Understanding print stability in material extrusion additive manufacturing of thermoset composites

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Understanding Print Stability in Material Extrusion Additive Manufacturing of Thermoset Composites

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Mohammed Islam
Michael Devinney
Dr. Chad E. Duty
Dr. Christopher J. Hershey
Dr. Brett G. Compton
Introduction – Direct ink writing

Direct ink writing (DIW)
- Subset of *material extrusion* additive manufacturing (AM)

Small-scale developments
- Bio-materials
- Elastomers
- Thermosets

Bio-materials

![Bio-materials](image)

Sun et al., *Advanced Materials*, 2012

Elastomers

![Elastomers](image)

Clausen et al., *Advanced Materials*, 2015

Thermoset composites

![Thermoset composites](image)

Hmeidat et al., *Compos Sci Technol*, 2018
Introduction – Large-scale thermoset DIW

Large-scale thermoset DIW
• Desirable characteristics
  • Extrusion does not require heat
  • Attractive mechanical properties
  • High thermal resistance
• Machine at Oak Ridge National Laboratory (ORNL)
• Limited by structural stability during printing

Fracture surface comparison

Rios et al., Mater. Today Commun., 2018
Background – Viscoelastic properties

Before cure, thermoset DIW inks
- Low specific stiffness

\[ E^{1/3}/\rho = 700 \]

\[ E^{1/3}/\rho = 160 \]
Background – Viscoelastic properties

Before cure, thermoset DIW inks
- Low specific stiffness
- Low specific strength
Background – Challenges

Collapse on small scale

Falling of thin walls

Image courtesy of Madeline Wimmer

Compton et al., JOM, 2017

Slumping of lower layers

Suiker, Int. J. Mech. Sci., 2018

Romberg, SAMPE J, 2019

Collapse on large scale

0.2 m

0.06 m
Background – Stability models

Buckling under self-weight
• Greenhill (1881)*
  • Inspired by the height capacity of trees
  • \( h_{column,b} = \left( 7.8373 \frac{E I}{\rho g A} \right)^{1/3} \)

Yielding under self-weight
• \( h_y = \frac{\sigma_y}{\rho g} \)
• Suiker (2018) – concrete print stability
  • Stiffening
  • Strengthening

*Greenhill predicted a maximum height of 300 feet for a pine tree with a 20-inch diameter
Hypothesis – Stability of DIW inks

Collapse of thermoset DIW walls is caused by self-weight and depends on 3 ink properties

- Density ($\rho$)
- Shear plateau storage modulus ($E$)
- Shear yield stress ($\sigma_y$)

\[ \sigma(z) = \rho g (h - z) \]
Stability tests – Setup

Nozzle diameters
- 0.404 mm
- 0.872 mm

Number of beads
- 1
- 2
- 3
- 6
- Enough to yield
- 1 image/layer
Approach – Material

Two epoxy-based systems
• Printed and cured properties can be filler dependent
• Nanoclay is more anisotropic than fumed silica
• Cross-polarized images highlight differences

Hmeidat, et. al., Compos Sci Technol, 2018

Cross-polarized transmitted light

Fumed silica-filled ink Nanoclay-filled ink

Transmitted light

Nanoclay filler

Fumed silica filler

Hmeidat, et. al., Addit. Manuf., in review 2020

Hmeidat, et. al., Compos Sci Technol, 2018
Approach – Material

Two epoxy-based systems
• Printed and cured properties can be filler dependent
• Nanoclay is more anisotropic than fumed silica
• Cross-polarized images highlight differences

• 10 wt% nanoclay (NC)
  • Garamite 7305
• 10 wt% fumed silica (FS)
  • Cab-o-sil TS-720

Without curing agent
• Minimize time-dependence

Hmeidat, et. al., Compos Sci Technol, 2018
Approach – Research plan

1. Rheology
   - $G'_p$ and $\tau_y$
   - Initial and recovered properties
Approach – Research plan

1. Rheology
   - $G'_P$ and $\tau_y$
   - Initial and recovered properties

2. Model wall height predictions
   - $G'_P \rightarrow$ Self-buckling
   - $\tau_y \rightarrow$ Self-yielding

![Graph of Nanoclay 10 wt% showing $G'_l$, $G'_R$, $\tau_{y,l}$, and $\tau_{y,R}$ vs. $t$ (mm)]
Approach – Research plan

1. Rheology
   • $G'_P$ and $\tau_y$
   • Initial and recovered properties

2. Model wall height predictions
   • $G'_P$ → Self-buckling
   • $\tau_y$ → Self-yielding

3. Print walls to assess model
Rheological tests

Extrusion may affect $G'_p$ and $\tau_y$

Oscillatory recovery studies
1. Began in linear viscoelastic region (LVR)
2. Ramped to a maximum stress
3. Held at maximum stress
4. Retraced stress back to LVR

Maximum stress
- Just past yield (lowest)
- Intermediate
- Before material loss (highest)

Time hold at each stress
- No hold
- 5-min hold
- 60-min hold

<table>
<thead>
<tr>
<th>Maximum stress</th>
<th>Nanoclay ink</th>
<th>Fumed silica ink</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowest max stress (Pa)</td>
<td>700</td>
<td>1200</td>
</tr>
<tr>
<td>Intermediate max stress (Pa)</td>
<td>1200</td>
<td>2000</td>
</tr>
<tr>
<td>Highest max stress (Pa)</td>
<td>2000</td>
<td>3000</td>
</tr>
</tbody>
</table>

40-mm upper platen
Peltier plate (22°C)
Rheological definitions

$G'_p$
- Averaged $G'$ in the LVR
Rheological definitions

$G'_P$
- Averaged $G'$ in the LVR

$\tau_y$
- $G'_P$ and post-yield fit intersection
Rheological definitions

\( G'_P \)
- Averaged \( G' \) in the LVR

\( \tau_y \)
- \( G'_P \) and post-yield fit intersection

\( G'_I \) and \( \tau_{y,I} \)
- Determined on the “initial curve”

\( G'_R \) and \( \tau_{y,R} \)
- Determined on the “recovered curve”
Rheological results – Nanoclay

Increased maximum stress decreases recovery

Recovery is dependent on shear history
  • Extrusion defines the shear history
Rheological results – Nanoclay

Holding at maximum stress decreases recovery
- Vertical drop at maximum stress

Again, recovery is dependent on shear history
- Extrusion defines the shear history
Rheological results – Nanoclay

Result: Array of potential material properties
Rheological results – Fumed silica

Nanoclay 10 wt%

Fumed silica 10 wt%
Rheological results – Fumed silica

Comparison to nanoclay:
- \( G' \) decreases
- \( \tau_y \) increases in modulus and in yield
- Loss upon recovery decreases
Rheological results – Time hold behavior

5 minutes – $G'$ is still decreasing

60 minutes – Near asymptotic behavior
• Most aggressive shear history
Rheological results – Time hold behavior

Hold at max stress - Nanoclay 10 wt%

Hold at max stress - Fumed silica 10 wt%
Rheological results – $G'_p$

Summary of oscillatory shear curves

$G'_p$ is inversely proportional to:
- Maximum stress
- Time held at maximum stress

1200 Pa returns the lowest recovered modulus
- Warrants further investigation
Rheological results – $G'_p$

For Nanoclay 10 wt%:
- Maximum stress (Pa): 700, 1200, 2000
- $G'_p$ values: 10
- Error band:
  - No hold
  - 5-min hold
  - 60-min hold

For Fumed silica 10 wt%:
- Maximum stress (Pa): 700, 1200, 2000
- $G'_p$ values: 10
- Error band:
  - No hold
  - 5-min hold
  - 60-min hold
Rheological results – $G'_P$

Nanoclay 10 wt%:
- Maximum stress (Pa): 700, 1200, 2000
- Error band
- No hold
- 5-min hold
- 60-min hold

Fumed silica 10 wt%:
- Maximum stress (Pa): 700, 1200, 2000
- Error band
- No hold
- 5-min hold
- 60-min hold
Rheological results – Model inputs

Rheological properties are used as wall height model inputs

<table>
<thead>
<tr>
<th>Material</th>
<th>$G'_I$ (Pa)</th>
<th>$G'_R$ (Pa)</th>
<th>$\tau_{y,I}$ (Pa)</th>
<th>$\tau_{y,R}$ (Pa)</th>
<th>$\rho$ (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoclay</td>
<td>76,282</td>
<td>11,990</td>
<td>393</td>
<td>80</td>
<td>1199</td>
</tr>
<tr>
<td>Fumed silica</td>
<td>38,040</td>
<td>12,080</td>
<td>944</td>
<td>360</td>
<td>1202</td>
</tr>
</tbody>
</table>
Model predictions

Buckling under self-weight

\[ \sigma(z) = \rho g (h - z) \]

Yielding under self-weight

*Greenhill predicted a maximum height of 300 feet for a pine tree with a 20-inch diameter*
Model predictions – Self-weight buckling

Self-weight column buckling height
- Greenhill 1881: $h_{c,b} = \left(7.8373 \frac{EI}{\rho g A}\right)^{1/3}$

Generalize column expression to plates
- Plane-strain modulus: $\tilde{E} = \frac{E}{1-\nu^2}$

Below yield, elastic behavior is assumed
- $G = G'$

Isotropy is assumed
- $E = 2G(1+\nu) = 2G'(1+\nu)$

Printed wall buckling height:

$$h_b = \left(7.8373 \left(\frac{G' t^2}{6\rho g}\right) \left(\frac{1+\nu}{1-\nu^2}\right)\right)^{1/3}$$
Model predictions – Self-weight yielding

- Yield height: \( h_y = \frac{\sigma_y}{\rho g} \)
- Rheological tests provide \( \tau_y \)
- Max shear (Tresca) yield criterion for uniaxial loading: \( \sigma_y = 2\tau_y \)
Model predictions – Results

Buckling at small thickness
- Red

Buckling or yielding at intermediate thickness
- Blue

Yielding at large thickness
- Green
Model predictions – Results

Yielding at large thickness

Nanoclay 10 wt%

Fumed silica 10 wt%
Stability tests – Data analysis

Image processing – onset of buckling
1. Identifies wall edges
2. Calculates wall thickness
3. Identifies the onset of buckling ($h_b$)

Full collapse ($h_u$) is defined when material is no longer deposited on the top of the wall.
Stability tests – Results

Nanoclay ink
- Data follows “Buckling ($G'_R$)” at low thickness
- Transitions to “Yielding ($\tau_{y,l}$)” around 13 mm
Stability tests – Results

Fumed silica ink
- Between Buckling ($G'_R$) and ($G'_I$)

Nanoclay 10 wt%
Stability tests – Wall profile

Nanoclay ink
• Slender walls buckle
Stability tests – Wall profile

Nanoclay ink
• Thick walls yield then buckle
Stability tests – Wall profile

Fumed silica ink
- Thick walls buckled without yield
# Stability tests – Wall profile

<table>
<thead>
<tr>
<th>Deposition layer</th>
<th>Δt (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td>200</td>
<td>0.2</td>
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Legend:
- Blue: Layers 1-5
- Red: Layers 6-10
- Orange: Layers 11-15
- Green: Layers 16-20
- Yellow: Layers 21-25
- Black: Layers 26-30

- Images show the progression of wall profile during deposition layers.

- Graphs illustrate the Δt (mm) changes over deposition layers.
Summary

Established a link between measurable rheology and stability

Geometry also plays a role in collapse
- Thinner walls exhibited buckling behavior
- Thicker walls demonstrated yielding behavior

Recovery is key to appropriately bounding predictions

Filler type affects recovery and therefore stability

Unclear whether initial or recovered properties dominate behavior
Future work

Informed material design

Characterize the time-dependence of recovery

Understand collapse during heated cure

Evaluate materials that cure during printing

Images courtesy of Madeline Wimmer

Video showing exothermic behavior of in-situ curing
Acknowledgements
Thank you for your attention!

Stian Romberg
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Questions?
Stability challenges

Images courtesy of Madeline Wimmer
Future work – Recovery vs time