State of the Art of Rheology of Concentrated Suspensions

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Prepreg Platelet Composite Molding and Performance Workshop
Composites Manufacturing and Simulation Center, Purdue University
October 26, 2017

VirginiaTech

Macromolecules Innovation Institute
At the intersection of science, engineering, and society

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)

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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

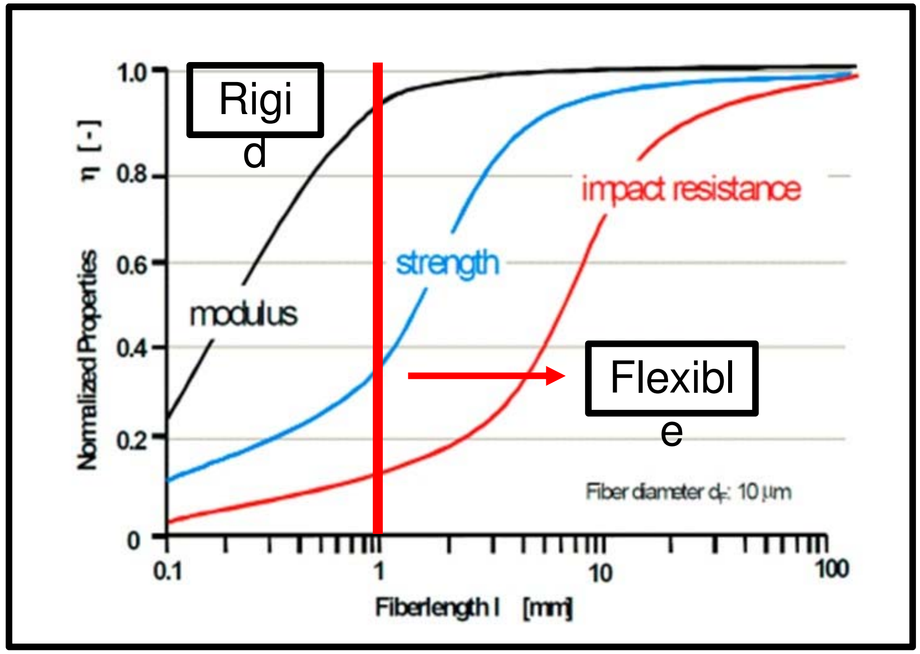
Motivation: Mechanical Properties

Orientation Effects

System (glass/epoxy)	Strength (10^3 psi)	Stiffness (10^6 psi)	Volume fraction
Unfilled resin	10-12	0.3-0.4	0
Spherical particles	9-10.5	1.5-1.7	0.50
Short fiber (transverse)	5.5	1.4	0.50
Short fiber (longitudinal)	40	4.5	0.50

Carlson, L.A., "Thermoplastic Composite Materials: Composite Materials Series, Vol 7." Elsevier, NY, 1991.

Length Effects

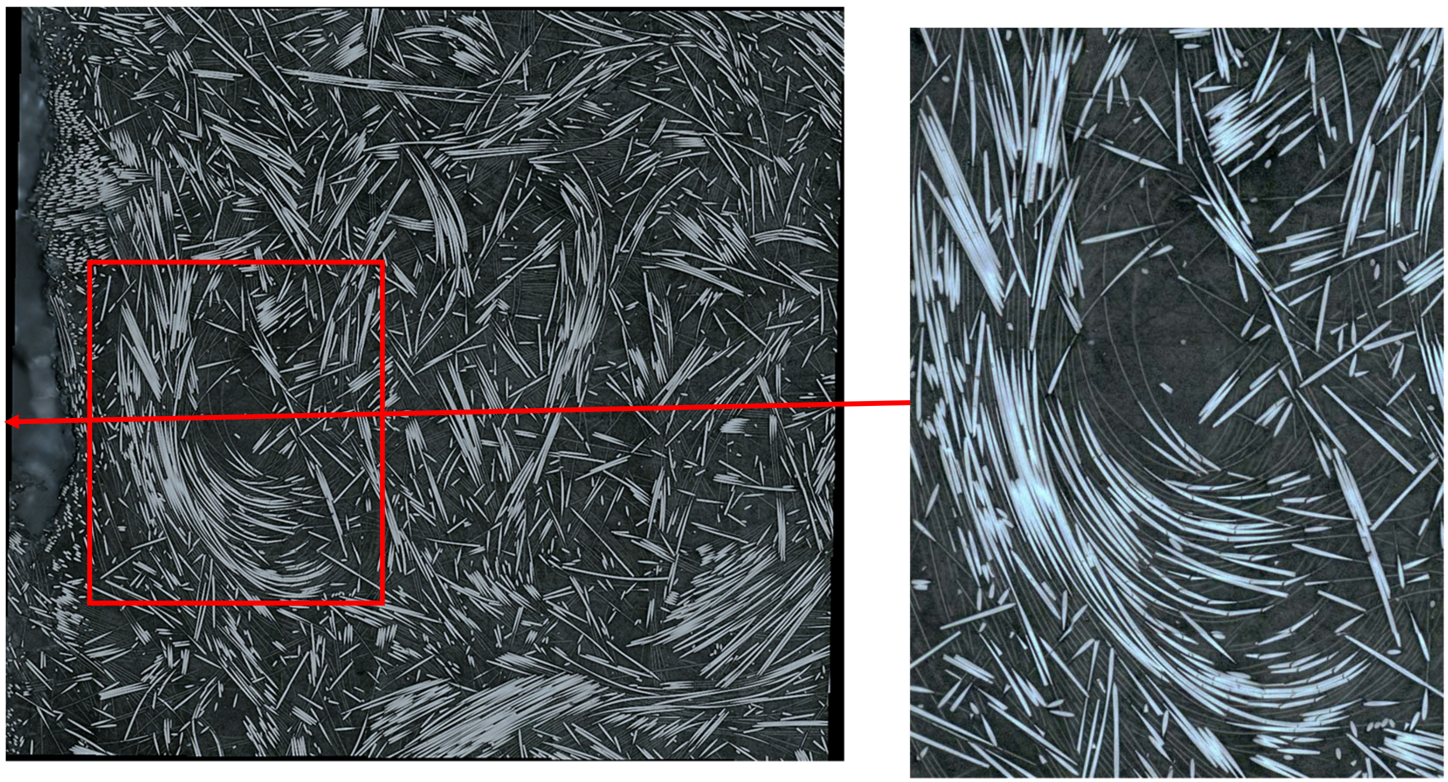


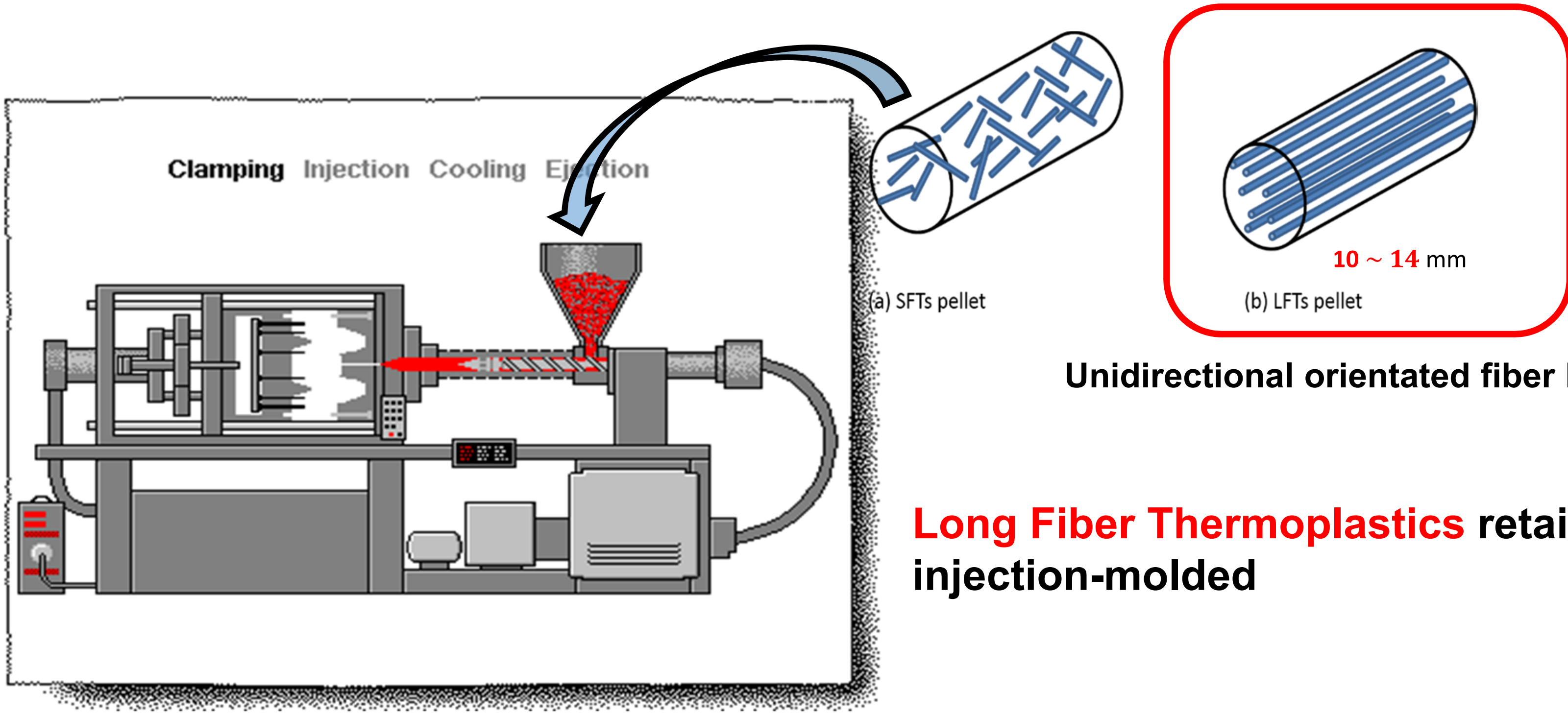
Cieslinski, M., Baird, D. *Progress in Assessing Fiber Orientation and Flexibility with Increased Fiber Lengths.* ANTEC 2015. 23-25 March 2015.

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

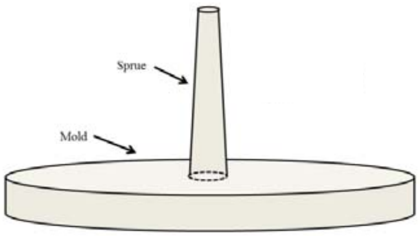
Widely Used in Industry & Suitable for Fiber Thermoplastic Composites

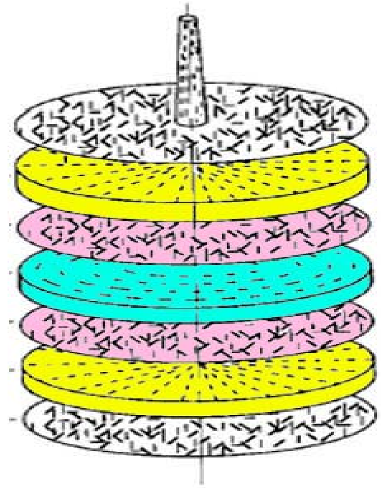
- Rapid & Automatic
- Repeatability & Geometrical Complexity

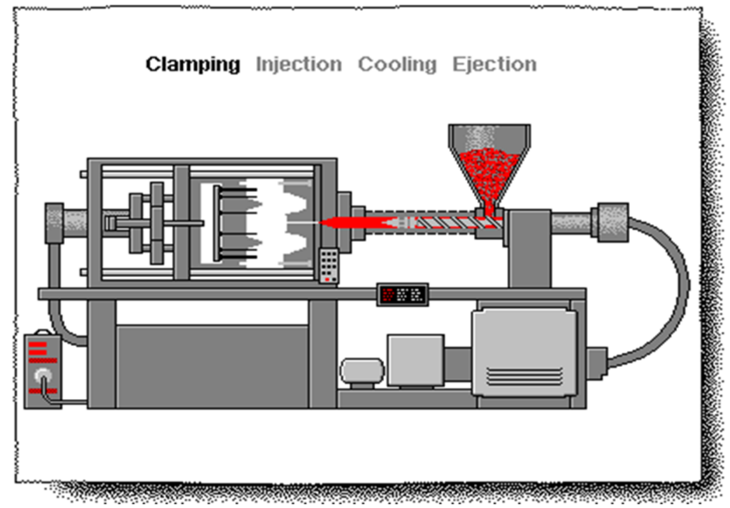
Two issues/facts of IM Long Fiber Thermoplastic Composites

- Flow induced variable orientation (Mold Cavity)

Center gated disk





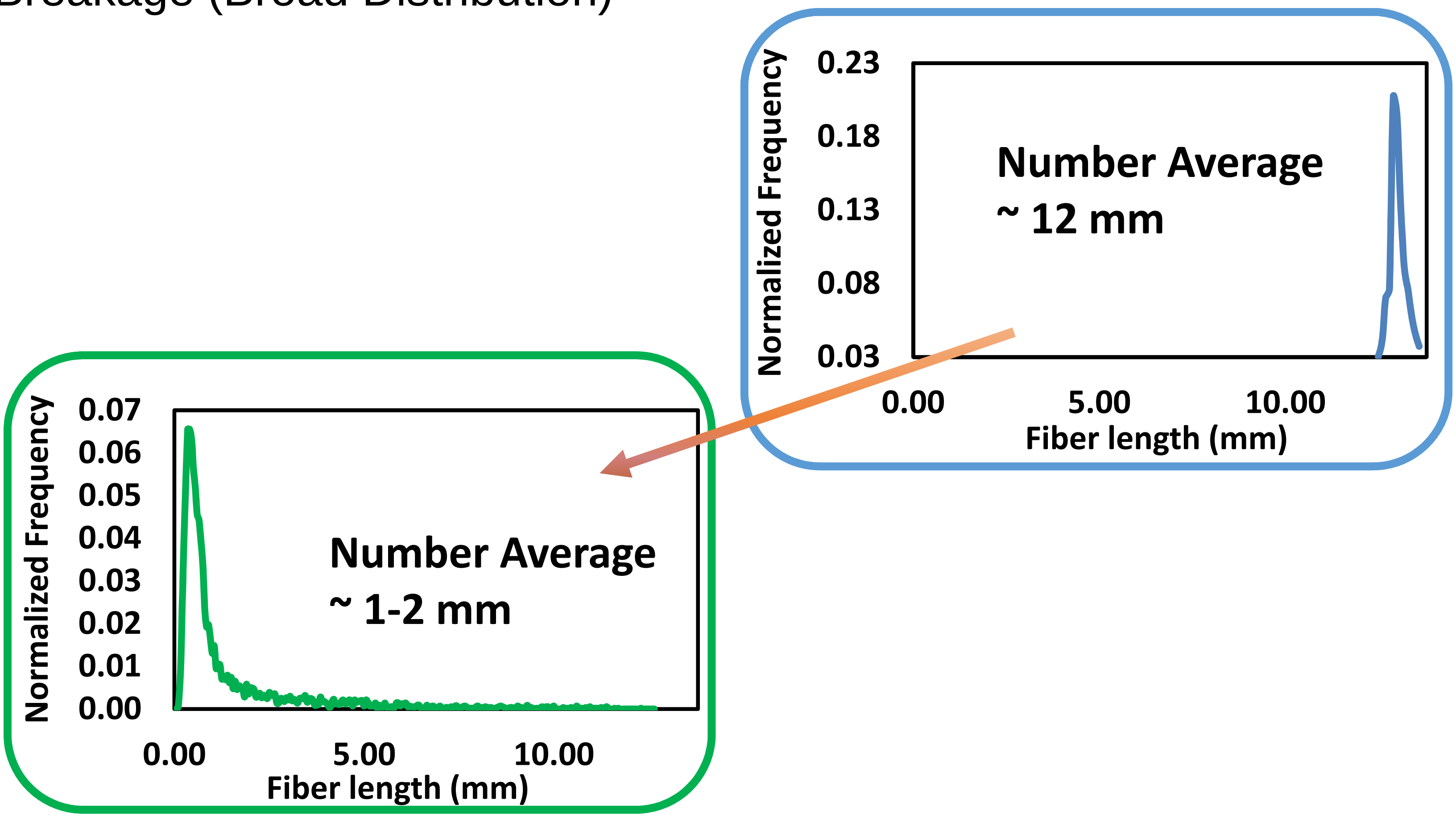


3~4 distinguishable layers:

Region		Orientation	Source
(black)	Skin	Random in *r*θ plane	Thermal + Fountain
(yellow)	Shell	Flow Aligned	Shear flow
(magenta)	Transition	No preferential	Shear & extension
(cyan)	Core	Transverse to flow	Extensional flow
(magenta)	Transition	No preferential	Shear & extension
(yellow)	Shell	Flow Aligned	Shear
(black)	Skin	Random in rθ plane	Thermal + Fountain

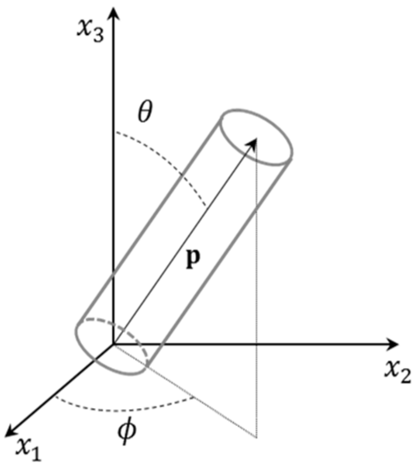
Factors Affecting Properties in Injection Molding

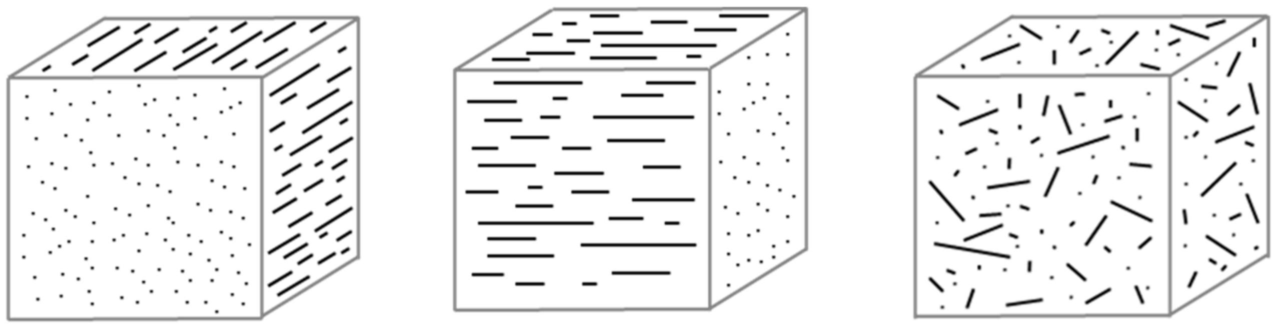
- Fiber Breakage (Broad Distribution)



Nguyen, 2008
Huq and Azaiez, 2005

Background: Orientation





$$\mathbf{A} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{A} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{A} = \begin{pmatrix} 1/3 & 0 & 0 \\ 0 & 1/3 & 0 \\ 0 & 0 & 1/3 \end{pmatrix}$$

$$\mathbf{A} = \int \mathbf{pp}\psi(\mathbf{p}, t)d\mathbf{p}$$

$$\mathbf{A_4} = \int \mathbf{pppp}\psi(\mathbf{p}, t)d\mathbf{p}$$

Advani, S.G. and C.L. Tucker III, *The Use of Tensors To Describe and Predict Fiber Orientation in Short Fiber Composites.* Journal of Rheology, 1987. **31**(8).

Background: Orientation Dynamics

$$\frac{D\boldsymbol{A}}{Dt} = \alpha\left((\boldsymbol{W}\cdot\boldsymbol{A} - \boldsymbol{A}\cdot\boldsymbol{W}) + \xi(\boldsymbol{D}\cdot\boldsymbol{A} + \boldsymbol{A}\cdot\boldsymbol{D} - 2\boldsymbol{D}:\boldsymbol{A}_4) + 2C_I\dot{\gamma}(\boldsymbol{I} - 3\boldsymbol{A})\right)$$

Matrix Contribution

Isotropic Rotary Diffusion

Empirical Parameters	
α	Fiber slip relative to matrix
C_I	Fiber interactions

Folgar, F. and C.L. Tucker III, *Orientation behavior of fibers in concentrated suspensions.* Journal of Reinforced Plastics and Composites, 1984. **3**(2): p. 98-119.
Huynh, H.M., *Improved Fiber Orientation Predictions for Injection-Molded Composites*. 2001, University of Illinois at Urbana-Champaign.

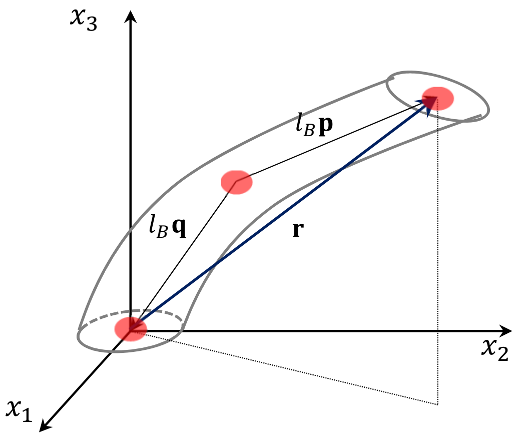
Semi-Flexible Fibers

$$\frac{D\mathbf{A}}{Dt} = \alpha\left[\mathbf{W}\cdot\mathbf{A} - \mathbf{A}\cdot\mathbf{W} + \xi\left(\mathbf{D}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{D} - 2\mathbf{D}:\mathbf{A}_4\right) + 2C_I\dot{\gamma}\left(\mathbf{I} - 3\mathbf{A}\right) + \frac{l_B}{2}\left[\mathbf{Cm} + \mathbf{mC} - 2\left(\mathbf{m}\cdot\mathbf{C}\right)\mathbf{A}\right] + 2k\left(\mathbf{B} - \mathbf{A}\,tr\left(\mathbf{B}\right)\right)\right]$$

$$\frac{D\mathbf{B}}{Dt} = \alpha\left[\mathbf{W}\cdot\mathbf{B} - \mathbf{B}\cdot\mathbf{W} + \xi\left(\mathbf{D}\cdot\mathbf{B} + \mathbf{B}\cdot\mathbf{D} - \left(2\mathbf{D}:\mathbf{A}\right)\mathbf{B}\right) - 4C_I\dot{\gamma}\mathbf{B} + \frac{l_B}{2}\left[\mathbf{Cm} + \mathbf{mC} - 2\left(\mathbf{m}\cdot\mathbf{C}\right)\mathbf{B}\right] + 2k\left(\mathbf{A} - \mathbf{B}\,tr\left(\mathbf{B}\right)\right)\right]$$

$$\frac{D\mathbf{C}}{Dt} = \alpha\left[\nabla\mathbf{v}^t\cdot\mathbf{C} - \left(\mathbf{A}:\nabla\mathbf{v}^t\right)\mathbf{C} - 2C_I\dot{\gamma}\mathbf{C} + \frac{l_B}{2}\left[\mathbf{m} - \mathbf{C}\left(\mathbf{m}\cdot\mathbf{C}\right)\right] - k\mathbf{C}\left(1 - tr\left(\mathbf{B}\right)\right)\right]$$

Hydrodynamic | IRD | Bending From Flow | Bending Potential



$$\mathbf{A} = \iint \mathbf{pp}\,\psi(\mathbf{p},\mathbf{q},t)\,d\mathbf{p}\,d\mathbf{q}$$

$$\mathbf{B} = \iint \mathbf{pq}\,\psi(\mathbf{p},\mathbf{q},t)\,d\mathbf{p}\,d\mathbf{q}$$

$$\mathbf{C} = \iint \mathbf{p}\,\psi(\mathbf{p},\mathbf{q},t)\,d\mathbf{p}\,d\mathbf{q}$$

$$\mathbf{A}_4 = \iint \mathbf{pppp}\,\psi(\mathbf{p},\mathbf{q},t)\,d\mathbf{p}\,d\mathbf{q}$$

$$\mathbf{m} = \sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}\frac{\partial^2 v_i}{\partial x_j \partial x_k} A_{jk}\mathbf{e}_i$$

$$\mathbf{r} = l_B\left(\mathbf{p} - \mathbf{q}\right)$$

$$\mathbf{R} = \frac{\langle\mathbf{rr}\rangle}{tr\left(\mathbf{rr}\right)} = \frac{\mathbf{A} - \mathbf{B}}{1 - tr\left(\mathbf{B}\right)}$$

Strautins and Latz, 2007

Ortman et al., 2012

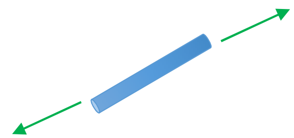
Coupling Orientation to Flow

Stress Equation for Rigid Fibers:

$$\boldsymbol{\sigma} = -P\mathbf{I} + 2\eta_m\mathbf{D} + 2\eta_m\phi(\,\mu_1\mathbf{D} + \mu_2\mathbf{D} : \mathbf{A_4})$$

Matrix

Fibers



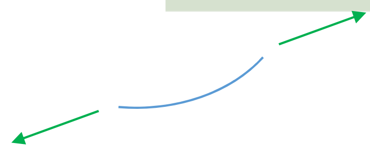
Proposed Stress Equation for Semi-Flexible Fibers:

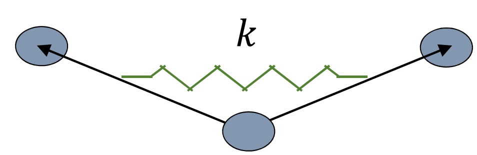
$$\boldsymbol{\sigma} = -P\mathbf{I} + 2\eta_m\mathbf{D} + 2\eta_m\phi(\,\mu_1\mathbf{D} + \mu_2\mathbf{D} : \mathbf{R_4}) + \eta_m k\,\frac{3\phi a_r}{2}(\mathbf{B} - \mathbf{A}tr\mathbf{B})$$

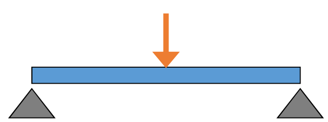
Matrix

Fibers

Fiber Bending



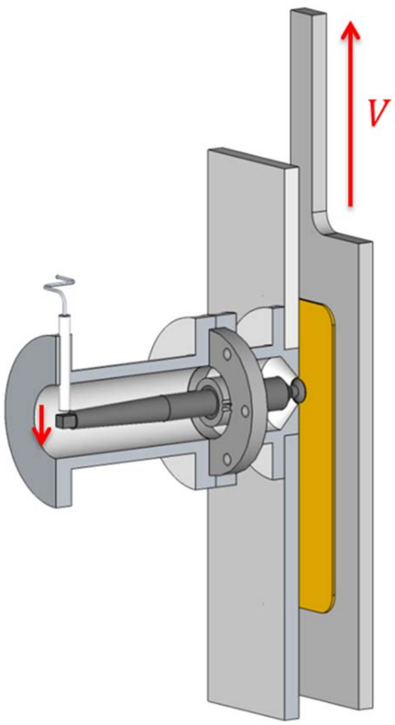




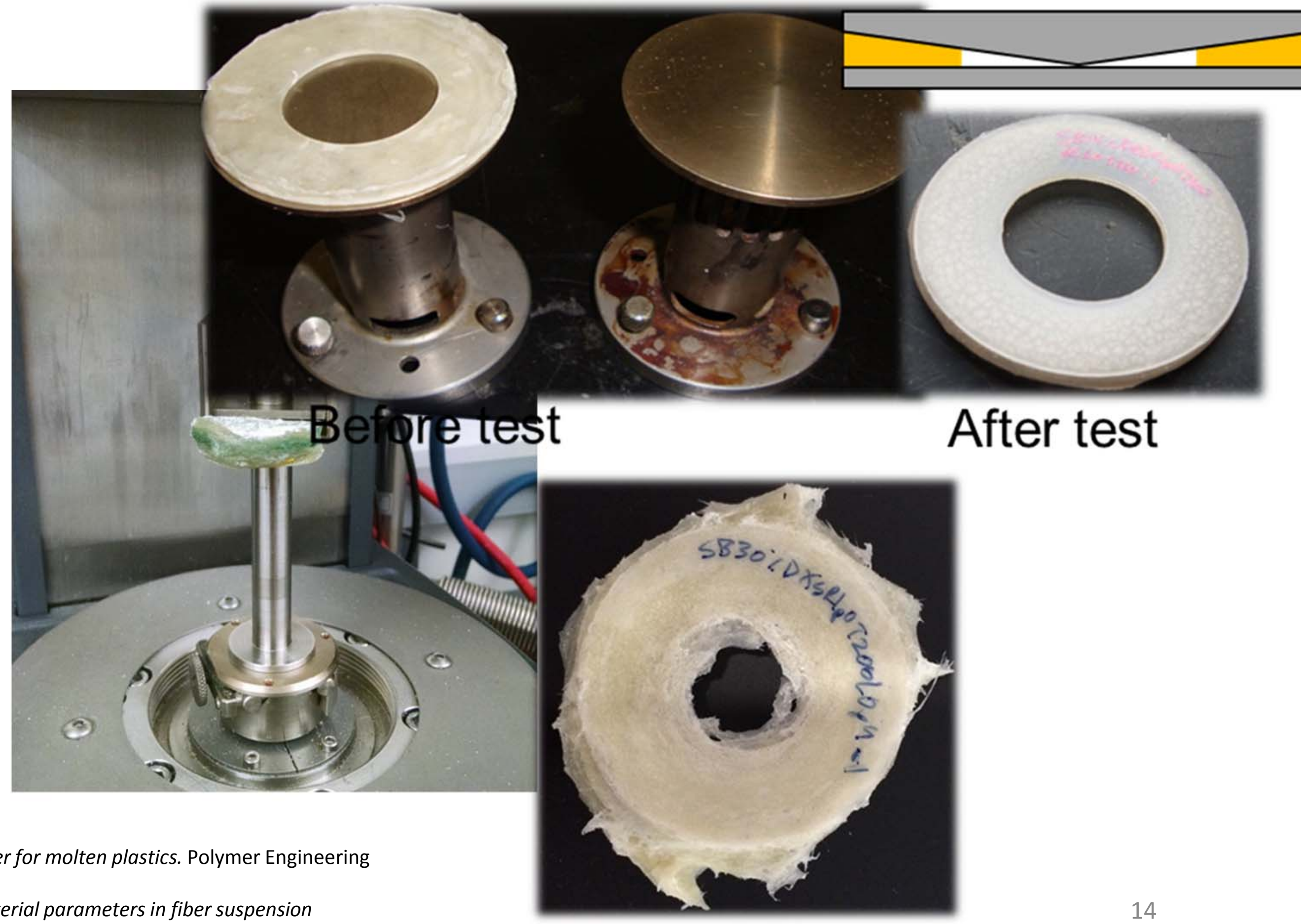
$$k = \frac{E_y}{8\eta_m}\left(\frac{1}{a_r}\right)^3$$

Lipscomb et al. 1988, Ortman et al. 2012

Experiments

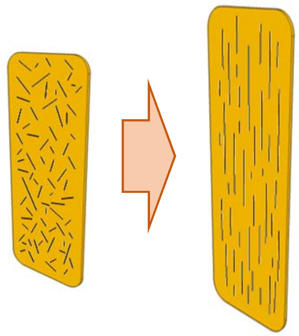


Cone and Plate – Donut, Short Fibers

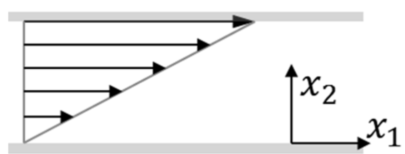


Oakley, J.G. and A.J. Giacomin, *A sliding plate normal thrust rheometer for molten plastics.* Polymer Engineering and Science, 1994. **34**(7): p. 580-4.
Eberle, A.P.R., et al., *Using transient shear rheology to determine material parameters in fiber suspension theory.* Journal of Rheology, 2009. **53**(3): p. 685-705.

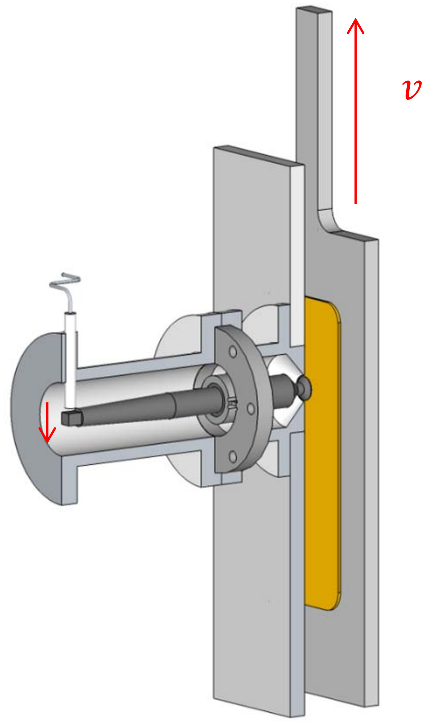
Model Parameter Obtaining



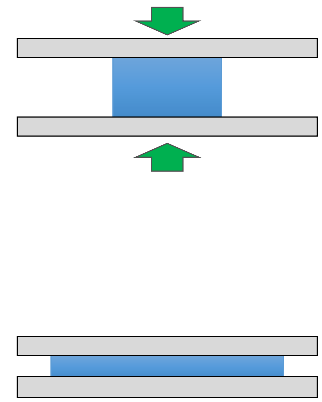
$$v_1(x_2) = \dot{\gamma}_o x_2$$



Startup of Simple Shear



Shear-free Flow
(Lubricated Squeeze Flow)



Giacomin, 1987
Dealy and Soong, 1984

$$\boldsymbol{\nabla}\cdot\mathbf{v} = 0 \qquad \text{(Continuity)}$$

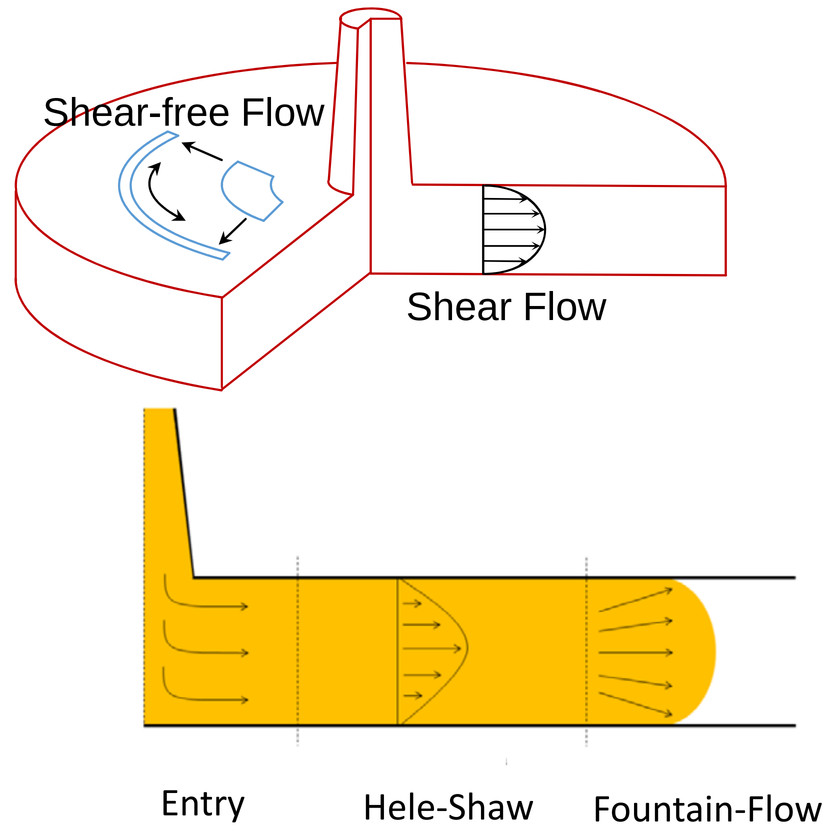
$$\boldsymbol{\nabla}\cdot\boldsymbol{\sigma} = \mathbf{0} \qquad \text{(Momentum)}$$

$$\boldsymbol{\sigma} = -P\mathbf{I} + 2\eta_m\mathbf{D} \qquad \text{(Stress)}$$

$$\frac{\partial c}{\partial t} + \mathbf{v}\cdot c = 0 \qquad \text{(Pseudo-concentration)}$$

Decoupled

$$\frac{\partial \mathbf{A}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{A} - c\mathbf{F}(\boldsymbol{\nabla}\mathbf{v},\mathbf{A}) = \mathbf{0}$$

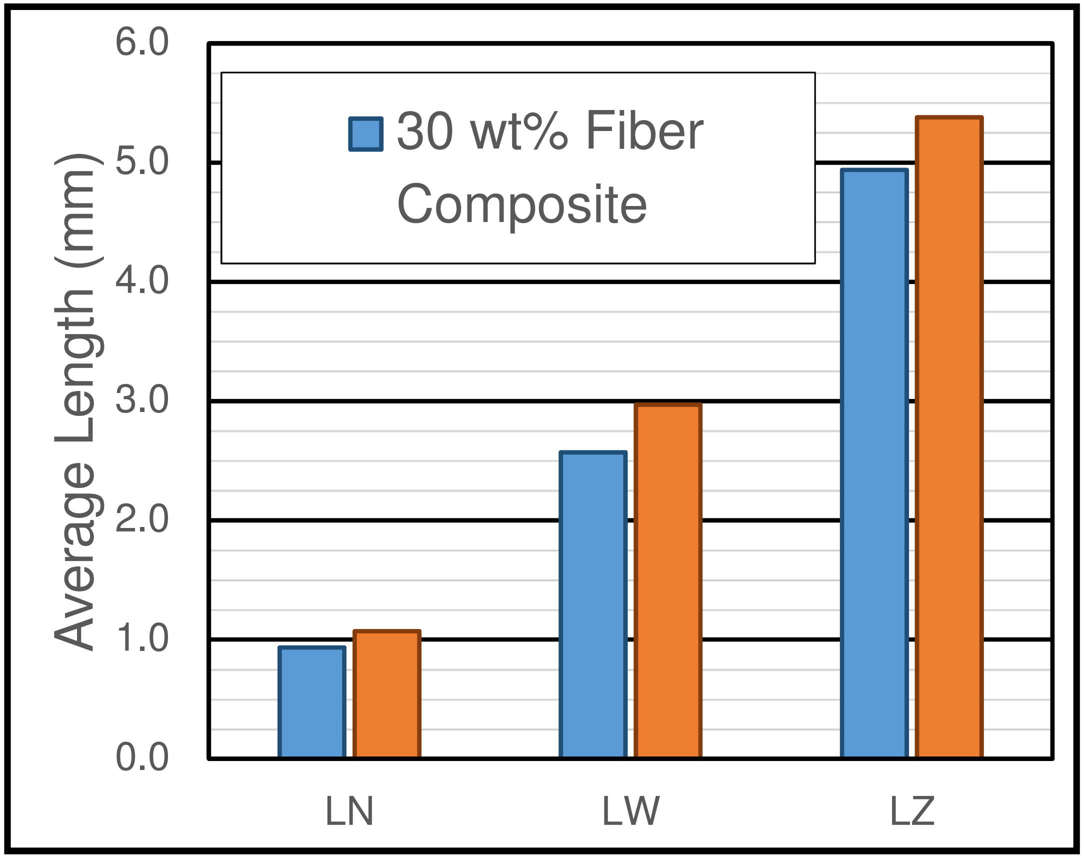


Nonlubricated Squeeze Flow

$$L_N = \frac{\sum N_i L_i}{\sum N_i}$$

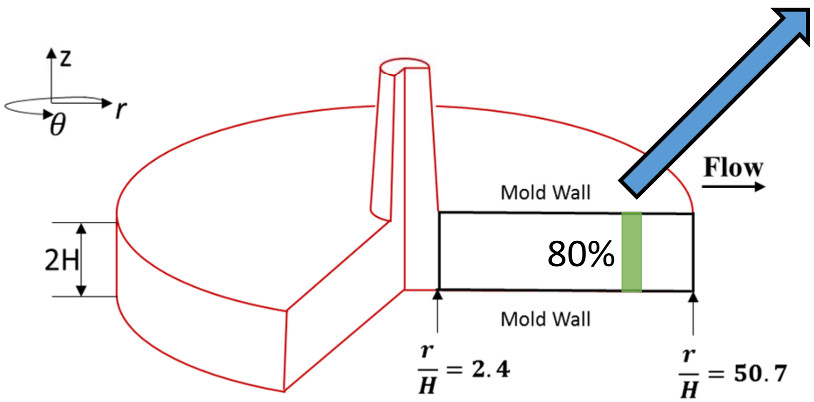
$$L_W = \frac{\sum N_i L_i^2}{\sum N_i L_i}$$

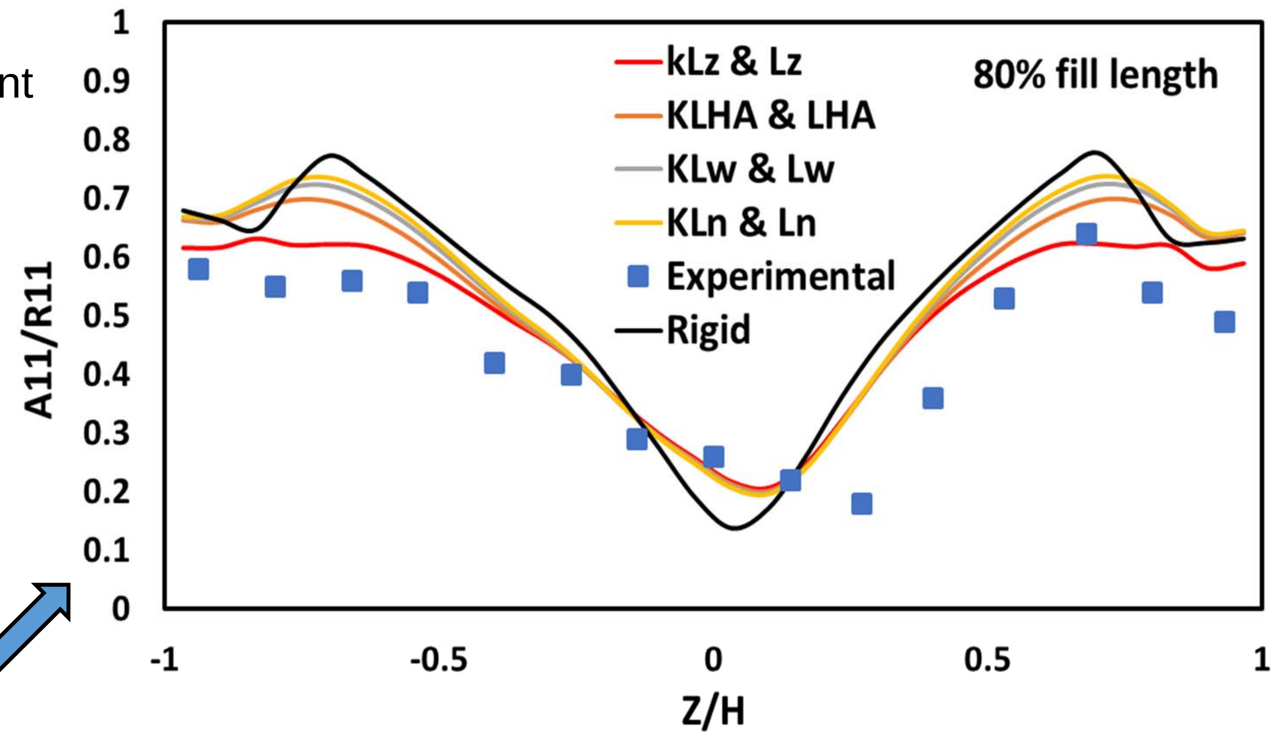
$$L_Z = \frac{\sum N_i L_i^3}{\sum N_i L_i^2}$$



Flow Direction Fiber Orientation

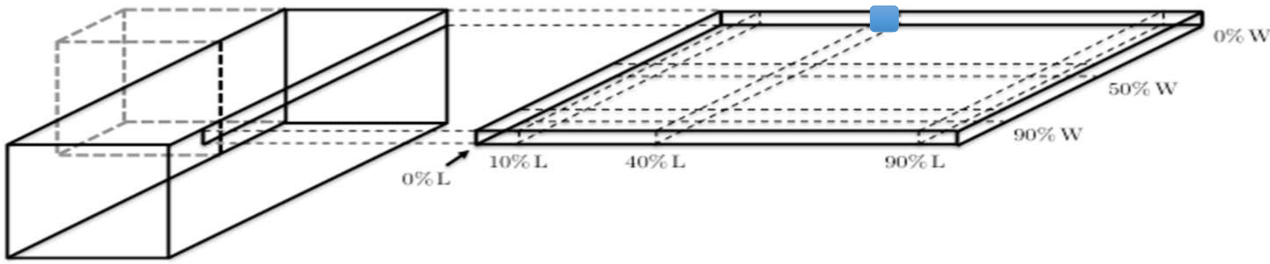
Location Close to the Advancing Front





- 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):

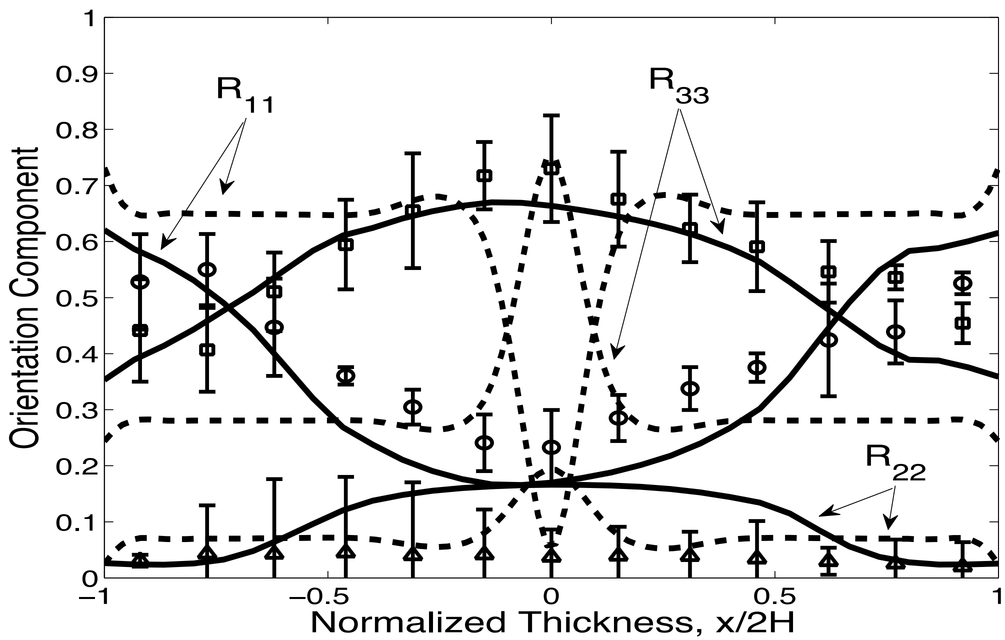
$\alpha = 0.0039$

$C_I = 0.4843$

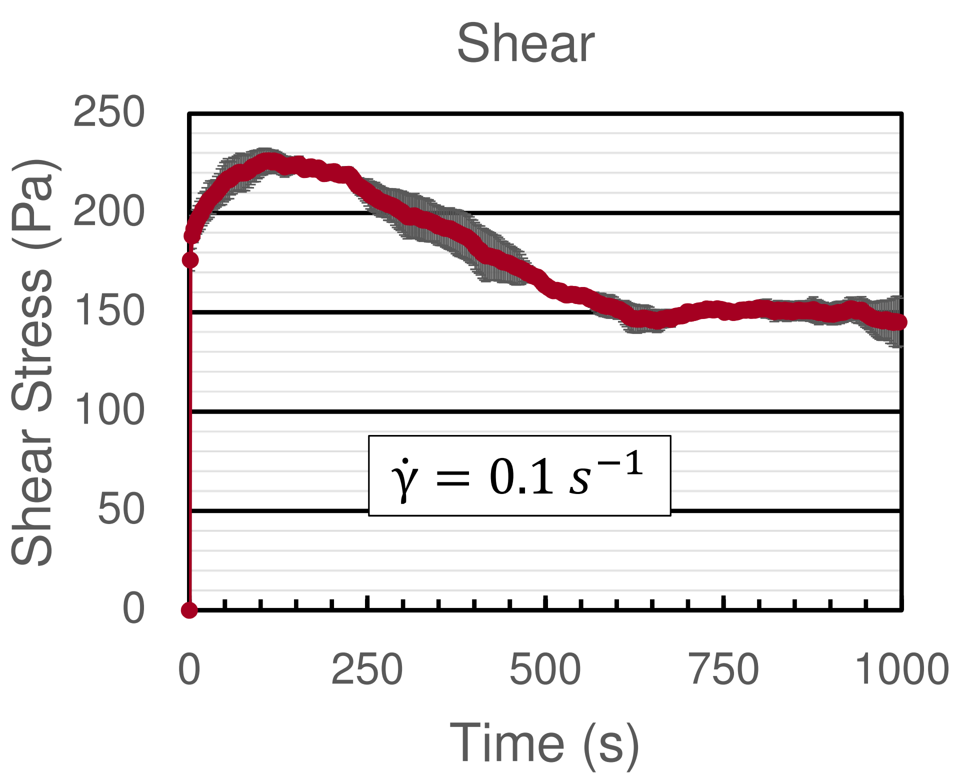
Fitted to Rheology (Dashed):

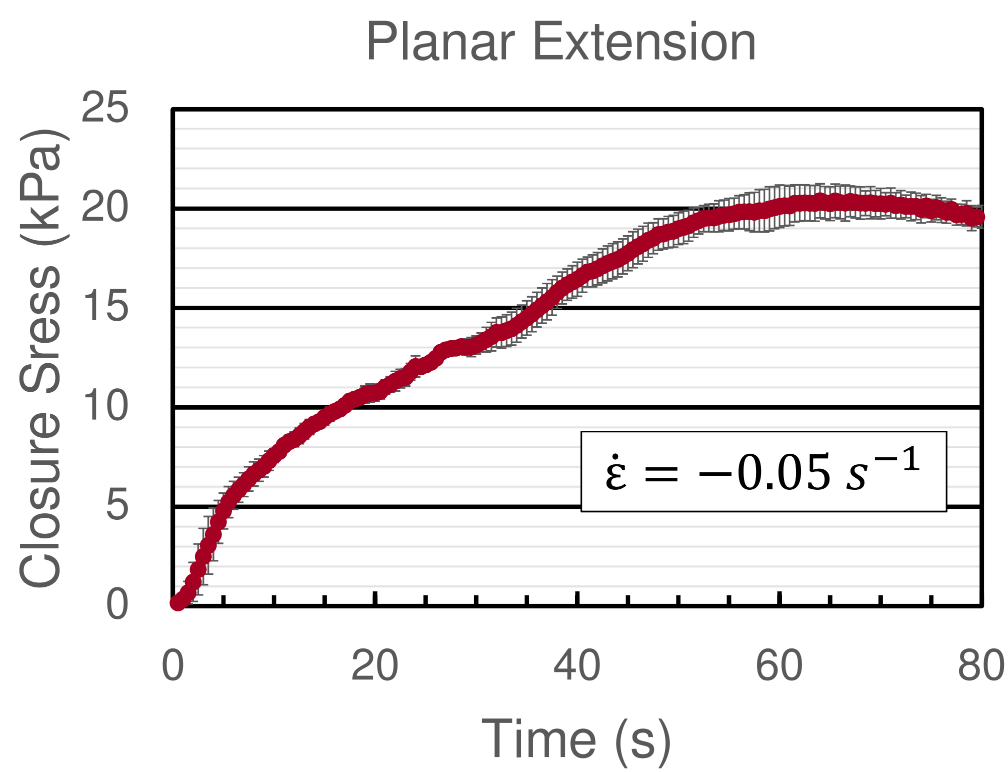
$\alpha = 0.13$

$C_I = 0.0530$



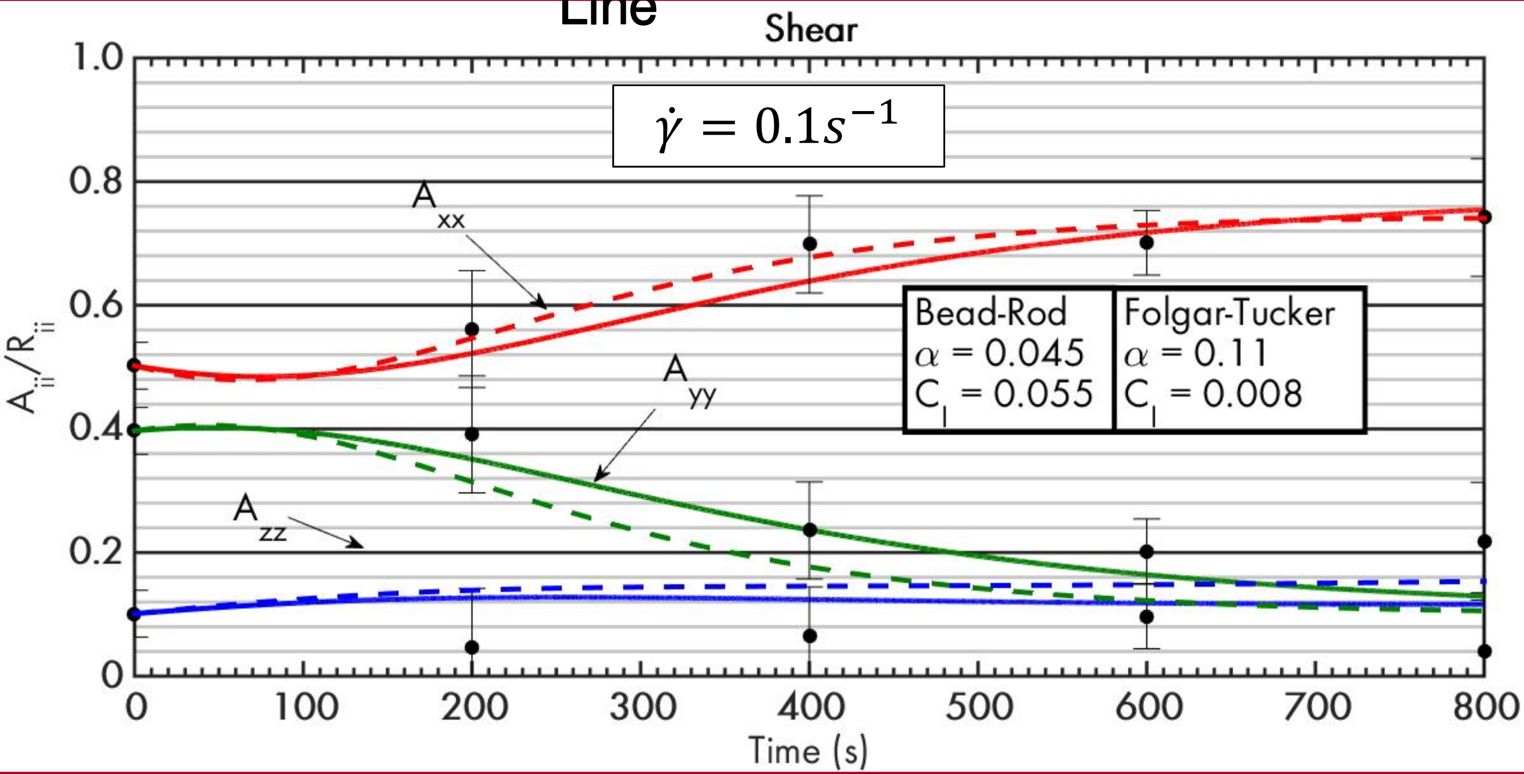
Experiments





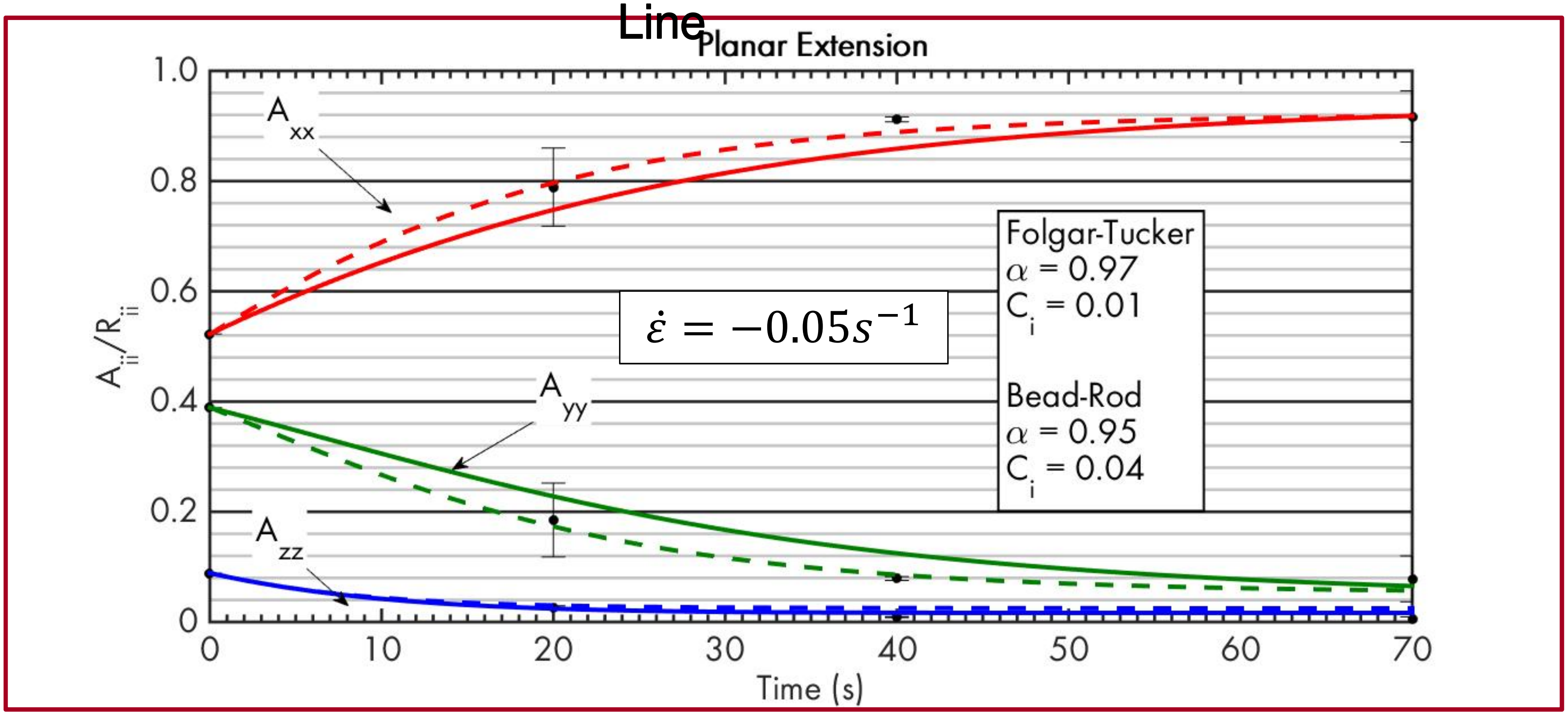
Experiments

Rigid: Solid Line
Flexible: Dashed Line



Experiments

Rigid: Solid Line
Flexible: Dashed Line



Background: Empirical Parameters

	Parameter	Shear	Extension
Rigid	α	0.11	0.97
	C_I	0.008	0.01
Flexible	α	0.045	0.95
	C_I	0.055	0.04

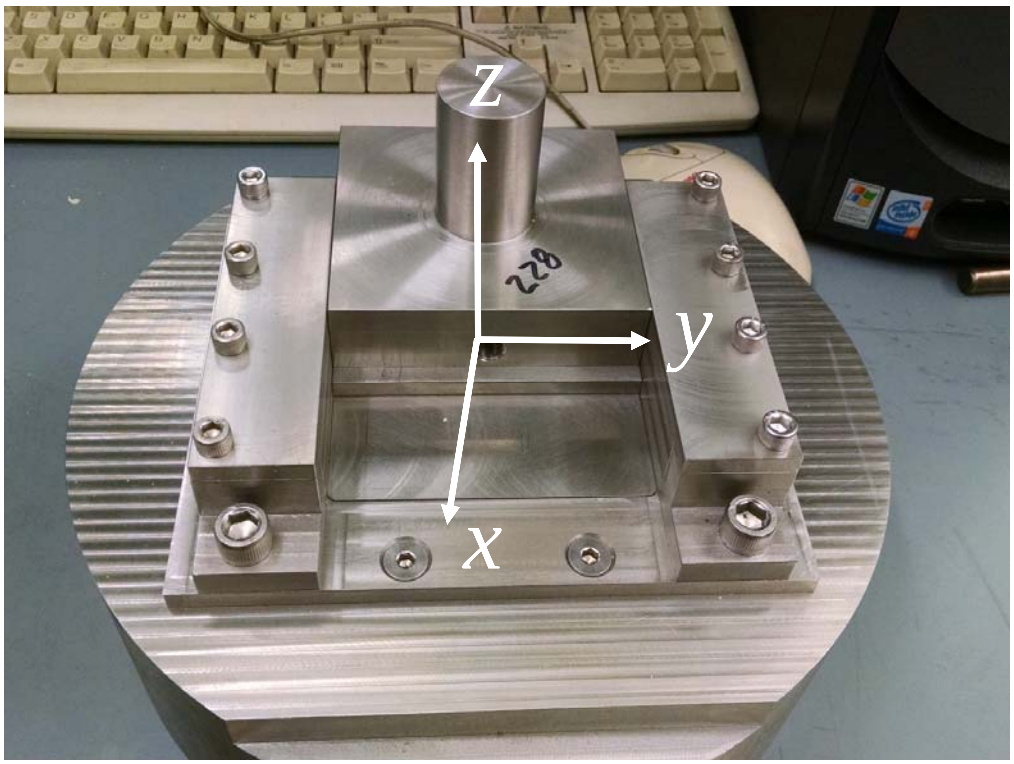
Lambert, G.M. and D.G. Baird, *Evaluating Rigid and Semiflexible Fiber Orientation Evolution Models in Simple Flows.* Journal of Manufacturing Science and Engineering, 2017. 139(3): p. 031012.

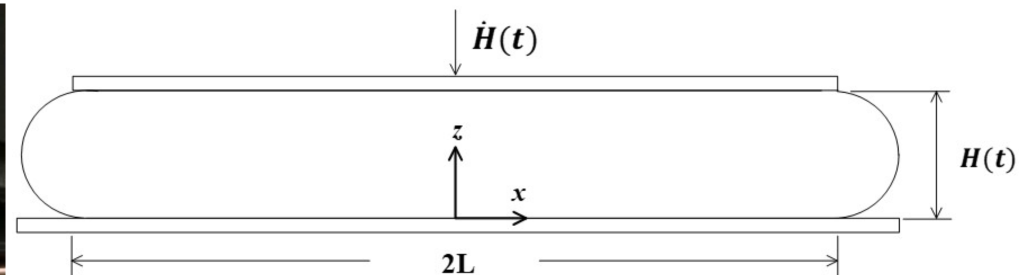
Ongoing and Future Efforts

- 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

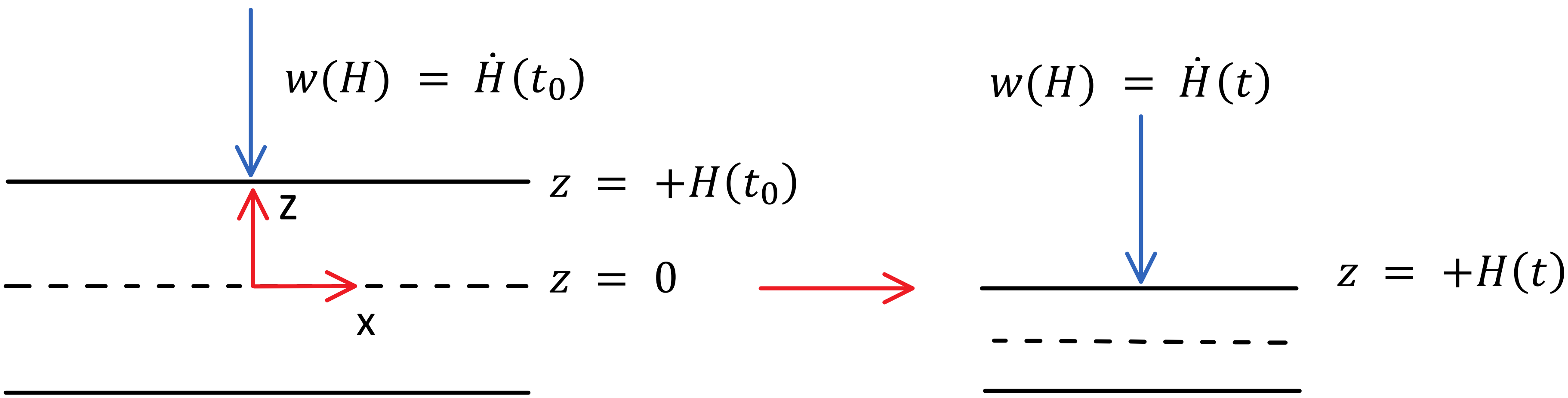
Experimental: NLSF





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

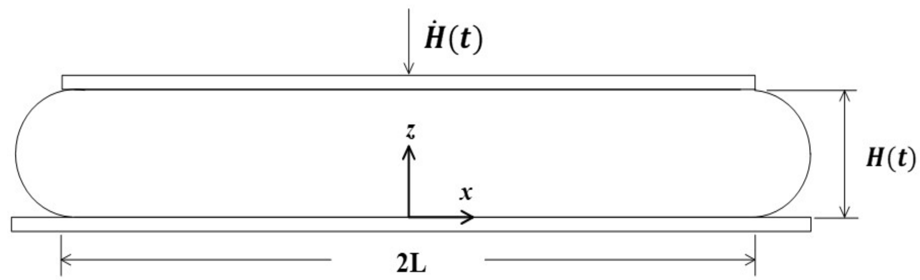
NLSF Schematic



Experimental: NLSF

$$u(x,z,t) = -6\frac{\dot{H}}{H}x\left[\left(\frac{z}{H}\right)-\left(\frac{z}{H}\right)^2\right]$$

$$w(z,t) = \dot{H}\left[3\left(\frac{z}{H}\right)^2 - 2\left(\frac{z}{H}\right)^3\right]$$

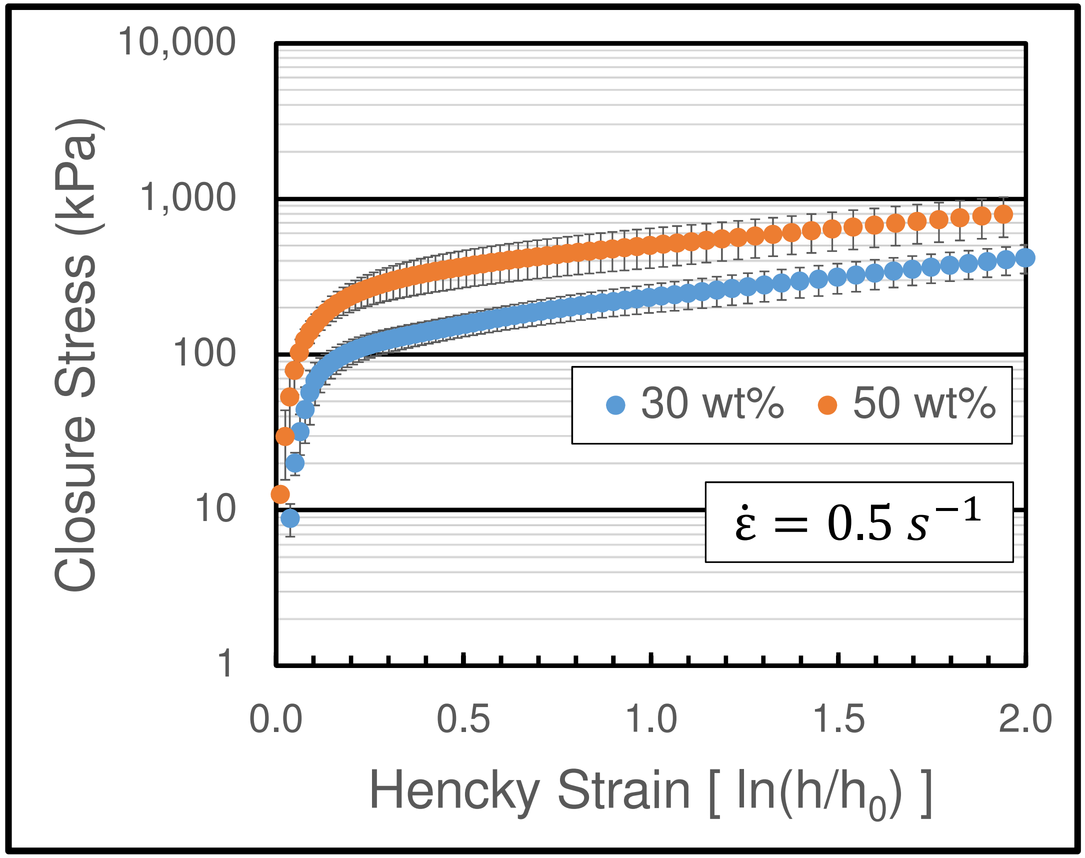


$$P(x,z,t) = 6\eta\frac{\dot{H}}{H}\left[\frac{x^2}{H^2}+\frac{z}{H}-\frac{z^2}{H^2}\right]+P_a$$

Lambert, G.M. et al. *Obtaining short fiber orientation model parameters using non-lubricated squeeze flow.* Phys. Fluids, 2017 (in press)

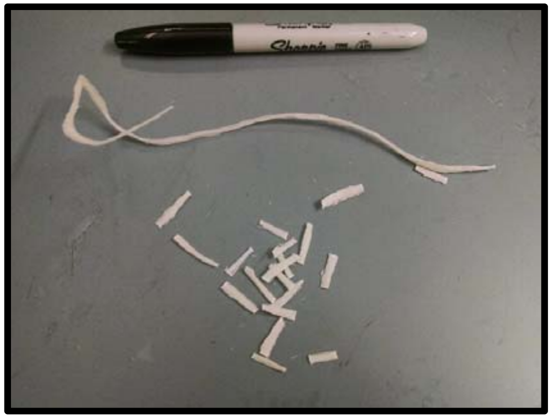
Nonlubricated Squeeze Flow

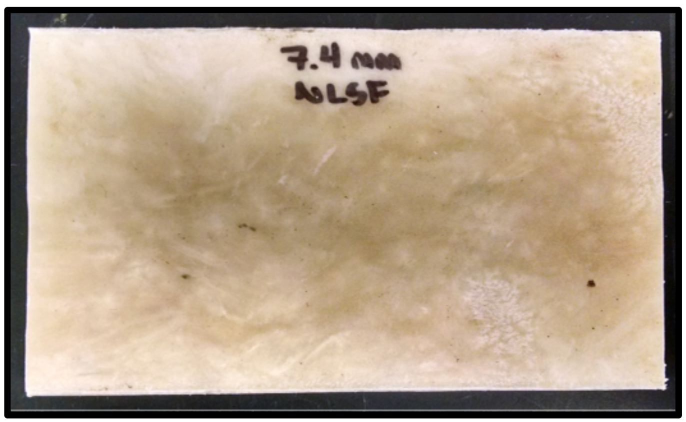
- Stress increases with fiber content
- Similar behavior in each case
- Increase from zero
  - GNF-based stress models cannot predict this



❖ *Error bars represent 95% CI*

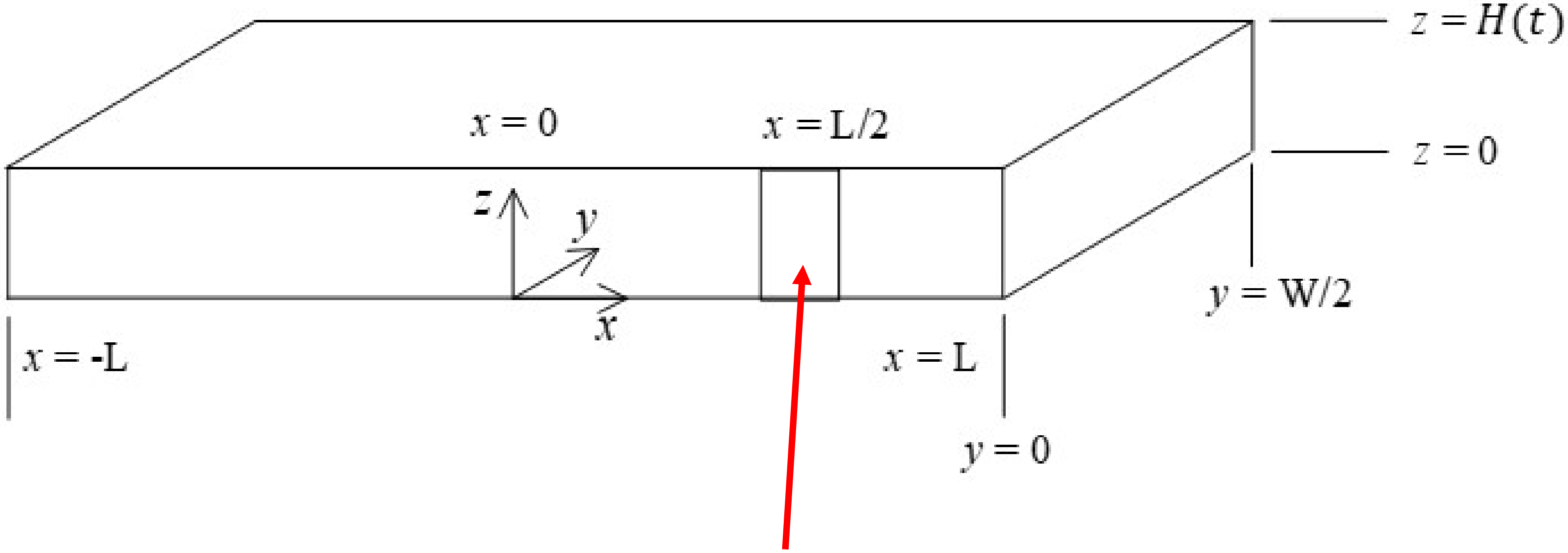
Experimental: Sample Prep





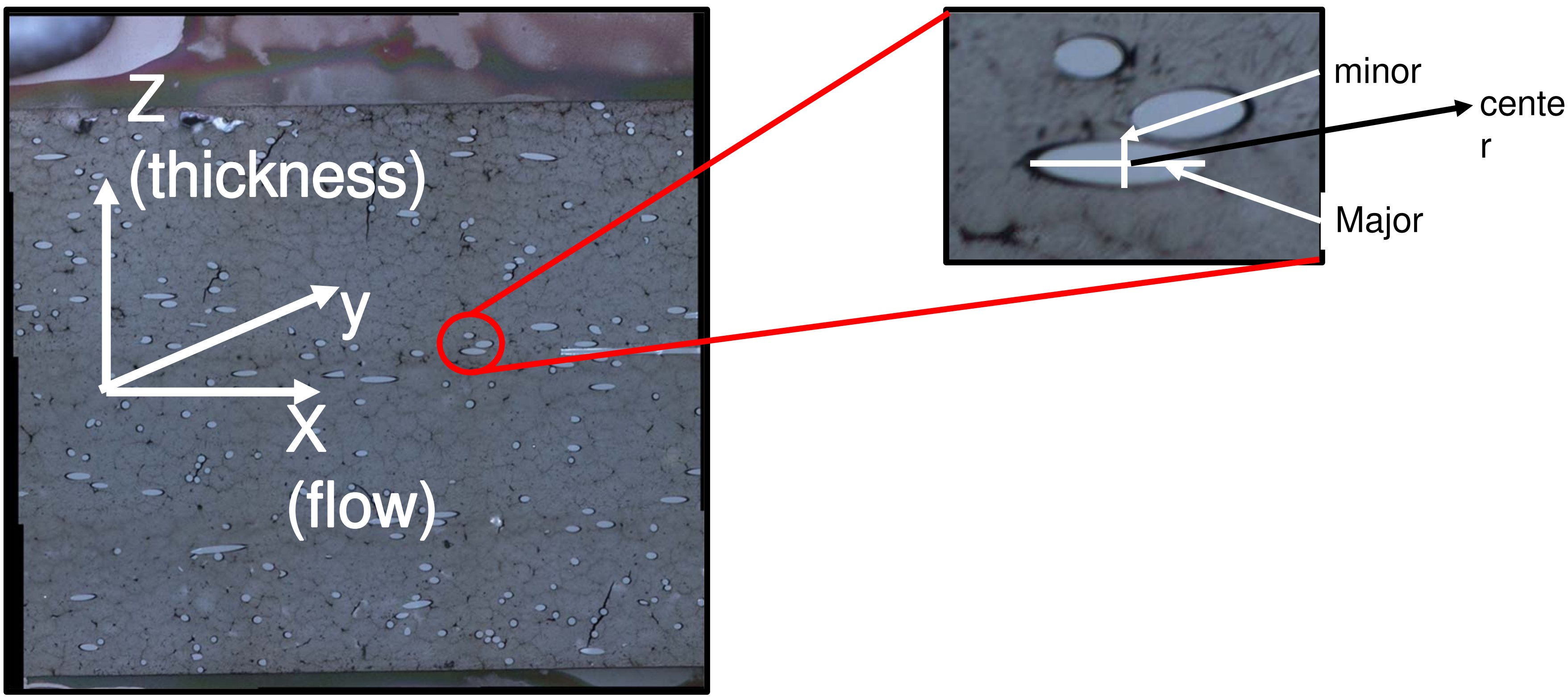
- Samples made of nozzle purge produced using the same conditions as injection-molded CGDs
- Testing Temperature: 200°C
- Constant Hencky Strain Rate: -0.50 s^{-1}
- Sample Dimensions
  - 3.75 in (95.25 mm) wide
  - 2 in (50.8 mm) long
  - 7.50 mm thick
- Initial planar random fiber orientation
  - Compression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

Experimental: Sample Prep



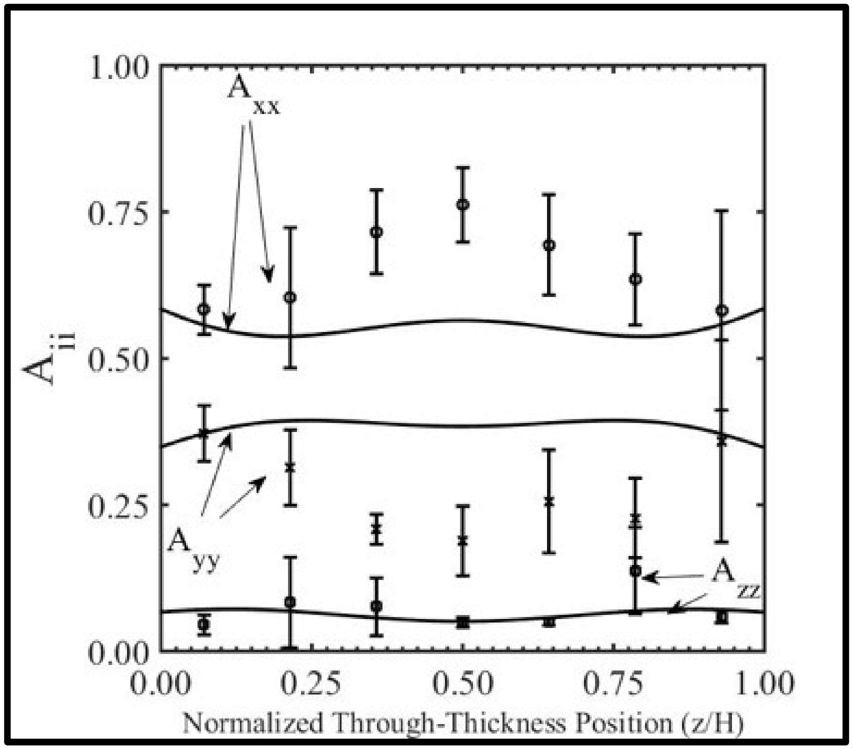
Through-Thickness
Orientation Observation

Experimental: Sample Prep

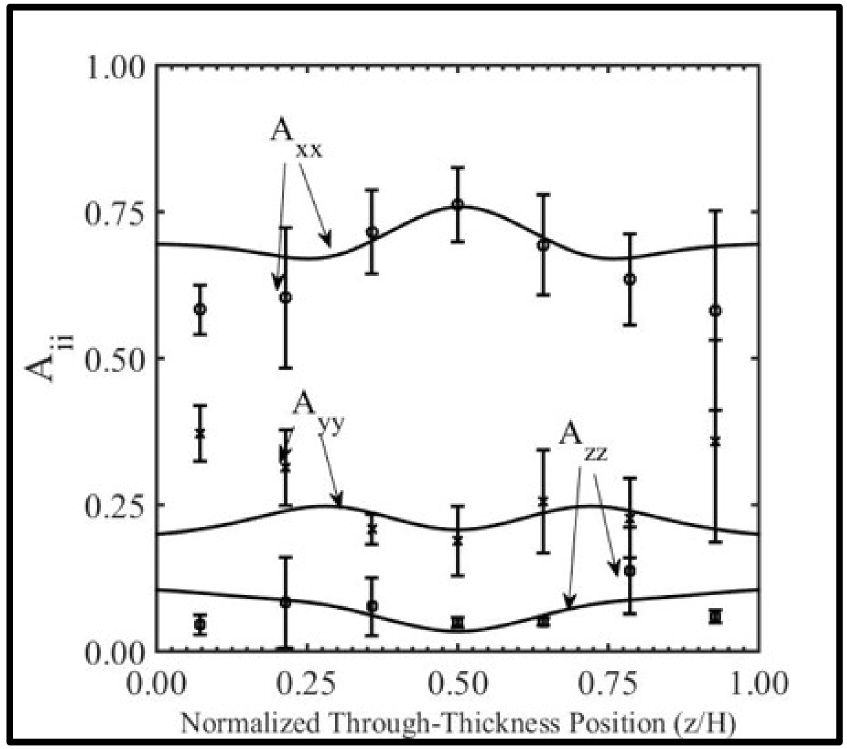


Results: Orientation

Parameters from Startup of Simple Shear



Parameters from NLSF



Lambert, G.M. et al. *Obtaining short fiber orientation model parameters using non-lubricated squeeze flow.* Phys. Fluids, 2017 (in press)

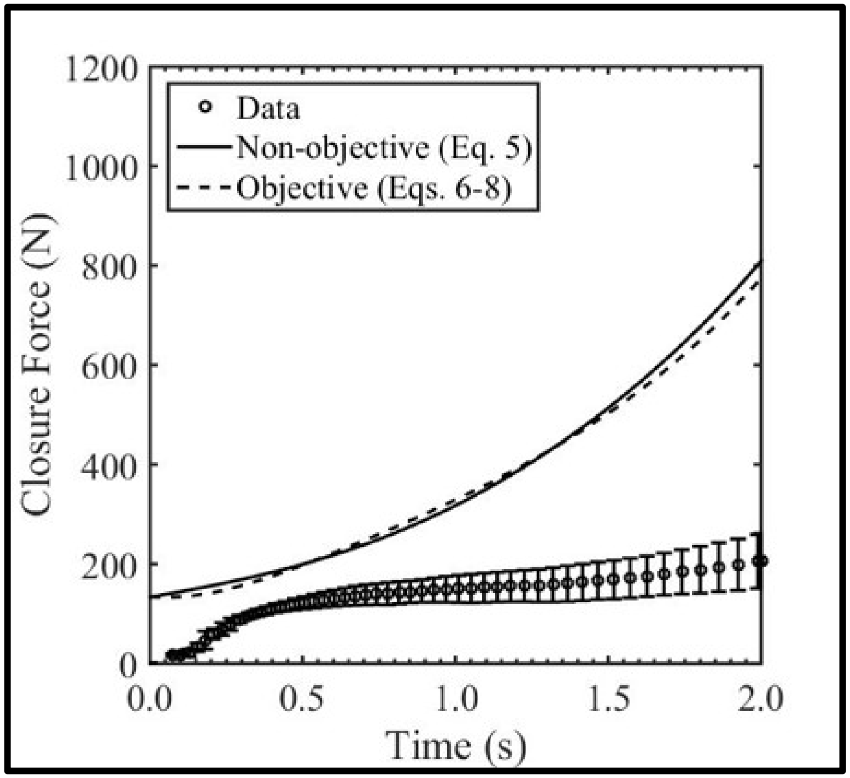
Results: Orientation

Parameter	Cieslinski et al.[1] (simple shear)	NLSF[2]
α	0.20	1.00
C_I	0.005	0.020

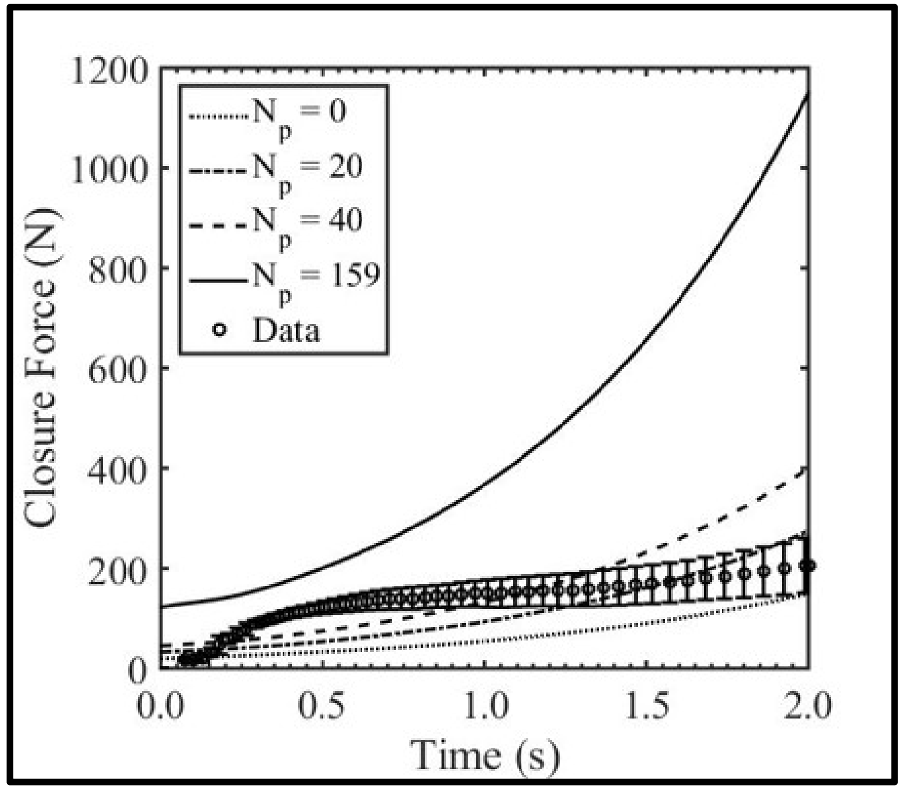
1. Cieslinski, M.J., P. Wapperom, and D.G. Baird, *Fiber orientation evolution in simple shear flow from a repeatable initial fiber orientation.* J. Non-Newton. Fluid Mech., 2016. **237**: p. 65-75.
2. Lambert, G.M. et al. *Obtaining short fiber orientation model parameters using non-lubricated squeeze flow.* Phys. Fluids, 2017 (under review)

Results: Stress Growth

Parameters from Simple Shear



Parameters from NLSF



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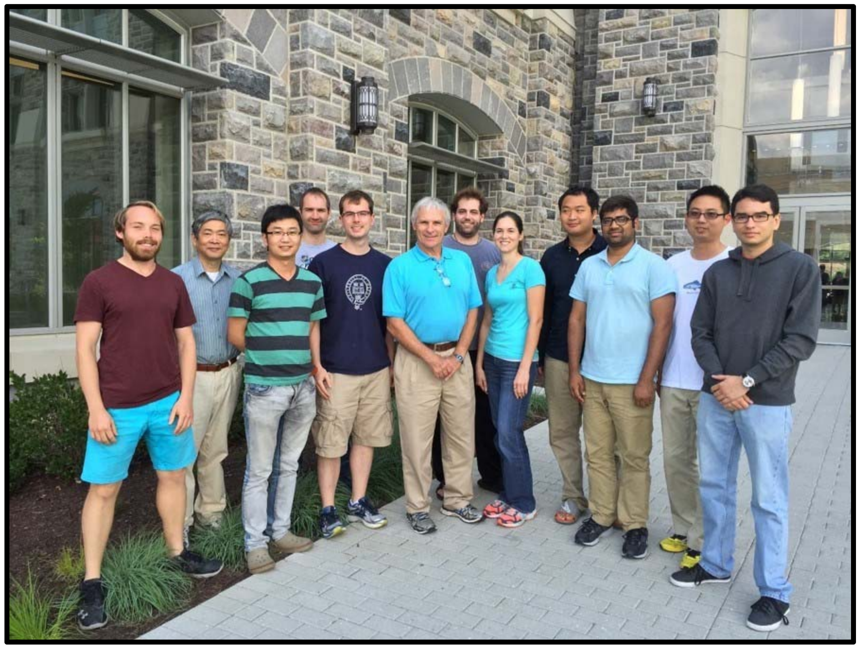
Conclusions

- 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



GM

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