AM11: Diagnostics for Measuring and Modelling Dispersion in Nanoparticulate Reinforced Polymers

Polymers: Multiscale Properties

8 November 2007

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Aims

- Provide diagnostic tools for quantitative measurement of nanoparticle dispersion in components for production and service inspection purposes
- Provide predictive models for determining thermal and mechanical properties of nanoparticulate reinforced polymers

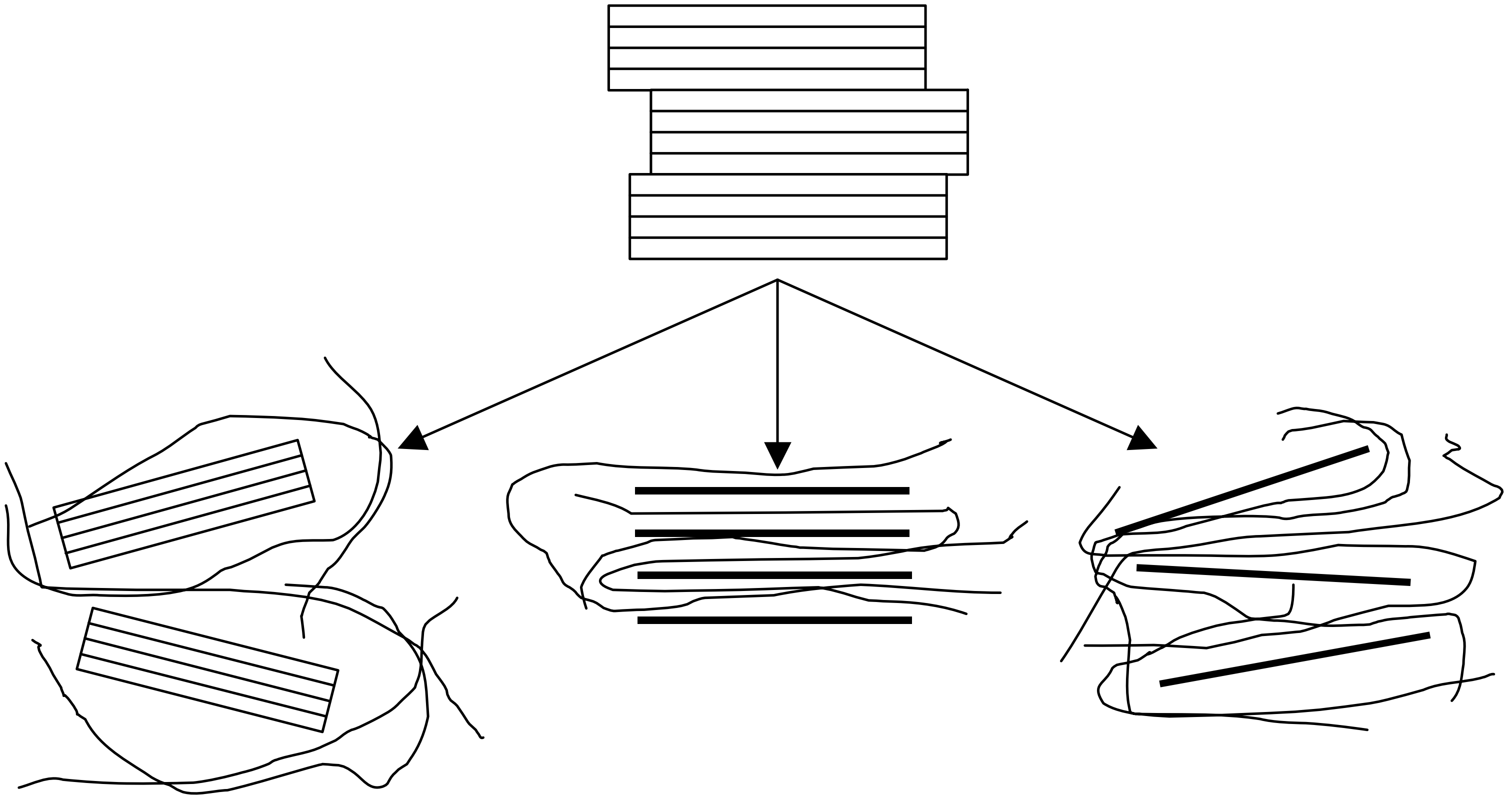
Rationale

Primary industrial impetus is ensuring sustainability of material properties and functionality of nanoparticulate reinforced polymeric materials throughout product lifetime through ensuring that nanoparticles remain in a highly dispersed uniform state, independent of external forces

Current Status

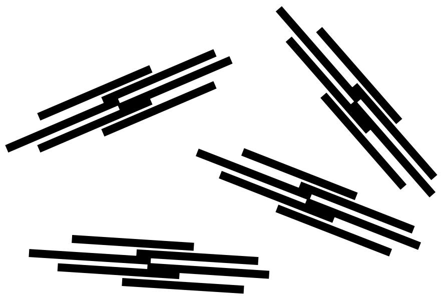
- No (direct) method available for production or service inspection that can provide accurate quantitative data on the nano-level of size, orientation and spatial distribution of nanoparticles
- No predictive models for determining the effects of non-uniformity on thermal and mechanical properties.

Polymer-Layered Silicate Structure

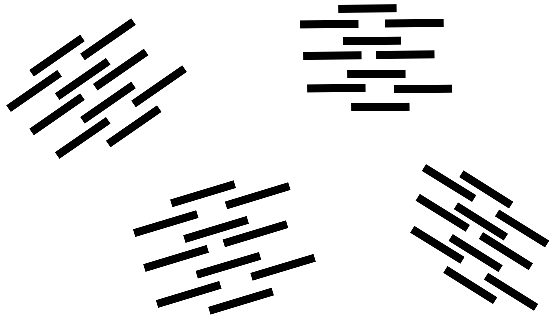


Conventional Intercalated Exfoliated

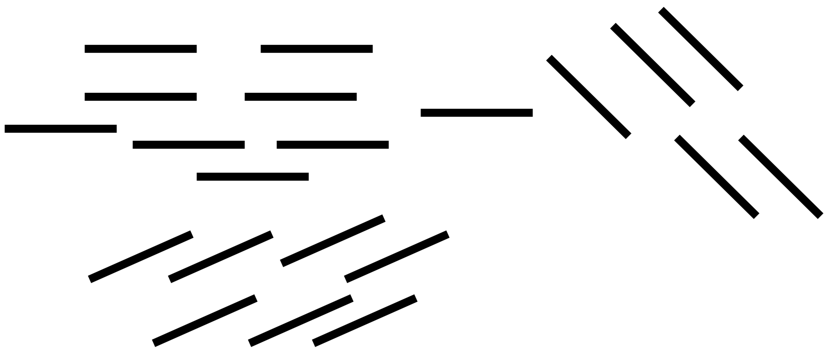
Polymer-Layered Silicate Structure



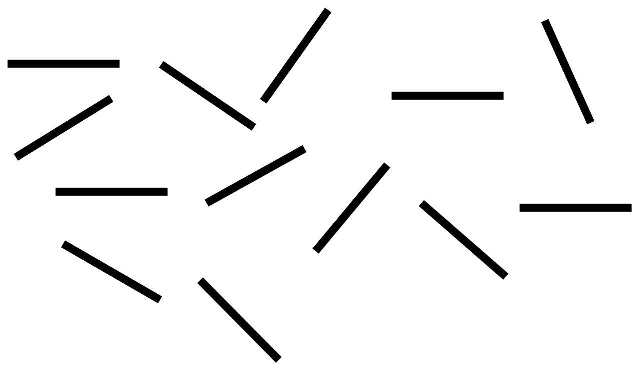
Conventional composite



Intercalated nanocomposite



Ordered exfoliated nanocomposite



Disordered exfoliated nanocomposite

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Functionality

Dependent on the following:

- ◆Spatial and compositional nature of the nanoparticulate filler
- ◆Size, orientation and spatial distribution of the nanoparticles in the matrix
- ◆Interfacial region between filler and matrix

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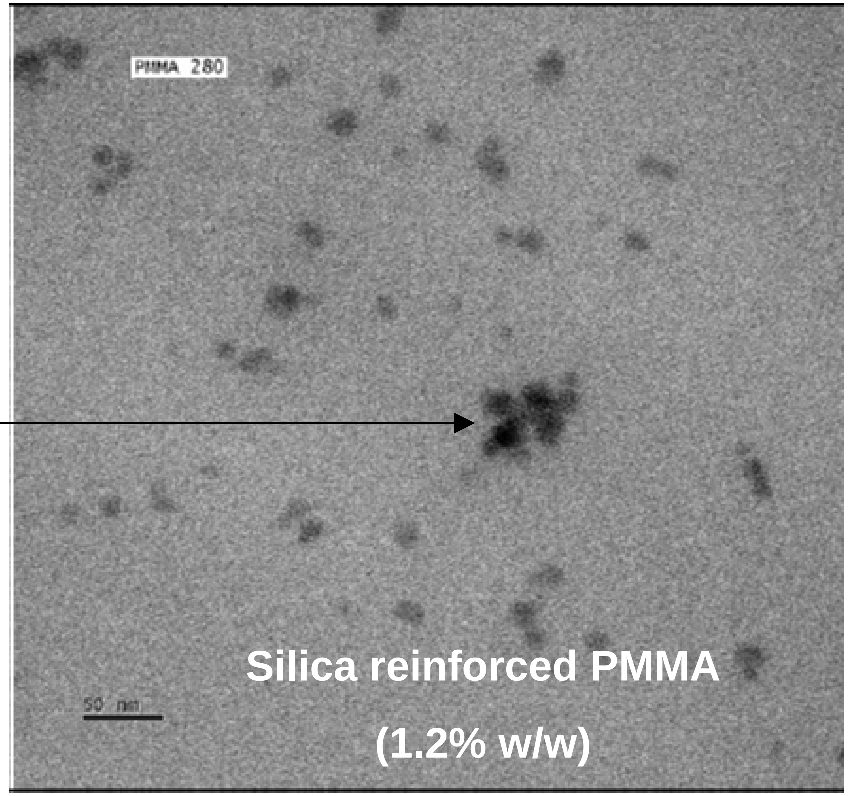
Characteristics

- Low percolation threshold (~0.1-2.0 vol%)
- Particle-particle interactions arising at low volume fractions affecting orientation and position of adjacent particles (short range order or correlation)
- High particle density per particle volume (10^6-10^8 particles/mm^3)
- High surface (interfacial) area to volume ratio (10^3-10^4 m^2/ml)
- Short inter-particle separation (~10-50 nm for 1-8 vol%)
- Comparable dimensions for particulate particle separation and relaxation volume of polymer chains

Concern

clustering



Electrical, thermal or chemical exposure, or subsequent processing activities may cause nanoparticle clustering, thus compromising the beneficial effects, such as improved thermal stability, stiffness, strength and impact resistance through the addition of small volumes of nanoparticles (1-5 vol %)

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Deliverables

- **D1: Critique of techniques and predictive analysis for characterising nanoparticle dispersion and thermal and mechanical properties of nanocomposite materials**
  NPL Report (December 2007)
- **D2: Dispersion monitoring technique to enable rapid quantifiable spatial and temporal distribution data of nanoparticles in polymeric materials (inc. case study)**
  Scientific paper (March 2010)
- **D3: Predictive model(s) for characterising dispersed nanoparticulate polymeric materials.**
  Scientific paper/CoDA module (February 2010)

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Work Programme

D2: Dispersion Monitoring Technique

- **Development of a new measurement tool to enable rapid quantifiable spatial and temporal distribution data of nanoparticles in polymeric materials resulting from post-processing migration due to electrical, thermal and chemical effects. Evaluation to include a number of industrial supplied nanoparticulate polymeric systems (case study) exposed to controlled test environments.**

D3: Predictive Models

- **Development of structure-property relationships for characterisation of thermal and mechanical properties of dispersed nanoparticulate polymeric materials. Modelling to accommodate various degrees of dispersion (i.e. clustering). Predictive analysis to be compared with case study results to be carried out in D2.**

Dispersion Measurement Techniques

- **Laboratory Based**
  - **Atomic force microscopy (AFM)**
  - **Nuclear magnetic resonance (NMR)**
  - **Raman spectroscopy**
  - **Scanning electron microscopy (SEM)**
  - **Small angle neutron scattering (SANS)**
  - **Transmission electron microscopy (TEM)**
  - **X-ray diffraction (XRD)**
    - **Wide-angle X-ray spectroscopy (WAXS)**
    - **Small-angle X-ray spectroscopy (SAXS)**
- **In-situ Measurements**
  - **Dielectric spectroscopy**
  - **Optical (diffraction – dynamic light scattering (DLS))**
  - **Raman spectroscopy**
  - **Thermal (rheology)**
  - **Ultrasonics**
  - **X-ray diffraction (XRD) - possibly**

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Dielectric Spectroscopy

- **Measures the capacitive and conductive properties of materials as a function of temperature, time and frequency under controlled environments**
- **Provides information on molecular mobility (relaxation) of materials, and can measure permittivity, loss factor and ionic conductivity of solids**
- **Dielectric dispersion parameters sensitive to percolation structure, state of dispersion and degree of exfoliation**

Clay/Polyamide Loading

Material	Weight Fraction (%)	Volume Fraction (%)	Density (kg/m^3)
Nylon 6 PA-6	-	-	1,123 ± 1
PNC1	1.37 ± 0.05	0.76 ± 0.08	1,130 ± 1
PNC2	2.79 ± 0.01	1.67 ± 0.05	1,136 ± 1

Slight increase in density with loading

Clay/Polyamide Mechanical Properties

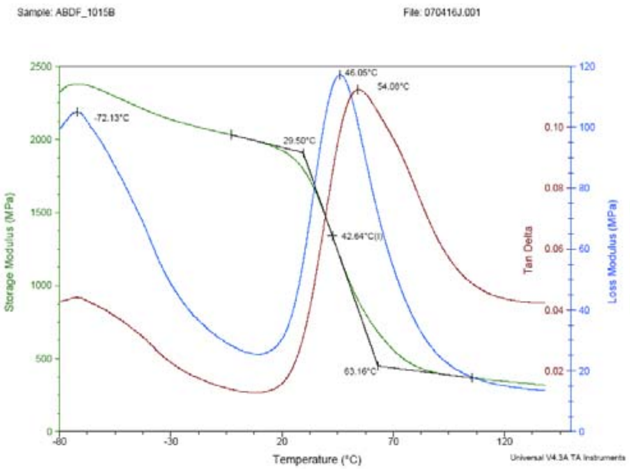
Material	Tensile Strength (MPa)	Tensile Modulus (GPa)	Poisson's Ratio	Failure Strain (%)
Nylon 6 PA-6	64.9 ± 2.0	2.93 ± 0.06	0.44 ± 0.01	228 ± 84
PNC1	81.3 ± 1.5	3.91 ± 0.04	0.43 ± 0.01	180 ± 57
PNC2	84.8 ± 0.7	4.52 ± 0.02	0.42 ± 0.01	30.8 ± 1.9

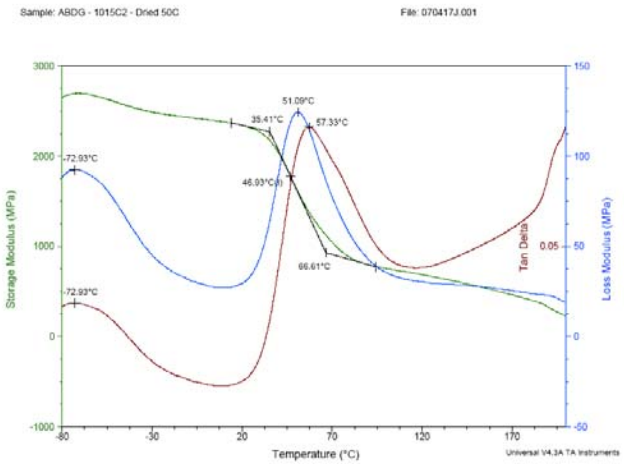
Material	Flexure Strength (MPa)	Flexure Modulus (GPa)
Nylon 6 PA-6	109.9 ± 1.0	2.89 ± 0.04
PNC1	137.9 ± 1.5	3.73 ± 0.11
PNC2	143.6 ± 0.9	4.29 ± 0.04

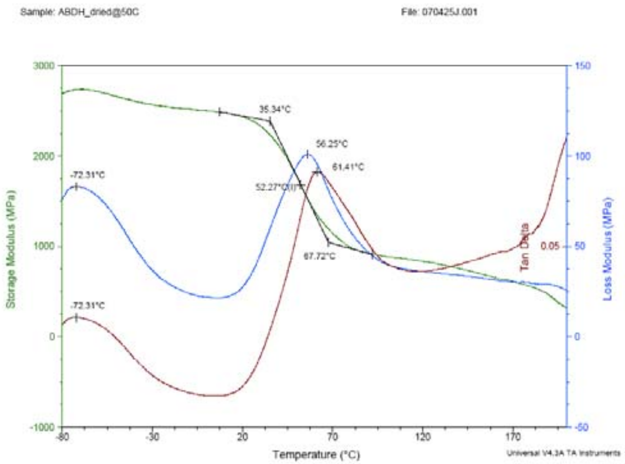
Increase in tensile/flexure strength/modulus with loading

Modulus more sensitive to small changes in loading

DMA Results – Clay/Polyamide Glass Transition Temperature (T_g)







Nylon 6 PA-6	PNC1	PNC2
(42.6 °C)	(46.9 °C)	(52.3 °C)

Tg increases with an increase in loading

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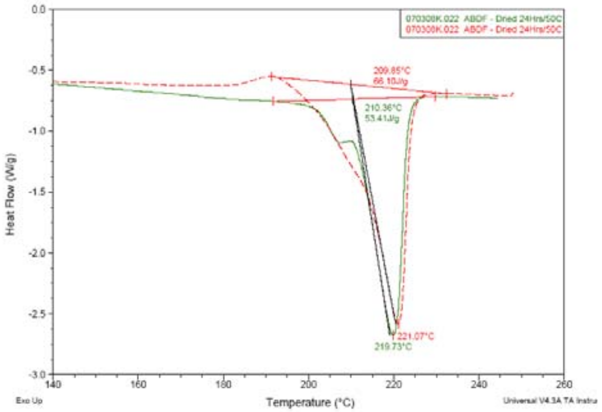
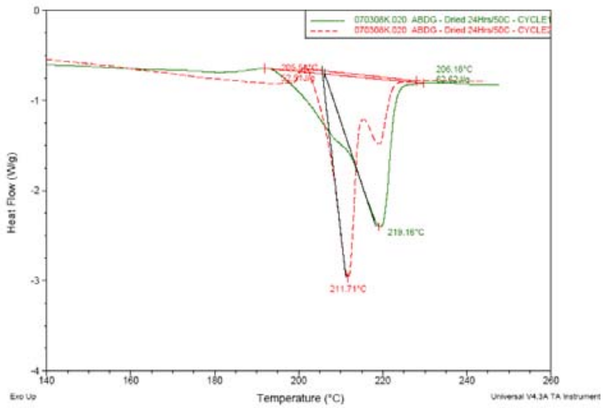
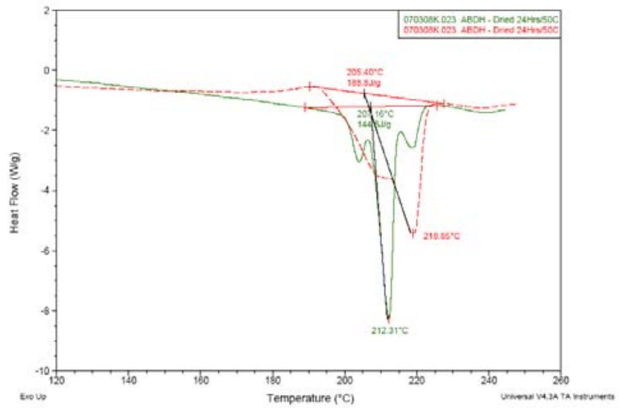
DSC Results – Clay/Polyamide T_{melt} and $T_{crystallinity}$







Nylon 6 PA-6	PNC1	PNC2
(219.7/210.4 °C)	(219.2/206.2 °C)	(218.9/207.2 °C)

Decrease in T_{melt} and $T_{crystallinity}$ with addition of clay nanoparticles

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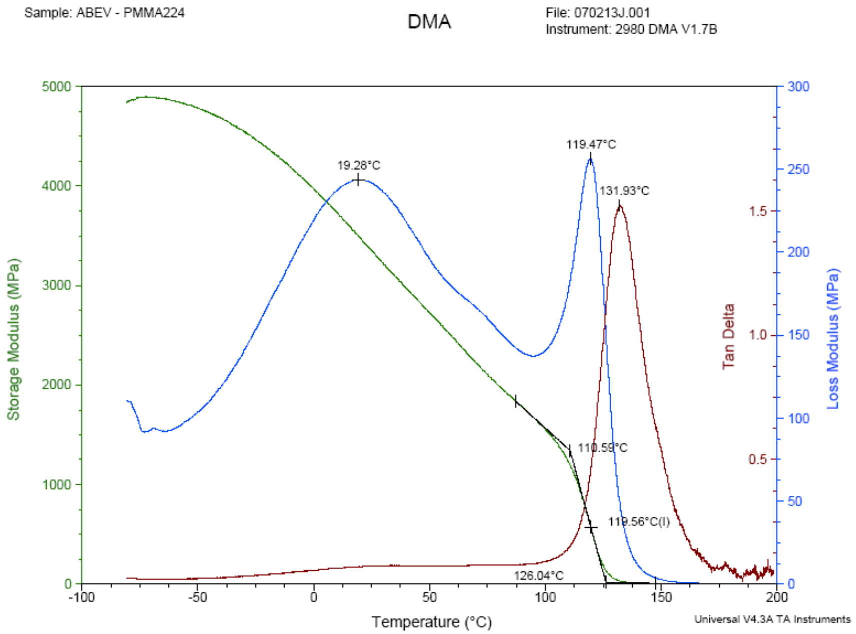
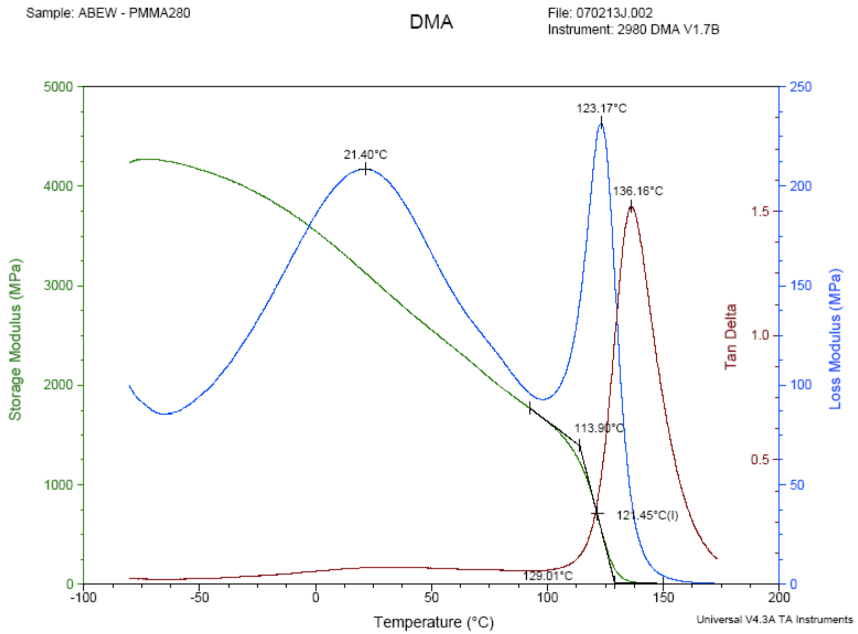
DMA Results – Silica/PMMA Glass Transition Temperature (T_g)

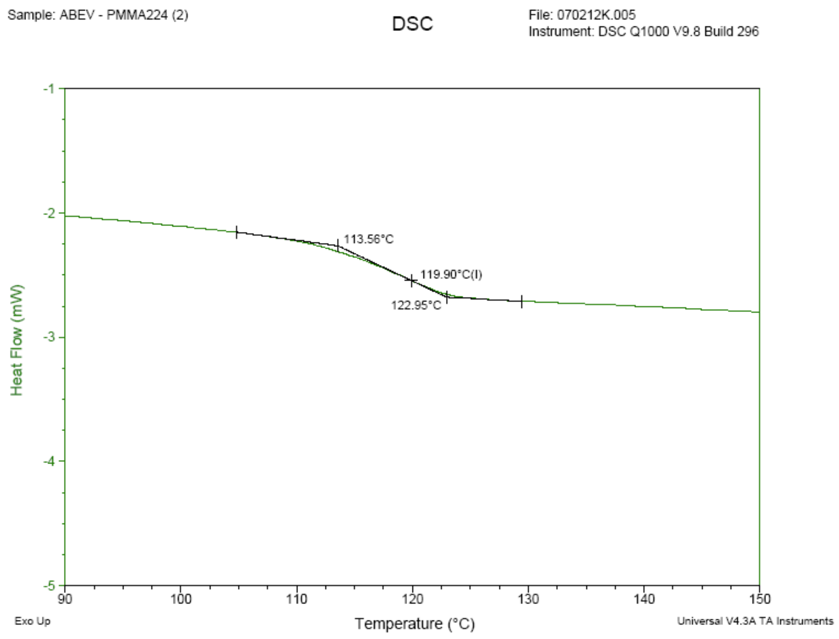


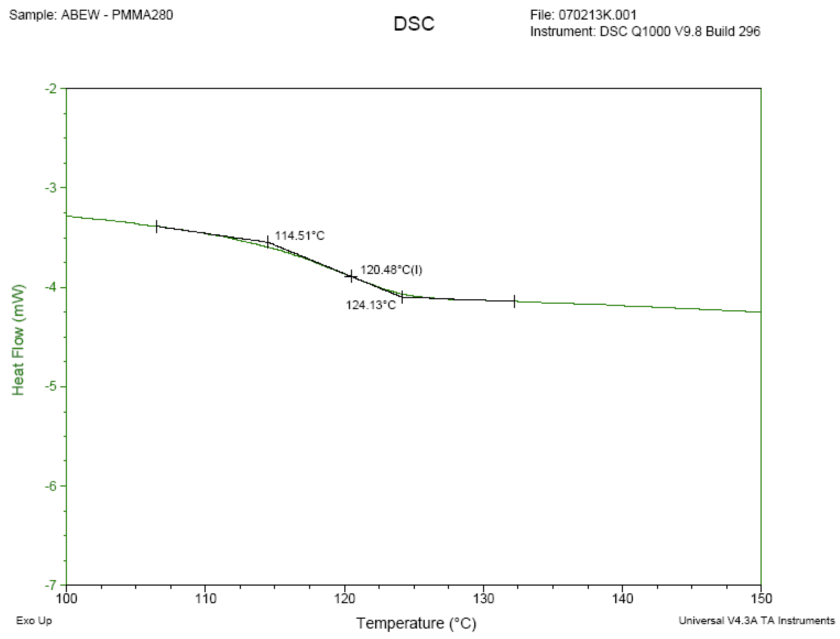


PMMA	Silica/PMMA
(119.6 °C)	(121.5 °C)

Tg higher with addition of silica nanoparticles

DSC Results – Silica/PMMA
Glass transition Temperature (T_g)





PMMA (119.9 °C)	Silica/PMMA (120.4 °C)

Tg higher with addition of silica nanoparticles

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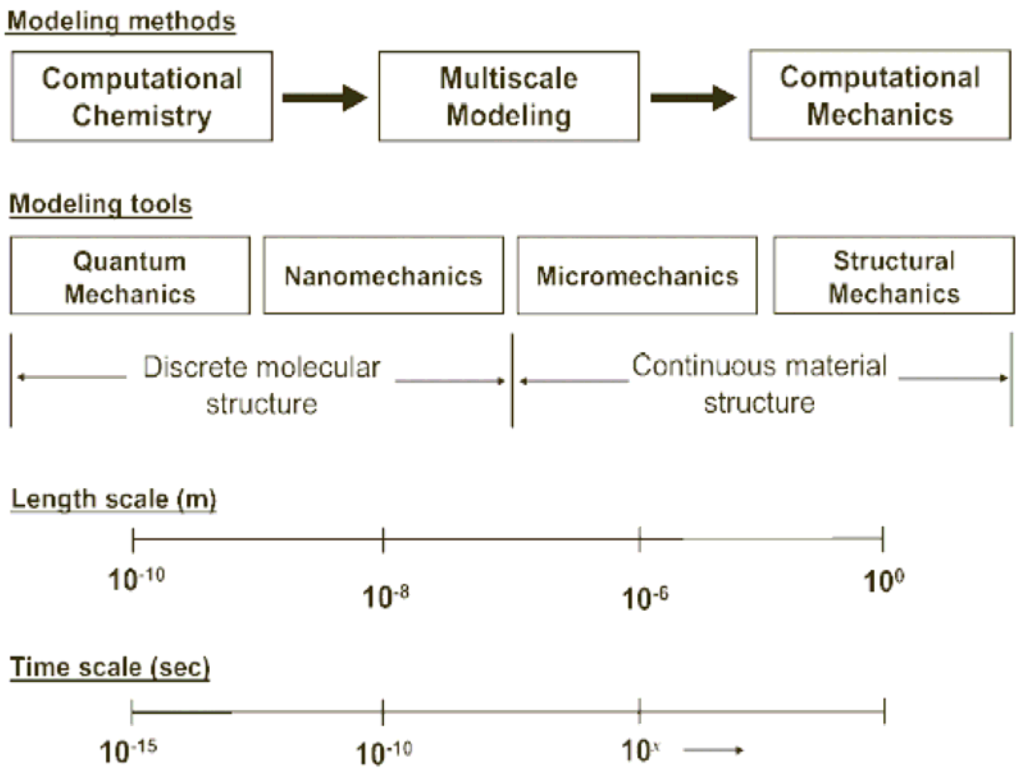
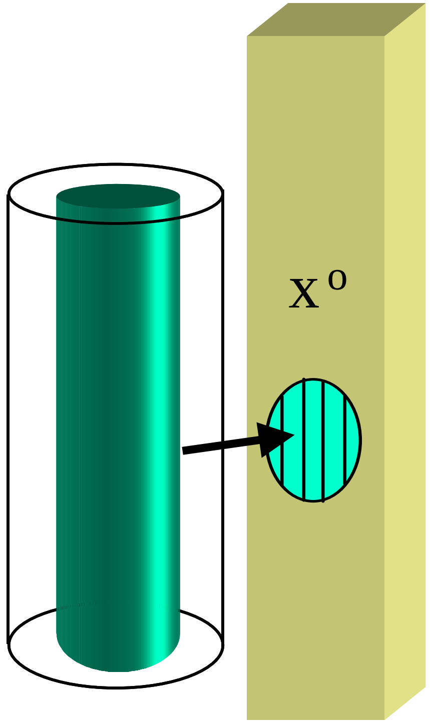
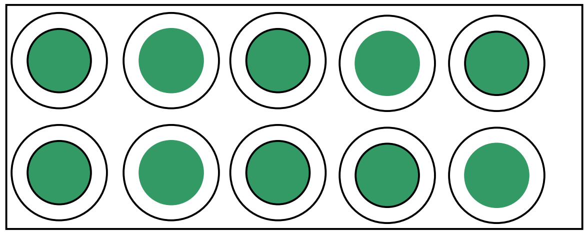
Modelling Approaches







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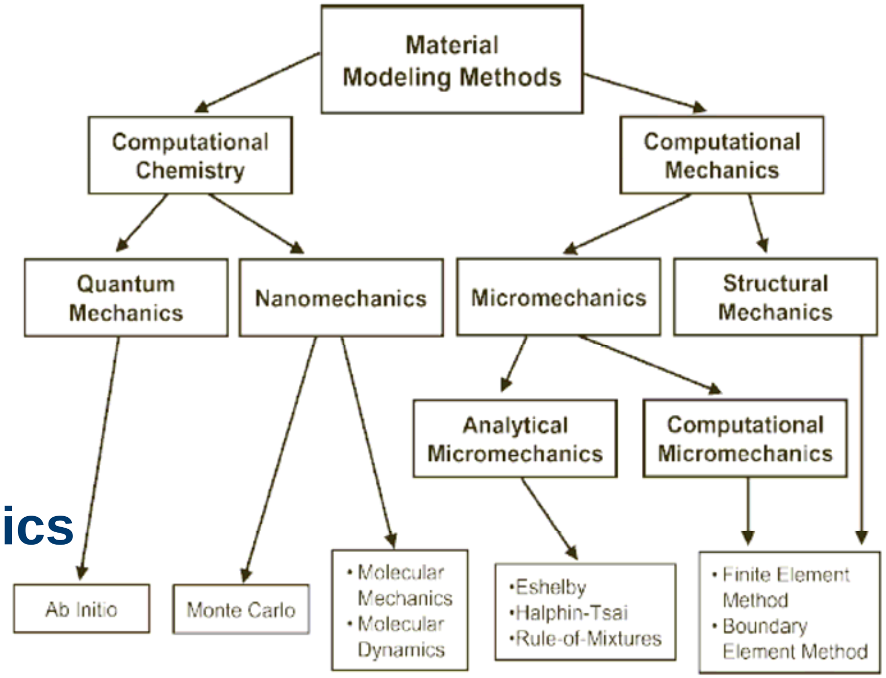
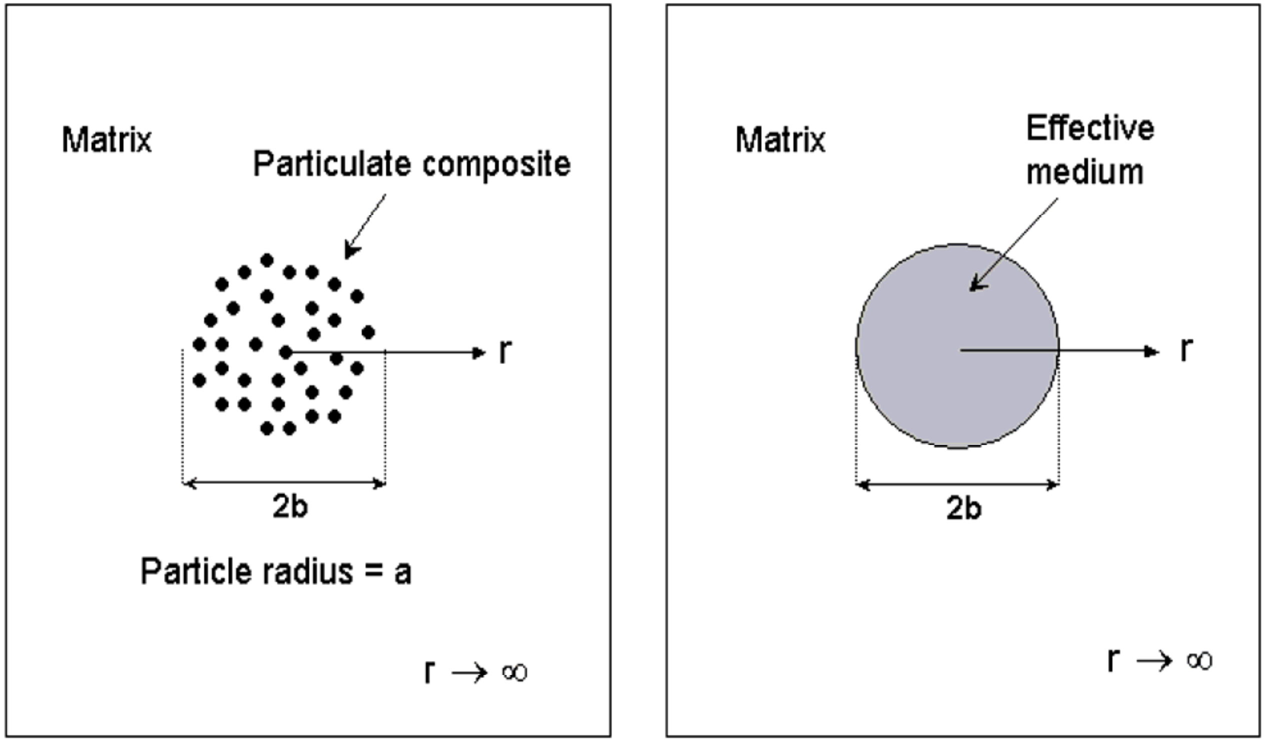
Modelling Approaches

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



Maxwell’s Far-Field Methodology - Properties of Multi-Phase Isotropic Particulate Composites



a) Discrete particle model   b) Smoothed effective medium model

Maxwell's Far-Field Methodology - Properties of Multi-Phase Isotropic Particulate Composites

The volume fractions of particles of type i within the enclosing sphere of radius b are given by:

$$V_p = n_i a_i^3 / b^3,\ i = 1,\ldots,N, \text{ such that } \quad V_m + \sum_{i=1}^{N} V_p^i = 1$$

where V_m is the volume fraction of matrix.

For just one type of particle, with n particles of radius a within the enclosing sphere of radius b, the particulate volume fraction V_p is such that:

$$V_p = na^3 / b^3 = 1 - V_m$$

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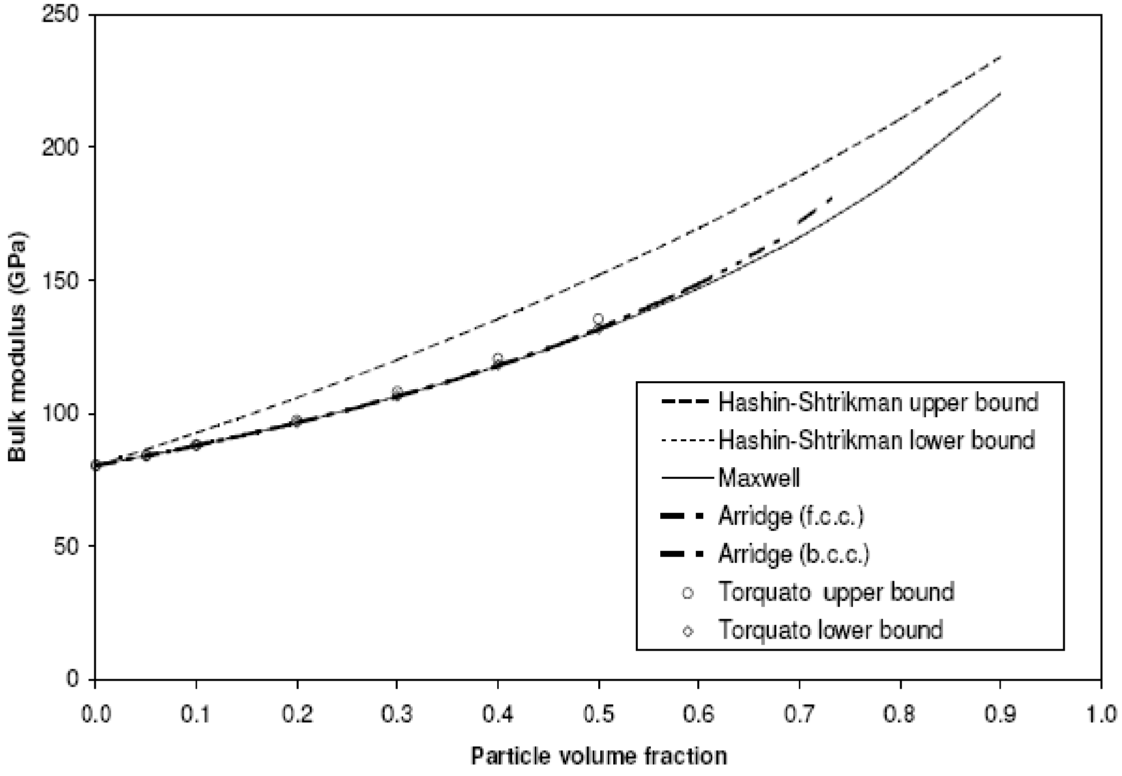
Maxwell's Far-Field Methodology – Bulk Modulus of Silicon Carbide Composite



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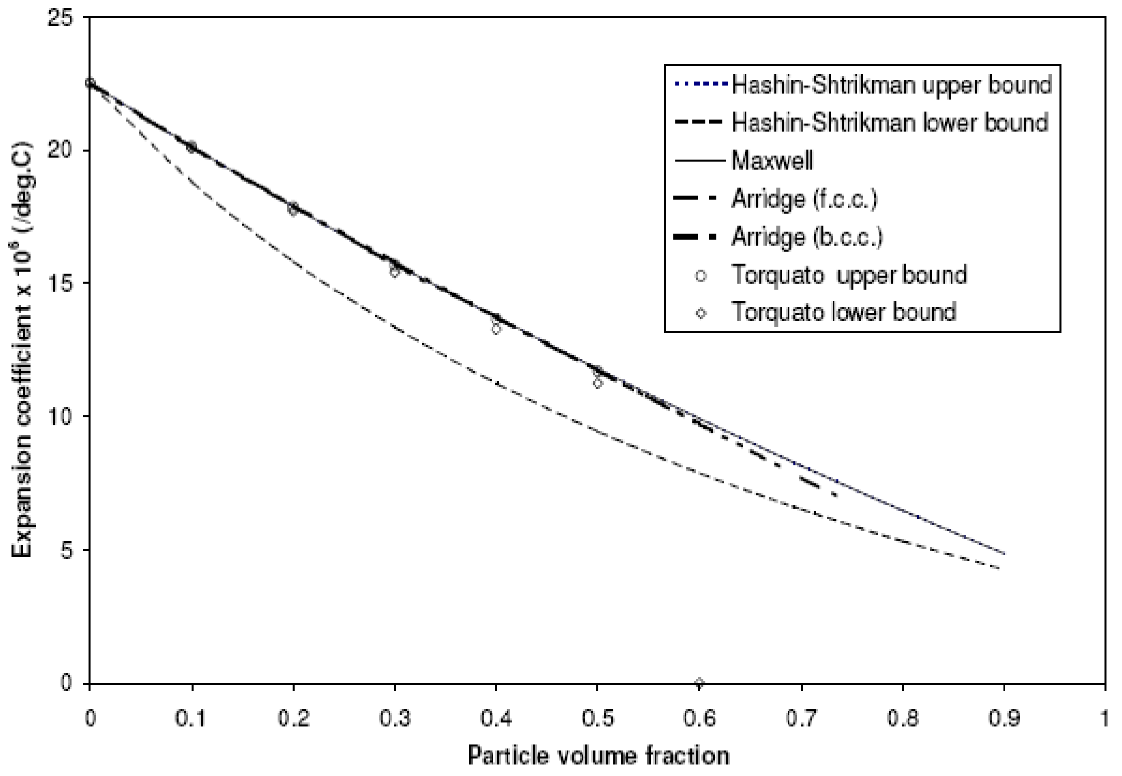
Maxwell's Far-Field Methodology – Coefficient of Thermal Expansion of Silicon Carbide Composite



Case Study: Nanocomposite

- **PNCs: Clay and silica nanoparticle reinforced PMMA composites**
- **Weight additional levels (wt %)**
- **Mechanical properties:**
  - **Fracture toughness (impact resistance)**
  - **Tensile properties**
  - **Permeation**
- **Supplier: Lucite International UK Ltd**

Others are welcome

Thank you for listening

Any Questions?

Case Studies?

Traceable Size and Shape Measurement on Nanoparticles

and

Dispersion in Polymeric Nano-composites

A project proposal for the Knowledge based programme

Contact: Martin Rides

8 November 2007

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Traceable Size and Shape Measurements

- Particle imaging in concentrated suspensions
  - Size, shape and distribution
- TEM to provide calibration standards for metrology of nanoparticles
- 3-D Dynamic Light Scattering (DLS)
- Surface properties/activiation

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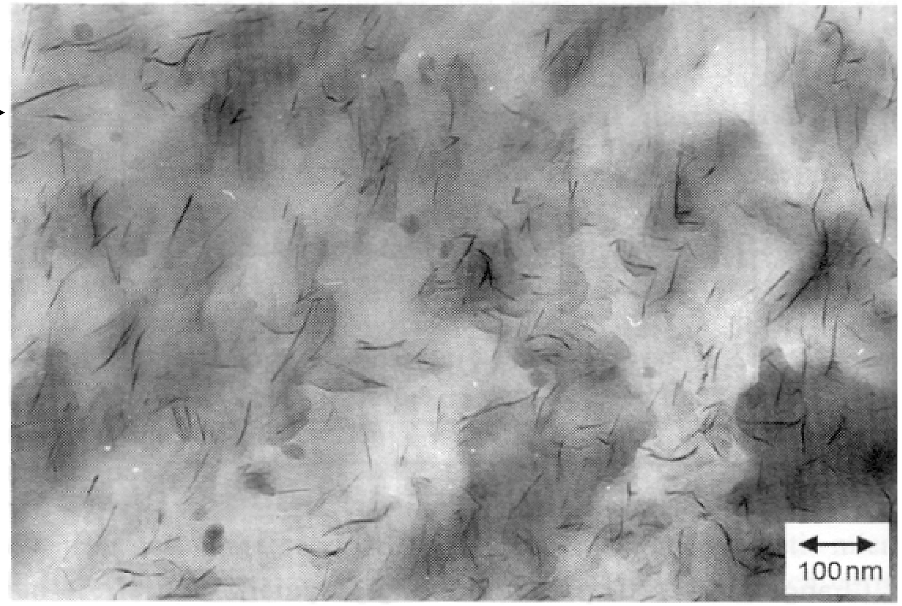
A problem – how well are nano-fillers dispersed?

TEM of nylon 6-clay nano-composite

Measurements for dispersion



Good dispersion (exfoliation) essential to achieve beneficial properties

volume ≈ 10^{-18} m^3

mass ≈ 10^{-15} kg

"Polymer-clay nano-composites"
Eds. T J Pinnavaia and G W Beall, Wiley, 2001.

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Dispersion in Polymeric Nano-composites

- Investigation of thermal and rheological techniques for assessing dispersion

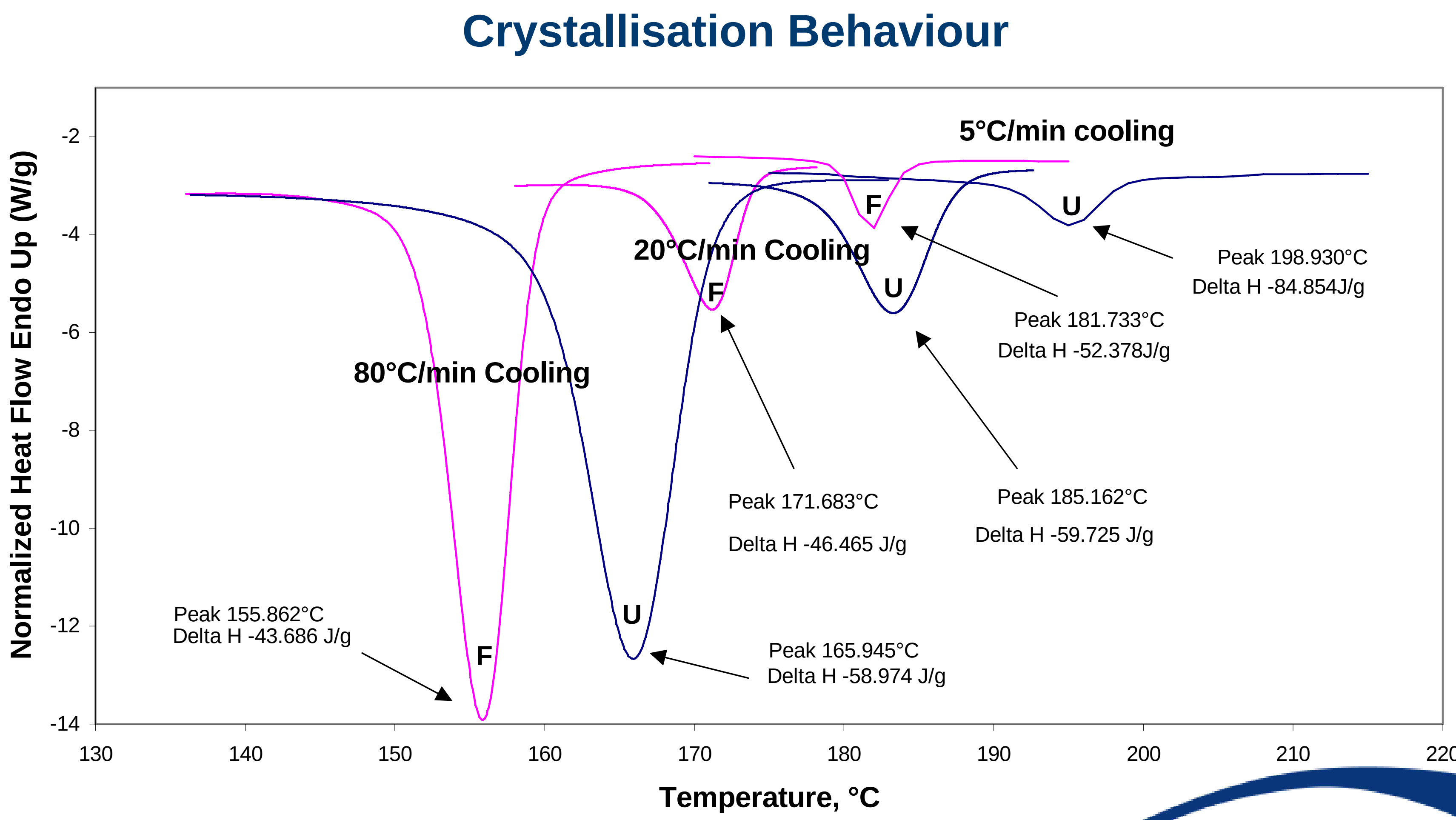
- Thermal: DSC measurement of crystallisation behaviour and glass transition temperature

- Rheological: Dynamic rheological measurements

- Other properties

- Case Studies

DSC test data of nylon 6 unfilled (blue) and nano-clay filled (pink) materials: 5, 20 and 80°C/min cooling rates.



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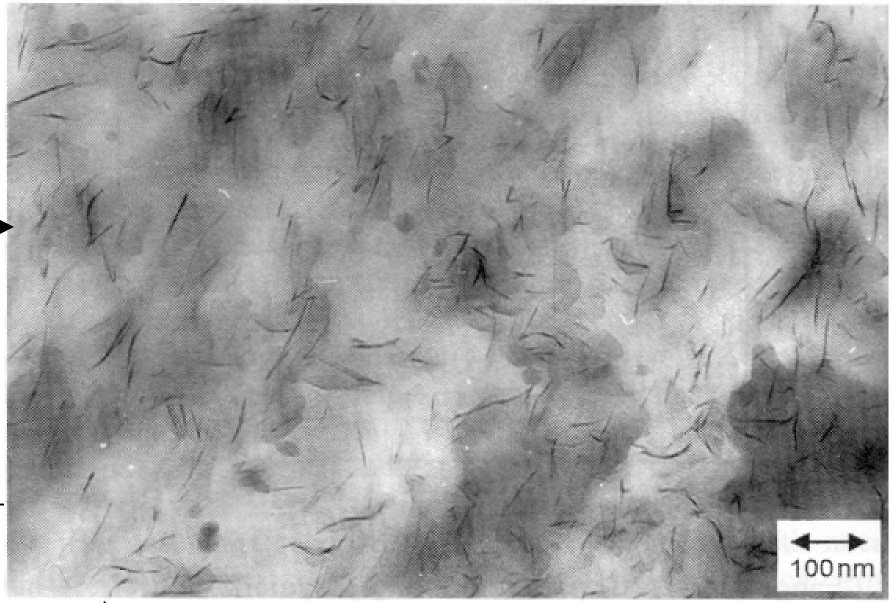
Dispersion

TEM of nylon 6-clay nano-composite



Measurements for dispersion

Crystallisation temperature/T_g combined with rheometry, ...

QC techniques

"Polymer-clay nano-composites" Eds. T J Pinnavaia and G W Beall, Wiley, 2001.

Your input to development of this proposal welcomed

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