State of the Art of Rheology of Concentrated Suspensions

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Composites Manufacturing and Simulation Center, Purdue University
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Current Projects and Titles-2017

- Numerical simulation of injection molding of long fiber thermoplastic composites (American Chemical Council)
- Benign processing of polymers using water or super-critical carbon dioxide-PAN (ORNL/DOE)
- Generation of sustainable composites based on thermoplastics reinforced with TLCP’s, rod-like molecules; automotive applications, and H2 storage (SRNL/DOE)
- Role of processing on the burst behavior of polyethylene pipes and tubing (Lyondell-Basell).
- High performance materials for use in additive manufacturing/3-D printing (NAI/NASA, 1 position)
- Polymer composites from plants (hemp) (2 positions)
- Novel polymer blends for removal of cancer cells in blood (BioTherapeutics/NIH)
Outline

• Motivation
  • Long fiber-reinforced plastic composites
  • Mechanical properties and manufacturing

• Background
  • Orientation models
  • Stress tensor
  • Fiber flexibility
  • Rheological testing: Shear and Extension

• Non-lubricated Squeeze Flow
  • Stress Growth
  • Orientation Evolution

• Conclusions & Future Plans
Objectives

• Develop a rheological test that will induce fiber flexing
  • Allows for testing of semi-flexible models
• Generate experimental stress growth data
  • Ultimate goal is to obtain orientation model parameters through stress-fitting
  • Currently obtain parameters by fitting to orientation data
  • Tedious and labor-intensive
Motivation: Mechanical Properties

Orientation Effects

<table>
<thead>
<tr>
<th>System (glass/epoxy)</th>
<th>Strength ($10^3$ psi)</th>
<th>Stiffness ($10^3$ psi)</th>
<th>Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled resin</td>
<td>10-12</td>
<td>0.3-0.4</td>
<td>0</td>
</tr>
<tr>
<td>Spherical particles</td>
<td>9-10.5</td>
<td>1.5-1.7</td>
<td>0.50</td>
</tr>
<tr>
<td>Short fiber (transverse)</td>
<td>5.5</td>
<td>1.4</td>
<td>0.50</td>
</tr>
<tr>
<td>Short fiber (longitudinal)</td>
<td>40</td>
<td>4.5</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Length Effects

Top Down

50 wt% Nylon 6,6

0% W and 10% L
Unidirectional orientated fiber bundles

Long Fiber Thermoplastics retain the ability to be injection-molded

Widely Used in Industry & Suitable for Fiber Thermoplastic Composites
- Rapid & Automatic
- Repeatability & Geometrical Complexity
Two issues/facts of IM Long Fiber Thermoplastic Composites

- Flow induced variable orientation (Mold Cavity)

Center gated disk

3~4 distinguishable layers:

<table>
<thead>
<tr>
<th>Region</th>
<th>Orientation</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Skin</td>
<td>Random in r$\theta$ plane</td>
<td>Thermal + Fountain</td>
</tr>
<tr>
<td>Shell</td>
<td>Flow Aligned</td>
<td>Shear flow</td>
</tr>
<tr>
<td>Transition</td>
<td>No preferential</td>
<td>Shear &amp; extension</td>
</tr>
<tr>
<td>Core</td>
<td>Transverse to flow</td>
<td>Extensional flow</td>
</tr>
<tr>
<td>Transition</td>
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Factors Affecting Properties in Injection Molding

- Fiber Breakage (Broad Distribution)

Nguyen, 2008
Huq and Azaiez, 2005
Background: Orientation

\[ A = \int pp\psi(p, t) dp \]
\[ A_4 = \int pppp\psi(p, t) dp \]

Background: Orientation Dynamics

\[
\frac{DA}{Dt} = \alpha \left( (W \cdot A - A \cdot W) + \xi (D \cdot A + A \cdot D - 2D : A_4) \right) + 2C_1\gamma (I - 3A)
\]

Empirical Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)</td>
<td>Fiber slip relative to matrix</td>
</tr>
<tr>
<td>(C_1)</td>
<td>Fiber interactions</td>
</tr>
</tbody>
</table>


Semi-Flexible Fibers

\[ \frac{DA}{Dt} = \alpha \left[ W \cdot A - A \cdot W + \xi (D \cdot A + A \cdot D - 2D : A) + \frac{I_B}{2} (Cm + mC - 2(m \cdot C)A) + 2k (B - A tr (B)) \right] \]

\[ \frac{DB}{Dt} = \alpha \left[ W \cdot B - B \cdot W + \xi (D \cdot B + B \cdot D - (2D : A)B) - 4C_i \hat{B} + \frac{I_B}{2} (Cm + mC - 2(m \cdot C)B) + 2k (A - B tr (B)) \right] \]

\[ \frac{DC}{Dt} = \alpha \left[ \nabla v^t \cdot C - (A : \nabla v')C - 2C_i \hat{C} + \frac{I_B}{2} (m - C (m \cdot C)) - kC (1 - tr (B)) \right] \]

Hydrodynamic \quad IRD \quad Bending From Flow \quad Bending Potential

\[
A = \iint pp \psi(p, q, t) \, dp \, dq \\
B = \iint pq \psi(p, q, t) \, dp \, dq \\
C = \iint p \psi(p, q, t) \, dp \, dq \\
A_4 = \iint pppp \psi(p, q, t) \, dp \, dq
\]

\[
m = \sum_{i=1}^3 \sum_{j=1}^3 \sum_{k=1}^3 \frac{\partial^2 v_i}{\partial x_j \partial x_k} A_{jk} e_i
\]

\[
r = l_B (p - q)
\]

\[
R = \frac{\langle rr \rangle}{tr(rr)} = \frac{A - B}{1 - tr (B)}
\]
Coupling Orientation to Flow

Stress Equation for Rigid Fibers:
\[ \sigma = -P I + 2 \eta_m D + 2 \eta_m \phi (\mu_1 D + \mu_2 D : A_4) \]

Proposed Stress Equation for Semi-Flexible Fibers:
\[ \sigma = -P I + 2 \eta_m D + 2 \eta_m \phi (\mu_1 D + \mu_2 D : R_4) + \eta_m k \frac{3 \phi a_r}{2} (B - AtrB) \]

Matrix  Fibers

Matrix  Fibers  Fiber Bending

\[ k = \frac{E_y}{8 \eta_m} \left( \frac{1}{a_r} \right)^3 \]

Lipscomb et al. 1988, Ortman et al. 2012
Experiments


Model Parameter Obtaining

\[ \dot{v} \left( x_2 \right) = \dot{\gamma} \cdot x_2 \]

Startup of Simple Shear

Shear-free Flow
(Lubricated Squeeze Flow)

Giacomin, 1987
Dealy and Soong, 1984
\[ \nabla \cdot \mathbf{v} = 0 \quad \text{(Continuity)} \]
\[ \nabla \cdot \sigma = 0 \quad \text{(Momentum)} \]
\[ \sigma = -P \mathbf{I} + 2\eta \mathbf{D} \quad \text{(Stress)} \]
\[ \frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = 0 \quad \text{(Pseudo-concentration)} \]
Nonlubricated Squeeze Flow

\[ L_N = \frac{\sum N_i L_i}{\sum N_i} \]

\[ L_W = \frac{\sum N_i L_i^2}{\sum N_i L_i} \]

\[ L_Z = \frac{\sum N_i L_i^3}{\sum N_i L_i^2} \]
Both models predict noticeable drops of the values near the wall due to the fountain flow effect.

- Bead-Rod model shows improvement over the rigid model especially when the longest length parameters are used.
LGF Orientation Predictions in a EGP Parameters

Fitted to Experimental Data (Solid):
\[\alpha = 0.0039\]
\[C'_{I} = 0.4843\]
Fitted to Rheology (Dashed):
\[\alpha = 0.13\]
\[C'_{I} = 0.0530\]
Experiments

Shear

\[ \dot{\gamma} = 0.1 \text{ s}^{-1} \]

Planar Extension

\[ \dot{\varepsilon} = -0.05 \text{ s}^{-1} \]
Experiments

Rigid: Solid Line
Flexible: Dashed Line

\[ \dot{\gamma} = 0.1s^{-1} \]

- Bead-Rod
  - \( \alpha = 0.045 \)
  - \( C_1 = 0.055 \)
- Folgar-Tucker
  - \( \alpha = 0.11 \)
  - \( C_1 = 0.008 \)
Experiments

Rigid: Solid Line
Flexible: Dashed Line

Planar Extension

$\dot{\epsilon} = -0.05 \text{s}^{-1}$

Folgar-Tucker
$\alpha = 0.97$
$C_i = 0.01$

Bead-Rod
$\alpha = 0.95$
$C_i = 0.04$
## Background: Empirical Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Shear</th>
<th>Extension</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rigid</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.11</td>
<td>0.97</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.008</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Flexible</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.045</td>
<td>0.95</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.055</td>
<td>0.04</td>
</tr>
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Ongoing and Future Efforts

• Develop a test that will induce fiber flexing
  • Allows for testing of semi-flexible models

• Generate experimental stress growth data
  • Ultimate goal is to obtain orientation model parameters through stress-fitting
  • Currently obtain parameters by fitting to orientation data
    • Tedious and labor-intensive

• Identifying bending parameter through stress relaxation tests
Experimental: NLSF

- Combination of shear and extension
- Second-order velocity gradients
- Closure stress easily measured
NLSF Schematic

\[ w(H) = \dot{H}(t_0) \]

\[ z = +H(t_0) \]

\[ z = 0 \]

\[ w(H) = \dot{H}(t) \]

\[ z = +H(t) \]
Experimental: NLSF

\[
\begin{align*}
u(x, z, t) &= -6 \frac{\dot{H}}{H} x \left[ \left( \frac{Z}{H} \right) - \left( \frac{Z}{H} \right)^2 \right] \\
w(z, t) &= \dot{H} \left[ 3 \left( \frac{Z}{H} \right)^2 - 2 \left( \frac{Z}{H} \right)^3 \right] \\
P(x, z, t) &= 6\eta \frac{\dot{H}}{H} \left[ \frac{x^2}{H^2} + \frac{z}{H} - \frac{Z^2}{H^2} \right] + P_a
\end{align*}
\]

Nonlubricated Squeeze Flow

- Stress increases with fiber content
- Similar behavior in each case
- Increase from zero
  - GNF-based stress models cannot predict this

Error bars represent 95% CI
Experimental: Sample Prep

• Samples made of nozzle purge produced using the same conditions as injection-molded CGDs
• Testing Temperature: 200°C
• Constant Hencky Strain Rate: -0.50 s⁻¹
• Sample Dimensions
  ▪ 3.75 in (95.25 mm) wide
  ▪ 2 in (50.8 mm) long
  ▪ 7.50 mm thick
• Initial planar random fiber orientation
  ▪ Compression molded “unidirectional” strands
  ▪ 30 wt% Short Glass Fiber + Polypropylene (SABIC)
Experimental: Sample Prep

Through-Thickness Orientation Observation
Experimental: Sample Prep

- **Z** (thickness)
- **X** (flow)
- **Y**

Arrows indicating:
- **Minor**
- **Major**
- **Center**
Results: Orientation

Parameters from Startup of Simple Shear

Parameters from NLSF

## Results: Orientation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cieslinski et al.(^1) (simple shear)</th>
<th>NLSF(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)</td>
<td>0.20</td>
<td>1.00</td>
</tr>
<tr>
<td>(C_I)</td>
<td>0.005</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Results: Stress Growth

Parameters from Simple Shear

Parameters from NLSF

Conclusions

• Parameters in orientation models obtained from planar extension are different from those in shear flow.

• These parameters lead to a significant difference in the prediction of orientation distribution in an injection molded disk (center-gated) especially in the semi-flexible fiber model.

• Homogeneous flows tend to not test the bending contribution to stress and fiber orientation.

• Non-lubricated squeeze flow will potentially lead to a method for obtaining the parameters in the orientation models from basic flow properties.

• Existing stress tensors have a flaw in the startup of flow which needs to be addressed.
Future Work

• Obtain orientation data on samples subjected to non-lubricated squeeze flow
• Obtain orientation parameters in the Bead-Rod Model from this orientation data
• Compare the values obtained above with those obtained from fitting stress growth data and possibly stress relaxation data
• Use wet-layed prepared samples to control fiber length and minimize fiber breakage
Acknowledgements