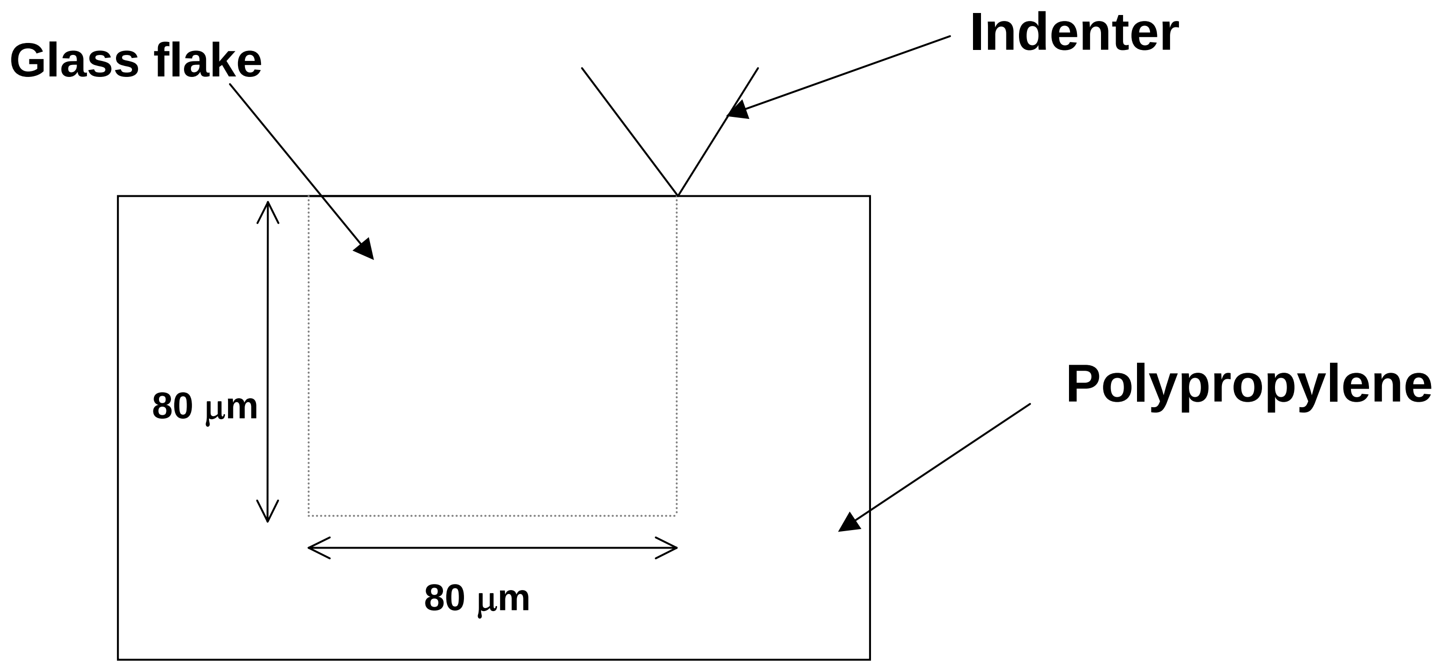
FEA Modelling - Nanoindentation

- Nanoindentation of glass flakes in polypropylene
- Due to symmetry, half structure can be modelled



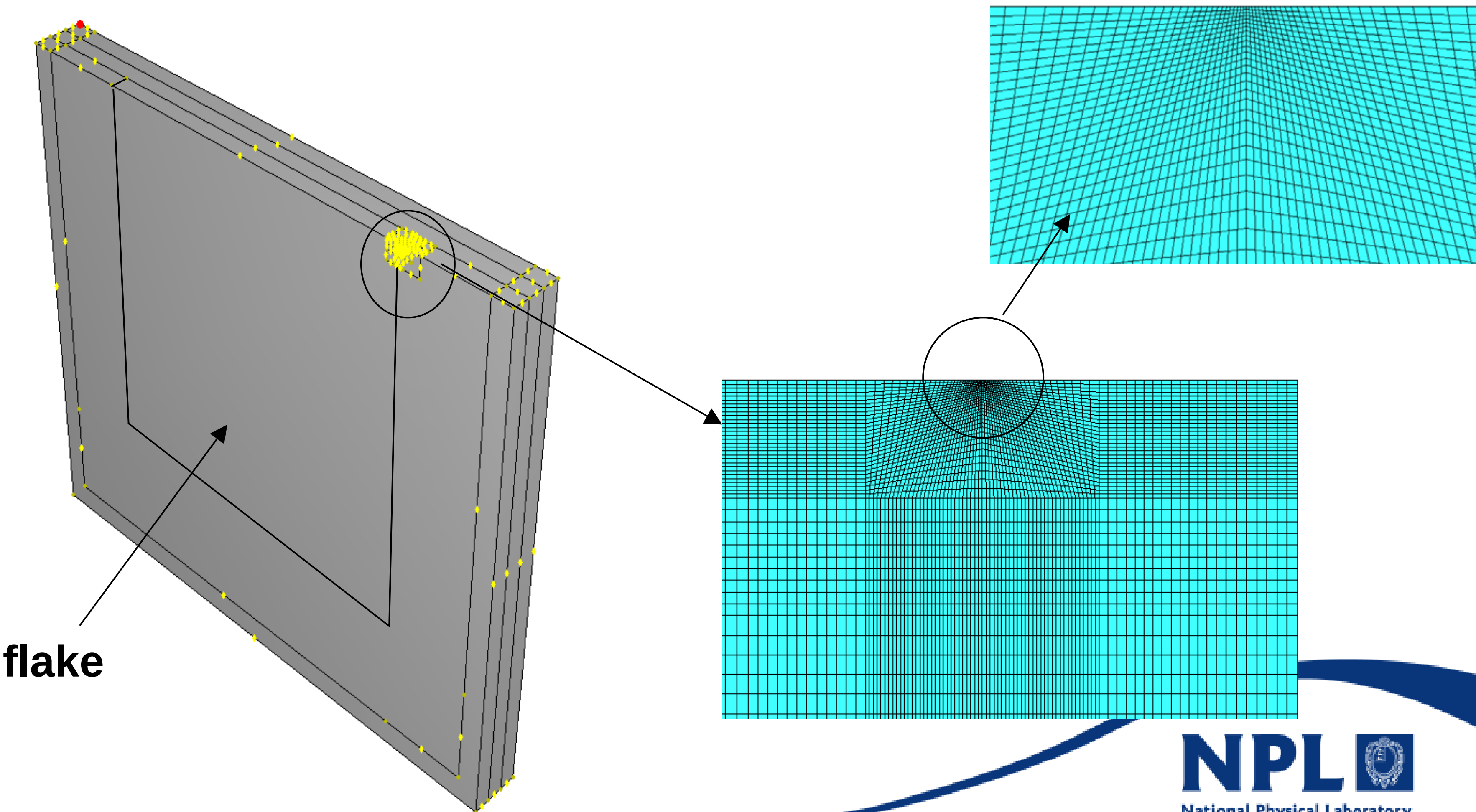
FEA Modelling - Nanoindentation

- Initially indenter will be located at interphase
- Different indenter locations and indentation depths will be investigated



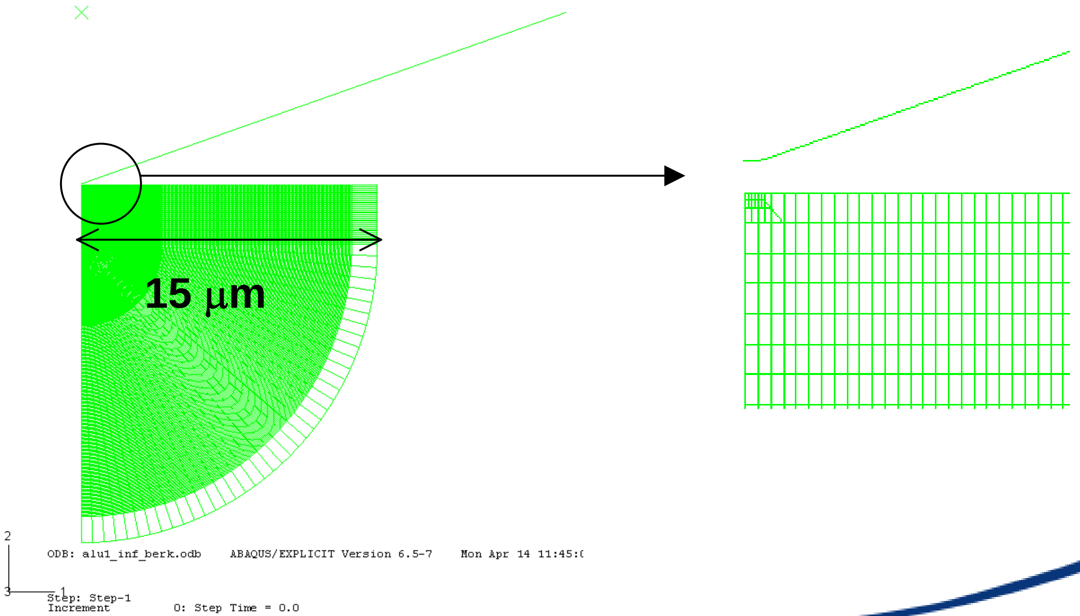
FEA Modelling - Nanoindentation

- FE geometry shown below
- Very refined mesh needed in area of contact with indenter



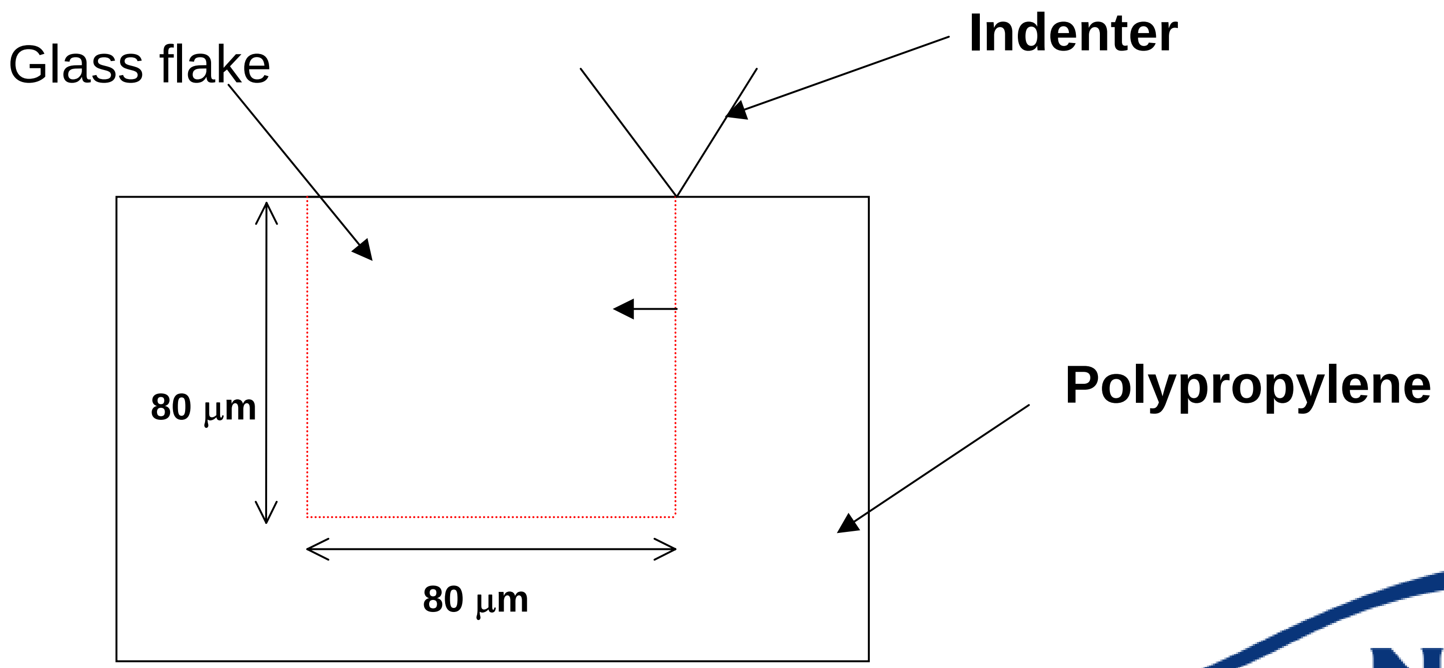
FEA Modelling - Nanoindentation

- FE geometry is not fully meshed yet
- Scale issues are a problem.
- Need an element size of ~ 0.01 micron in region of contact for accurate contact predictions with tips such as Berkovich
- Need large elements if possible throughout bulk to minimise size of the model
- Previous indentation model - much smaller scale and only 2D



FEA Modelling - Nanoindentation

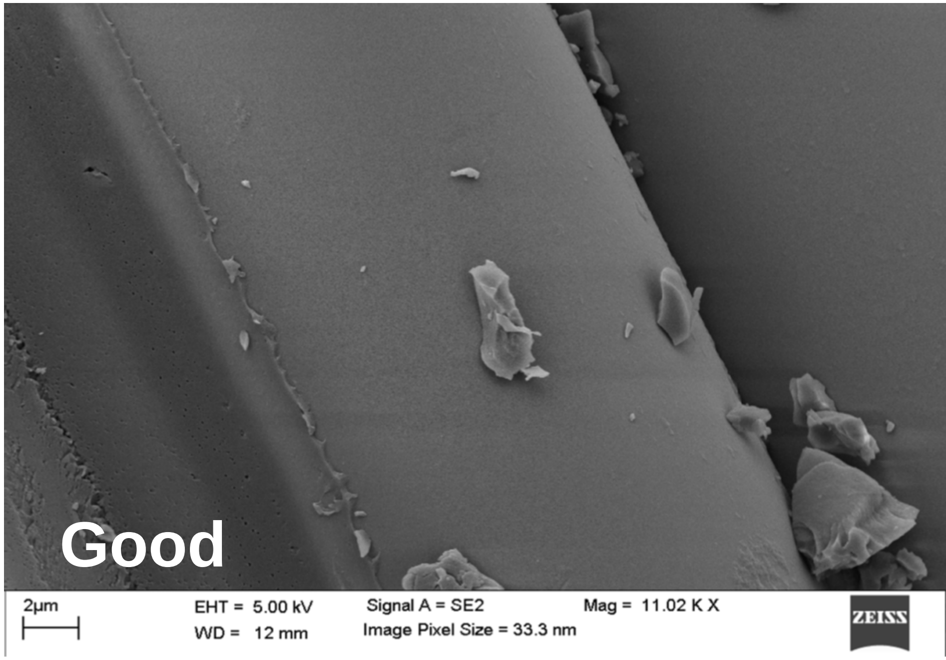
- To allow relocation of indenter without needing a very fine mesh over a large area, the model will be set up so that the mesh stays the same, while the material definitions change
- To move the indenter to the right, the boundaries of the glass flake will be moved to the left so that the indenter now impacts refined elements with polypropylene material definitions



Case Study 1: GRP Pultruded Rods

- Fibre products: E-glass and ECR glass
- Resin: Vinylester
- Surface treatment: Organosilane
- Properties:
  - Flexure strength/stiffness
  - Glass transition temperature
  - Environmental durability/permeation
    - Water immersion at elevated temperature
    - Alkaline solution/elevated temperature
- Suppliers:
  - Exel Composites Ltd (Fibreforce)
  - Owens Corning (Saint-Gobain Vetrotex)

GRP Pultruded Rods – SEM Images



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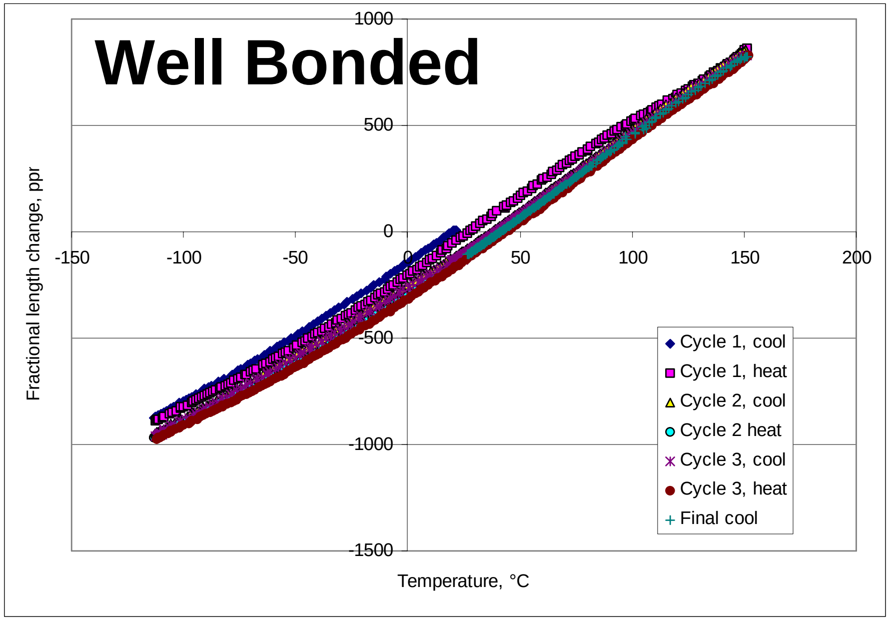
GRP Pultruded Rods – Test Data

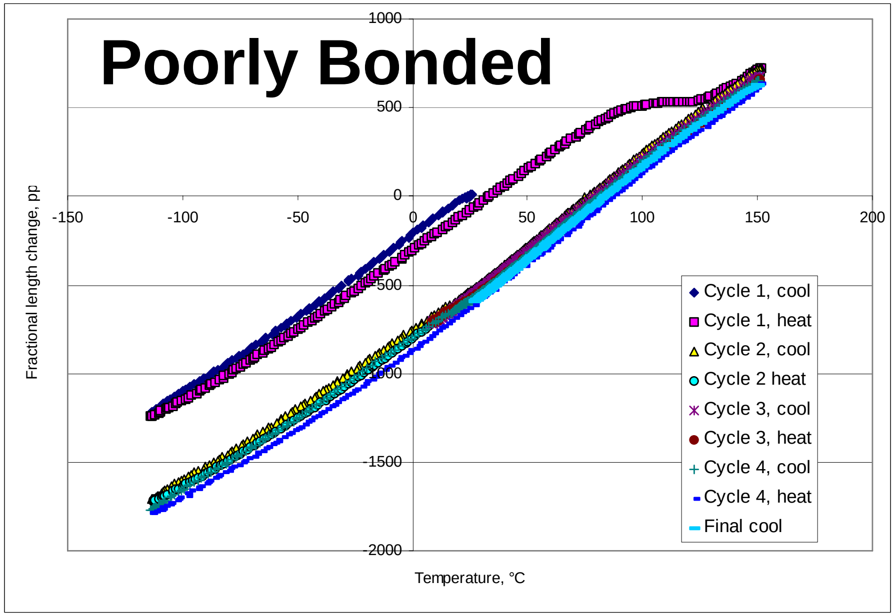
- Fibre Volume Fraction (%)
  - Well bonded: 56.2 ± 0.7
  - Poorly bonded: 55.8 ± 0.8
- Flexural Modulus (GPa)
  - Well bonded: 33.8 ± 0.8
  - Poorly bonded: 30.1 ± 1.1
- Flexural Strength (MPa)
  - Well bonded: 853 ± 39
  - Poorly bonded: 371 ± 56
- Interlaminar Shear Strength (MPa)
  - Well bonded: 54.6 ± 3.1
  - Poorly bonded: 20.0 ± 1.4
- Moisture Content (%) – 3 months in deionised water at 23°C
  - Well bonded: 0.27 ± 0.04
  - Poorly bonded: 0.83 ± 0.22

Observations

- Interphase region
  - < 50 nm (well bonded)
  - 100-350 nm (poorly bonded)
- Longitudinal flexure and interlaminar shear strengths severely compromised by weak fibre/matrix interface
- Flexural stiffness not significantly affected by a weakened fibre/matrix interface
- Poorly bonded system absorbs higher levels of moisture (lowers chemical resistance)

GRP Pultruded Rods – CTE Data





- **Coefficient of Thermal Expansion (CTE) at ambient**
  - **7 x 10^{-6}/°C (well bonded)**
  - **10 x 10^{-6}/°C (poorly bonded)**
  - **Strain difference between relaxed state and following annealing 450-500 με (poorly bonded)**

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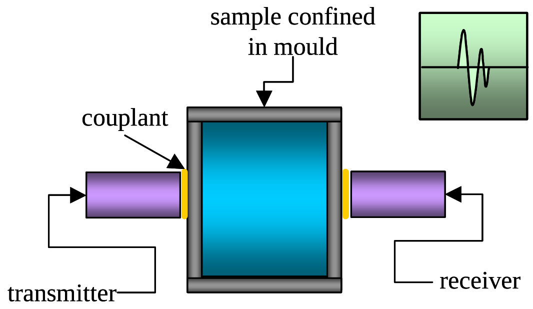
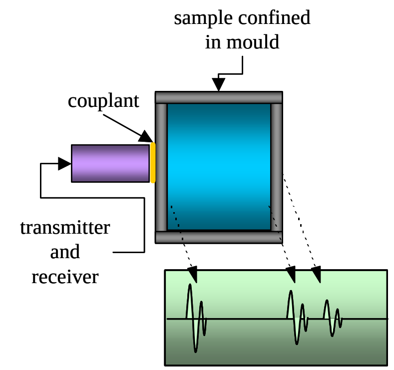
Ultrasonic Elastic Properties



Through-transmission mode

(inset – received signal)



Pulse-echo mode

(inset – received signal + signals from mould walls)

Velocity of a sound wave is directly related to the modulus (stiffness) and density of the material, through the relationship:

$$E_l = \rho V_l^2$$

E_l is the longitudinal elastic modulus

ρ is the density

V_l is the longitudinal wave velocity.

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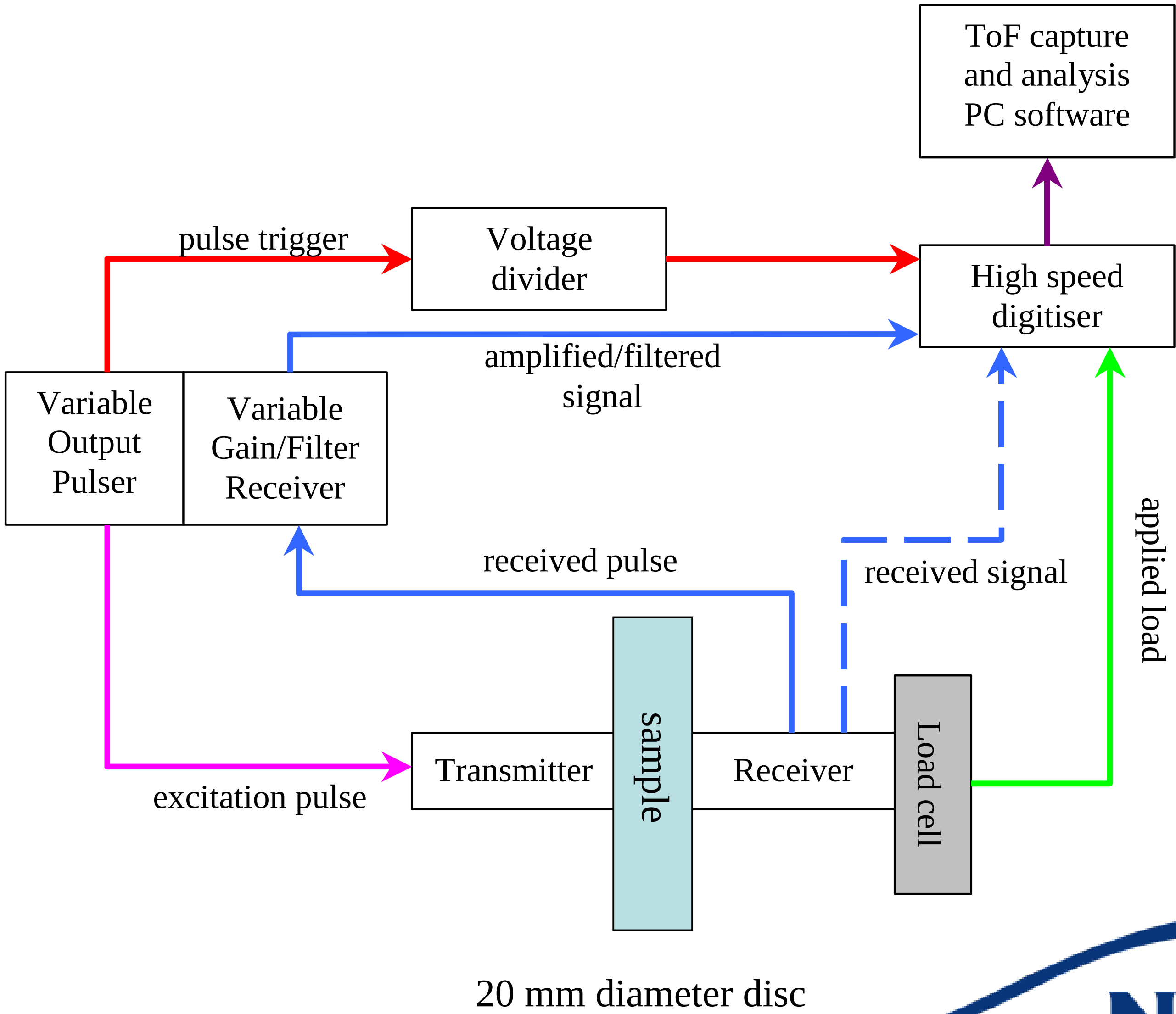
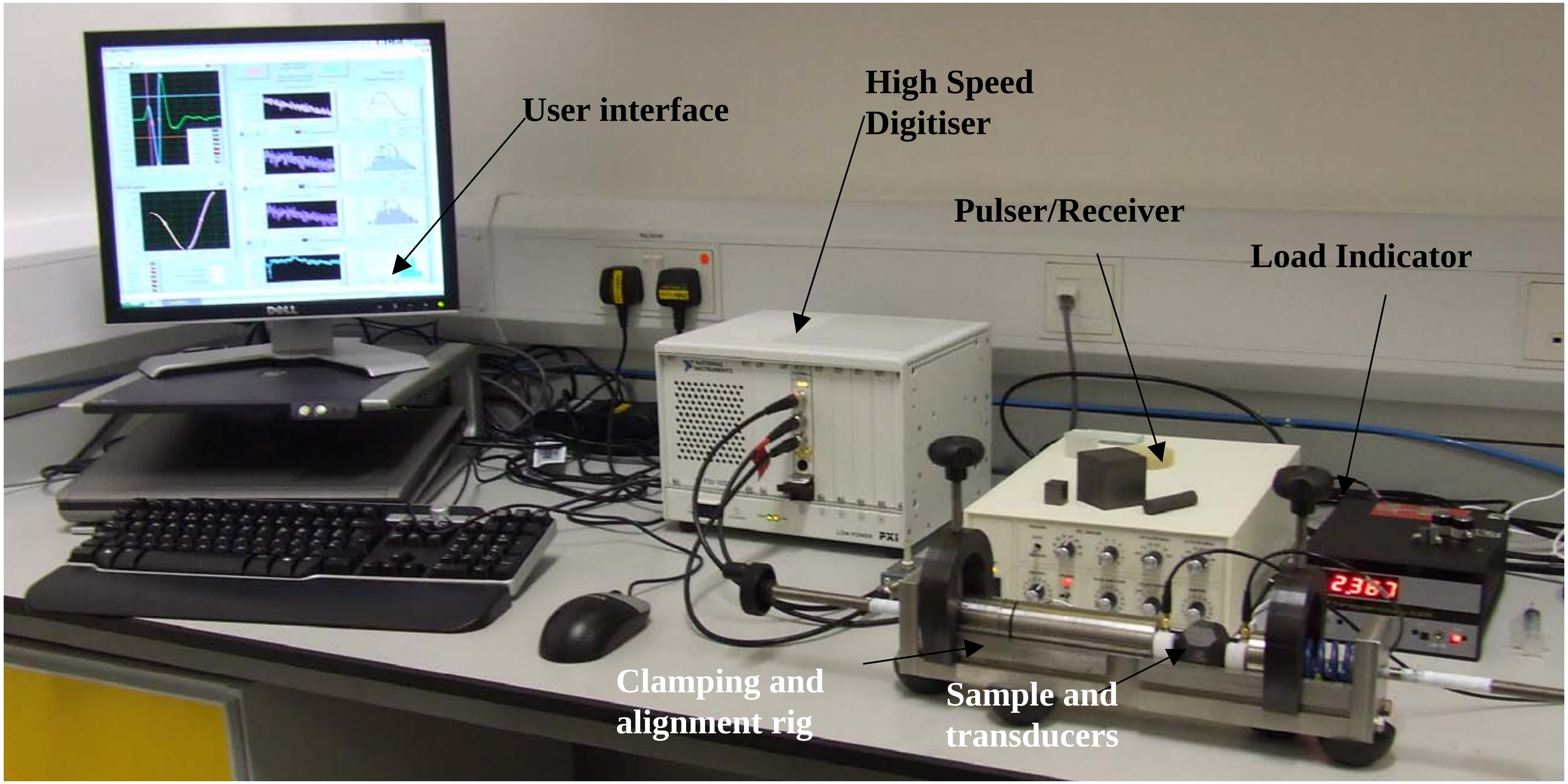
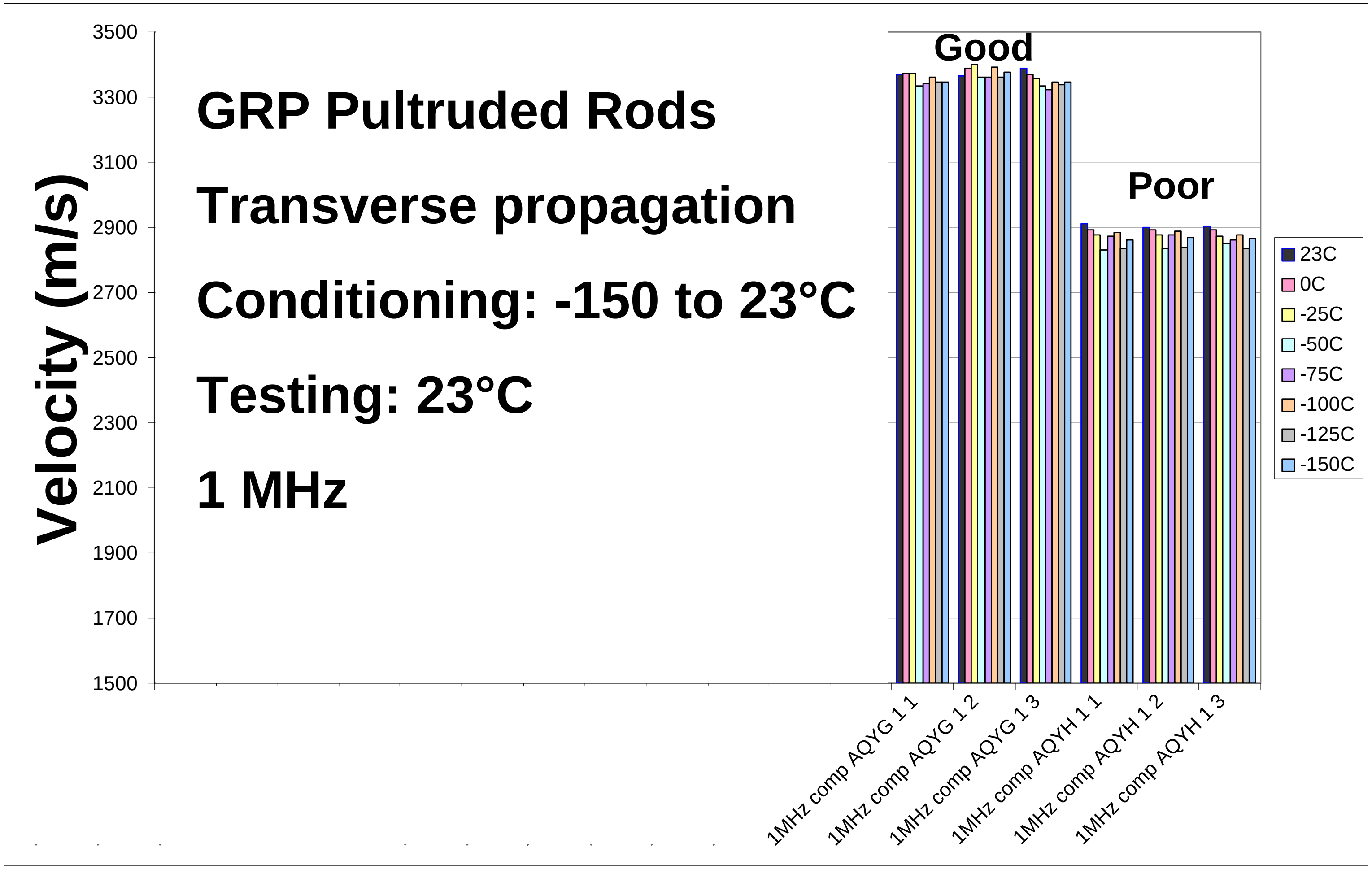
Ultrasonic Elastic Measurements – Time of Flight



Ultrasonic Elastic Measurements – Time of Flight



GRP Pultruded Rods – Velocity Measurements



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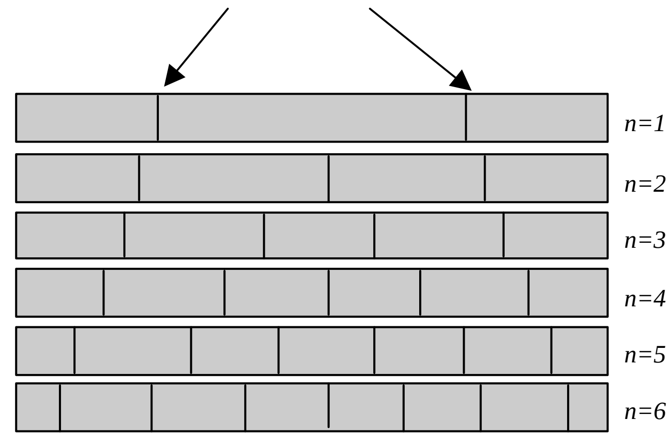
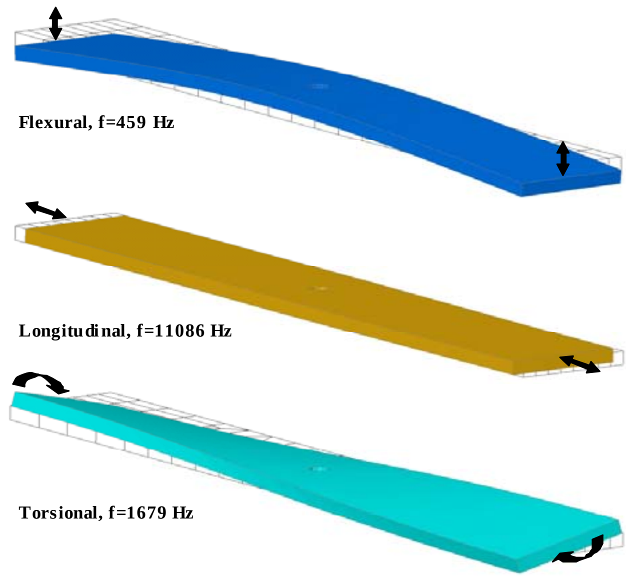
Impact Excitation – Determination of Elastic Moduli

- Technique used to measure stiffness changes due to damage
- All objects have a frequency or set of frequencies at which they naturally vibrate when struck
- Characteristic vibration frequencies of a specimen (round, square or rectangular) can be determined by striking it causing 'ringing' and then deconvoluting the recorded sound spectrum
- Formulae can then be used to relate the resonant frequencies to elastic moduli
- For flexure, at the lowest resonant or natural frequency (the fundamental mode), the nodes are 0.223 of the beam length from each end, with anti-nodes at each end and in the centre – support at nodes, listen at anti-nodes
- Interested in the fundamental mode frequencies for flexural, longitudinal and torsional excitation

Positions of minimum vibration

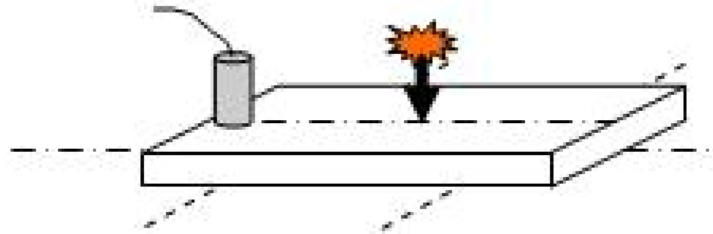
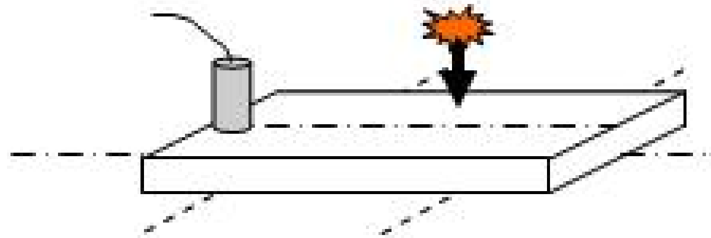
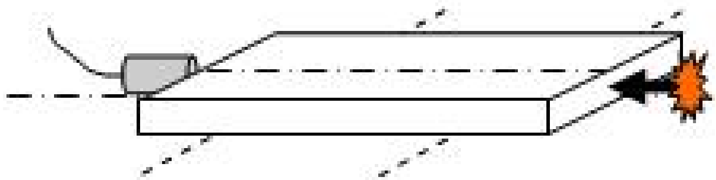
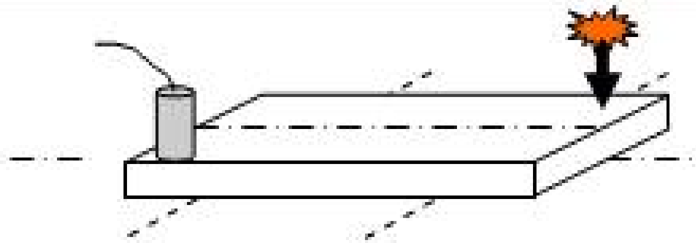


Out-of plane flexure

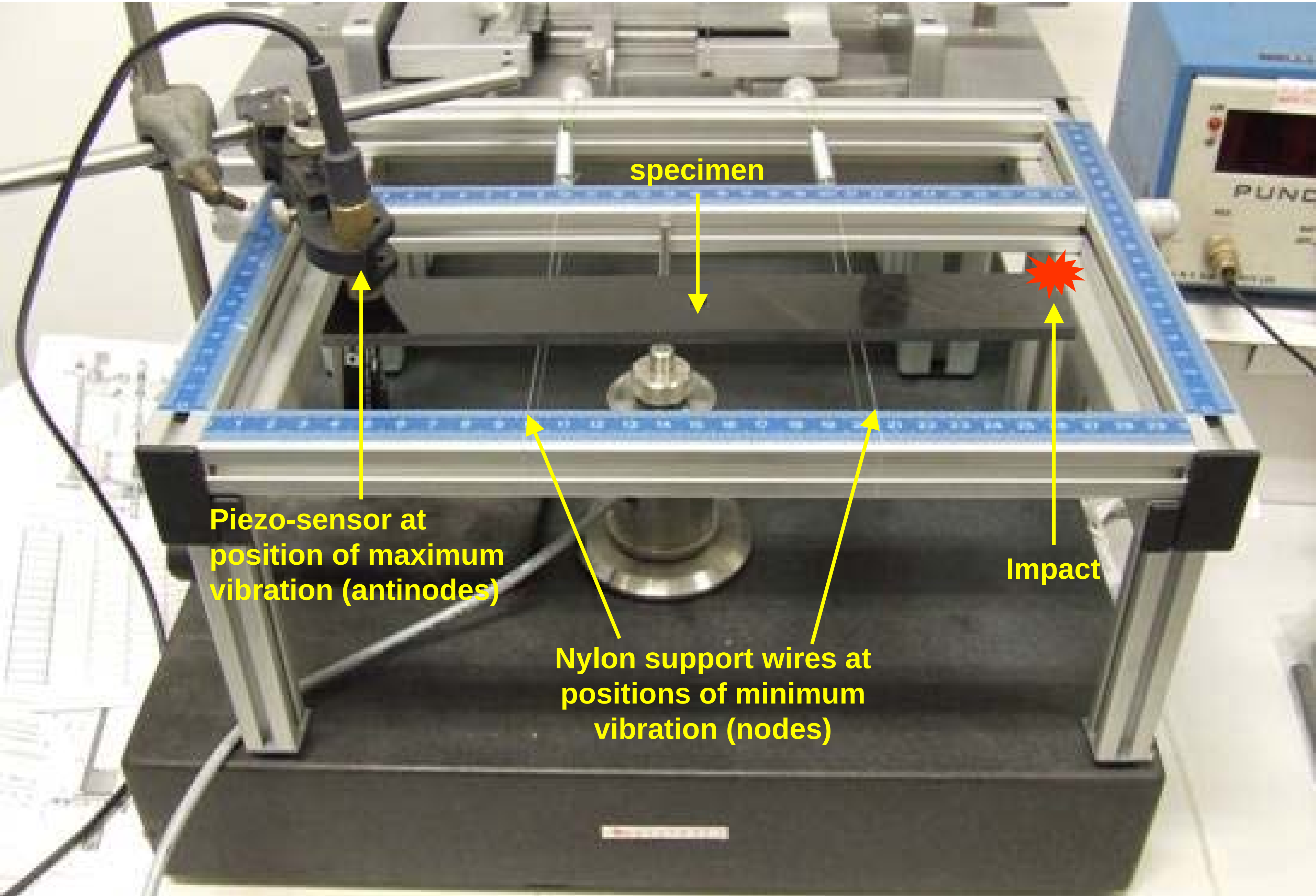


FE modal analysis to identify fundamental frequencies

Impact Excitation – Modes and Moduli Measured

Impact mode	Schematic of impact and vibration detection locations	Elastic modulus measured
Flexural - centre strike		Flexural, E_f
Flexural - off-centre strike		Flexural, E_f
Longitudinal end strike		Axial, E_{xx}
Flexural and torsion - end strike		Shear, G_{xy} Flexural, E_f

Impact Excitation Apparatus



Flexure Modulus (GPa) – Ambient Conditions

- Four-Point Bend
  - Well bonded: 33.8 ± 0.8
  - Poorly bonded: 30.1 ± 1.1
- Impact Excitation
  - Well bonded: 30.9 ± 0.1
  - Poorly bonded: 28.2 ± 0.1
- Damping
  - Well bonded: 0.00137 ± 0.00007
  - Poorly bonded: 0.00501 ± 0.00045
- Loss Factor
  - Well bonded: 2.96 ± 0.15
  - Poorly bonded: 10.46 ± 0.95

Insensitive to sub-zero temperature excursions

Summary

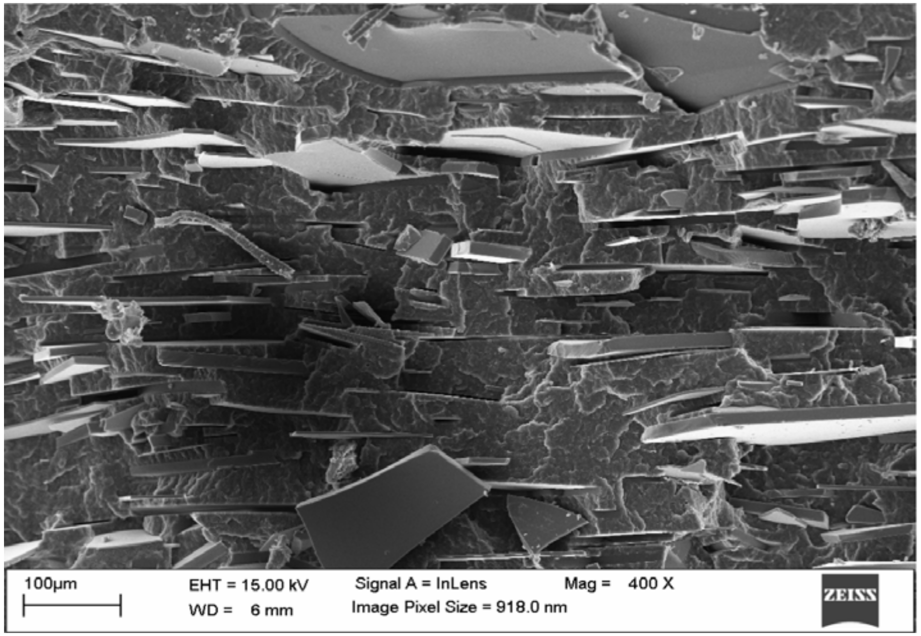
- Longitudinal CTE measurements sensitive to fibre/matrix interfacial strength – stress relaxation observed for poorly bonded system
- Longitudinal flexure and interlaminar shear strengths severely compromised by weak fibre/matrix interface
- Flexural stiffness not significantly affected by a weakened fibre/matrix interface
- Ultrasonic (ToF) technique – capable of detecting differences in stiffness between GRP pultrusions
- Impact excitation method – capable of detecting differences in stiffness and damping/loss factor between GRP pultrusions

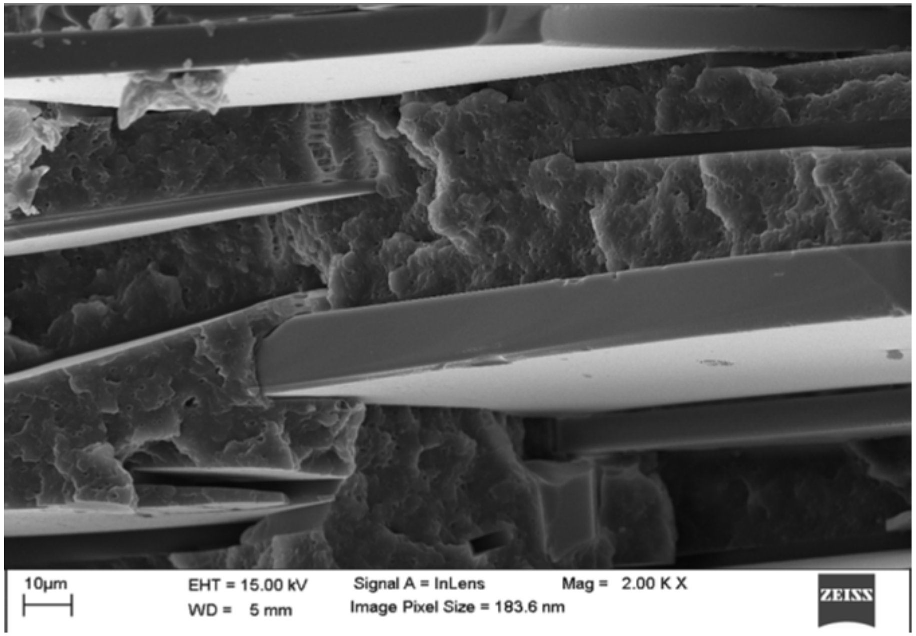
Case Study 2: Glass Flake/Polypropylene

- Glass format: Flake
- Matrix: Polypropylene
- Surface treatments:
  - Unreinforced polypropylene (ABEC)
  - Untreated (ABED)
  - Aminosilane (0.05% - ABEE and 0.28% - ABEF)
  - Titanate (0.09% - ABEG and 0.42% - ABEH)
- Mechanical properties:
  - Hardness
  - Impact resistance
  - Flexure strength/stiffness
  - Residual stress (strain)/thermal expansion
  - Crystallinity
- Supplier: NGF Europe

Glass-Flake/Polypropylene – SEM Images

Untreated





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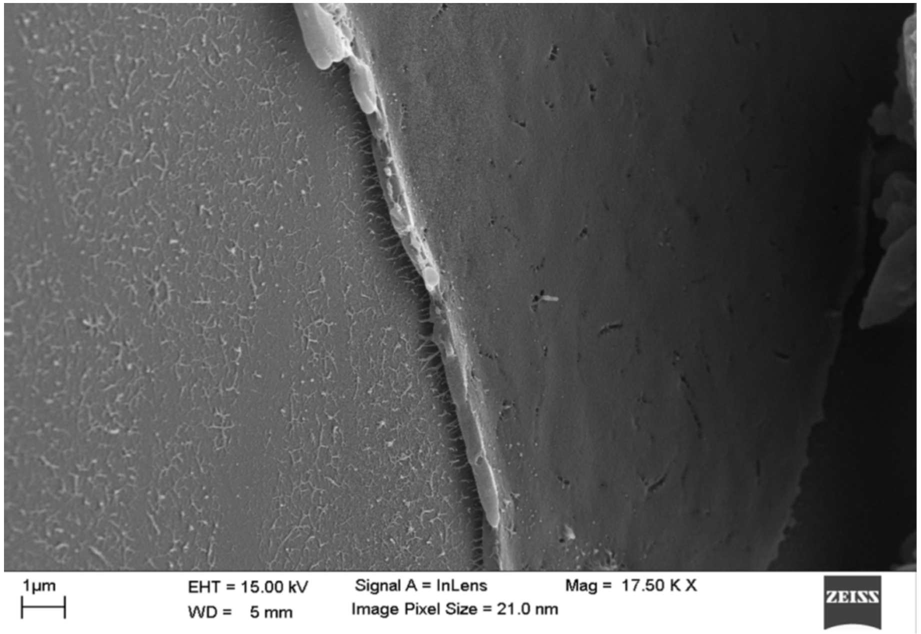
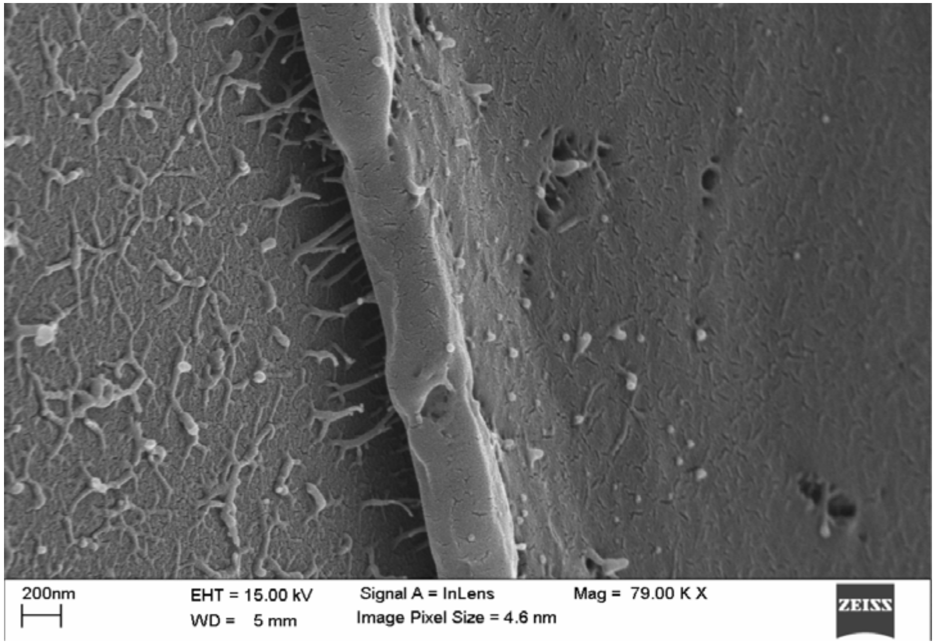
Glass-Flake/Polypropylene – SEM Images

Aminosilane (0.28%)





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Glass-Flake/Polypropylene – Physical Properties

Material	Density (kg/m^3)	Volume Fraction (%)	Shore Hardness D
Polypropylene	908 ± 1	**N/A**	21.9 ± 0.1
Untreated Flake	1,126 ± 1	13.3 ± 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
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

- **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/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
Aminosilane		
0.05%	4.34 ± 0.17	4.13 ± 0.09
0.28%	4.30 ± 0.03	4.05 ± 0.16
Titanate		
0.09%	3.28 ± 0.09	3.27 ± 0.16
0.42%	3.04 ± 0.22	3.05 ± 0.11

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

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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
Aminosilane		
0.05%	55.31 ± 3.02	53.50 ± 0.31
0.28%	56.12 ± 1.03	53.91 ± 0.57
Titanate		
0.09%	44.47 ± 3.73	43.46 ± 0.59
0.42%	41.57 ± 0.62	40.51 ± 0.62

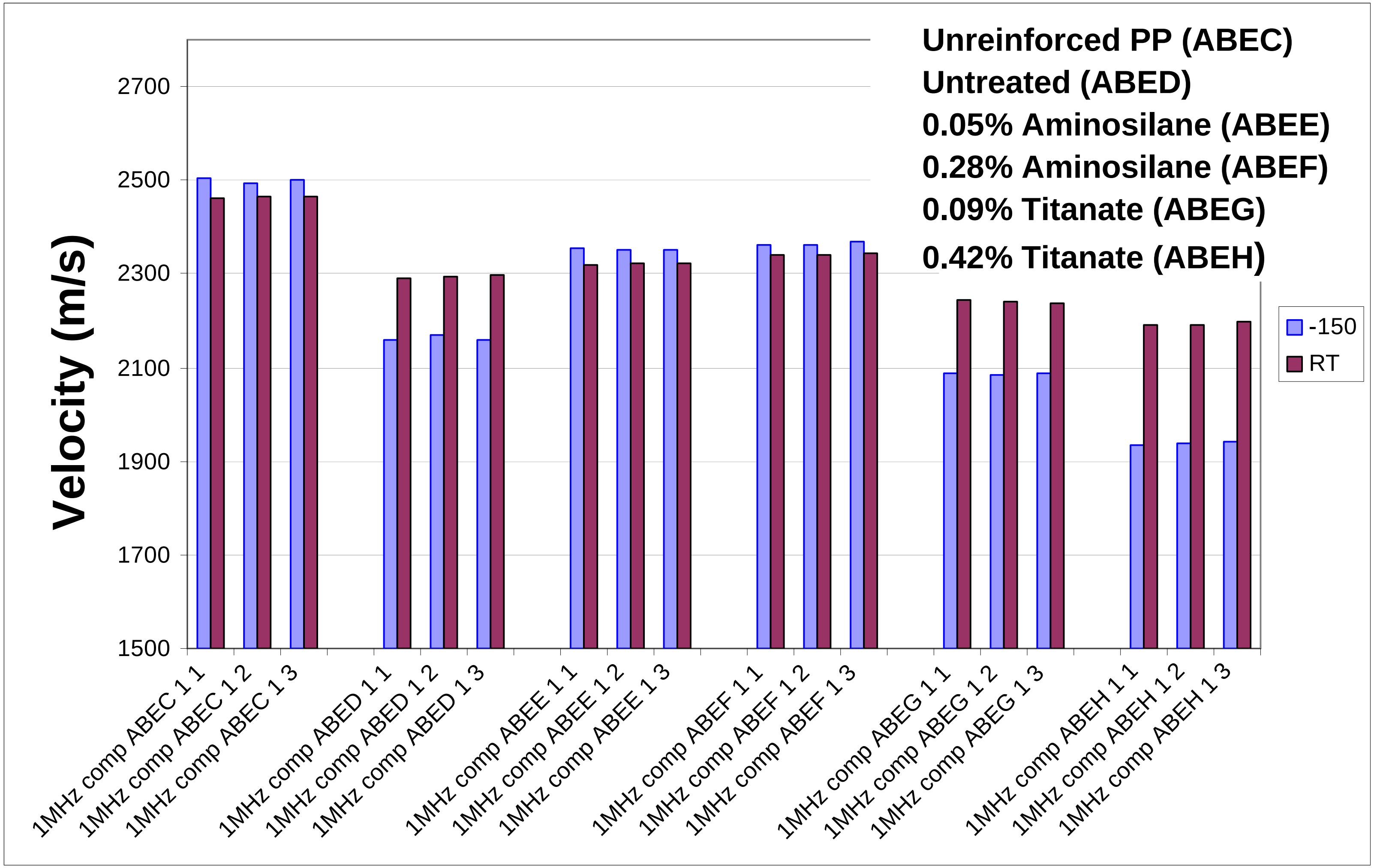
- **Flexural strength increases with increasing filler/matrix interfacial strength**
- **Poorly bonded systems tend to exhibit lower flexure strength**

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
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
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

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

Ultrasonic Elastic Properties – Time of Flight



Samples conditioned at –150°C for 30 minutes, warmed to room-temperature for ~ 30 minutes and tested

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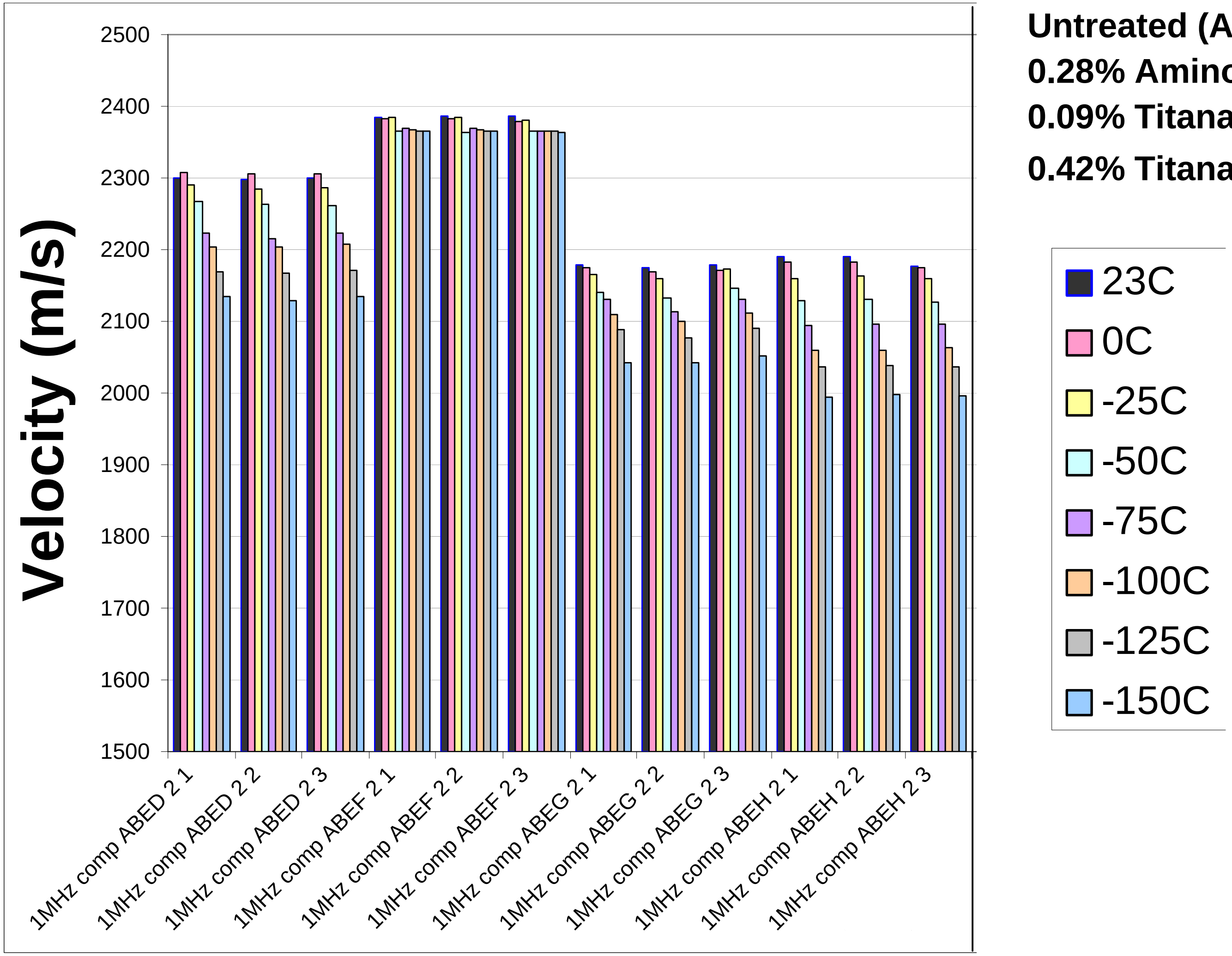
Ultrasonic Elastic Properties – Time of Flight



Untreated (ABED)
0.28% Aminosilane (ABEF)
0.09% Titanate (ABEG)
0.42% Titanate (ABEH)

Samples conditioned at sub-zero temperatures for 30 minutes, warmed and tested at ambient

Glass-Flake/Polypropylene – Thermal Properties

Material	T_g (°C)	T_{melt} (°C)	Heat of Fusion (J/g)
Polypropylene	12.8	152.7	100.5
Untreated Flake	14.1	153.2	64.39
Aminosilane			
0.05%	12.5	153.5	59.63
0.28%	14.2	153.5	68.22
Titanate			
0.09%	14.0	152.7	65.88
0.42%	14.1	152.9	69.31

- T_g and T_{melt} independent of surface treatment and presence of fibres
- Enthalpy (heat flow) reduced with introduction of glass flakes

T_{melt} – onset value measured using DSC

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Glass-Flake/Polypropylene – Crystallinity

- Crystallinity of PP and glass flake/PP composites determined using the following methods:
  - Volumetric Method
    - Density measurements
  - Thermal Analysis (DSC)
    - Heat flow (heat fusion) measurements
  - X-ray Diffraction (XRD)
- Reference samples
  - Isostatic polypropylene homopolymer
  - Samples (2 off) supplied by Basell UK Ltd
  - Heat fusion of 100% crystalline PP – 163 J/g
  - Density of fully amorphous PP – 853 kg/m^3
  - Density of fully crystalline PP – 946 kg/m^3
  - Density of flake – 2,560 kg/m^3?

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Glass-Flake/Polypropylene – Thermal Properties

Material	Density (kg/m3)	Heat of Fusion (J/g)	Crystallinity (%)	
			Volumetric Method	Thermal Analysis
Isostatic PP				
Reference 1	895 ± 3	79.19	47.73	49.44
Reference 2	897 ± 3	81.08	49.90	50.82
Polypropylene	908 ± 1	100.5	61.61	61.66
Untreated Flake	1,126 ± 1	64.39	59.07	56.67
Aminosilane				
0.05%	1,129 ± 1	59.63	58.54	52.77
0.28%	1,117 ± 1	68.22	59.65	59.13
Titanate				
0.09%	1,115 ± 1	65.88	58.47	57.03
0.42%	1,121 ± 2	69.31	56.90	60.73

- **Crystallinity independent of surface treatment and presence of fibres**

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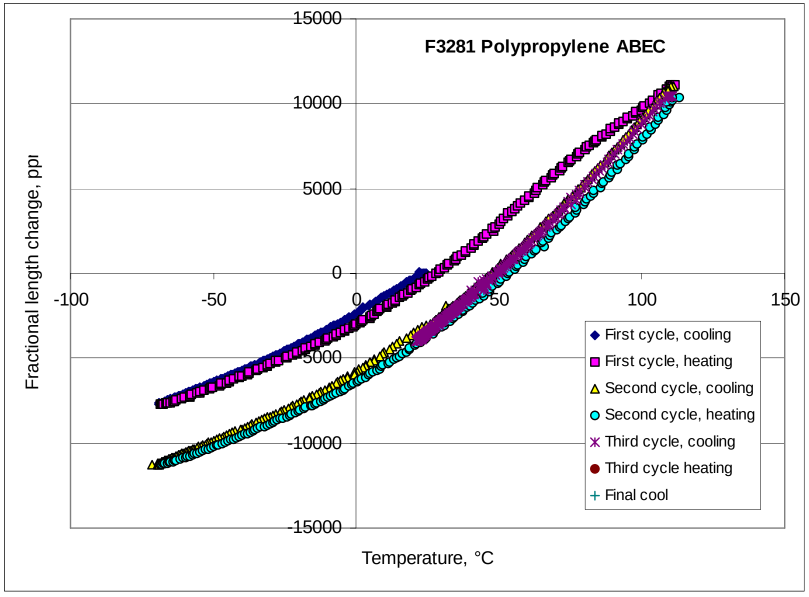
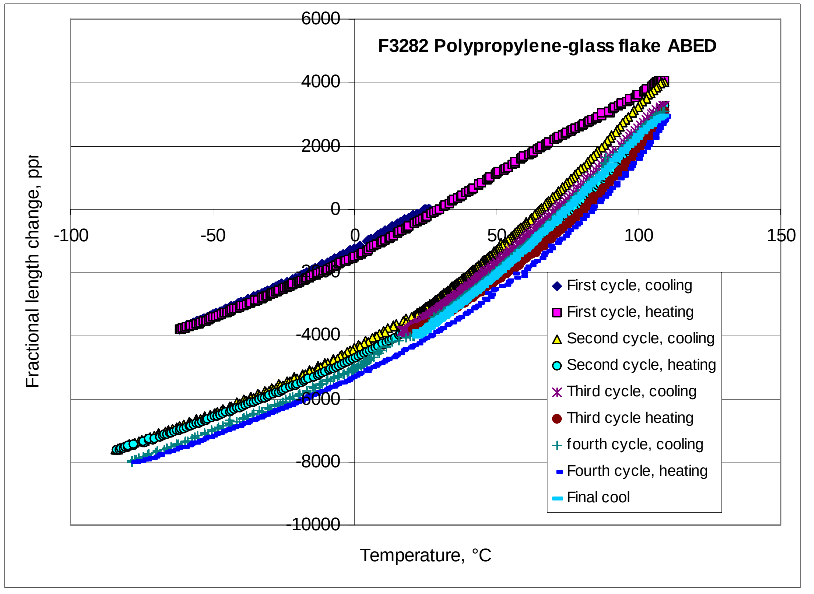
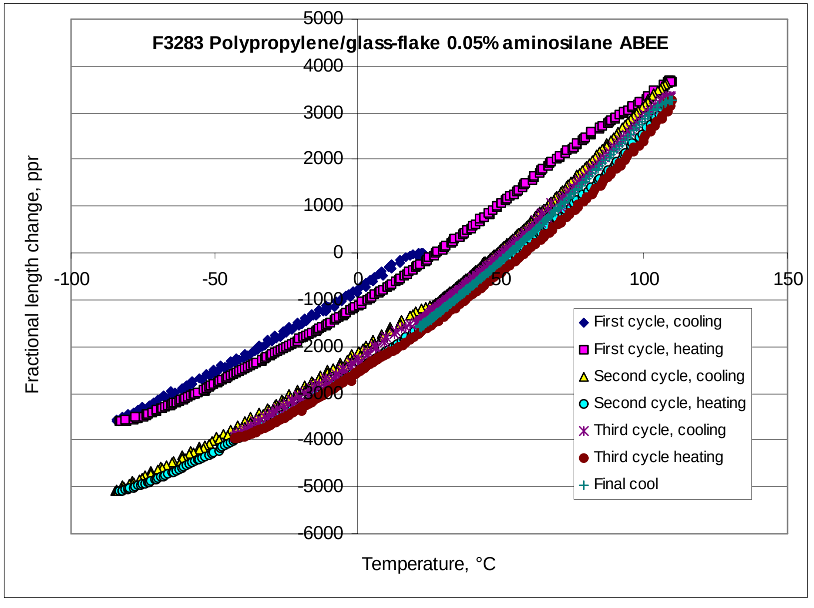
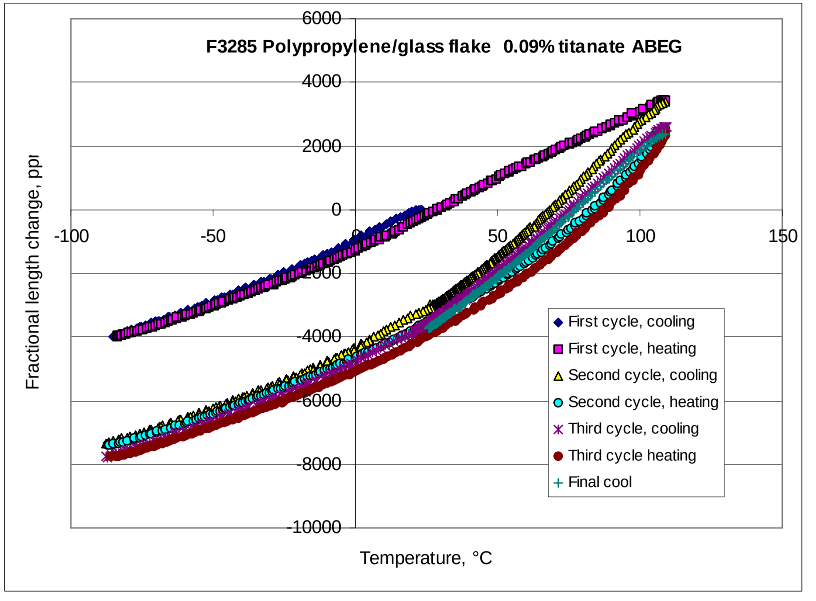
Glass-Flake/Polypropylene - CTE









Glass-Flake/Polypropylene – Strain Difference Dilatometry – CTE Measurements

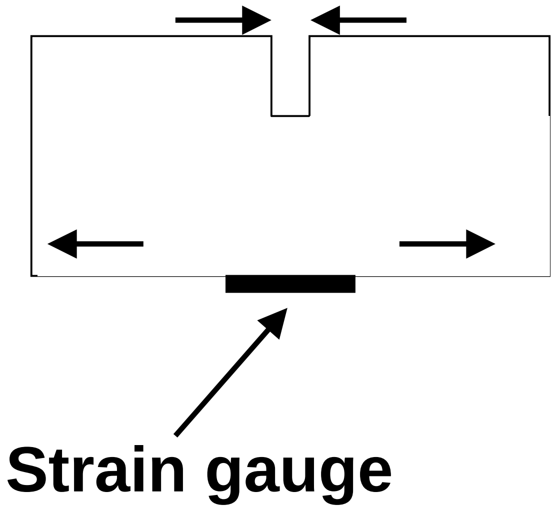
Material	Strain Difference (%)	CTE (10^{-6}/°C)
Polypropylene	0.31	67
Untreated Flake	0.35	45
Aminosilane		
0.05%	0.11	39
0.28%	0.14	40
Titanate		
0.09%	0.35	48
0.42%	0.25	41

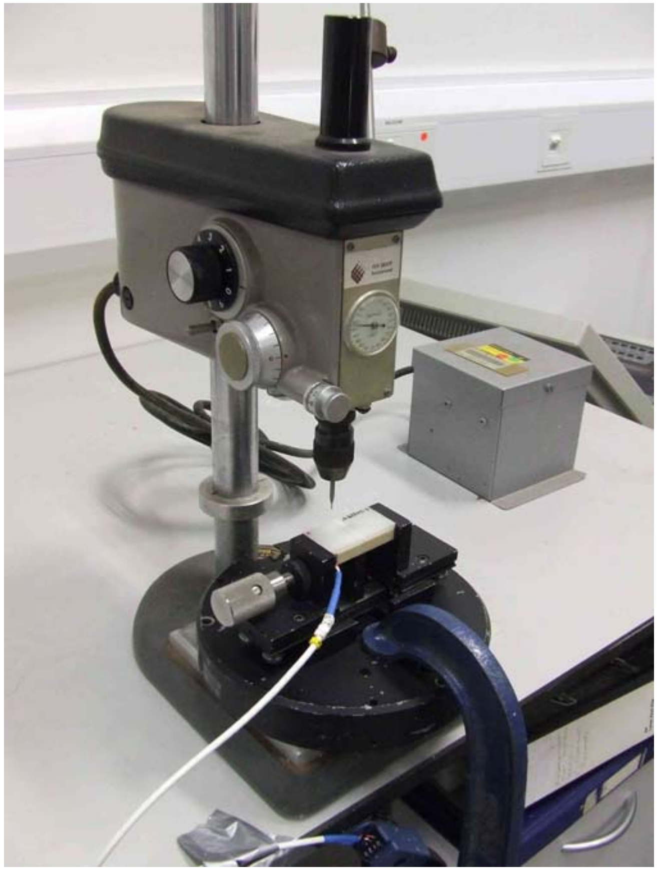
- **Strain difference lowest for aminosilane treated glass flakes following annealing at 110°C – indicative of lower residual strain (stress)**

Residual Strain Measurement Techniques

- Feasibility study in SM09 to examine:
  - Layer removal
  - Incremental slitting
  - Hole drilling
  - Raman spectroscopy
  - Embedded fibres (Fibre Bragg Grating)
- Dilatometry (strain relaxation)

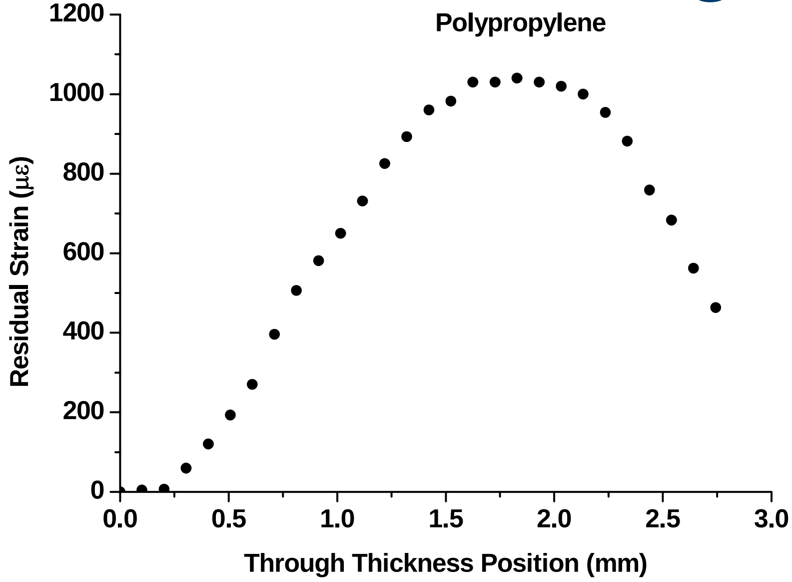
Incremental Slitting Method

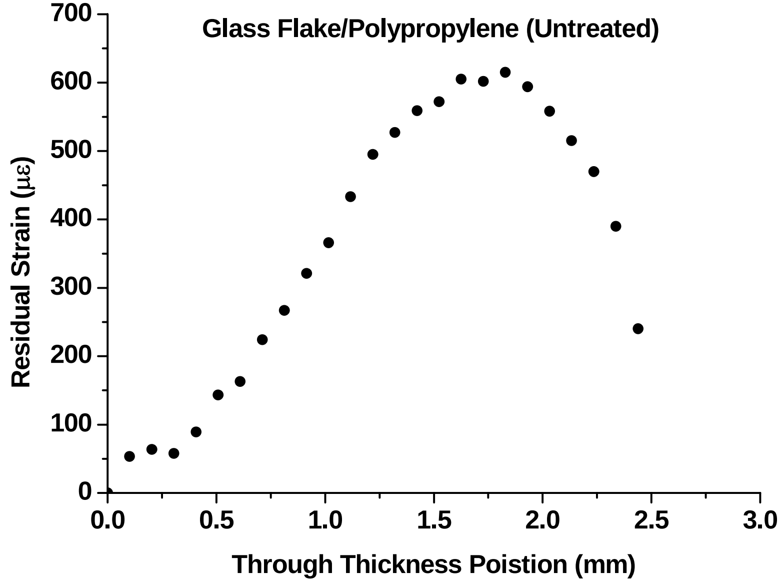


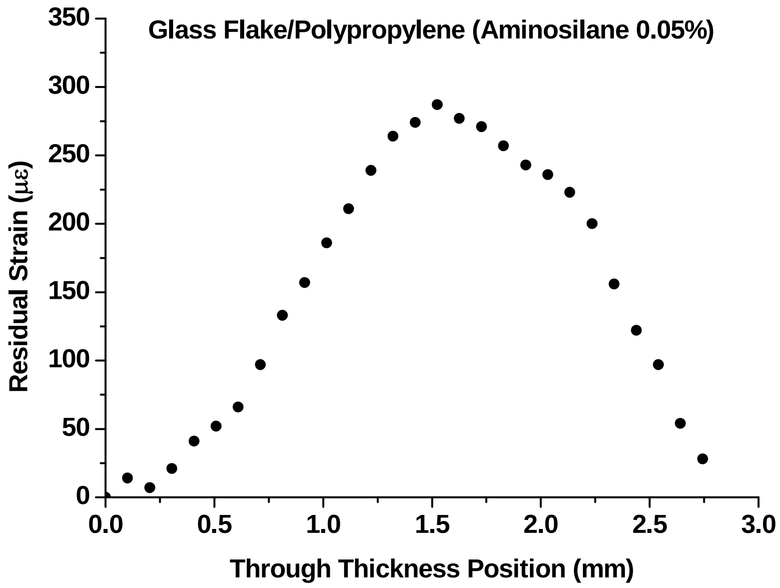


- **Residual strain can be measured using a strain gauge attached to the back surface of the test specimen**

Incremental Slitting Method – Residual Strain







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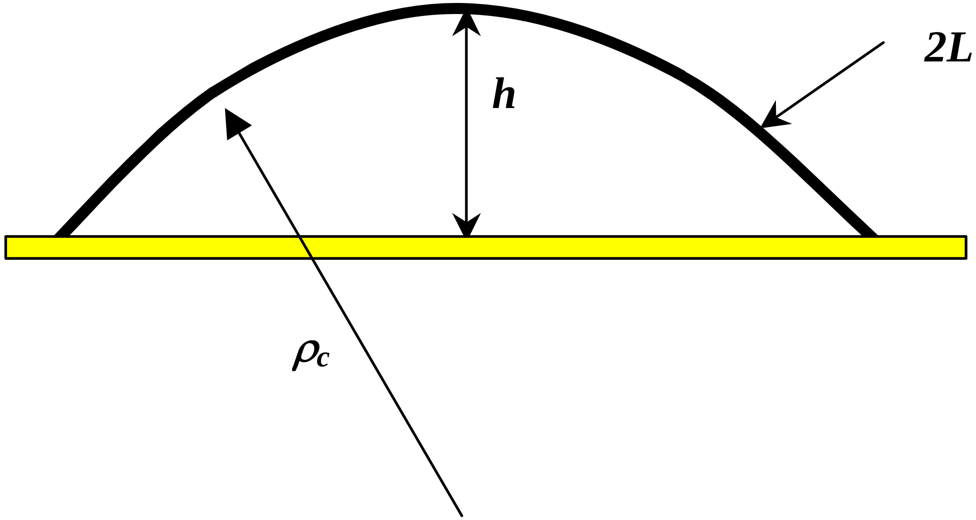
Curvature Measurements



- Residual strain can be determined from the curvature of a beam that results from removal of layers

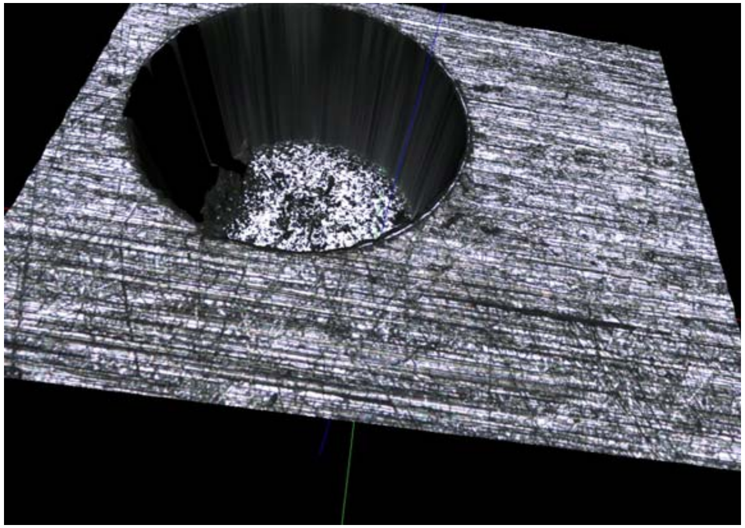
Glass-Flake/PP – Maximum Residual Strain (με)

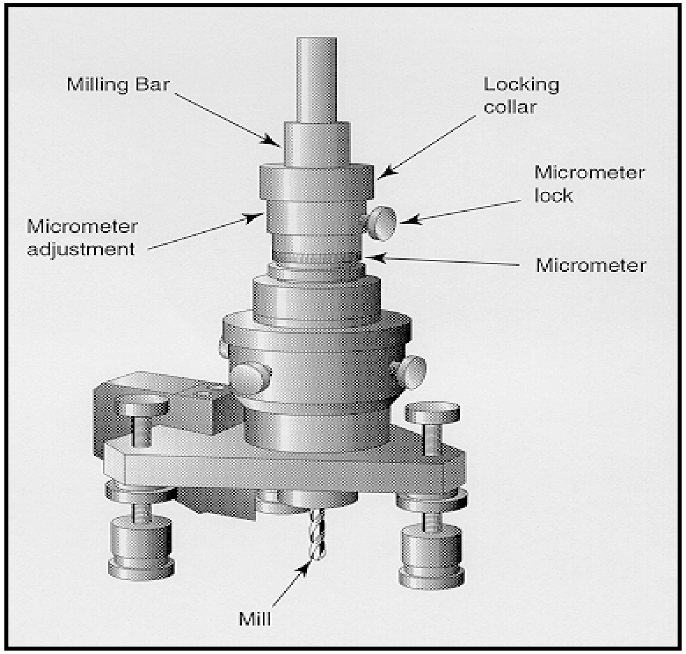
Ambient Conditions

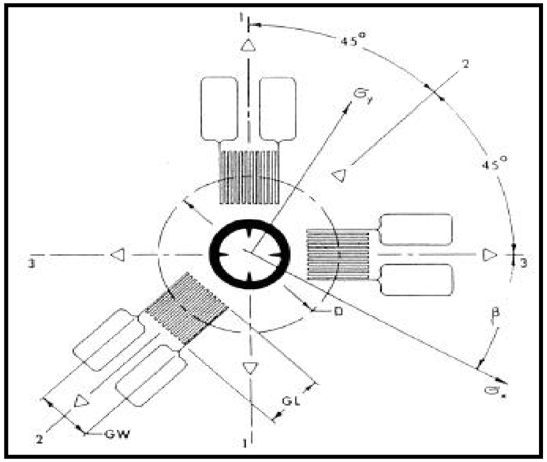
Material	Incremental Slitting Method	Layer Removal Method	
		Relaxed State	Heated to 80 °C
Polypropylene	1040	2083	3829
Untreated Flake	615	858	1970
Aminosilane			
0.05%	287	586	1102
0.28%	439	785	1749
Titanate			
0.09%	732	925	2179
0.42%	429	864	2104

- Residual strain measurements dependent on technique
- Residual strain lowest for 0.05% aminosilane
- Layer removal method – higher residual strain values
  - Possibly heating during layer removal

Residual Stress Hole Drilling ASTM 837-E

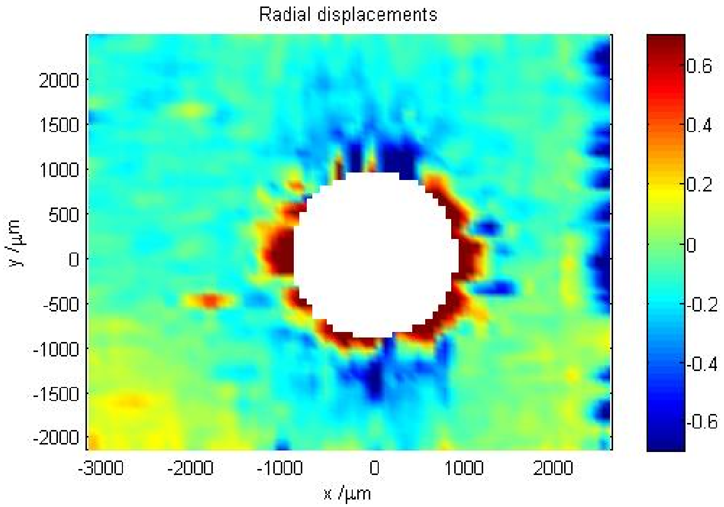


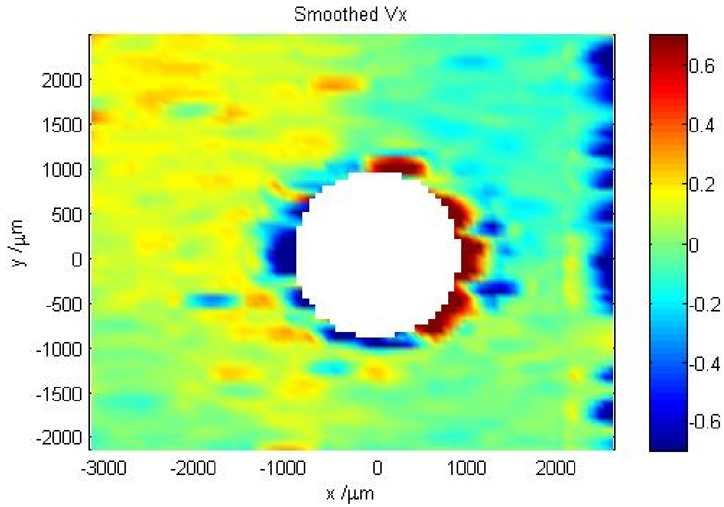


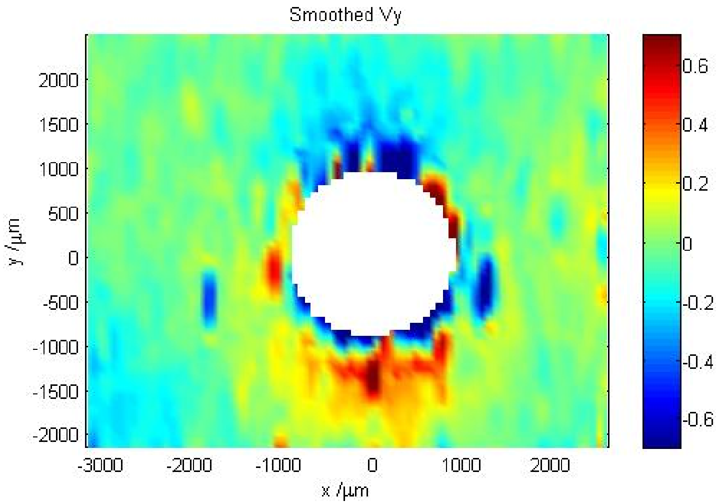


A hole is drilled into the composite and the residual stress calculated from the strains that develop around the hole

Glass Flake/PP – Untreated
Residual Stress – DIC Images of Drilled Hole







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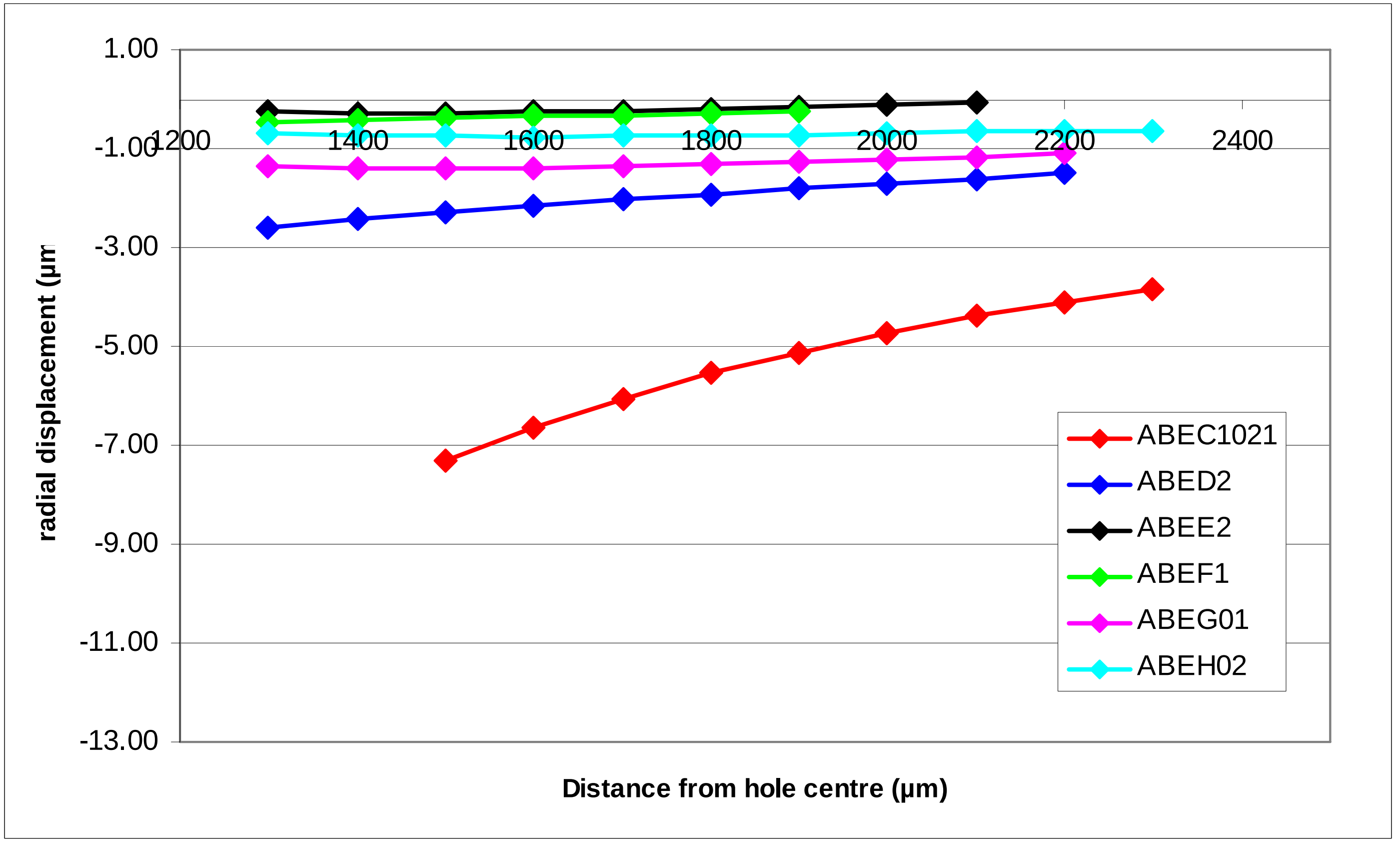
Glass Flake/PP
Radial Displacement around Drilled Holes



ABEC – Polypropylene

ABED – Untreated

ABEE/ABEF – Aminosilane (0.05%/0.28%)

ABEG/ABEH – Titanate (0.09%/0.42%)

Future Work

- Glass Flake/Polypropylene
  - DIC strain analysis
  - XRD crystallinity measurements (CU02)
  - Incremental slitting method – stress analysis
- Modelling of interfacial properties
  - AXIS – stress transfer predictions
  - Multi-model – elastic property predictions
  - Particle reinforced systems
  - FEA – interfacial strength/interphase properties

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Thank you for listening

Any Questions?