Characterisation of the flow properties of filled materials and update on standards

Polymeric Materials IAG
Wednesday 12 March 2008

Martin Rides & Crispin Allen

H4 - Flow properties of filled materials (2005-08)
U4: Dynamic properties of solid/liquid materials systems at the nano and micro-scale (2005-08)
Outline

• Introduction
• Melt flow rate testing – moisture sensitive materials
• Piezoelectric device for rheometry
• Rheology of fast curing filled systems
• Gels
• Summary / future work
H4: Flow properties of filled materials

Project objectives:

• development of the Melt Flow Rate method for moisture sensitive materials (e.g. PET, PBT, nylon) to avoid the need for solvent-based testing

• development of Melt Flow Rate precision and uncertainty statements in support of ISO standardisation activities, through intercomparison

• evaluation of the use and capability of innovative piezoelectric devices, to facilitate rheological measurement and improved process monitoring

• development of new/improved measurement methods/procedures for monitoring flow properties of filled materials, with particular emphasis on mixing/compounding processes (mix quality)
Developments in rheology standards

ISO TC 61 (Plastics) SC5 (Thermophysical properties) WG9 (Rheology) - Chairman

Represent UK interests in the revision of ISO rheological standards and the drafting of new standards

- Melt flow rate (MFR/MVR) – ISO 1133
- Capillary extrusion rheometry – ISO 11443
- Extensional viscosity (tensile drawing method) – ISO 20965
- Drawing characteristics of molten thermoplastics (fibre-spinning method) – ISO 16790
- Oscillatory rheometry - ISO 6721-10
- Pressure-volume-temperature (pVt) – ISO 17744
Potential future developments in standards in rheology

- On-line viscosity measurement
- Rotational rheometry
  - Calibration of, steady shear, creep/stress relaxation
- TAPPI Method 702
  - Rheological measurements for characterization of polyolefins: Low Density Polyethylene (LDPE) for extrusion coating
- Short-die MVR/MFR for extensional characterisation
- Determination of no-flow temperature
- Others – your say
ISO 1133 Melt mass-flow rate (MFR) and melt volume-flow rate (MVR)

Recently revised (published 2005):
- Incorporation of additional die (half normal length and half normal diameter) to enable higher MFR/MVR value materials (MFR>75) to be measured
- Removal of dead-weight specification
- Revised temperature tolerances

Future revisions:
- Moisture sensitive materials (Part 2)
- Preparation of a consolidated charge
- Possible inclusion of short die (extensional measurement)
Melt flow rate testing for moisture sensitive materials

Solution:
Greater control on time-temperature history occurring during test.

Plastics — Determination of the melt mass-flow rate (MFR) and the melt volume-flow rate (MVR) of thermoplastics — Part 1: Standard method

Plastics — Determination of the melt mass-flow rate (MFR) and melt volume-flow rate (MVR) of thermoplastic materials — Part 2: Method for materials sensitive to time-temperature history and/or moisture

This International Standard specifies a procedure for the determination of the melt volume-flow rate (MVR) of thermoplastic materials that exhibit a high rheological sensitivity to the time-temperature history experienced by the sample during the test and/or moisture.

Examples of these materials are:

- Materials affected by hydrolysis or condensation, e.g. PET, PBT, PAs.
- Materials affected by crosslinking and/or other phenomena.
Intercomparison on MVR and MFR testing of moisture sensitive materials – in support of development of ISO 1133

<table>
<thead>
<tr>
<th>Material</th>
<th>Grade</th>
<th>MVR/MFR test conditions</th>
<th>Drying requirement (required maximum moisture level)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP – A</td>
<td>Polypropylene</td>
<td>2.16 kg, 230 °C</td>
<td>Not applicable</td>
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<tr>
<td>PBT – E</td>
<td>Fibre–filled poly(butylene terephthalate)</td>
<td>2.16 kg, 250 °C</td>
<td>150 ppm (0.015%)</td>
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<tr>
<td>PET – B</td>
<td>Poly(ethylene terephthalate)</td>
<td>5 kg, 280 °C</td>
<td>50 ppm (0.005%)</td>
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<tr>
<td>PA6(1) – C</td>
<td>Polyamide 6</td>
<td>1.2 kg, 250 °C</td>
<td>300 ppm (0.03%)</td>
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<tr>
<td>PA6(2) – D</td>
<td>Filled polyamide 6</td>
<td>5 kg, 275 °C</td>
<td>300 ppm (0.03%)</td>
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<tr>
<td>PA66 – F</td>
<td>Polyamide 66</td>
<td>2.16 kg, 275 °C</td>
<td>300 ppm (0.03%)</td>
</tr>
</tbody>
</table>

Relevant to ALL rheological testing of moisture sensitive materials
<table>
<thead>
<tr>
<th>Lab ref.</th>
<th>MVR</th>
<th>MFR</th>
<th>MFR cut-off</th>
<th>Instrument</th>
<th>Temperature compliant (1133-2)</th>
<th>Moisture measurement y/n</th>
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<tbody>
<tr>
<td>1</td>
<td>Yes</td>
<td>-</td>
<td>-</td>
<td>Gottfert 011.5</td>
<td>not reported at 0mm, &lt;= 0.2°C, not reported at 0mm (230°C)</td>
<td>EN ISO 15512/B</td>
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<tr>
<td>2</td>
<td>Yes</td>
<td>Yes</td>
<td>automatic</td>
<td>UNIBS (MODULAR MELT FLOW TESTER)</td>
<td>&lt;= 0.6°C (230°C)</td>
<td>ISO 15512/C</td>
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<tr>
<td>4</td>
<td>Yes</td>
<td>Yes</td>
<td>automatic</td>
<td>Zwick 4106.01-00</td>
<td>&lt;=0.4°C (only 230°C reported)</td>
<td>No</td>
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<td>5</td>
<td>Yes</td>
<td>-</td>
<td>-</td>
<td>Goettfert 98 MI Robot</td>
<td>&lt;=1°C (230°C)</td>
<td>No</td>
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<tr>
<td>6</td>
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<td>Göttfert MPS - D</td>
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<td>ISO 15512, method B</td>
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<td>7</td>
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<td>Yes</td>
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<td>MFR/MVR TESTER</td>
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<td>-</td>
<td>Goettfert MI4/20188</td>
<td>&lt;=0.2°C, not reported at 0mm (300°C)</td>
<td>Karl-Fischer-Titration</td>
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<tr>
<td>9</td>
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<td>Manual</td>
<td>Toyo Seiki Seisaku-sho Ltd.</td>
<td>&lt;=0.4°C (230°C)</td>
<td>Karl Fischer Coulometric titration method</td>
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<td>Yes</td>
<td>Manual</td>
<td>J1</td>
<td>&lt;0.4°C, not reported at 0mm (230°C)</td>
<td>Karl Fischer Coulometric titration method</td>
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<td>11</td>
<td>Yes</td>
<td>Yes</td>
<td>Manual</td>
<td>J1</td>
<td>&lt;0.4°C, not reported at 0mm (230°C)</td>
<td>Karl Fischer Coulometric titration method</td>
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<tr>
<td>13</td>
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<td>Yes</td>
<td>-</td>
<td>12148 (Zwick 4106-200)</td>
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<td>Mettler HG53 Halogen Moisture analyser</td>
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<td>-</td>
<td>CEAST 7027.000</td>
<td>&lt;=0.2°C, not measured at 0mm and 70mm (230°C)</td>
<td>Karl Fischer</td>
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<tr>
<td>16</td>
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<td>Yes</td>
<td>automatic</td>
<td>Goettfert MI4/20188</td>
<td>reported meets specification: no data presented</td>
<td></td>
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<tr>
<td>18</td>
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<td>-</td>
<td>Goettfert Type MI-4</td>
<td>&lt; 0.3°C at 230C, 250C &amp; 275C</td>
<td>Coulometric ISO 15512</td>
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<tr>
<td>19.0</td>
<td>Yes</td>
<td>Yes</td>
<td>automatic</td>
<td>CEAST 7023000</td>
<td>&lt;=1.7°C, not measured at 60mm and 70mm (250°C)</td>
<td>Karl-fisher at 180°C</td>
</tr>
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<td>19.5</td>
<td>Yes</td>
<td>-</td>
<td>-</td>
<td>GOTTFERT MPS/E</td>
<td>&lt;=1°C, &lt;= 0.9°C at 0mm (275°C) at least 0.6°C</td>
<td>Karl-fisher at 180°C</td>
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<td>20</td>
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<td>Yes</td>
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<td>046TF51 ATSFAAR MEP2/PC</td>
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<td>ISO 15512 C</td>
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<td>TINIUS &amp; OLSEN - MP993</td>
<td>&lt;=2.8°C, not measured at 0mm and 70mm (230°C)</td>
<td>Karl-fisher</td>
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<td>Yes</td>
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<td>-</td>
<td>Ray Ran 5 series</td>
<td>&lt;=4.1°C (230C)</td>
<td>mass loss</td>
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<td>Yes</td>
<td>automatic</td>
<td>Zwick Mflow</td>
<td>&lt;= 0.4°C (230°C)</td>
<td>No</td>
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<tr>
<td>25.5</td>
<td>Yes</td>
<td>Yes</td>
<td>automatic</td>
<td>Zwick 4106</td>
<td>&lt;= 1.0°C (230°C)</td>
<td>No</td>
</tr>
</tbody>
</table>
MVR intercomparison results - PP

All data

A - PP unfilled, 230 °C, 2.16 kg

MVR, cc/10 mins

Max temperature variation, °C
MVR intercomparison results - PBT

![Graph showing MVR intercomparison results for PBT with data points and error bars.](image-url)
MVR intercomparison results - PBT

All data

E - PBT filled, 250 °C, 2.16 kg

MVR, cc/10 mins

Max temperature variation, °C

Lab No.
MFR intercomparison results - PBT

All data

E - PBT filled, 250 °C, 2.16

Moisture content, %

MFR, g/10 mins
MFR intercomparison results - PBT

All data

E - PBT filled, 250 °C, 2.16 kg

MFR, g/10 mins

Max temperature variation, °C

Lab No.

Average
Moisture sensitivity of MVR/MFR intercomparison results - PBT

![Graph showing the relationship between moisture content, % and scaled MVR or MFR. The graph includes a red dashed line indicating the drying requirement.](image-url)
MVR intercomparison results - PET

![Graph showing MVR results for PET samples.](image-url)
MVR intercomparison results - PET

![Graph showing MVR intercomparison results for PET samples. The graph includes data points for MVR (in cc/10 mins) and Max temperature variation (°C) across different lab numbers.](image)
MFR intercomparison results - PET

![Graph showing MFR intercomparison results for PET with moisture content and lab numbers plotted.](image)
MFR intercomparison results - PET

B - PET unfilled, 280 °C, 5 kg

Max temperature variation, °C
Moisture sensitivity of MVR/MFR intercomparison results
- PET

Scaled MVR or MFR

Moisture content, %

Drying requirement

MFR - PET

MFR - PET

0 0.005 0.01 0.015 0.02 0.025 0.03 0.035 0.04 0.045 0.05

0 0.5 1 1.5 2 2.5 3 3.5 4

Moisture content, %

Scaled MVR or MFR
Effect of temperature on PET - MVR

Temperature sensitivity ≈ 5 %/°C
MVR intercomparison results – PA6(1)

C - PA6(1) unfilled, 250 °C, 1.2 kg
MVR intercomparison results – PA6(1)

C - PA6(1) unfilled, 250 °C, 1.2 kg
MFR intercomparison results – PA6(1)

C - PA6(1) unfilled, 250 °C, 1.2 kg

MFR, g/10 mins

Moisture content, %
MFR intercomparison results – PA6(1)

C - PA6(1) unfilled, 250 °C, 1.2 kg
Moisture sensitivity of MVR/MFR intercomparison results – PA6(1)
MVR intercomparison results – PA6(2)

All data

D - PA6(2) filled, 275 °C, 5

Moisture content, %

MVR, cc/10 mins

Lab No.

Average
MVR intercomparison results – PA6(2)

![Graph showing MVR intercomparison results for PA6(2). The graph includes data points for different labs, with labels for each lab number along the x-axis. The y-axis represents MVR, cc/10 mins, and the x-axis represents lab numbers. The graph also includes a section labeled 'All data' and another labeled 'D - PA6(2) filled, 275 °C, 5 kg.' There are error bars for each data point to indicate variability.]
MFR intercomparison results – PA6(2)

D - PA6(2) filled, 275 °C, 5
MFR intercomparison results – PA6(2)

All data

D - PA6(2) filled, 275 °C, 5 kg

Max temperature variation, °C

MFR, g/10 mins

Lab No.

Average
Moisture sensitivity of MVR/MFR intercomparison results – PA6(2)

Moisture content, %

Scaled MVR or MFR

Drying requirement

MFR - PA6(2)

MFR - PA6(2)
MVR intercomparison results – PA66

Average Lab No.

F - PA66 unfilled, 275 °C, 2.16 kg

MVR, cc/10 mins

Moisture content, %
MVR intercomparison results - PA66

All data

F - PA66 unfilled, 275 °C, 2.16 kg

MVR, cc/10 mins

Max temperature variation, °C

Average

Lab No.
MFR intercomparison results – PA66

All data

F - PA66 unfilled, 275 °C, 2.16 kg

Max temperature variation, °C
Moisture sensitivity of MVR/MFR intercomparison results – PA66

![Graph showing moisture sensitivity of MVR/MFR intercomparison results for PA66. The x-axis represents moisture content (%), and the y-axis represents scaled MVR or MFR. The graph includes data points for MFR - PA66 and a line indicating drying requirement.](image-url)
MVR intercomparison results

Analysis of MVR results with initial outliers removed

<table>
<thead>
<tr>
<th>Material</th>
<th>No. labs</th>
<th>Mean, m cm³/10 mins</th>
<th>Standard deviation, sr</th>
<th>Repeatability limit (2.8* sr)</th>
<th>Within laboratory</th>
<th>Between laboratories</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP - A</td>
<td>16</td>
<td>59.3 16</td>
<td>1.6</td>
<td>4.5</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>B PET</td>
<td>17</td>
<td>12.2 17</td>
<td>8.3</td>
<td>23.2</td>
<td>3.7</td>
<td>10.5</td>
</tr>
<tr>
<td>C PA6(1)</td>
<td>18</td>
<td>28.0 18</td>
<td>2.0</td>
<td>5.7</td>
<td>8.0</td>
<td>22.3</td>
</tr>
<tr>
<td>D PA6(2)</td>
<td>15</td>
<td>24.1 15</td>
<td>3.8</td>
<td>10.6</td>
<td>15.1</td>
<td>42.3</td>
</tr>
<tr>
<td>E PBT</td>
<td>17</td>
<td>19.6 17</td>
<td>2.3</td>
<td>6.3</td>
<td>4.9</td>
<td>13.8</td>
</tr>
<tr>
<td>F PA66</td>
<td>13</td>
<td>24.1 13</td>
<td>5.8</td>
<td>16.2</td>
<td>32.4</td>
<td>90.8</td>
</tr>
</tbody>
</table>
## MVR intercomparison results

Analysis of MVR results where method compliant with both moisture and temperature tolerance criteria

<table>
<thead>
<tr>
<th>Compliant data only</th>
<th>No. labs</th>
<th>MVR mean</th>
<th>Within laboratory</th>
<th>Between laboratories</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>cm³/10 mins</td>
<td>Standard deviation, ( s_r )</td>
<td>Repeatability limit (2.8* ( s_r ))</td>
</tr>
<tr>
<td>PP - A</td>
<td>9</td>
<td>58.6</td>
<td>1.4%</td>
<td>3.9%</td>
</tr>
<tr>
<td>B PET</td>
<td>5</td>
<td>12.17</td>
<td>4.4%</td>
<td>12.3%</td>
</tr>
<tr>
<td>C PA6(1)</td>
<td>4</td>
<td>26.24</td>
<td>1.2%</td>
<td>3.2%</td>
</tr>
<tr>
<td>D PA6(2)</td>
<td>6</td>
<td>21.66</td>
<td>3.1%</td>
<td>8.7%</td>
</tr>
<tr>
<td>E PBT</td>
<td>9</td>
<td>19.63</td>
<td>2.1%</td>
<td>6.0%</td>
</tr>
<tr>
<td>F PA66</td>
<td>4</td>
<td>18.93</td>
<td>3.4%</td>
<td>9.7%</td>
</tr>
</tbody>
</table>

|                     |          |          | Standard deviation, \( s_R \) | Repeatability limit (2.8* \( s_R \)) |
| PP - A              | 9        | 58.6     | 3.7%             | 10.2%                |
| B PET               | 5        | 12.17    | 30.9%            | 86.6%                |
| C PA6(1)            | 4        | 26.24    | 6.2%             | 17.2%                |
| D PA6(2)            | 6        | 21.66    | 9.9%             | 27.8%                |
| E PBT               | 9        | 19.63    | 5.8%             | 16.1%                |
| F PA66              | 4        | 18.93    | 18.8%            | 52.6%                |
### MVR intercomparison results

#### Analysis of MVR results where method compliant with both moisture and temperature tolerance criteria

<table>
<thead>
<tr>
<th>Compliant data only</th>
<th>No. labs</th>
<th>MVR mean</th>
<th>Within laboratory</th>
<th>Between laboratories</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>cm³/10 mins</td>
<td>Standard deviation, $s_r$</td>
<td>Repeatability limit (2.8*$s_r$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>PP - A</td>
<td>9</td>
<td>58.6</td>
<td>1.4</td>
<td>3.9</td>
</tr>
<tr>
<td>B PET</td>
<td>5</td>
<td>12.17</td>
<td>4.4</td>
<td>12.3</td>
</tr>
<tr>
<td>C PA6(1)</td>
<td>4</td>
<td>26.24</td>
<td>1.2</td>
<td>3.2</td>
</tr>
<tr>
<td>D PA6(2)</td>
<td>6</td>
<td>21.66</td>
<td>3.1</td>
<td>8.7</td>
</tr>
<tr>
<td>E PBT</td>
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<td>6.0</td>
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<td>F PA66</td>
<td>4</td>
<td>18.93</td>
<td>3.4</td>
<td>9.7</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Ratio, compliant / all excluding outliers</th>
<th>Ratio, mean</th>
<th>Ratio, repeatability limit</th>
<th>Ratio, reproducibility limit</th>
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<tbody>
<tr>
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<td>0.99</td>
<td>0.98</td>
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<tr>
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<td>C PA6(1)</td>
<td>0.94</td>
<td>0.57</td>
<td>0.77</td>
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<td>0.90</td>
<td>0.82</td>
<td>0.66</td>
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<tr>
<td>E PBT</td>
<td>1.00</td>
<td>0.95</td>
<td>1.17</td>
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<tr>
<td>F PA66</td>
<td>0.79</td>
<td>0.60</td>
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</table>
MVR/MFR intercomparison results

MFR repeatability and reproducibility values - with initial outliers removed

<table>
<thead>
<tr>
<th>MFR (outliers removed)</th>
<th>No. labs</th>
<th>Mean, m g/10 mins</th>
<th>Standard deviation, sr %</th>
<th>Repeatability limit (2.8* sr) %</th>
<th>Standard deviation, sR</th>
<th>Repeatability limit (2.8*sR) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>PP - A</td>
<td>8</td>
<td>43.4</td>
<td>2.2</td>
<td>6.2</td>
<td>7.4</td>
<td>20.8</td>
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<tr>
<td>B PET</td>
<td>10</td>
<td>15.0</td>
<td>9.1</td>
<td>25.5</td>
<td>20.7</td>
<td>57.9</td>
</tr>
<tr>
<td>C PA6(1)</td>
<td>8</td>
<td>26.3</td>
<td>3.2</td>
<td>9.0</td>
<td>9.6</td>
<td>26.7</td>
</tr>
<tr>
<td>D PA6(2)</td>
<td>9</td>
<td>33.9</td>
<td>3.8</td>
<td>10.5</td>
<td>15.2</td>
<td>42.5</td>
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<tr>
<td>E PBT</td>
<td>12</td>
<td>26.3</td>
<td>2.2</td>
<td>6.0</td>
<td>5.8</td>
<td>16.1</td>
</tr>
<tr>
<td>F PA66</td>
<td>9</td>
<td>28.7</td>
<td>6.2</td>
<td>17.3</td>
<td>40.7</td>
<td>114.0</td>
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</tbody>
</table>
Summary of intercomparison results – MVR and MFR testing

95% confidence limits quoted

- **MVR** temperature sensitivity up to 5 %/°C (for PET)

- PP repeatability and reproducibility limits (ex. outliers):
  - 5% and 13% repeatability for **MVR**
  - 7% and 21% **reproducibility** for MFR

- For moisture sensitive materials, not compliant to ISO 1133-2:
  - **MVR** repeatability varies from 6% to 24%
  - **MVR** reproducibility varies from 14% to 91%
  - MFR repeatability varies from 6% to 26%
  - MFR reproducibility varies from 16% to 114%

- For moisture sensitive materials, compliant to ISO 1133-2:
  - **MVR** repeatability varies from 4% to 13%
  - **MVR** reproducibility varies from 17% to 87%
Summary of intercomparison results – MVR and MFR testing

- PET and PA66 highly sensitive to moisture content.
- PBT and PA6s less sensitive to moisture content.
- Decreasing the value for the temperature tolerance (to $\pm 0.5 \degree C$) and limiting the moisture value (material specific) resulted in lower repeatability and reproducibility limit values, but still greater than that for PP.
- PET rapid moisture pick up from atmosphere.
- Contribution of moisture content to measurements indicated.
- Sample preparation and handling prior to and during MVR/MFR measurements potentially very significant source of error.
A piezoelectric device for rheological measurement

Applications:
in-situ measurement,  
quality control

Additional equipment:  
Impedance analyser,  
Origin curve fitting software
Results for glycerol and a range of Newtonian oils

\[ y = 1.497E-18 x + 1.801E-17 \]

Viscosity, mPa.s

- Newtonian oils, resonant peak 1
- Glycerol
- Air
Characterisation of fast-curing systems by capillary extrusion rheometry

Disposable extrusion rheometer
Rheological testing of filled curing systems

Average viscosity error: 2% for 500 Pa.s reference oil

Constant load extrusion test

Clear indication of application time

60 N load
FM07: Characterisation of gels

Monitoring mass transport through gel-like materials

Biomedical Applications:
• Tissue regeneration (as tissue scaffold)
• Drug delivery
• Diagnostics

Characteristics
• Biocompatibility
• Ease of fabrication
• Low cost

Desired properties
• High permeability
• Cell attachment and growth
• Mechanical support

Characterisation of viscoelastic properties of the gel under defined conditions
  – effect of different level of cross-linking
  – effect of concentration
  – effect of gel type (physical or chemical)

Significant drying out of specimen
  – use of solvent trap essential

Significant slip at gel-plates is considered to occur
  – assessing forming gels in-situ

‘slow’ cool  ‘fast’ cool
Abstract

The ISO committee ISO TC61/SC5/WG 9 Plastics Melt Rheology is responsible for developing standards on polymer melt rheology in ISO, covering melt flow rate, capillary extrusion, extensional viscosity and pvT testing.

Currently only ISO 1133 on the measurement of melt flow rate properties is being revised. It is being developed so that it can also be used for testing moisture sensitive materials that degrade at the testing conditions.

Potential proposals for new work items include standardisation of in-process rheological measurements and calibration of oscillatory and rotational rheometers.
Abstract

The current melt flow rate method as described in ISO 1133 (1) does not adequately cover the measurement of materials that degrade or further polymerise at the melt flow rate test conditions. Materials such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), polyamide 6 (PA6) and polyamide 66 (PA66) tend to degrade at processing temperatures if they contain excessive amounts of absorbed water, sometimes rapidly. This will result in poor repeatability and reproducibility of melt flow rate results. The ISO Plastics Melt Rheology committee (ISO TC61/SC5/WG 9) is currently developing a modified melt flow rate method for reliable measurement of moisture sensitive materials thereby providing an alternative to intrinsic viscosity measurements. The modified method controls more tightly the time-temperature history experienced by the material and thus the resultant variability in measured properties due to degradation. Results for a moisture sensitive material, poly(ethylene terephthalate) (PET), are presented demonstrating the effect of moisture content and temperature on measurements. Repeatability of measurements of melt flow rate using a non-optimised handling procedure was up to 10% (1 standard deviation). This poor level of repeatability was considered to be due to moisture absorption during handling of the sample whilst charging the instrument. The need to tightly control the sample preparation (e.g. drying) and sample handling procedures is highlighted as being critical to reliable rheological measurements of such materials.
INTERLABORATORY COMPARISON OF MELT FLOW RATE TESTING OF MOISTURE SENSITIVE PLASTICS

Martin Rides, Crispin Allen, Huub Omloo, Kazuo Nakayama and Gianpiero Cancelli

Abstract

The current melt flow rate method (ISO 1133) does not adequately cover the measurement of materials that degrade or further polymerise at the melt flow rate test conditions. Materials such as PET, PBT and PA containing absorbed water tend to degrade, sometimes rapidly, at processing temperatures. This will result in poor repeatability and reproducibility of melt flow rate results. The ISO Plastics Melt Rheology committee (TC61/SC5/WG 9) is currently developing a modified melt flow rate method for reliable measurement of moisture sensitive materials, e.g. PBT and PET, thereby providing an alternative to intrinsic viscosity measurements. The modified method controls more tightly the time-temperature history experienced by the material and thus the resultant variability in measured properties due to degradation. This paper presents the results of an interlaboratory comparison of testing of moisture sensitive polymers using the melt volume flow rate and melt mass flow rate methods.
ANALYSIS AND USE OF PIEZOELECTRIC CANTILEVERS FOR DETERMINATION OF THE RHEOLOGICAL PROPERTIES OF FLUIDS

Martin Rides, Feng Yan and Crispin Allen

Abstract

In-process measurement of the rheological properties of fluids can provide very valuable information for process monitoring and control. However, obtaining an acceptable solution for in-process measurement can be difficult. Piezoelectric devices can potentially provide a solution for in-process monitoring; their small size and low cost being particular advantages. This paper evaluates the use of small-scale PZT1 piezoelectric cantilevers for measuring the rheological properties of a range of fluids.

The PZT piezoelectric cantilever is excited by a dynamic voltage over a range of frequencies using an impedance analyser. At frequencies near a resonant frequency of the cantilever the electrical conductance and capacitance of the piezoelectric device change, with the conductance reaching a peak at the resonant frequency. When the cantilever is surrounded by a fluid, the fluid modifies the resonant behaviour of the cantilever. A model has been developed to relate the resonant behaviour, described by the capacitance-frequency and conductance-frequency curves, to the viscosity of the surrounding medium.

Results of investigations using the piezoelectric cantilever as a rheological sensor are reported. The piezoelectric device was calibrated using known viscosity reference liquids. It has been demonstrated that the device can operate over at least seven decades in viscosity. Issues of repeatability and sensitivity of measurements and the use of different resonant modes will be discussed along with results on a range of materials.
THE USE OF THE MELT FLOW RATE METHOD FOR MOISTURE SENSITIVE MATERIALS AND AN EVALUATION OF THE UNCERTAINTIES IN MELT FLOW RATE MEASUREMENT

Martin Rides and Crispin Allen

NPL REPORT MAT 3, SEPTEMBER 2007

Abstract

The current melt flow rate method (ISO 1133) does not adequately cover the measurement of materials that degrade or further polymerise at the melt flow rate test conditions. Materials such as PET, PBT and PA containing absorbed water tend to degrade, sometimes rapidly, at processing temperatures. This will result in poor repeatability and reproducibility of melt flow rate results. The ISO Plastics Melt Rheology committee (TC61/SC5/WG 9) is currently developing a modified melt flow rate method for reliable measurement of moisture sensitive materials, e.g. PBT and PET, thereby providing an alternative to intrinsic viscosity measurements. The modified method controls more tightly the time-temperature history experienced by the material and thus the resultant variability in measured properties due to degradation. Results on a range of moisture sensitive materials are presented, demonstrating the effect of moisture content on measurements. Repeatability of measurements of melt flow rate were up to 10% (1 standard deviation). The need to tightly control the sample preparation (e.g. drying) and sample handing procedures is considered critical to reliable measurements of such materials. Furthermore, an evaluation of the uncertainties in the measurement using the current ISO 1133 is reported and recommendations for improved measurements are made.
Abstract
The extrusion properties of highly filled, curing systems are difficult to characterise due to both their highly filled nature and the fact they are time dependant. These can result in complex flow behaviour that includes slip phenomena and rapidly increasing viscosity with time. This paper reports on the development of a disposable extrusion rheometer suitable for curing systems, and presents results obtained in both controlled rate and controlled stress measurement modes. The results of oscillatory rheometry testing on the curing, filled system are also reported.
Polymers

NPL's Polymers research activity develops and promotes good measurement practice to provide accurate, quantitative properties data for an extensive range of materials and properties. Improved measurement practices and models for predicting materials behaviour will enable industry to develop reliable design procedures and manufacturing processes, and thus produce reliable fit-for-purpose products in a more efficient and economical way.

Materials and products investigated include thermoplastics, thermosetting plastics, thermoplastic elastomers, rubbers, oils, cements, suspensions, slurries, paints, gels, foams, foods and biomaterials. The materials properties investigated are relevant to the many stages of the product lifecycle, for example from materials qualification and specification, through product and manufacturing process design, to the prediction of lifetime performance.

A significant and growing emphasis of the work is on the development of reduced length-scale measurement technology and measurements for nano-particle filled materials, with increasing emphasis on micro-processing technologies.

For more information: Martin Rider

Polymers research

Polymer Degradation
NPL is seeking to increase the use of plastics in more demanding environments through the development and standardisation of new test methods.

Characterising Interfaces in Continuous and Dispersed Materials
NPL aims to provide industry methods for measuring interfacial properties and dispersion, suitable for production and maintenance purposes, and for determining structure-property relationships.

Polymer Rheology
Reliable characterisation of the rheological behaviour of materials is important for the development of new materials, design of processes, and for quality control of materials in production.

Modelling Heat Transfer in Polymer Processing
Modelling can help predict cycle times in injection moulding, which can cut manufacturing costs.
Summary

- Standards – your input to standardisation welcome.

- MVR/MFR intercomparison for moisture sensitive materials – repeatability and reproducibility quantified.

- New disposable extrusion rheometry technique for filled curing systems – demonstrated in controlled load and rate modes for bone cement: average error 2% for viscosity of 500 Pa.s oil.

- Oscillatory rheometry of gels – slippage at interface significant issue.

- Piezoelectric device for rheological measurement demonstrated for Newtonian and viscoelastic fluids.
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ISO TC61 SC5 WG9 members

http://www.npl.co.uk/server.php?show=nav.600