Flow Properties of Filled Materials and Standards Update

Martin Rides
18 April 2007

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
- Characterisation of filled materials
- Piezoelectric devices for rheological measurements
- Rheology of fast curing filled systems
- Rheological standards in ISO
- Summary / future work
- Gels
The flow behaviour of multi-phase/filled materials can be complex

Multi-phase materials exhibit flow behaviours that are difficult to characterise, but are often essential to their processability, e.g.:

- extreme shear thinning (e.g. thixo-casting, foods)
- slip (e.g. plastics extrusion, biomedical materials)

The reliable measurement of the flow behaviour of multi-phase is relevant to many industrial sectors and is important to, for example:

- materials design, selection, quality control (mix quality)
- process modelling (design, optimisation)
- reducing scrap rates and time to market
H4: Flow properties of filled materials

Project objectives:

- development of new/improved measurement methods/procedures for monitoring flow properties of filled materials, with particular emphasis on mixing/compounding processes *(mix quality)*

  RAPRA – supply of nano-composite samples / mix quality

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

- 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
Investigation of thermal and rheological techniques for assessing mix quality

Thermal:
  Differential Scanning Calorimetry (DSC) measurement of crystallisation behaviour and Tg

Rheological:
  Dynamic rheological measurements

Case studies
Thermal and rheological characterisation of filled materials (PP + CNT)
Thermal and rheological characterisation of filled materials (PP + Cloisite)

Crystallisation:
- 114.83°C
- 116.62°C
- 114.71°C
- 116.29°C
- 115.29°C
- 116.19°C

Melting:
- 165.25°C
- 165.97°C
- 165.63°C
- 165.35°C
- 166.04°C
- 164.24°C

Cooling

Heating

Melting
DSC test data of nylon 6 unfilled (blue) and nano-clay filled (pink) materials at 5°C/min, 20°C/min and 80°C/min cooling rates.
H4: Flow properties of filled materials

Industrial input:
e.g. materials, industrial trials, equipment

Measurements for dispersion

Rheometry, T_g, other

Case studies:
Compounding for nano-fillers, micro-moulding

Simple QC / inline techniques

Your input
to steer the project to maximise the benefits to you
A piezoelectric device for rheological measurement

Crispin R.G. Allen

IAG
18 April 2007
Characterisation of fast-curing systems by capillary extrusion rheometry

Disposable extrusion rheometer
Rheological testing of filled curing systems

example viscosity values (Pa.s)
glycerol - 1
liquid honey - 10
golden syrup - 100
molten polymer - 1000

Oscillatory rheometry data using controlled strain and controlled stress modes of operation.
Rheological testing of filled curing systems

Effect of extrusion rate on measured extrusion force and increase in required force with time
Rheological testing of filled curing systems

Normalised extrusion forces for various extrusion rates (providing similar magnitude values from 150 s to 200 s) to provide scaling rule

\[ y = 1.9778x^{0.4813} \]
\[ R^2 = 0.9781 \]

Shift factor for extrusion force compared with that obtained for a piston speed of 0.33 mm/s
Rheological testing of filled curing systems

Comparison of extruder and oscillatory rheometer measurements of a filled curing system
International standards activities on rheological measurement of plastics

http://www.npl.co.uk/materials/polyproc/iso.html

Next ISO TC61 meeting to be held in September 2008
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

- Acquisition and presentation of comparable multipoint data: Thermal and processing properties – ISO 11403-2
- ISO guide for the acquisition and presentation of design data for plastics - ISO 17282
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
- inclusion of novel NPL test features
Melt flow rate testing for moisture sensitive materials

Application:
- PET, PBT, PEN, Nylons, other polyesters

Problems:
- hydrolysis
- low viscosity (high MVR)
- air entrapment problem and consequences (especially with recyclate, e.g. flake)
- greater sensitivity to thermal history

Avoidance of intrinsic viscosity measurement
- ISO 1628-5 Determination of the viscosity of polymers in dilute solution using capillary viscometers
  – Part 5: thermoplastic polyester (TP) homopolymers and copolymers
- Benefits in time, cost, not requiring toxic / hazardous solvents
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. poly (ethylene terephthalate) (PET), poly (butylene terephthalate) (PBT), poly (ethylene naphthalate) (PEN), other polyesters and polyamides.
Materials affected by crosslinking and/or other phenomena.
Melt flow rate testing: potential developments

Sample preparation:

Related problem for recycled polymer, flakes, film, shredded product samples, e.g. PET bottles (low bulk density).

Pre-forming of charge using cylinder (9.55 mm diameter) under vacuum.

- Temperature 241 °C +/- 1 °C
- Load 1.5 kN +/- 0.5 kN
- Charge 6 g to 10 g sample

Specification of barrel and piston sizes

Currently:
- ISO - relative specification between each
- ASTM – absolute specification on each

Is this a problem?
Limits and uncertainties in MFR testing

![Graph showing limits and uncertainties in MFR testing](image)

- Blue: resolution limit
- Red: imposed constraint
- Black: chosen range
- Purple: 3 measurements limit

Current ISO 1133 constraints
Fahrenholz proposal
ASTM D1238
0.02
0.05
0.1
0.15
0.4
0.5
1
5
10
20
50
75
100
200
500
1640

Time constraint
Upper piston travel constraint
Distance resolution
3 test time constraint
240 s limit
3 piston movement constraint
Method A constraint ext length
Time resolution
Distance resolution
MFR minimum extrudate length
Freefall time limit

Measurement time vs. Piston displacement, mm

Method A constraint ext length

Limits in MFR testing
Limits and uncertainties in MFR testing

MFR values for given time and displacement values
Limits and uncertainties in MFR testing

![Graph showing uncertainties in MFR testing]
Melt flow rate testing for moisture sensitive materials

**Intercomparison:**

To provide precision data and statement to ISO 1133-1 and ISO 1133-2 for both current and moisture sensitive parts

Materials: PET, PBT, PA6, PA66, PE

Led by NPL

Participants welcomed
Potential future developments in standards in rheology

- Rotational rheometry
  - calibration of, steady shear, creep/stress relaxation
- On-line viscosity measurement
- Short-die MVR/MFR for extensional characterisation
- Determination of no-flow temperature
- Other? – your say
Summary

• Crystallisation behaviour shows most promise of thermal techniques for differentiating filled materials
• Industrial input for case studies being developed

• Assessment of piezoelectric device for rheological measurement has identified potential capability of technique

• ISO standardisation of MVR/MFR testing of moisture sensitive materials progressing – intercomparison imminent
FM07: Characterisation of gels

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

Monitoring mass transport through gel-like materials
Gels

Porous network of interconnected molecules spans the volume of a liquid medium

- Wet (>90% water content)
- Soft
- Undergo large deformation in response to environment change

‘slow’ cool

‘fast’ cool
The polymer network which can be formed by chemical bonds or by physical aggregation with region of local order acting as network junctions.

- **Physically aggregated gels**
  - poly(vinyl alcohol) gel
  - agar and agarose gel (show heat reversible transition)

- **Chemical linked gel**
  - Alginate crosslinked with divalent cations (Ca$^{2+}$) or cationic polymer (chitosan)
  - Collagen gel crosslinked with gluteraldehyde
Gelling of agar (heat)

Random coil → Heat (thermal agitation) → Helix formation

Formation of junction points of the chains
Gelling of alginate (cations)

Ca\(^{2+}\)
• 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)
Gel viscoelasticity - shear moduli $G'$ & $G''$

Shear storage $G'$ or loss $G''$ modulus, Pa

- 2% Alginate, $G'$
- 2% Alginate, $G''$
- 1% Agar $G'$
- 1% Agar $G''$

37 ºC
Oscillatory testing of gels

• Measurements performed at 37ºC.
• Significant drying out of specimen
  – use of solvent trap essential
• Significant slip at gel-plates is considered to occur
  – assessing forming gels in-situ
• Gels predominantly elastic
• Further development of technique planned
Next twelve months

- Technical / industrial case studies on mix quality
- Further explore use of thermal and rheological techniques for evaluating dispersion quality (case studies)
- Further assessment of small-scale rheological devices (viscoelastic fluids, reduction in size issues)
- Progress standardisation of moisture sensitive MVR/MFR method
- Intercomparison on MFR/MVR in support of standards activity
Polymer Processing

Welcome to the Home page of the Polymer Processing Team

The team focuses on the development of measurement technologies to assist manufacturers and users of plastics materials and products.

- Industrial Advisory Group Meetings
- Next Polymer Processing IAG meeting
  Date: Wednesday 25th October 2006.
  Location: UK Space Centre, Leicestershire.
  For directions to the Space Centre: please use this link
  If you would like to receive an invitation to this meeting please contact: Lydia Solomon
  Date: Wednesday 25th November 2006.
- Next Polymer Performance IAG meeting
  Date: Wednesday 25th November 2006.
  Please use this link
- Progress on International Standards (ISO committee reports) Updated 10th November 2005

Current Projects:
- Heat Transfer in Polymer Processing (H1) (94Kb)
- Flow Properties of Filled Materials (H4) (104Kb)

For further information about these projects please contact: Martin Rides

Recent DTI-Funded Projects:

http://www.npl.co.uk/materials/polyproc/
http://www.npl.co.uk/materials/polyproc/

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