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

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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

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*

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**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°

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Barrel Zone 1</th>
<th>Barrel Zone 2</th>
<th>Barrel Zone 3</th>
<th>Clamp ring</th>
<th>Adapter 1</th>
<th>Adapter 2</th>
<th>Slit Die</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSE (single pass)</td>
<td>205</td>
<td>220</td>
<td>235</td>
<td>240</td>
<td>245</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>SSE (pre-compounded in TSE)</td>
<td>205</td>
<td>220</td>
<td>235</td>
<td>235</td>
<td>240</td>
<td>240</td>
<td></td>
</tr>
</tbody>
</table>

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

**d-spacing examined by XRD**

<table>
<thead>
<tr>
<th>Screw Speed</th>
<th>d-spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 rpm</td>
<td>3.09</td>
</tr>
<tr>
<td>65 rpm</td>
<td>3.53</td>
</tr>
<tr>
<td>90 rpm</td>
<td>3.25</td>
</tr>
</tbody>
</table>

\[ d\text{-spacing of Cloisite 20A} = 2.30 \text{ nm} \]
SSE - Off-line Characterisation

2% clay
- Significant decrease in agglomerates from 40rpm to 90rpm from x1000 SEM micrographs

\[ \text{d-spacing examined by XRD} \]

\[
\begin{array}{|c|c|}
\hline
\text{Screw Speed} & \text{d-spacing} \\
\hline
40 \text{ rpm} & 3.09 \text{ nm} \\
65 \text{ rpm} & 3.53 \text{ nm} \\
90 \text{ rpm} & 3.25 \text{ nm} \\
\hline
\end{array}
\]

\text{d-spacing of Cloisite 20A = 2.30 nm}

Lowest peak height

SSE - Off-line Characterisation

6% clay
- Significant decrease in agglomerates from 40rpm to 90rpm from x1000 SEM micrographs

\[ \text{d-spacing of 6\% clay} \]

\[
\begin{array}{|c|c|}
\hline
\text{Screw Speed} & \text{d-spacing} \\
\hline
40 \text{ rpm} & 3.21 \text{ nm} \\
65 \text{ rpm} & 3.23 \text{ nm} \\
90 \text{ rpm} & 3.22 \text{ nm} \\
\hline
\end{array}
\]

\text{d-spacing of Cloisite 20A = 2.30 nm}

\text{Little change with screw speed}
\text{slightly higher at 65rpm}

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

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

<table>
<thead>
<tr>
<th></th>
<th>SSE 40rpm</th>
<th>SSE 90rpm</th>
<th>TSE 90rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% d-spacing</td>
<td>3.37 nm</td>
<td>3.35 nm</td>
<td></td>
</tr>
<tr>
<td>6% d-spacing</td>
<td>3.22 nm</td>
<td>3.23 nm</td>
<td></td>
</tr>
<tr>
<td>6% d-spacing</td>
<td>3.06 nm</td>
<td>3.26 nm</td>
<td></td>
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</table>

Cloisite 20A = 2.30 nm
Greater peak heights

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**

- Extruder inputs: N, T1, T2, Tn...
- Pressure
- Viscosity Prediction model
- Viscosity
- Pressure model
- Signature of machine
- K

Low cost indicator of degradation

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**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

• 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

Temporal variations ±25deg

130 155 170 180 180 180 180

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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

Temporal variations ±15deg

140 170 185 200 200 200 200

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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

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