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

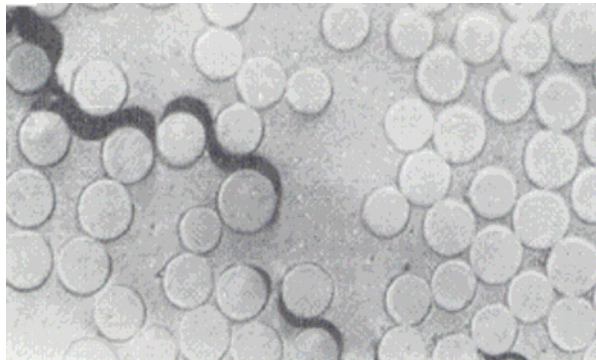
Polymer: Multiscale Properties IAG Meeting

6 September 2006

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, nanocomposites and toughened adhesives.

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.

Deliverables

- **D1: Critique of test methods and predictive analysis for characterising interfacial properties in filled systems (NPL Report).**

  Duration: 1 April 2006 – 30 September 2006 (W Broughton)

- **D2: Case studies (micro- to nano-scale) on the application of interfacial characterisation methods to filled systems (scientific paper).**

  Duration: 1 October 2006 – 31 March 2009 (W Broughton)

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

  Duration: 1 October 2006 – 31 March 2009. (L Crocker)

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Stage Plans

- Stage 1: Review and Organise IAG
  - Duration: 6 months
  - Critique of test methods/predictive analysis (NPL Report)
  - Agree Case Studies (3 off) for Stage 2
- Stage 2: Develop Measurement and Modelling Methods
- Stage 3: Evaluate Methods via case studies
- Stage 4: Validate and Report (scientific papers)

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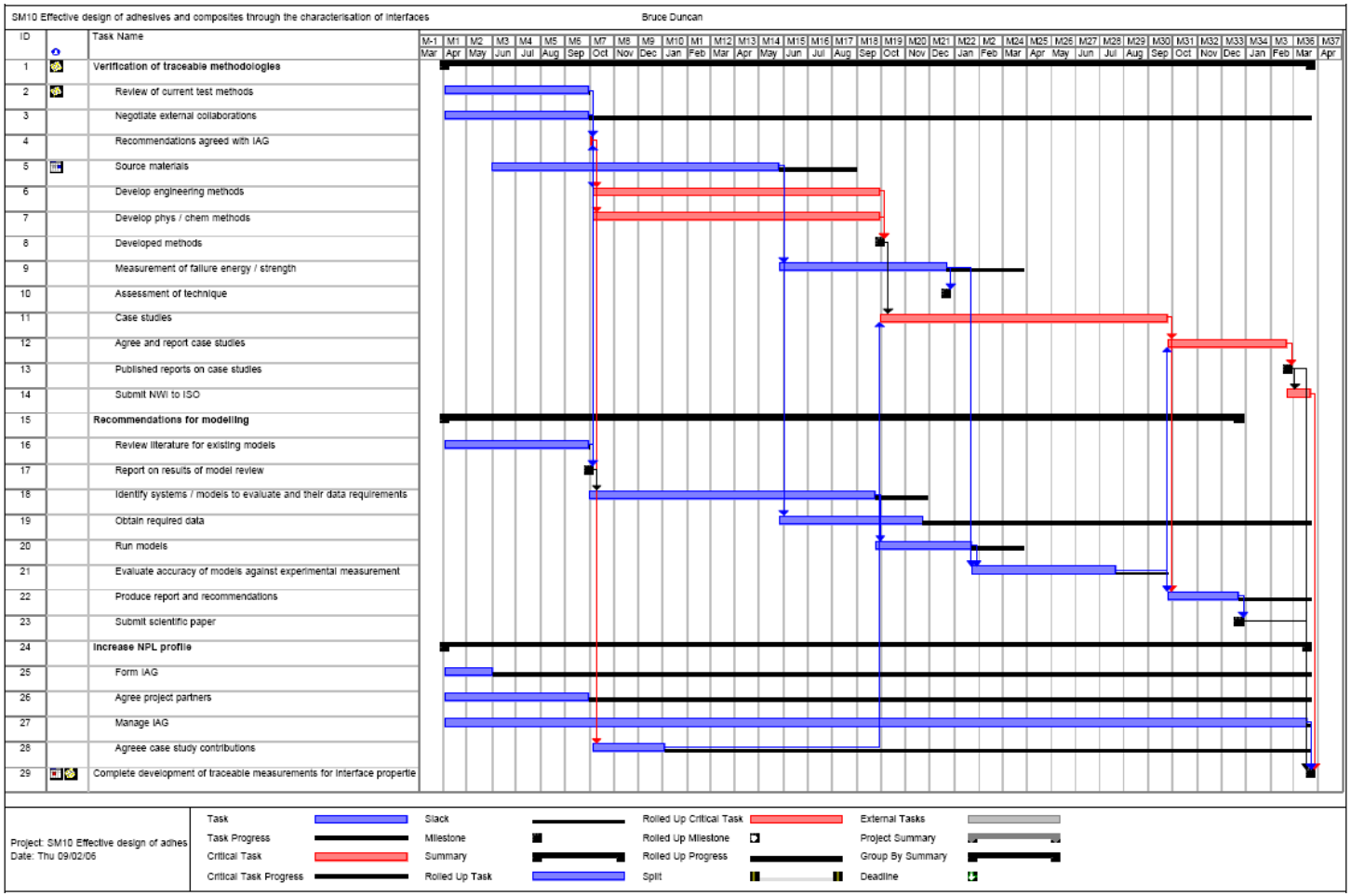
Gantt Chart – Project Plan



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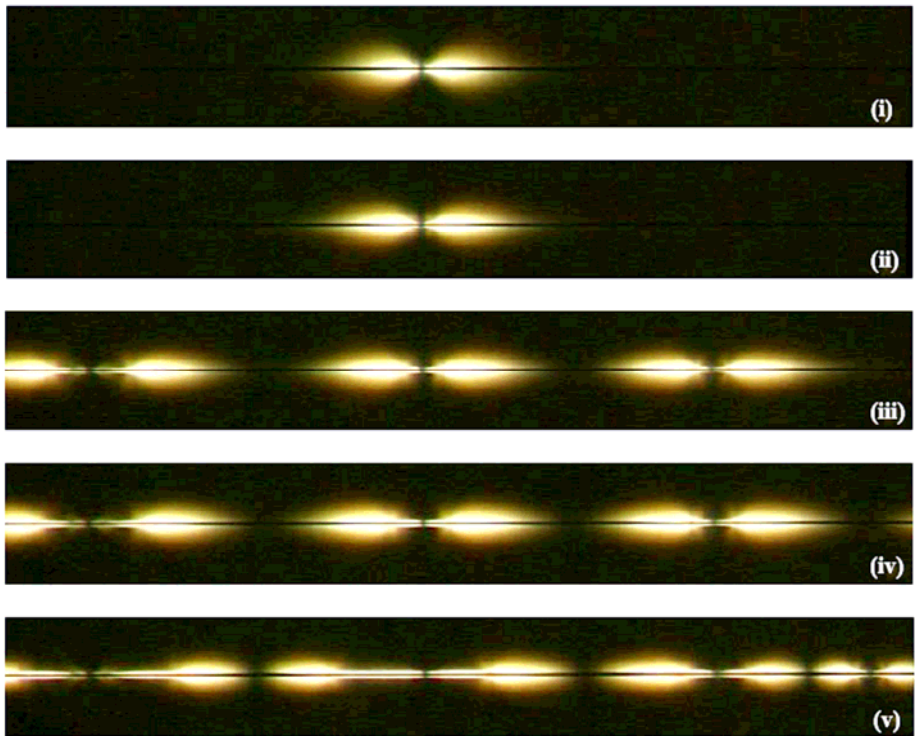
Test Method Review

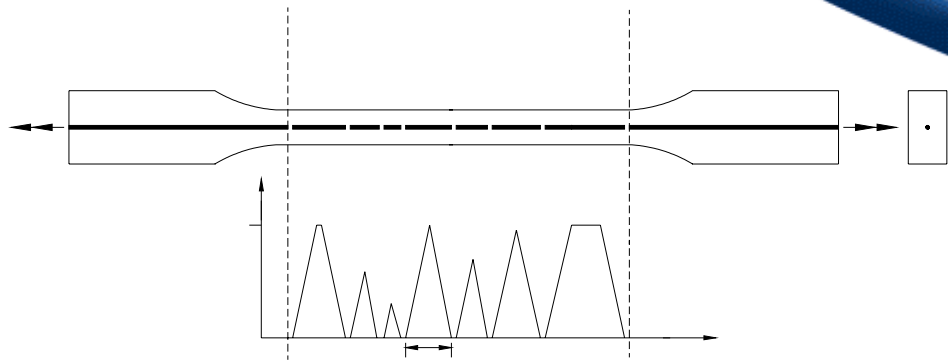
- Coupon Test Methods (Indirect)
  - Tension, compression, shear, flexure and fracture toughness
- Micromechanical Test Methods (Direct)
  - Fragmentation, fibre pull-out, microdrop/microbond and microindentation
- New/Novel Test Methods
  - Nanoindentation, nanoscratch, atomic force microscopy (AFM), scanning electrochemical microscopy (SECM), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy and ultrasonics

Coupon Tests (Indirect)

- **Transverse flexure strength versus transverse tension**
  - **Transverse flexure strength of continuous unidirectional laminates is the most appropriate mechanical property that could be used for assessing fibre/matrix adhesion, and preferable over transverse tensile strength.**
  - **Transverse flexure strength is less sensitive to the effects of flaws, and thus generally higher than transverse tensile strength.**
  - **Transverse flexural strength is strongly dependent on the degree of fibre/matrix adhesion with the surface appearance generally commensurate with the degree of interfacial bonding.**

Single-Fibre fragmentation Test





$$l_c = \frac{d\sigma_f}{2\tau_i}$$

τ_i = interfacial shear strength
σ_f = fibre tensile strength
L_c = critical fibre length
d = fibre diameter

Photoelastic microscopy images detailing damage progression in a single break in a carbon fibre fragmentation specimen under full extinction with increasing stress: (i) ~45 MPa, (ii) ~52 MPa, (iii) ~57MPa, (iv) ~60 MPa and (v) ~66 MPa.

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Single-Fibre fragmentation Test Advantages

- Simple specimen handling
- Large statistical sampling of the interface
- Replicates the stress transfer characteristics in real composites
- Critical length sensitive to changes in level of fibre-matrix adhesion
- Energy and fracture mechanics analysis methods being developed which do not require specimen saturation
- Variety of methods available for observing/analysing failure processes directly: acoustic emission, photoelasticity and Raman spectroscopy
- Variations on fragmentation test provide additional/complementary information: coaxial test, multi-fibre test, strand test and *in-situ* fibre strength test

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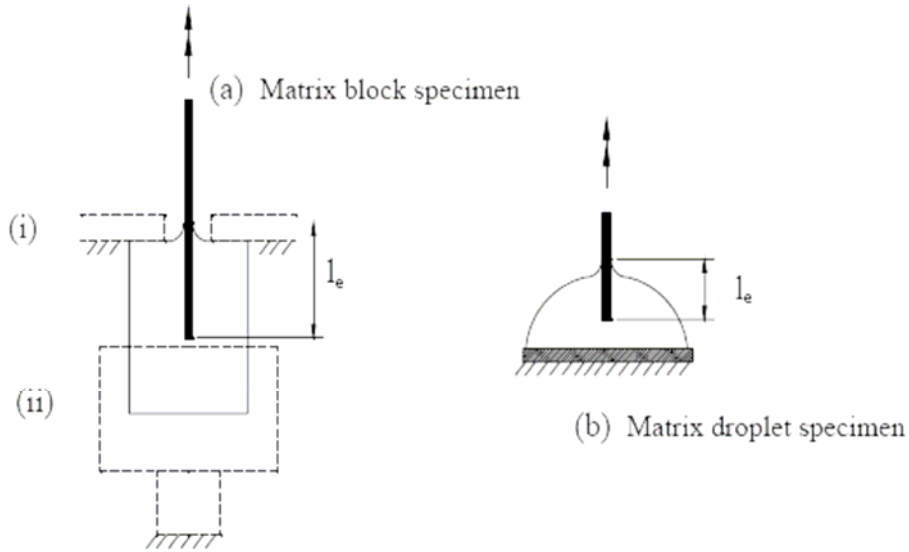
Single-Fibre fragmentation Test Disadvantages

- Indirect method of interface loading
- Time consuming: specimen preparation, testing, data collection/analysis
- Additional fibre strength tests required
- Limited material applicability (tough, high strain to failure matrices)
- Highly complex/non-uniform stress state at the interface
- Multiple failure events: interfacial debonding, matrix cracking, plastic yielding, frictional slip
- Does not allow determination of coefficient of friction/interface pressure
- Interfacial shear strength value depends on the constituent properties
- Relationship between critical fibre length and average fragment length unknown
- Extrapolation of Weibull fibre strength data to short fragment strengths is not understood
- High radial compression stresses result in overestimated interfacial strengths

Single-Fibre Pull-Out Test



$$\tau_i = \frac{F}{\pi d l_e}$$

τ_i = interfacial shear strength
F = debonding force
l_e = embedded fibre length
d = fibre diameter

Pull-out specimen geometries showing fibre embedded lengths and different geometries and loading configurations: (a) matrix block sample (i) restrained from above and (ii) restrained from below; and (b) matrix droplet sample.

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Single-Fibre Pull-Out Test
Advantages

- Direct method of loading interface
- Single force value recorded at failure
- Applicable to most fibre-matrix combinations
- Simple test to perform
- Simple basic analysis
- Provides information on friction coefficients and shrinkage pressures

Single-Fibre Pull-Out Test Disadvantages

- Difficult specimen preparation and handling
- Variability in specimen geometry and fabrication procedure
- Highly complex/non-uniform stress state at interface
- Restrictions on embedded length
- Large scatter obtained
- Single data point per test
- Local interface measurement
- Meniscus failures are invalid
- Test device stiffness affects nature of failure and results
- Radial stresses on fibre change with thermal and moisture expansion mismatch between fibre, resin and resin holder; fibre strength degradation due to environmental ageing

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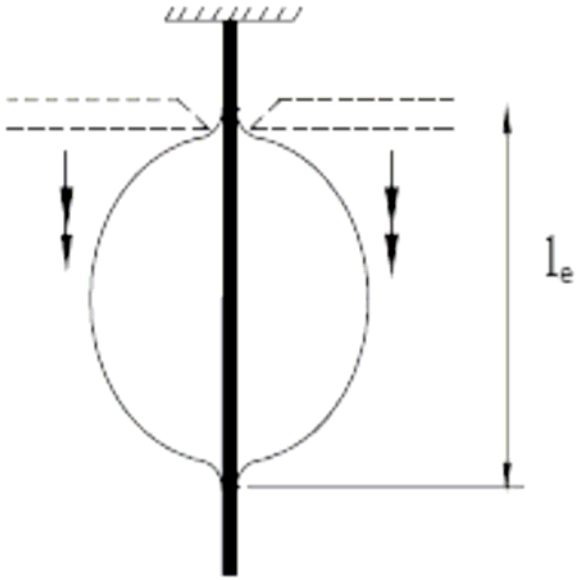
Microdrop/Microbond Test



$$\tau_i = \frac{F}{\pi d l_e}$$

τ_i = interfacial shear strength
F = debonding force
l_e = embedded fibre length
d = fibre diameter

Microdrop/Microbond pull-out specimen geometries showing fibre embedded length and loading configuration.

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Microdrop/Microbond Test Advantages

- Direct method of loading interface
- Single force value recorded at failure
- Applicable to most fibre-matrix combinations
- Simple: specimen preparation, test to perform, basic analysis
- Requires very small amounts of material
- Cohesive or adhesive nature of failure can be ascertained through SEM examination of the fibre surface after failure
- Reduced meniscus

Microdrop/Microbond Test Disadvantages

- Difficult specimen handling
- Variability in droplet shape and dimensions
- Restrictions on embedded length
- Highly complex/non-uniform stress state at interface affected by:
  - Location of loading points on droplet and shape of loading blades
  - Droplet shape and size
- Large scatter obtained
- Single data point per test - local interface measurement
- Meniscus failures are invalid
- Droplet mechanical properties vary with size
- Resin plasticisation at loading points following hygrothermal exposure; high diffusion rates demand prompt post-conditioning testing

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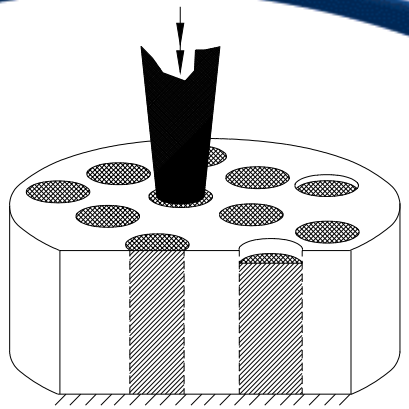
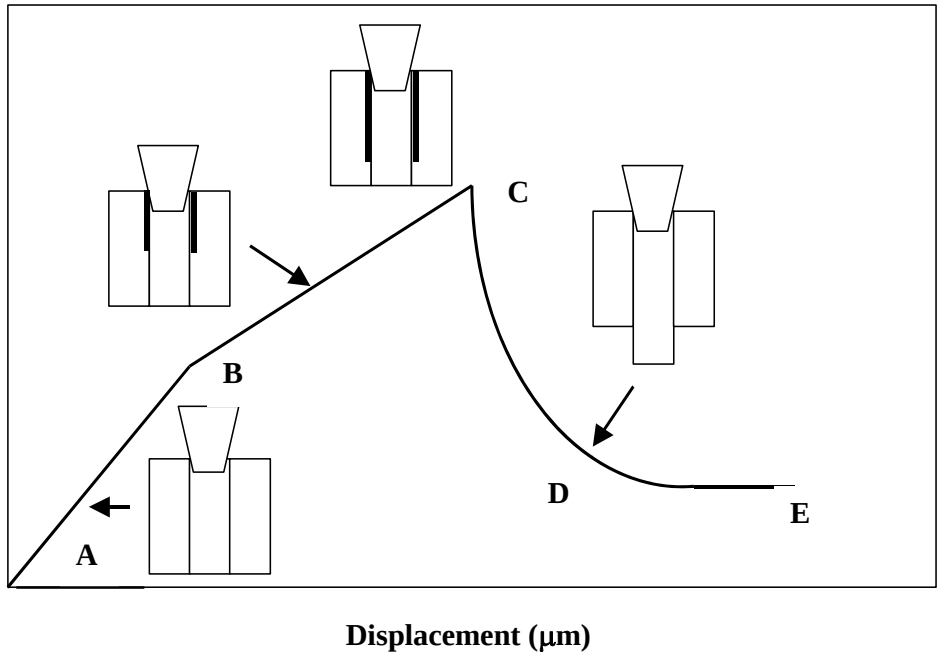
Microindentation Test



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



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

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Microindentation Test Advantages

- Direct method of loading interface
- Single force value recorded at failure
- One specimen provides many data points
- Applicable to most fibre-matrix combinations
- Simple specimen preparation
- Simple specimen handling
- *In-situ* test providing real environment for assessing interface
- Independent of fibre tensile strength
- **ASTM Working Group for ceramic matrix composites**

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Microindentation Test Disadvantages

- Difficult specimen testing:
  - High position accuracy required and difficulty detecting debonding load
- Failure criterion is subjective and arbitrary
- Highly complex/non-uniform stress state at interface:
  - Stress concentration at loading region of contact
  - Affected by proximity/configuration of neighbouring fibres
  - Affected by indenter shape/size/stiffness and position on the fibre cross-section
  - Affected by the polishing protocol
- Fibre damage is common, limiting material applicability
- Failure mode and locus cannot be observed
- Finite or boundary element analyses required for accurate data reduction.

Nanomechancial Test Methods Concerns

- Highly complex/non-uniform stress state at interface
- Multiple failure events
- Interfacial strength - physical meaning?
- High data scatter associated with all methods - results differ widely
- Data reduction methods is heavily oversimplified
- Large variability: specimen geometry, dimensions, method of specimen manufacture, test equipment and procedures used, parameters measured and/or monitored, and methods of data reduction and analysis employed
- Tests are generally difficult to perform and that only a small number of specialised laboratories are equipped for carrying out tests
- No standard procedures

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Nanoindentation/Nanoscratch

- Nanoindentation
  - Elastic modulus (Poisson's ratio using ultrasonic)
  - Interfacial strength/fracture energy (corner cube indenter)
  - Glass transition temperature
  - Interphase dimensions
  - Corner cube indenter $\Rightarrow$ smaller imprint $\Rightarrow$ improved spatial resolution (imprint spacing < 400 nm)
- Nanoscratch
  - Interphase dimensions (improved resolution m)
  - Coefficient of friction (continuous measurement < 200 nm)

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Nanoindentation
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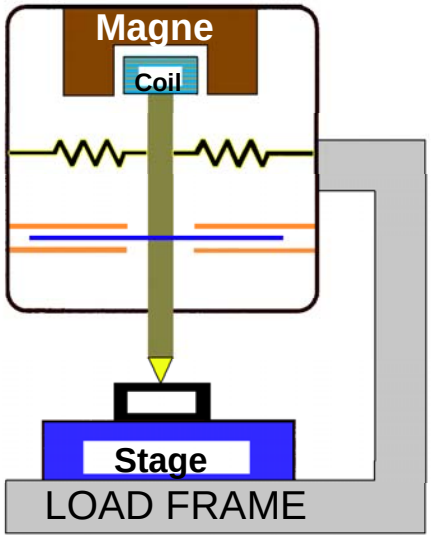
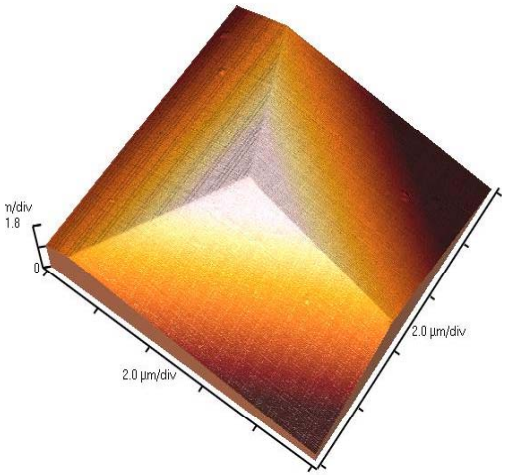
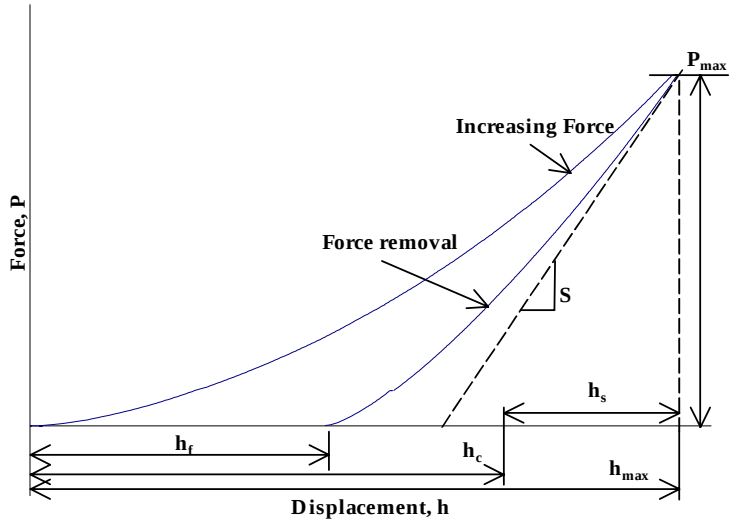
Nanoindenter





Force versus indentation depth



AFM Image of Modified Berkovich Indentation

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- **Hardness:** $H_{IT} = \frac{P}{A(h_c)}$

- **Modulus:** $E_{IT} = \left(1 - \nu_{IT}^2\right) \Big/ \left\{ \frac{2}{\sqrt{\pi}} \frac{\sqrt{A(h_c)}}{S} - \frac{\left(1 - \nu_{indenter}^2\right)}{E_{indenter}} \right\}$

P	Applied force
h_c	Contact depth
$A(h_e)$	Indenter surface area
E	Indenter stiffness
ν_{IT}	Sample Poisson's ratio
$\nu_{indenter}$	Indenter Poisson's ratio
S	Indenter stiffness

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Raman Spectroscopy

- Raman spectrum obtained from materials that inelastically scatter light
- Well-defined relationship between the peak frequency position of a strain sensitive Raman band and the applied strain
- Relation between strain or stress and the Raman frequency tends to be complex, however under uniaxial and biaxial loads tends to be linear
- Capable of measuring frequency changes as small as 0.02 cm^{-1}
- True axial strain distribution in an embedded fibre can be determined at the microscopic level (limited to non-amorphous reinforcement with strong Raman signals and transparent matrices)
- Strain mapping (inc. residual strains)
- Spatial resolution is 10 μm and for Micro Raman ~1 μm

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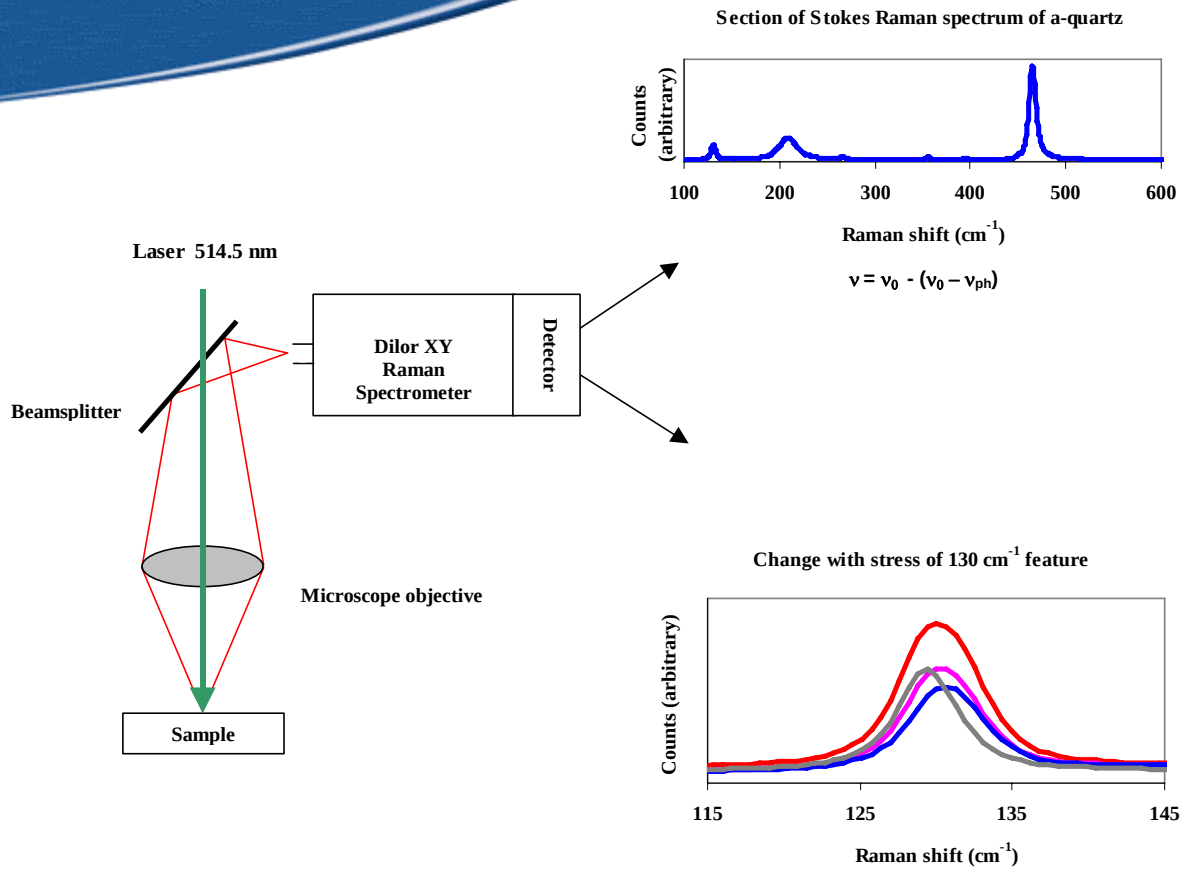
Raman Spectroscopy



Schematic of scattering from α-quartz (SiO_2) (Dilor XY Raman spectrometer)

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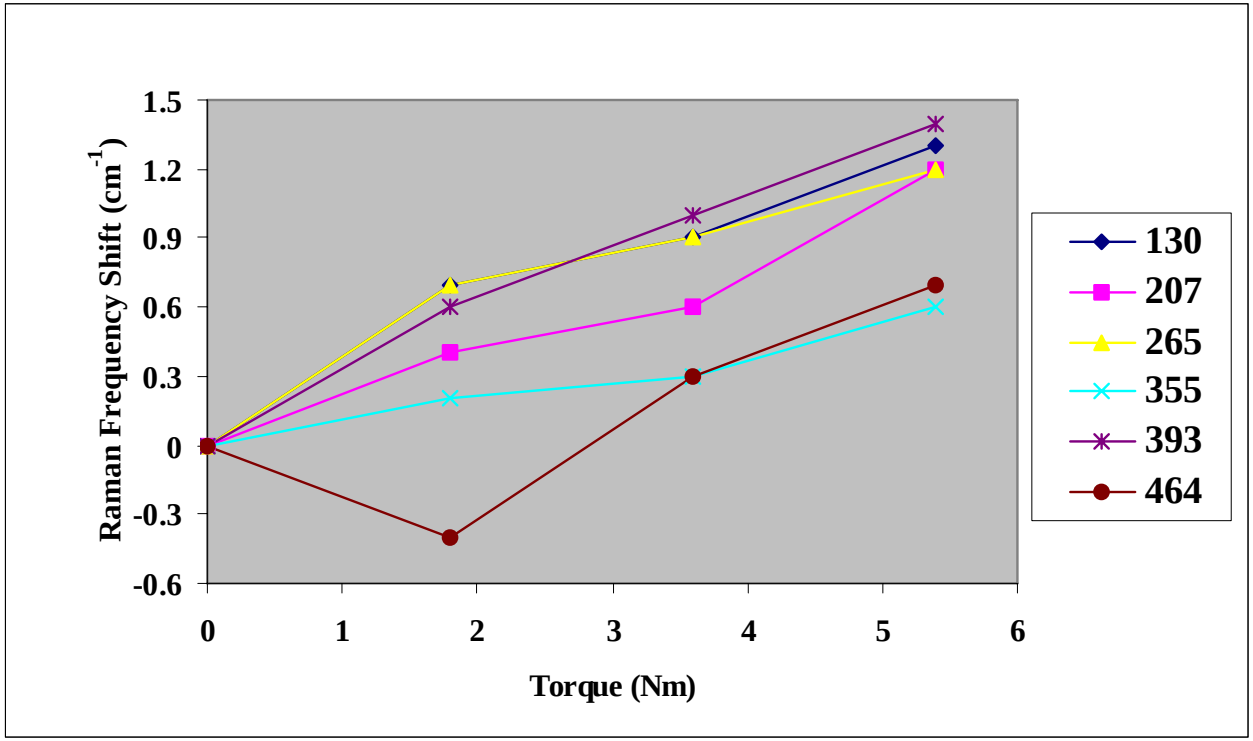
Raman Spectroscopy



Raman frequency shift as a function of applied torque

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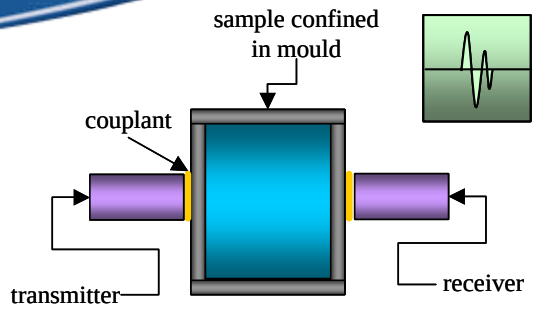
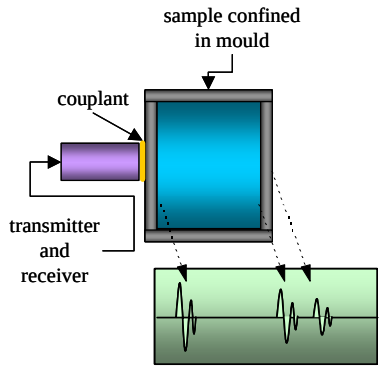
Ultrasonic Elastic Properties



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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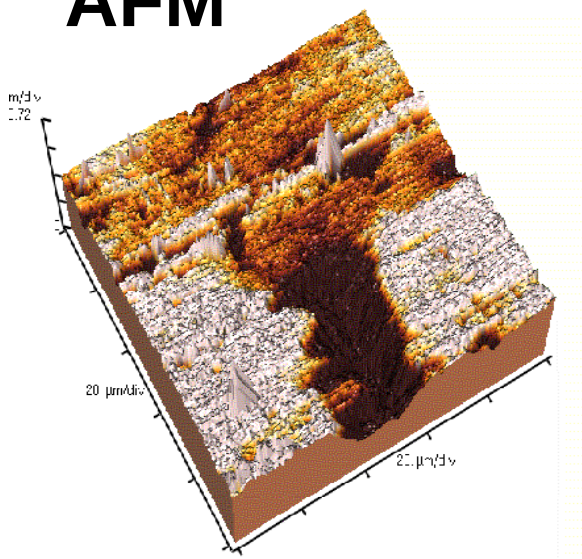
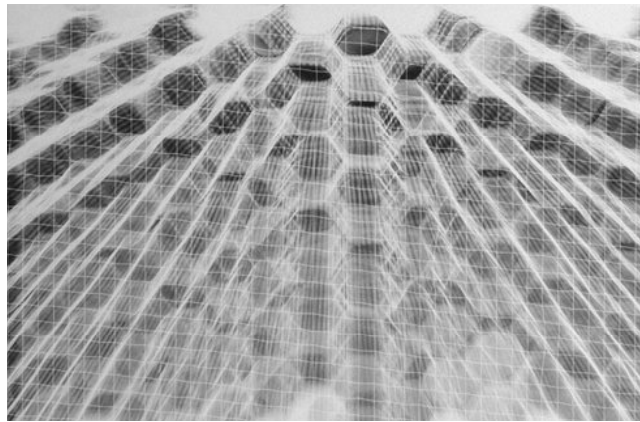
Other Techniques

- Atomic Force Microscopy (AFM)
  - Surface roughness/hardness/scratch
  - Spatial resolution ≤ 3 nm
  - Atomic Force Acoustic Microscopy (AFAM)
    - Elastic properties
- Scanning Electron Microscopy (SEM)
- Transmission Electron Microscopy (TEM)
- Scanning Electrochemical Microscopy (SECM)
- Absorption and Phase Contrast X-ray Imaging
  - X-ray tomography (3D imaging)
  - Spatial resolution 1 μm

AFM



XRT



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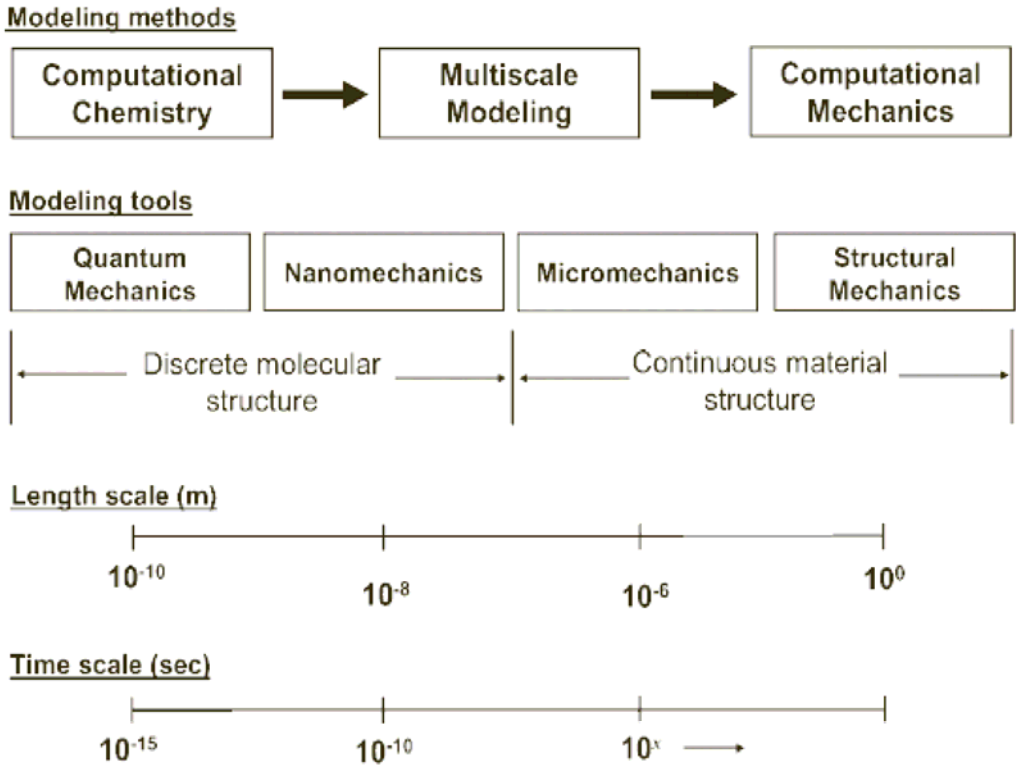
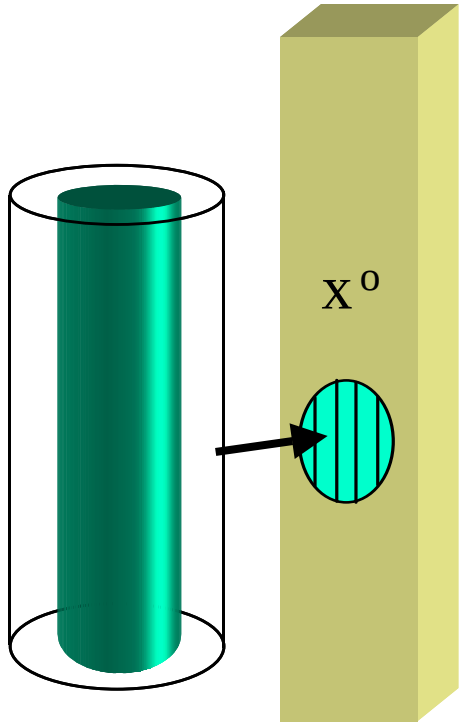
Micromechanical Modelling





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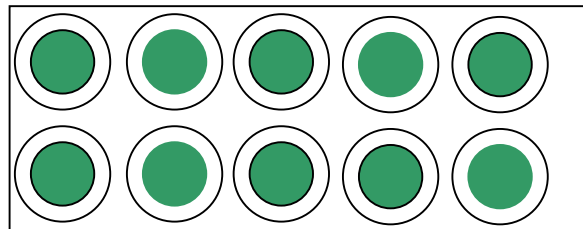
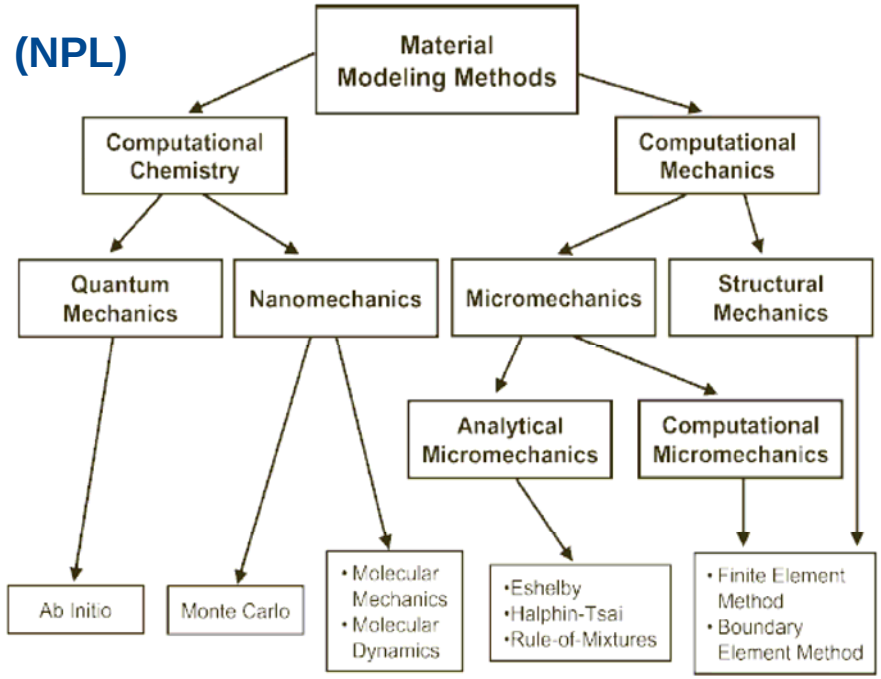


Multiscale Modelling

- **Interfacial/Interphase Models**
  - Multiple concentric cylinder model (NPL)
  - Continuum mechanics
  - Micromechanics
  - Energy-based models
  - FEA and BEM
- **Nanocomposites**
  - Atomistic/molecular dynamics
  - Continuum mechanics
  - Micromechanics
  - Statistical analysis



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Work Programme

D2: Interfacial Characterisation Methods

- Develop and evaluate new measurement techniques identified in D1 for characterising interfacial properties
- Case studies will be set-up around different reinforced systems ranging from the micro- to the nano-scale (i.e. continuous, discontinous and nanofilled) to assess the 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.
- The predictive analysis will be compared with the results from the case studies to be carried out in D2. The models to include filler/matrix adhesion and dispersion for nanocomposites, stress transfer and interfacial failure criteria.

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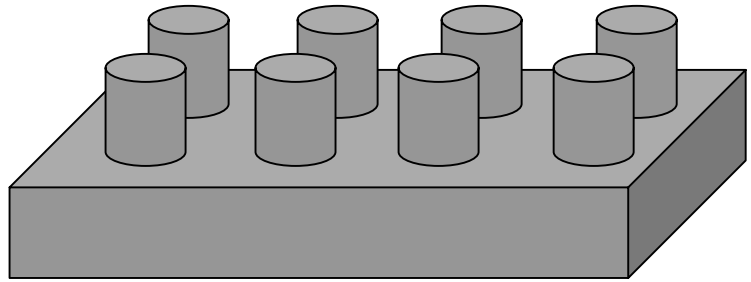
Case Study 1:
GRP Pultruded Rods

- Fibre products: E-glass, ECR glass, carbon
- Resins: Vinyl ester and polyurethane
- Surface treatments: Silanes
- Mechanical properties:
  - Flexure strength/stiffness
  - Glass transition temperature
  - Environmental durability/permeation
    - Alkaline solution/elevated temperature
    - Combinatorial analysis
- Supplier: Fibreforce Composites Ltd



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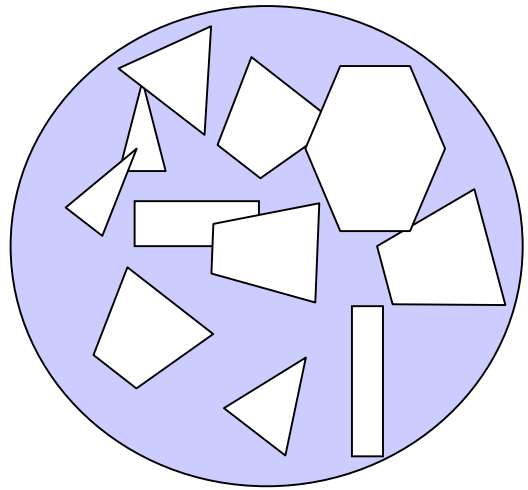
Case Study 2: Glass Flakes

- Flake products: REFG302, REFG101 and REF600 or REF160N
- Resins: Polyamide, PBT and PP
- Surface treatments: None, amino and acryl silanes and contaminated (oil)
- Mechanical properties:
  - Impact (fracture toughness)
  - Flexure strength
  - Thermal conductivity/thermal expansion
  - Permeation
- Supplier: NGF Europe



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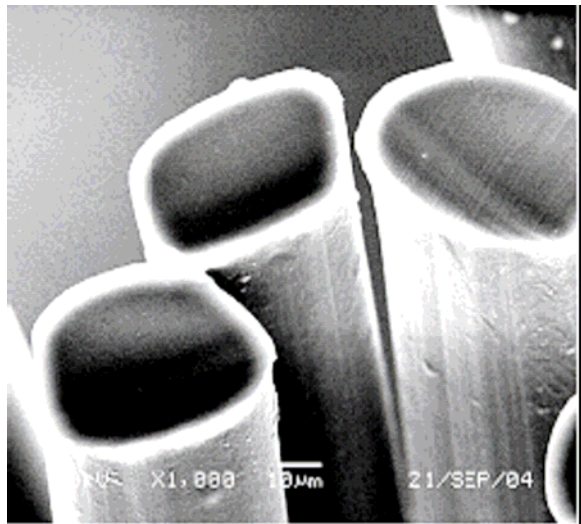
Case Study 3: Nanocomposite

- 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

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Processing Programme 2005 – 2008

H4 - Flow Properties of Filled Materials

For enquiries please contact Martin Rides
martin.rides@npl.co.uk

H4: Project Objectives

1. **Development of new/improved measurement methods/procedures for monitoring flow properties of filled materials, with particular emphasis on *mixing/compounding* processes.**
2. **Evaluation of the use and capability of innovative piezoelectric devices, to facilitate rheological measurement and improved *process monitoring*.**
3. **Development of the Melt Flow Rate method for *moisture sensitive materials* (e.g. PET, PBT, nylon), to avoid the need for solvent-based testing.**
4. **Development of Melt Flow Rate *precision and uncertainty statements* in support of ISO standardisation activities, through intercomparison.**

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H4: Objective 1

Industrial input: e.g. materials, industrial trials, equipment

Measurements of the dispersion of fillers in polymers – *"characterisation of the quality of mix"*

Case studies required: e.g. compounding of nano-filled materials, filled materials for micro-moulding

Evaluation and development of rheometry, DSC and potentially other methods

Development of simple QC / inline procedures / technique(s)

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U4: Dynamic Properties of Solid/Liquid Materials Systems at the Nano and Micro-Scale (2005-08)

Industry need to measure and understand the behaviour of materials on the *nano and micro-scale*, particularly where scale effects are significant, if they are to develop successfully micro- and nano-technologies (e.g HTT).

Process monitoring is key to improving quality and profitability but is often expensive to implement. Through the development of small-scale instrumentation, *process monitoring* will become more attractive and cost effective.

To address such issues this project aims to develop new innovative capability to measure the dynamic properties of materials

- **Development of a macro scale resonating piezoelectric cantilever device for fluid rheology, and validated using a range of reference fluids**
- **Design and development of prototype nano-mechanical tester (NTM3D) based in an SEM for measurement of solids**

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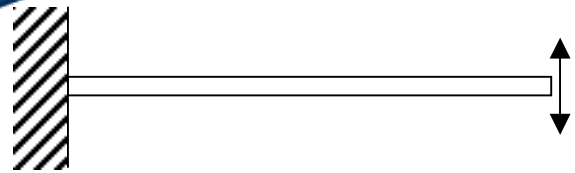
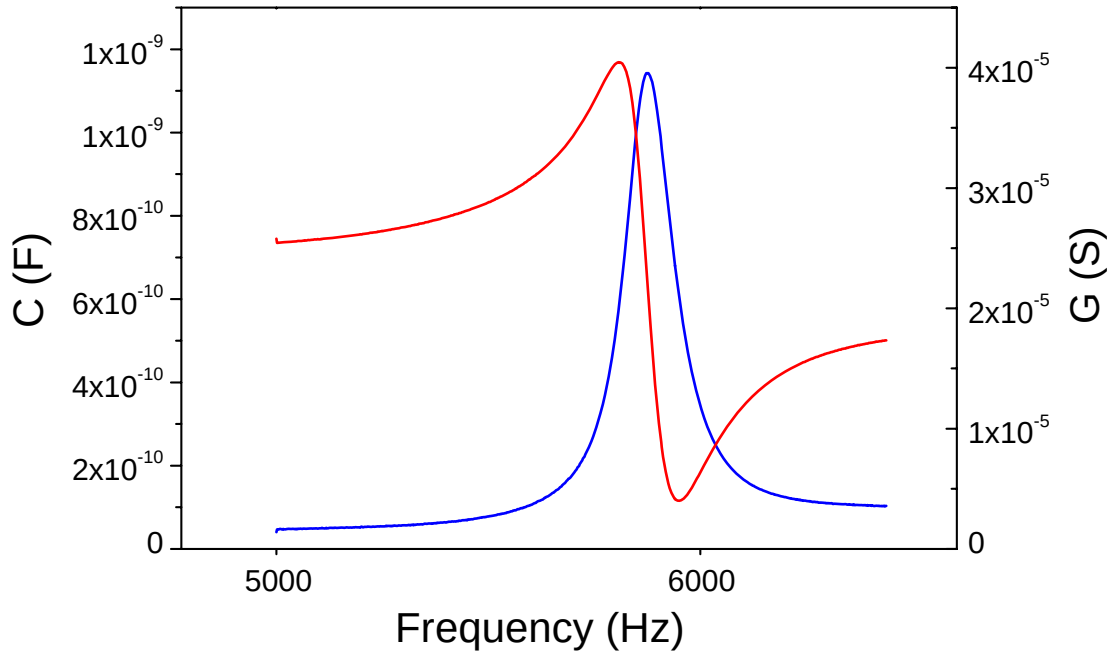
Use of Piezoelectric Devices for Small-Scale Rheological Measurement



Applications:
e.g. in-situ measurement



Resonant frequency dependant on surrounding fluid: measures of viscosity and density

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Polymer Processing

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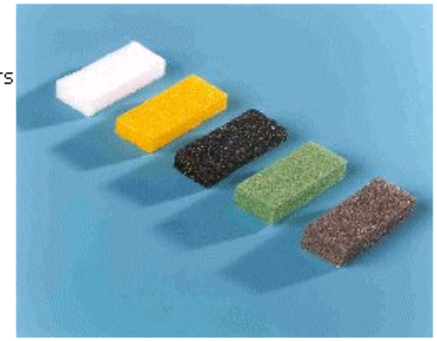
How can we improve the site for you?

Email Address

Welcome to the Home page of the Polymer Processing Team

The team focuses on the development of measurement technologies to assist manufacturers and users of plastics materials and products.



- Industrial Advisory Group Meetings
- **Next Polymer Processing IAG meeting**

  Date: Wednesday 25th October 2006.
  Location: UK Space Centre, Leicestershire.
  For directions to the Space Centre: please use this link

  If you would like to receive an invitation to this meeting please contact: Lydia Solomon
  Date: Wednesday 22nd November 2006.

- **Next Polymer Performance IAG meeting**

  Date: Wednesday 22nd November 2006.
  Please use this link

- Progress on International Standards (ISO committee reports) Updated 10 th November 2005

Current Projects:

- Heat Transfer in Polymer Processing(H1) (94Kb)
- Flow Properties of Filled Materials (H4) (104Kb)

  For further information about these projects please contact: Martin Rides

http://www.npl.co.uk/materials/polyproc/