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

Polymers: Multiscale Properties

22 April 2008

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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 polymers throughout product lifetime through ensuring that nanoparticles remain in a highly dispersed uniform state, independent of external forces

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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.

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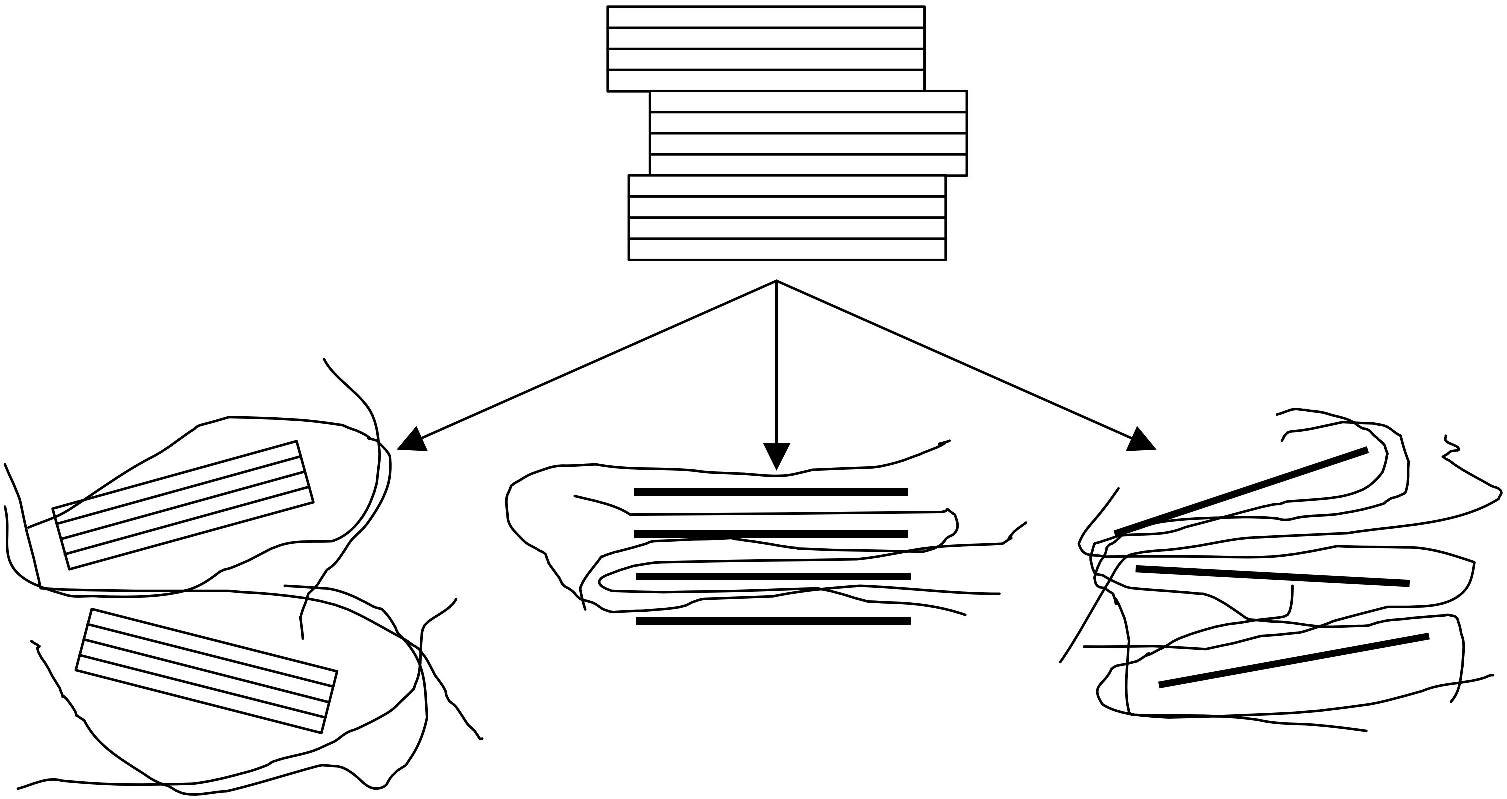
Polymer-Layered Silicate Structure



Conventional **Intercalated** **Exfoliated**

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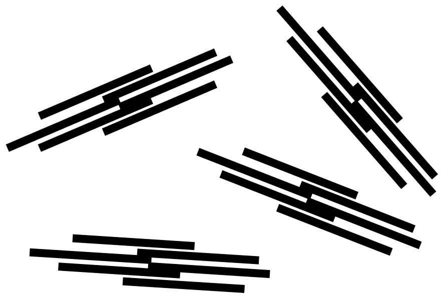
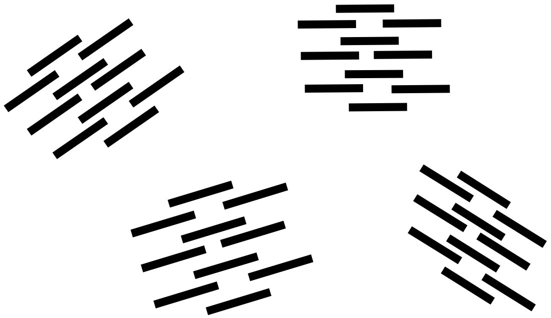
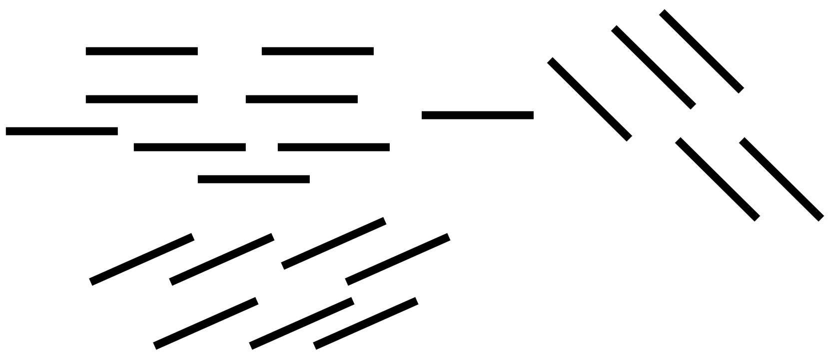
Polymer-Layered Silicate Structure



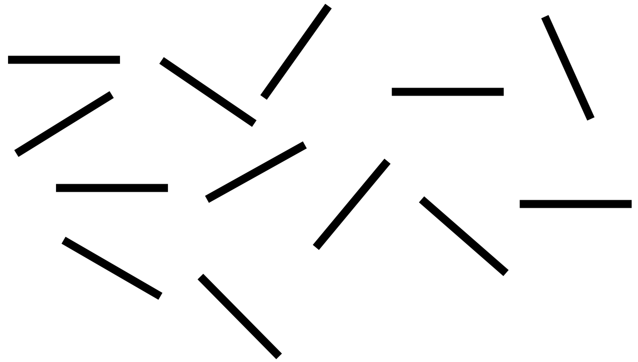
Conventional composite



Intercalated nanocomposite



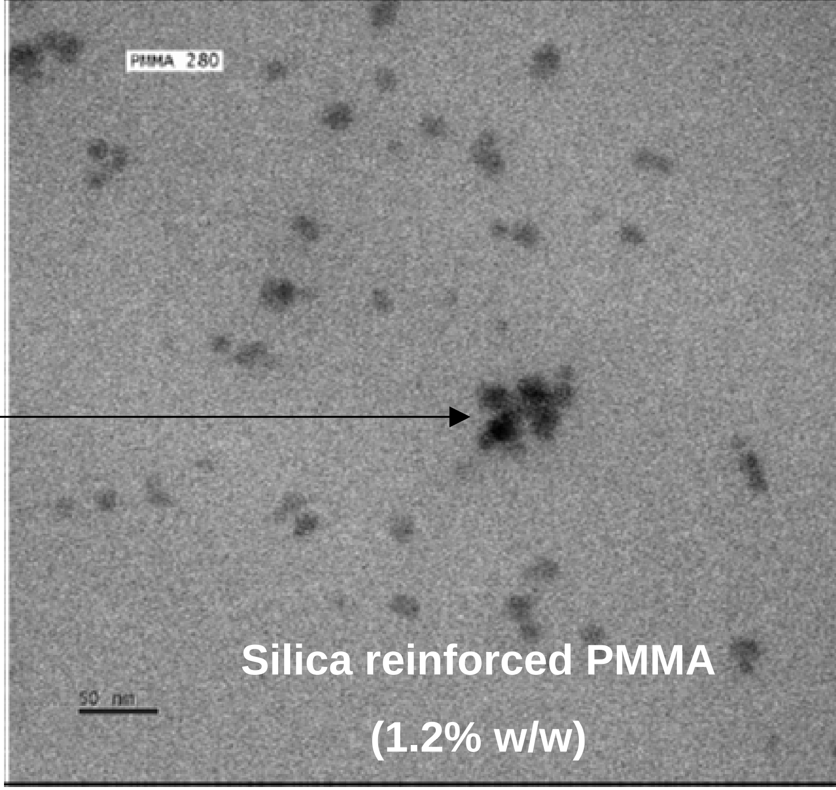
Ordered exfoliated nanocomposite



Disordered exfoliated nanocomposite

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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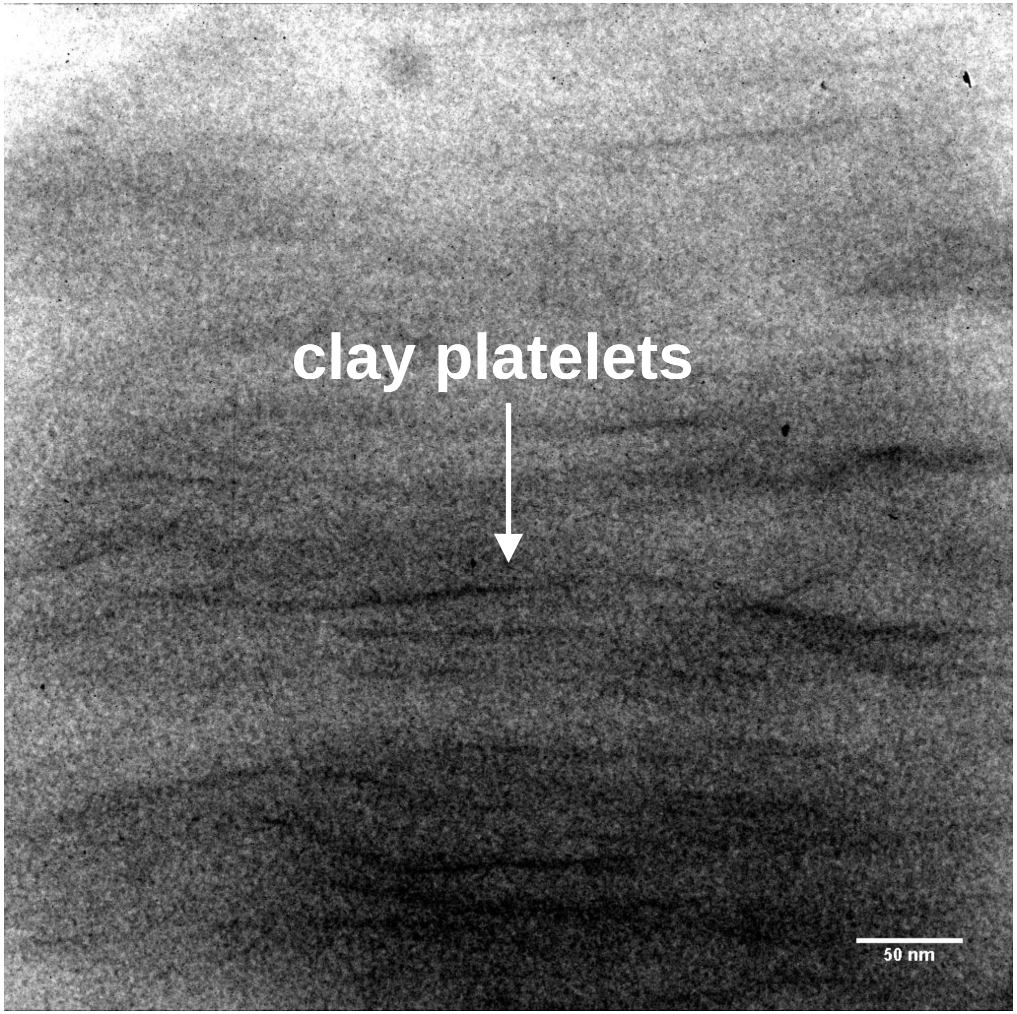
Clay Reinforced Polyamide (Nylon 6 PA-6)



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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Deliverables

- **D1: Critique of techniques and predictive analysis for characterising nanoparticle dispersion and thermal and mechanical properties of nanocomposite materials**

  NPL Report (December 2007) – completed

- **NPL Report MAT 12 “Characterization of Nanosized Filler Particles in Polymeric Systems: A Review”, W R Broughton**

Review

- Material Systems
- Processing
  - Processing Issues
  - Dispersion
  - Orientation Distribution
- Measurement Techniques*
- Modelling Nanocomposites
  - Continuum Based Modelling
    - Micromechanics approach
  - Molecular modelling
- Discussion and Conclusions
  - Recommendations

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Measurement Techniques

- X-ray diffraction (XRD)
- X-ray tomography
- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- Scanning tunnel microscopy (STM)
- Scanning probe microscopy
  - Atomic force microscopy (AFM)
- Nanoindentaion
- Infrared spectroscopy (IRS)
- Dielectrics
- Electrical impedance tomography (EIT)
- Eddy current
- Ultrasonic techniques
- Optical techniques
- Thermal techniques
- Rheological methods
- Nuclear techniques

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)
- In-situ Measurements
  - Dielectric spectroscopy
  - Optical properties
  - Raman spectroscopy
  - Thermal (CTE, DSC, DMA, Rheology)
  - Ultrasonic techniques (time of flight – velocity/attenuation)
  - X-ray diffraction (XRD) – possibly
  - Mechanical properties
    - Stiffness, strength and fracture toughness
    - Environmental stress cracking (ESC)

Deliverables

- **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 nanoparticles in polymeric materials**

  Scientific paper/CoDA module (February 2010)

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Case Studies

- **Case Study 1: Nanoclay/polyamide (Nylon 6 PA-6)**
  - **VAMAS Round-Robin exercise (completed)**
- **Case Study 2: Silica/PMMA**
  - **Lucite International UK Ltd**
- **Case Study 3: Nanoclay/PMMA**
  - **Lucite International UK Ltd (Durham University)**
- **Case Study 4: CNT/polypropylene**
  - **Security Composites Ltd**

Case Study 1 – Clay/Polyamide

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**

Clay/Polyamide – Thermal Properties

Material	Strain Difference (με)	CTE (10^{-6}/°C)
Nylon 6 PA-6	2,564	68
PNC1	3,880	83
PNC2	1,882	66

- **Reduction in residual strain for higher loading**

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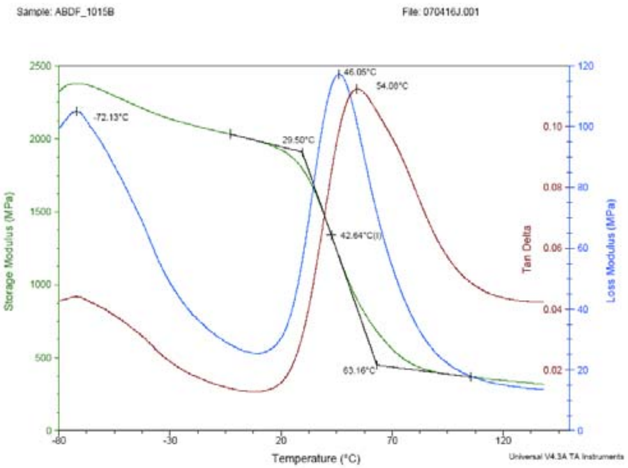
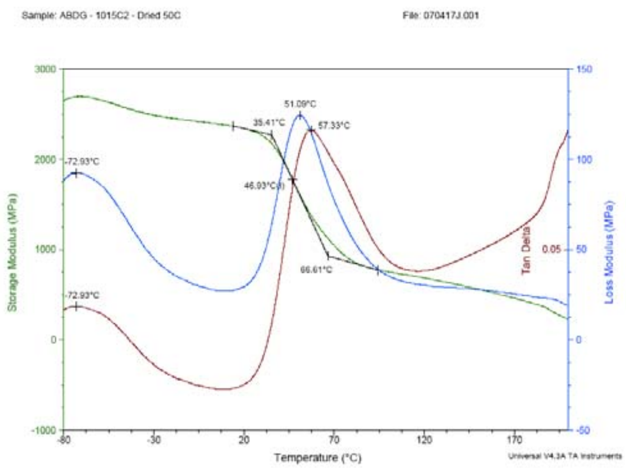
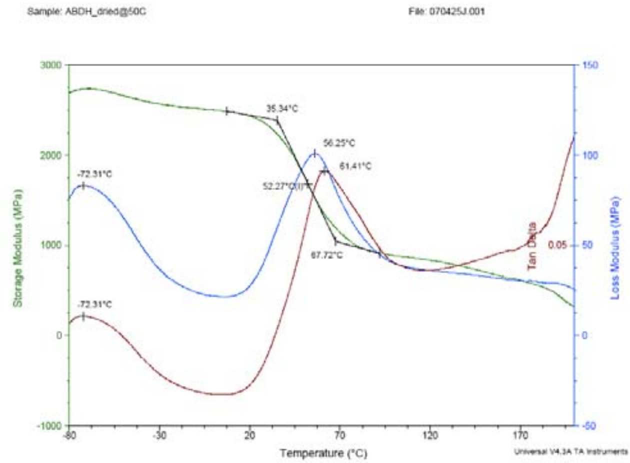
Clay/Polyamide – DMA Results
Glass Transition Temperature (T_g)







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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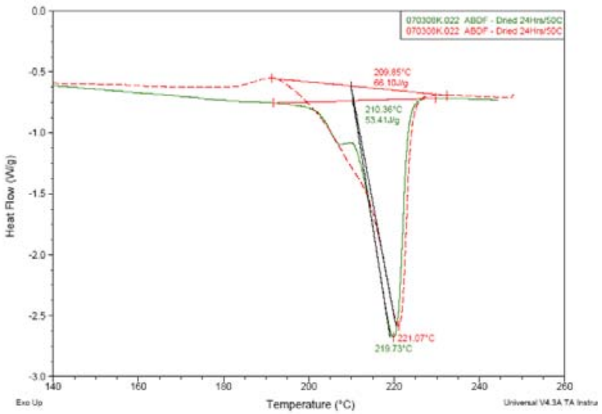
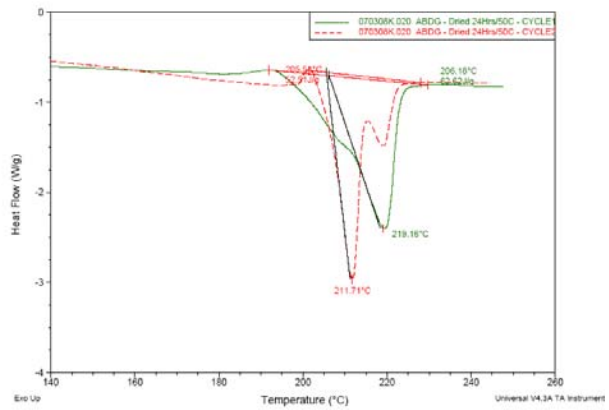
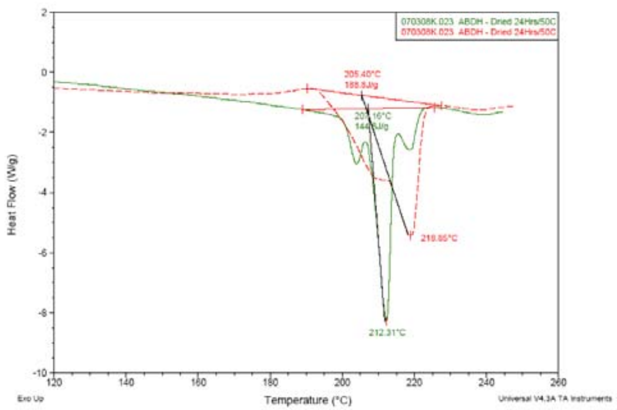
Clay/Polyamide – DSC Results

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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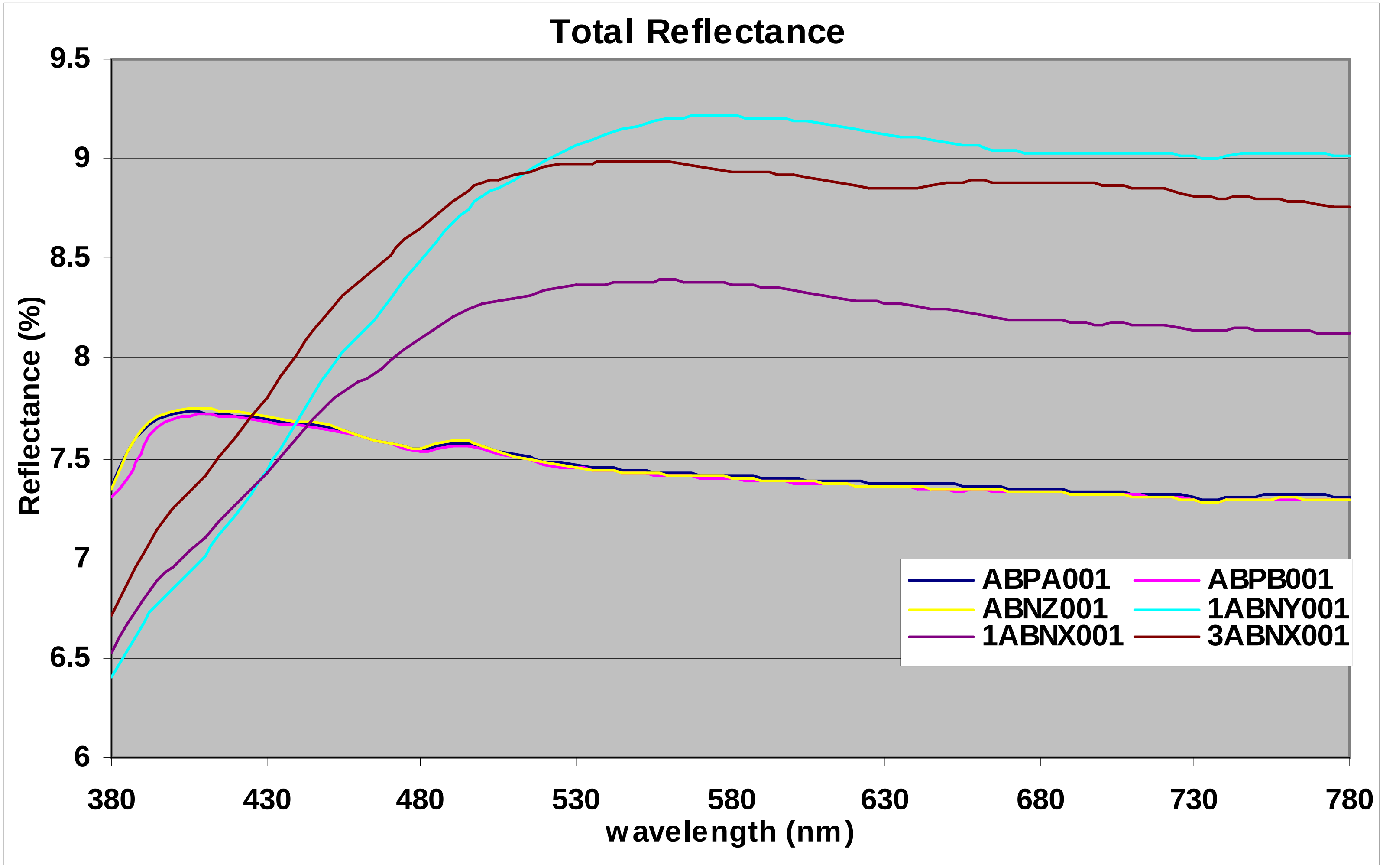
Case Studies 2/3 – Silica/PMMA + Clay/PMMA

Material	Density (kg/m^3)	Loading (wt %)	Shore Hardness D
PMMA 363 (Unreinforced)	1190 ± 1	**N/A**	22.1 ± 0.1
<u>Silica/PMMA</u>			
PMMA 364 (0.5%)	1,189 ± 1	0.5	22.0 ± 0.1
PMMA 365 (2.0%)	1,190 ± 1	2.0	22.0 ± 0.1
<u>Nanoclay/PMMA</u>			
2.0%	1,189 ± 1	2.0	22.0 ± 0.1
2.0% (poor dispersion)	1,188 ± 3	2.0	22.1 ± 0.1
4.0%	1,194 ± 1	4.0	22.1 ± 0.1

- Slight increase in density with loading

Silica/PMMA + Clay/PMMA – Reflectance



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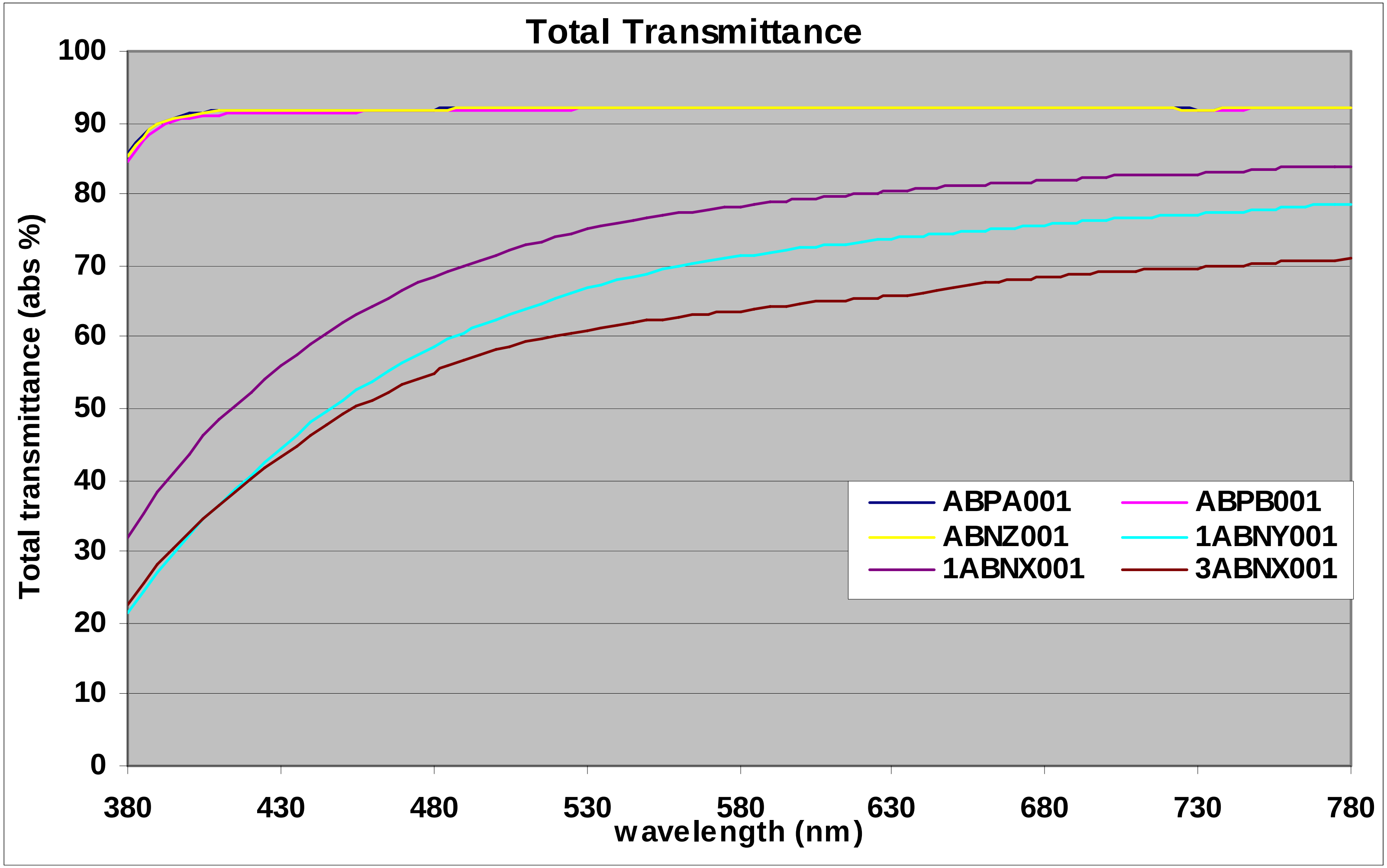
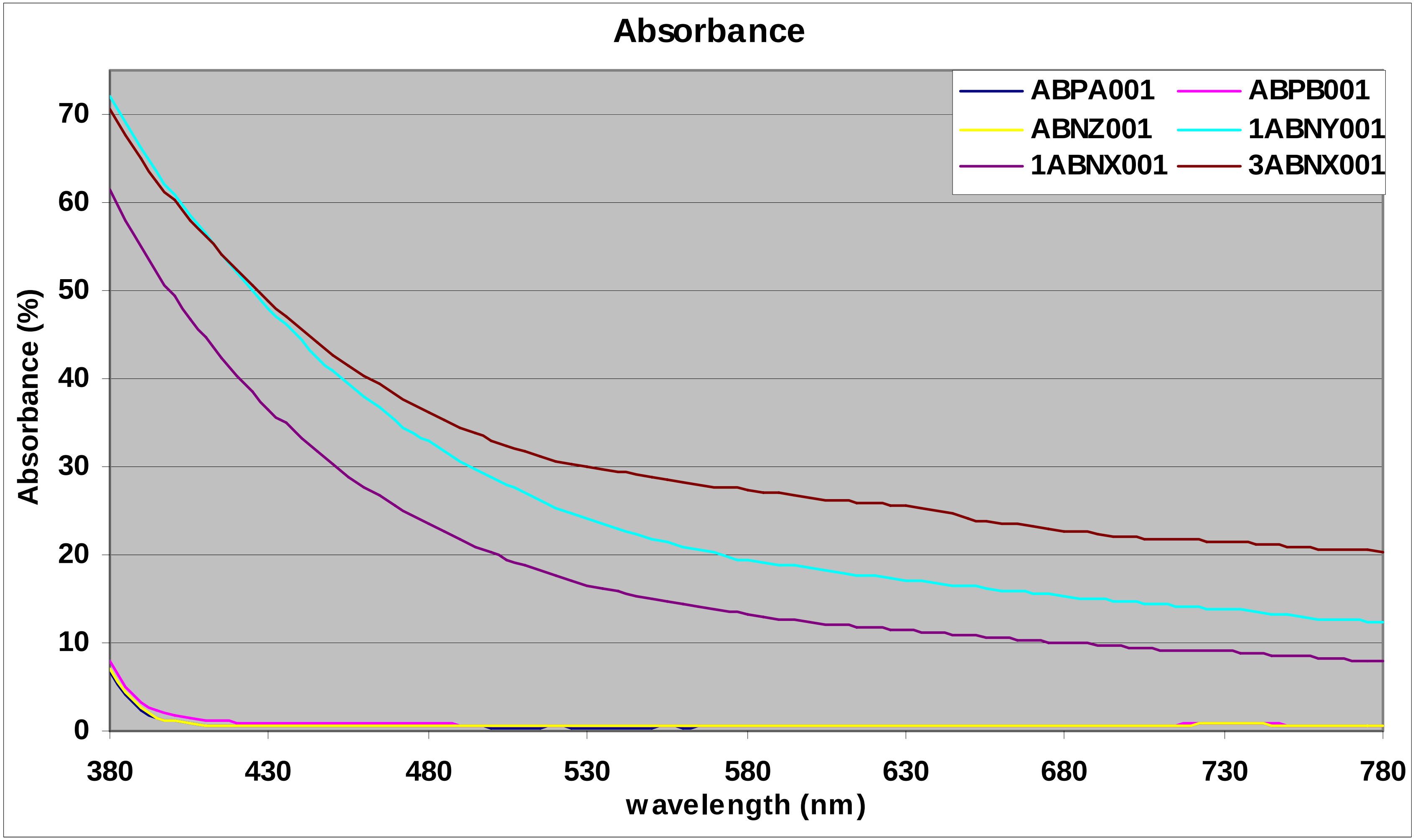
Silica/PMMA + Clay/PMMA – Transmittance



Silica/PMMA + Clay/PMMA – Absorbance



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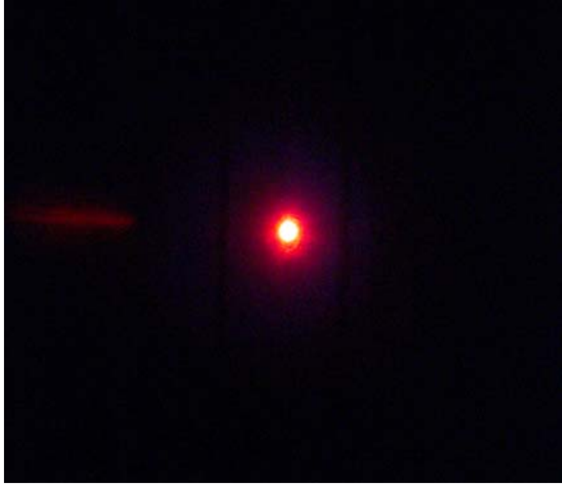
Silica/PMMA - Optical Properties



Triantafillos Koukoulas

- Minimal differences in total reflectance, transmittance and absorbance for PMMA and silica/PMMA materials
- Refractive Index (n)
  - PMMA - 1.49221921 (0.0001422)
  - Silica/PMMA (2.0%) - 1.49236546 (0.00042269)
- No significant difference in refractive index
- Static light scattering – work is on-going

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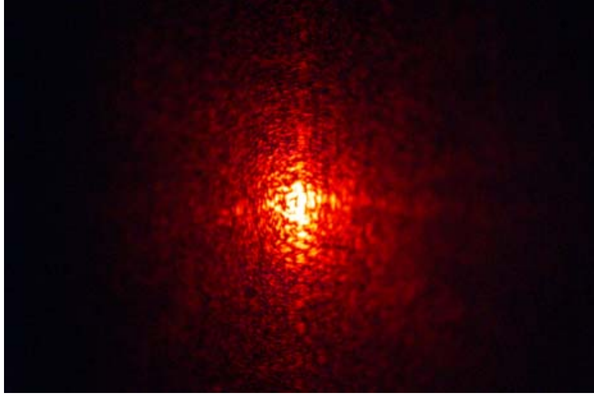
Clay/PMMA - Optical Properties



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- Total Transmittance
  - 2.0% (good) > 4.0% > 2.0% (poor)
- Absorbance
  - 2.0% (poor) > 4.0% > 2.0% (good)
- Total Reflectance
  - 4.0% > 2.0% (poor) > 2.0% (good)
- Static light scattering – work is on-going

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Silica/PMMA + Clay/PMMA - Tensile Properties

Material	Tensile Modulus (GPa)	Tensile Strength (MPa)	Strain to Failure (%)
PMMA 363 (Unreinforced)	3.40 ± 0.07	73.60 ± 0.28	8.13 ± 0.72
Silica/PMMA **PMMA 364 (0.5%)** **PMMA 365 (2.0%)**	 3.33 ± 0.10 3.37 ± 0.05	 72.64 ± 0.25 70.28 ± 0.21	 5.52 ± 0.48 6.95 ± 1.10
Nanoclay/PMMA **2.0%** **2.0% (poor dispersion)** **4.0%**	 3.46 ± 0.14 3.58 ± 0.08 3.70 ± 0.03	 Not measured	 Not measured

- **Loading has minimal effect on tensile strength/modulus**
- **Strain-to-failure sensitive to small changes in loading**

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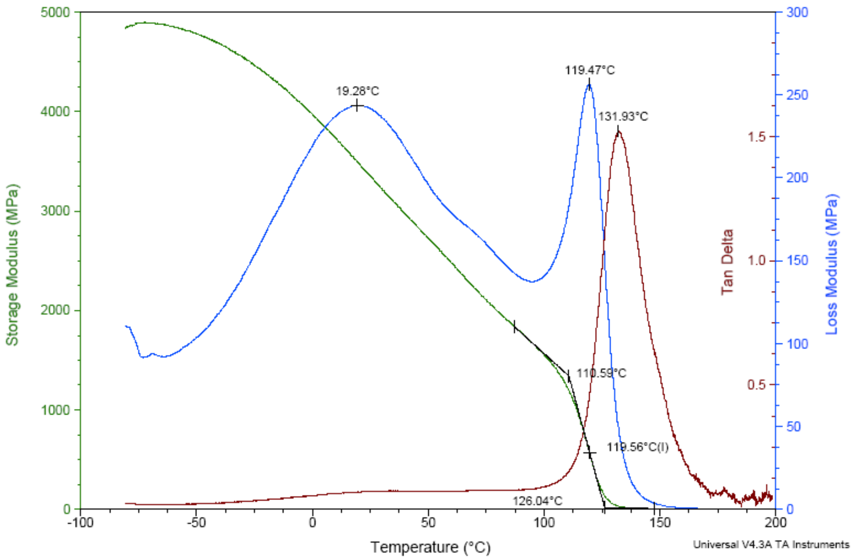
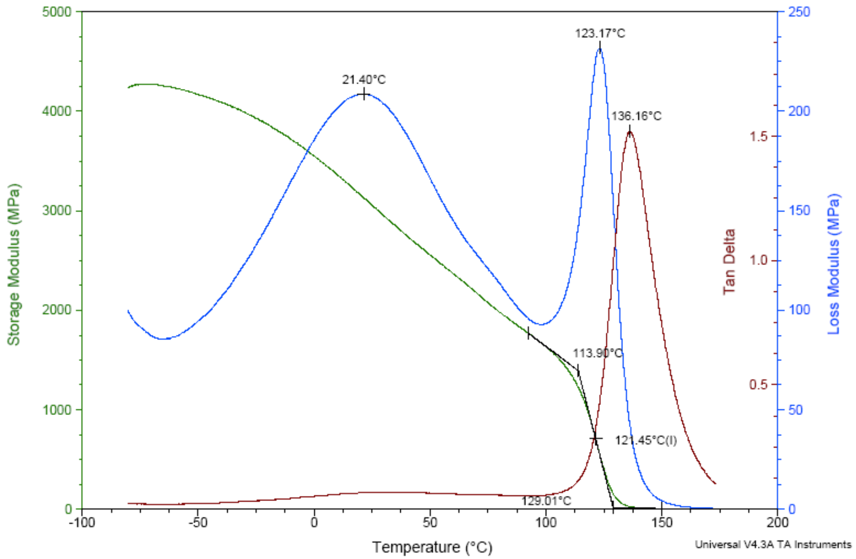
DMA Results – Silica/PMMA Glass Transition Temperature (T_g)





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

- Tg higher with addition of silica nanoparticles

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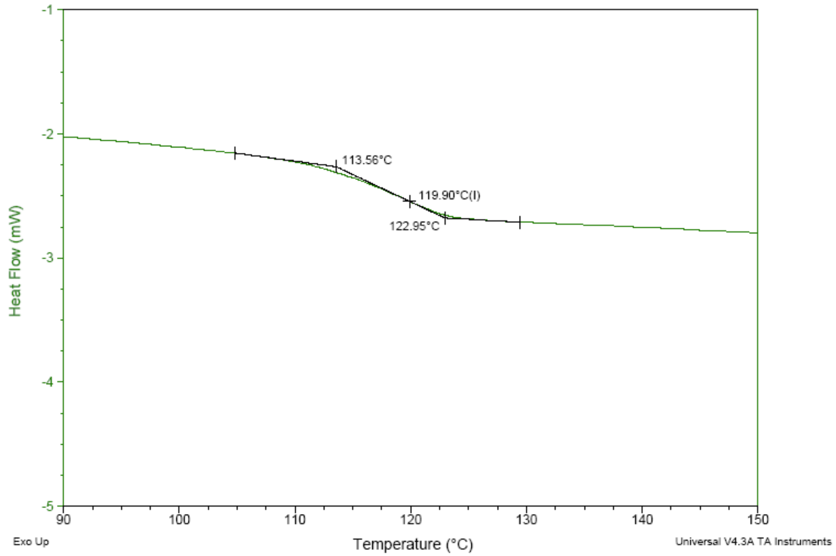
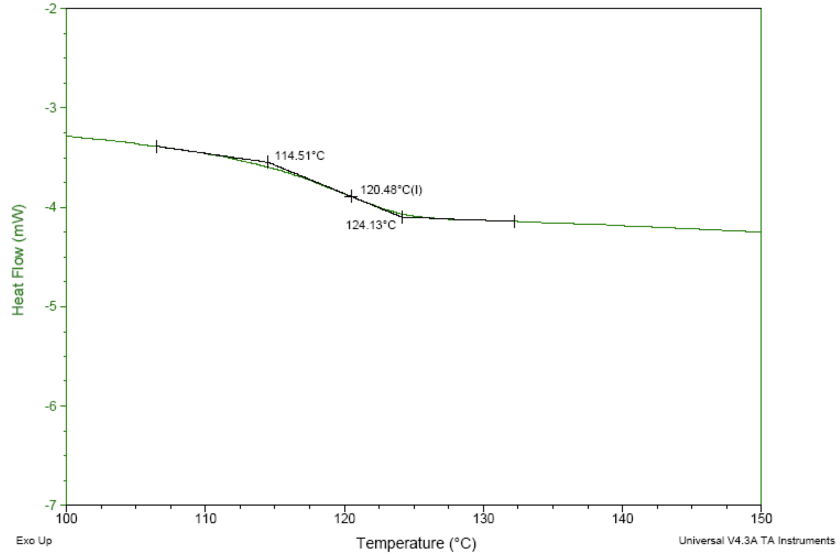
DSC Results – Silica/PMMA
Glass transition Temperature (T_g)





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

Tg relatively unaffected by addition of silica nanoparticles

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

Material	T_g (°C) DMA	T_g (°C) DSC
PMMA 363 (Unreinforced)	126.1	117.8
Silica/PMMA		
PMMA 364 (0.5%)	126.1	120.9
PMMA 365 (2.0%)	119.9	116.7
Nanoclay/PMMA		
2.0%	116.5	111.1
2.0% (poor dispersion)	115.3	109.9
4.0%	118.5	108.6

- **Data interpretation difficult due to uncertainty in measurements**

Thank you for listening

Any Questions?

Case Studies?