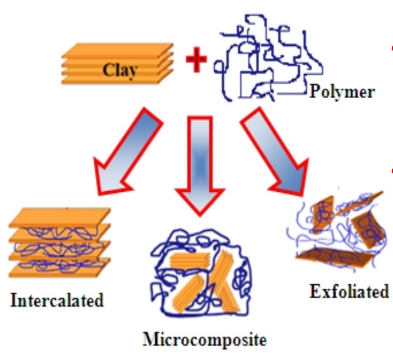
On-line Monitoring of Nanocomposite/Biomaterials Compounding for Process Optimization

Dr Marion McAfee

Polymers Cluster

School of Mechanical and Aerospace Engineering

Nanocomposites - potential and challenges

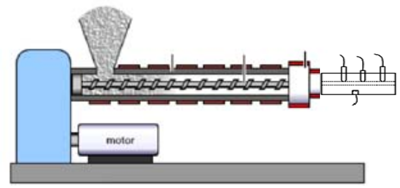


- In 2004 it was predicted that market for nanocomposites would grow at a rate of 76% per year
- Despite intense research effort there are to date a modest number of commercial applications

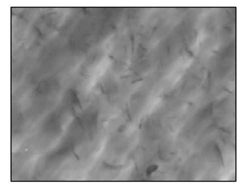
- Various methods of nanocomposite production – melt mixing of greatest commercial interest
- Majority of research effort focussed on polymer/clay interface chemistry
- Effect of processing/scale-up has more recently been recognised as a major factor in commercial success but is not well understood

Why on-line monitoring?

- Degree of clay dispersion depends on extruder/mixer design and processing parameters
- Off-line characterisation is time-consuming and expensive



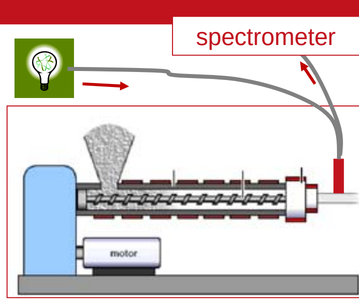
- Recent investigations into on-line monitoring solutions (Optical; Fluorescence; IR; Ultrasound; Dielectric)
- Effect of degradation, intercalation, exfoliation on sensor responses is not yet well understood

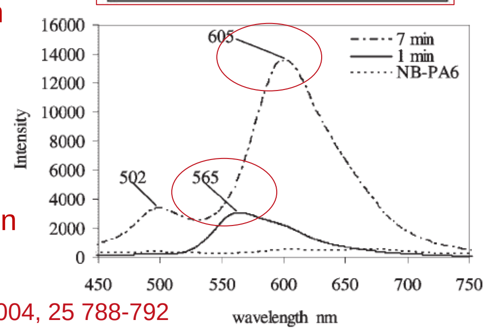


TEM image

Fluorescence Monitoring

- Clay is doped with Nile Blue fluorescent die
- Fluorescence is quenched at high concentrations and in nano-confinement
- As exfoliation occurs, die escapes - emission spectrum evolves with the extent of exfoliation
- Sensitivity to intercalation and exfoliation
- Useful for in-depth evaluation of mixing – not suitable in production

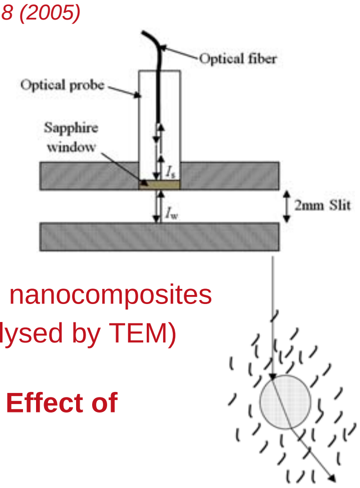




Maupin et al. Macro. Mol. rapid comms 2004, 25 788-792

Optical Transmission Monitoring

- Presented by Bur et al. *Polymer, 46, 10908-10918 (2005)*
- Optical probe carries light from source into the melt;
  Reflects off base of die and reflected signal is collected by return fibers
- Intensity of reflected signal is measured by photon counting
- Higher light transmission achieved with the nanocomposites exhibiting greater extent of exfoliation (analysed by TEM)

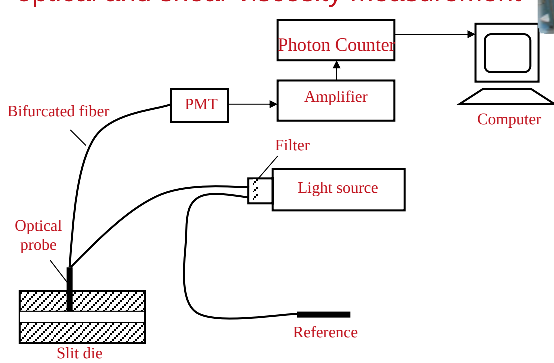


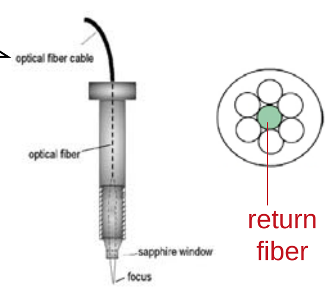
Effect of changes in screw speed/temp? Effect of degradation?

Aim here to assess optical transmission and in-line rheology as suitable tools for process optimisation

Experimental

- Nylon 6 loaded with various mass fractions of Cloisite 20A at different processing conditions
- 25mm Single Screw Extruder instrumented with a slit die for on-line optical and shear viscosity measurement





Processing Trials

Single Screw Extrusion (SSE)

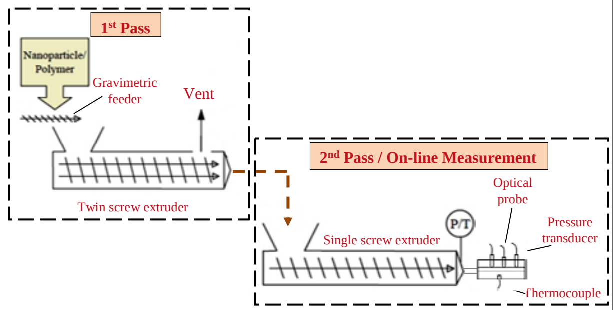
- 25mm Killion KTS-100
- 2%; 4%; 6% mass fraction – each run at 40; 65 and 90rpm

Pre-compounding in TSE

•Dr. Collin 25mm co-rotating

•2%; 4%; 6%

•150rpm at temp profile 210 °-240°

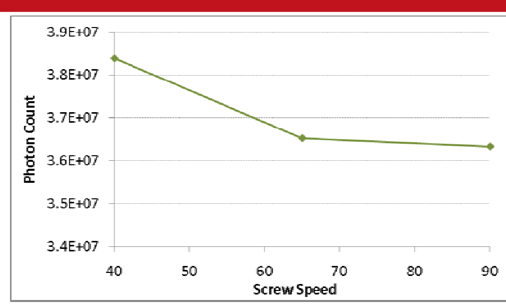


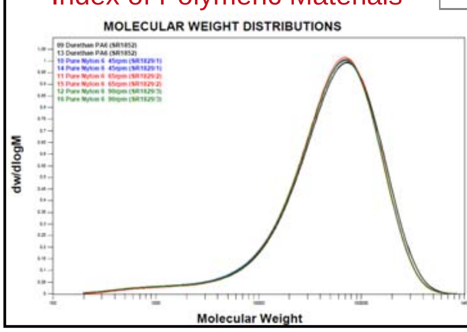
Temperature (°C)	Barrel			Clamp ring	Adapter 1	Adapter 2	Slit Die
	Zone 1	Zone 2	Zone 3				
SSE (single pass)	205	220	235	240	245	250	250
SSE (pre-compounded in TSE)	205	220	235	235	235	240	240

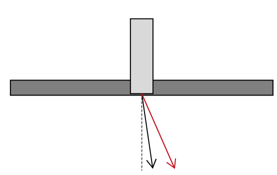
Optical transmission pure polymer

Pure Nylon

- Optical Transmission decreases 40-65rpm
- No sig change in Mw
- Changes in temp & stress levels affect the Refractive Index of Polymeric Materials



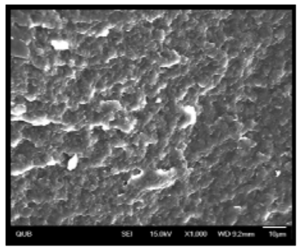




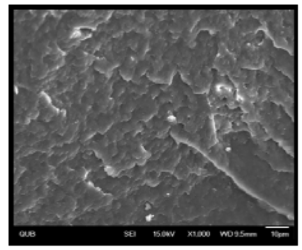
SSE - Off-line Characterisation

2% clay

- Significant decrease in agglomerates from 40rpm to 90rpm from x1000 SEM micrographs

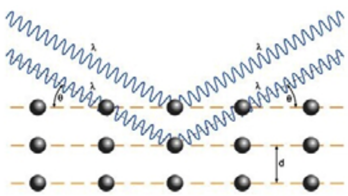


40rpm



90rpm

d-spacing examined by XRD



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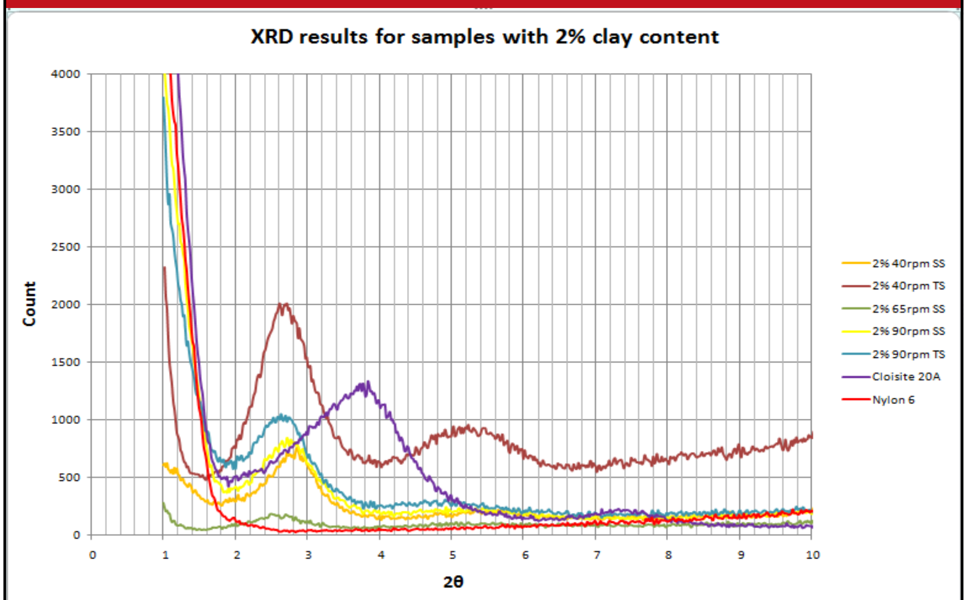

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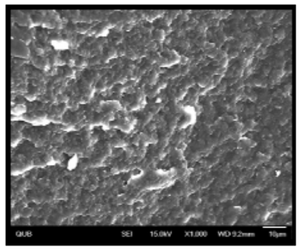
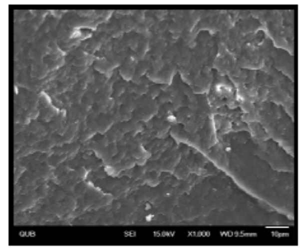


40rpm



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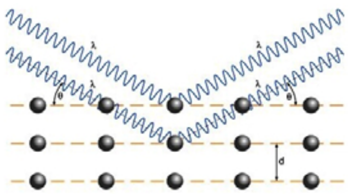


d-spacing of Cloisite 20A = 2.30 nm

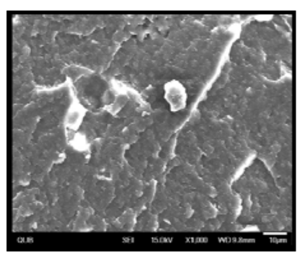
Screw Speed	d-spacing
40 rpm	3.09 nm
65 rpm	**3.53 nm**
90 rpm	3.25 nm

Lowest peak height

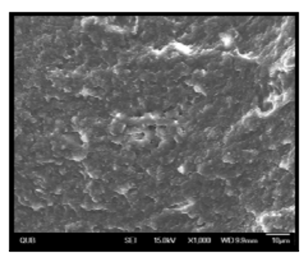
SSE - Off-line Characterisation

6% clay

- Significant decrease in agglomerates from 40rpm to 90rpm from x1000 SEM micrographs



40rpm



90rpm

d-spacing of Cloisite 20A = 2.30 nm

d-spacing of 6% clay

•Little change with screw speed

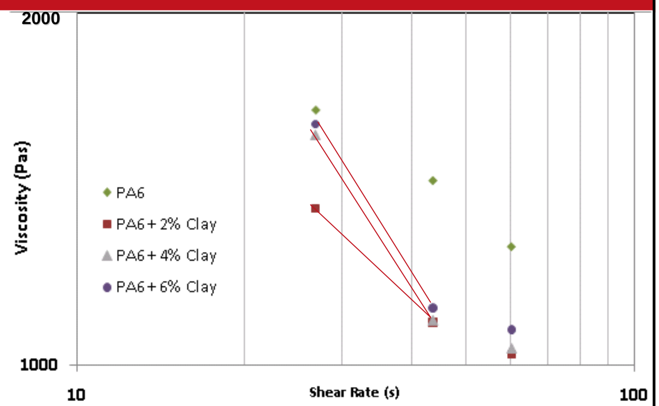
•slightly higher at 65rpm

Screw Speed	d-spacing
40 rpm	3.21 nm
65 rpm	3.23 nm
90 rpm	3.22 nm

Lowest peak height

SSE On-line results

- Optical Transmission – sig. changes between 40 and 65rpm
- Major changes in dispersion efficiency? Supported by XRD
- Viscosity decreases on addition of clay but increases with mass fraction

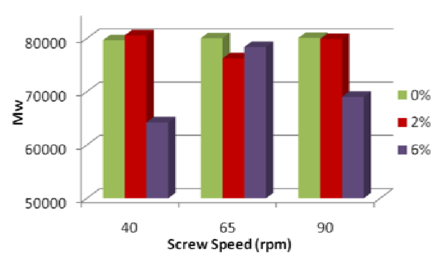


- Dramatic decrease in viscosity 40 – 65 rpm
  - reduction in agglomerates?
  - consequence of greater exfoliation?
  - degradation?

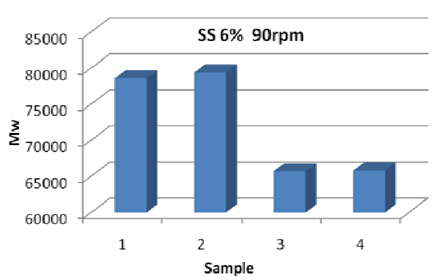
Molecular Weight Analysis

GPC for determination of M_w

- Slight decrease in Mw of 2% sample at 65rpm – may be contributing to viscosity changes
- Large reduction in Mw of 6% samples – but not at 65rpm!



$M_{w\ of}$ SSE samples



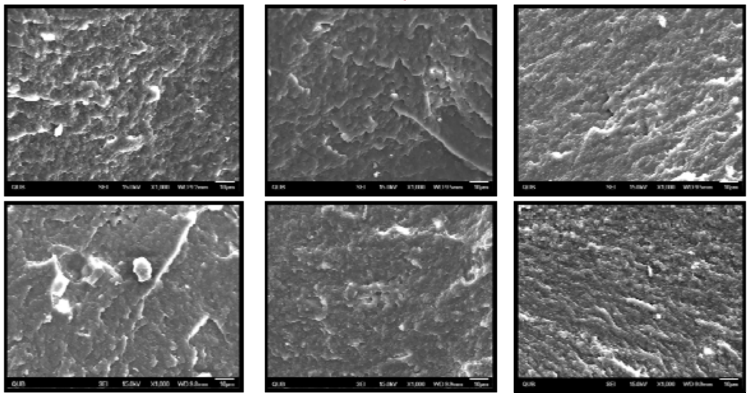
Further analysis of 6% 90rpm sample

- Two samples M_w equal to pure sample
- Two samples molecular weight sig. Lower (slightly higher than for 40rpm)
- Two distinct mechanisms – not a

TSE – Off-line Characterisation

SSE 40rpm | SSE 90rpm | TSE 90rpm

2% / 6%



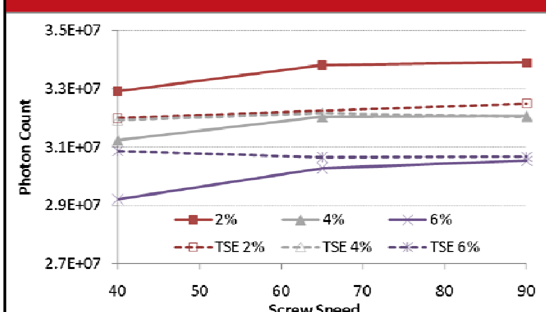
d-spacing

Cloisite 20A = 2.30 nm

Greater peak heights

(nm)	40 rpm	90 rpm
2%	3.37	3.35
4%	3.22	3.23
6%	3.06	3.26

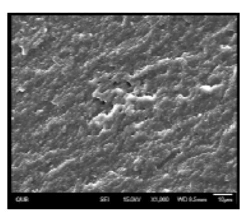
TSE – Online Results



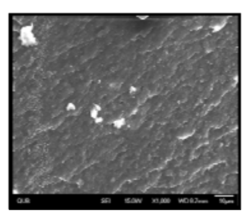
- For each mass fraction little change in light intensity
- 2%- lower light signal than SSE

Evidence of reagglomeration in second pass through SSE:

Greater degradation



2% TSE before 2nd Pass

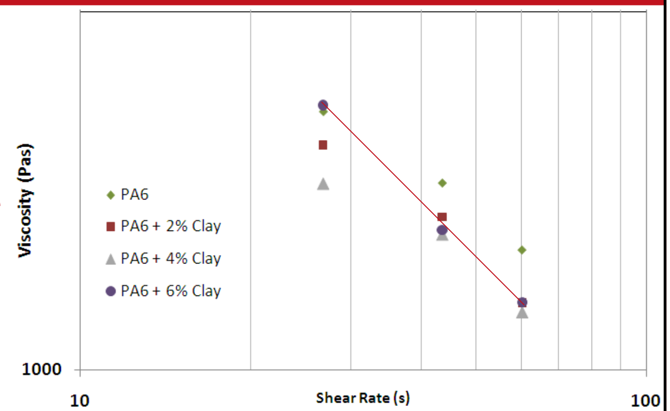


2% TSE after 2nd Pass at 90rpm

TSE – Online Results

In-line rheology closer to power law behaviour

- For 2% & 4% (little change in d-spacing)



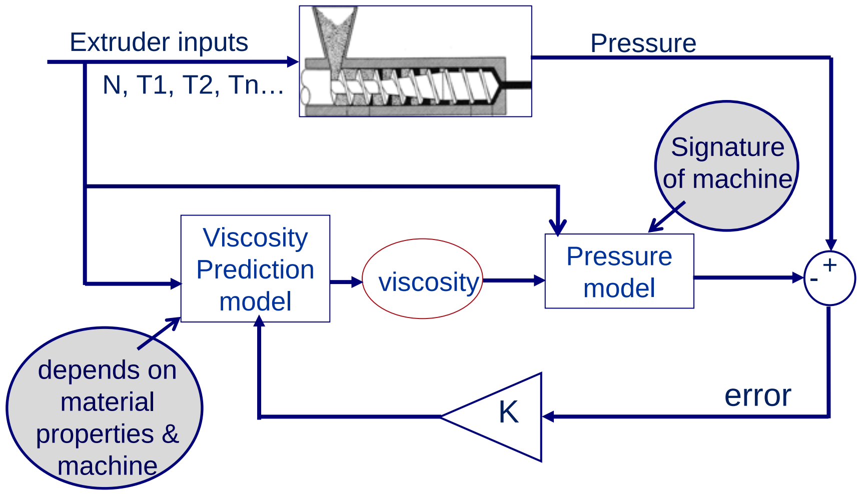
- 6% shows much higher ‘shear thinning’
  - Changes in structure at different conditions
  - Enhancement of d-spacing from 40rpm to 90rpm

Summary of findings

- Reflected light intensity sensitive to agglomerate break-up – correlates well with XRD and SEM analysis.

  Not capable of ‘absolute’ measurement
- In-line rheology showed significant decrease in viscosity with enhanced intercalation and reduced agglomeration – unclear mechanism
- Both techniques capable of identifying changes in conditions which led to significant changes in composite structure in real-time
- Modelling the effect of processing parameters on the quality of the composite is also necessary for process optimisation and control

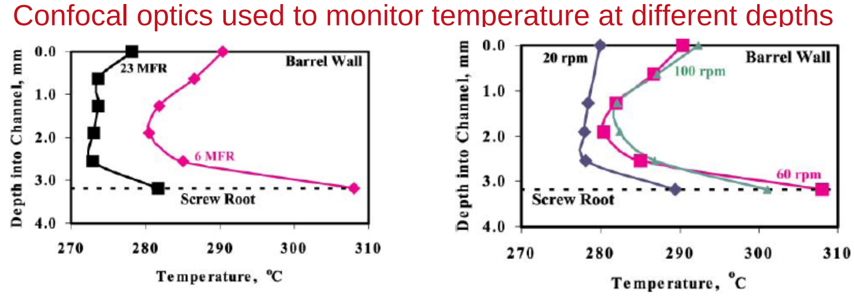
Viscosity 'Soft Sensor' Strategy



Low cost indicator of degradation

Monitoring and Control of Thermal Stability

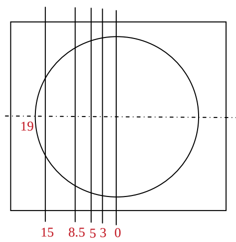
- Temperature control extremely important in biomaterial processing
- Large variations can exist in melt temp profile in extrusion/injection moulding – undetected by conventional instrumentation
- Temp-sensitive fluorescent probe used to investigate in-barrel temp profile
- Confocal optics used to monitor temperature at different depths



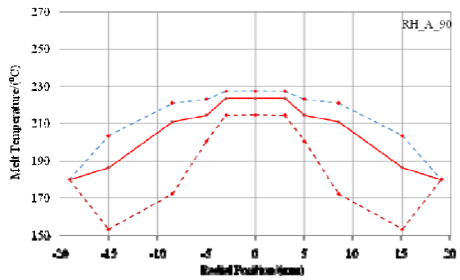
Bur et. Al, Polym Eng. Sci 2004, 44, 2148-2157

Monitoring and Control of Thermal Stability

- Interested in determining process settings to optimize rate with thermal stability
- Using thermocouple mesh to model effect of process settings and material properties on thermal profile



Thermocouple mesh
Applied before die



130	155	170	180	180	180	180

Temporal variations ±25deg

m.mcafee@qub.ac.uk

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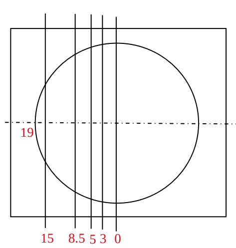

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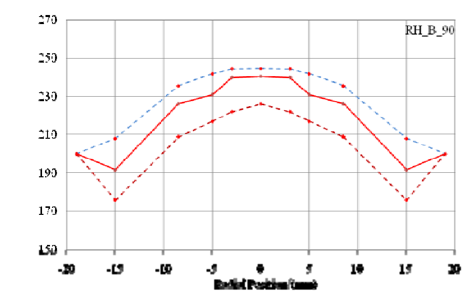

140	170	185	200	200	200	200

Temporal variations ±15deg

m.mcafee@qub.ac.uk

Applications

- Identifying industrially feasible solutions to process optimization in high-value areas
  - In manufacture of nanocomposites
  - In extrusion processing of medical devices with stringent quality specifications
  - In processing of degradation-prone biomaterials
  - Can be developed to apply to other processes

m.mcafee@qub.ac.uk

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m.mcafee@qub.ac.uk