J. Simulation of Injection Molding of Thermoplastics Reinforced with Short and Long Fibers

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Contractor: Virginia Polytech Institute and State University
Contract No.: DMI-052918

Objective

- Improve predictions of fiber orientation in thermoplastics during injection and compression molding by:
  - using a theory that couples fiber orientation with the flow field and incorporates the effects of fiber interaction and the viscoelastic behavior of the suspending medium.
  - incorporating the frontal flow region (which is dominated by extensional flow) into the finite-element simulation.
- Evaluate predicted-orientation distribution by comparing results to glass-fiber orientation found in injection-molded parts produced using basic mold geometries (end- and center-gated parts).

Approach

- Conduct shear and extensional, steady and transient rheological studies on glass-fiber-filled polypropylene (PP) and polybutylene terephthalate (PBT) systems in which fibers of various lengths (length: 0.2 - 11 mm, diameter: 12.5 microns) are used to asses the effects of both fiber length and the viscoelastic nature of the matrix on the transient rheology.
- Determine the relationship between fiber-orientation distribution and the nonlinear rheological behavior in shear flow.
- Identify the limitations of Doi theory for concentrated systems of rigid-rod molecules in a Newtonian suspending medium to represent the rheology and associated orientation distribution of glass fibers in a non-Newtonian matrix by comparing model predictions to experimental observations.
- Modify theory to address the limitations.

- Define and evaluate specific rheological tests to determine the material parameters in the constitutive equation which are unique and give consistent results when used in numerical simulations.
- Develop a finite-element-method simulation program capable of using multiple constitutive equations to simulate mold filling in injection molding, including the extensional flow kinematics of the advancing front region.
- Assess the performance of the simulation by comparing predicted fiber orientation against values determined experimentally from injection-molded samples containing fibers of varying length and of different matrix viscosity and viscoelasticity.
- Further assess the performance of the model by comparing the model predictions for fiber orientation to that of experimental findings for a tubular element (runner), an end-gated plaque, and center-gated disk injection-mold geometries.

Accomplishments

- Composite Materials: Various glass-fiber-filled composite materials were produced relating to the dilute, semi-dilute and concentrated concentration regimes with both polypropylene and polybutylene matrices.
- Rheology: Rheological characterization of the short-glass-fiber composites was performed, including intermittent stress growth/relaxation tests to elucidate the stress contribution of the fiber, matrix, and flow field on the transient evolution of fiber orientation. Rheological characterization of the long-glass- fiber composite has been initiated.
- Model: A constitutive relation is currently being developed that incorporates stress contributions from the fiber and the viscoelastic suspending medium. Model predictions compared to rheological data suggests a term accounting for fiber interaction in the evolution equation for fiber motion is needed.
- Simulation: A computer simulation of mold filling in injection molding is being developed. Currently, the program is capable of performing simulations with the discontinuous Galerkin finite-element method for 2-D flows using the Hele-Shaw approximation.
- Injection molding: Center-gated disks of polypropylene containing long glass fibers were injection molded and determination of fiber orientation within these samples was initiated with Oak Ridge National Laboratory (ORNL) using x-ray tomography. End-gated plaques of incrementally increasing size “short-shots” have been made and characterization of the advancing front has been initiated.
- Equipment design: A sliding-plate rheometer has been designed and is 80% completed. The sliding-plate rheometer is being fabricated primarily for the purpose of performing unbiased and reproducible rheological experiments on long-glass-fiber-filled polymeric fluids. In addition, the rheometer with be used in tracking the transient evolution of long-fiber orientation upon startup and cessation of shear flow.

Future Direction

- Accurately characterize the rheological behavior of the long-glass-fiber-filled polypropylene composite samples.
- Establish the relationship between the fiber-orientation distribution and the nonlinear rheological behavior in shear for short- and long-fiber composites.
- Extend the model to incorporate fiber interaction in the equation governing fiber motion.
- Determine a protocol for attaining unique material parameters for the model.
- Extend the numerical technique to track the frontal flow to an axisymmetric coordinate system.
- Determine the impact on the fiber orientation of the Hele-Shaw approximation when compared to simulations including the fontal flow and compare with experimental results.

Introduction

Glass fibers have been used for decades to improve the mechanical, thermal and isolative properties of polymers. These property improvements are highly dependent on the orientation distribution of the fiber. This makes it desirable to not only be able to predict the flow behavior of the composite fluid but the orientation distribution of the fiber within the fluid or melt generated during processing. Previous work on modeling glass-fiber-composite melts has primarily been accomplished by using a decoupling method, where the flow field is calculated using a purely viscous constitutive equation and the fiber orientation is post-calculated. The primary objective of this project is to improve on current simulated predictions of fiber orientation during processing of composite fluids and, hence, the ability to predict stiffness and part dimensional stability.

Materials

Three commercially-available, glass-fiber-filled composites have been chosen for this study: a 30 wt% short-glass-fiber-filled polybutylene terephethalate (commercial name Valox 420), a 30 wt% short-glass-fiber-filled polypropylene (commercial name RTP 105), and a 40 wt% long-glass-fiber-filled polypropylene (commercial name VLF 8017 cc). Three additional fiber concentrations relating the dilute, semi-dilute, and concentrated concentration régimes were made for each of the short-glass-fiber-filled composites by diluting the 30 wt% composite with the neat suspending medium. The following table outlines all the samples.

Table 1. Composition of the various composite materials that is used in this research.

	Mass fraction	Volume fraction	Aspect ratio	Concentration regime
PBT-Valox	0.3	0.1766	~29	concentrated
PBT-C	0.0842	0.044	~29	concentrated
PBT-SD	0.04071	0.0208	~29	semi-dilute
PBT-D	0.00287	0.00144	~29	dilute
SGF-PP-105	0.3	0.1288	~35	concentrated
SGF-PP-C	0.0809	0.0295	~35	concentrated
SGF-PP-SD	0.03884	0.01375	~35	semi-dilute
SGF-PP-D	0.001869	0.000646	~35	dilute
LGF-PP	0.4	0.187	~375	concentrated

Rheological Behavior

Subsequently, we outline the pertinent rheological behavior, in shear flow, exhibited by glass-fiber-composite fluids as it will aid in the discussion on model development. When the steady-state rheology of a suspension is compared to its neat counterpart, it typically has an enhanced Newtonian plateau and can exhibit a shear-thinning behavior at lower shear rates than the neat resin. At high shear rates the viscosity curves typically merge. In some cases, typically at very high fiber loading, the suspensions can exhibit yield-like behavior, the point being that the steady-state viscosity can be predicted with a number of shear-rate-dependent empiricisms, i.e., Carreau-Yasuda model. Conversely, the transient shear rheology of fiber suspensions is typically easily distinguishable from that of a neat resin. For example, when a sample with an isotropic fiber orientation is subjected to a stress growth upon inception of steady-shear-flow test, the sample will exhibit a large stress overshoot in both the shear stress and the normal stress differences. This is believed to be a result of the fiber aligning itself in the principal flow direction. Once aligned, the stresses reach a steady state. Hence, the transient rheological behavior is coupled with the fiber orientation and being able to model the evolution of orientation is imperative for correctly predicting the rheology.

A key aspect of this research is to be able to determine the cause of the enhanced rheological properties of glass-fiber-filled composites compared to the virgin matrix. If it is possible to separate the contributions from the fiber, matrix, and their interaction, then it is much easier to correctly model the behavior**.** One way to do this is to look at intermittent stress growth/relaxation behavior. This is accomplished by imposing a constant strain rate on the material until a steady state is reached in the stresses, and then the displacement is stopped and the stresses are allowed to relax for some period of time, after which the flow (constant strain rate) is turned on again. This gives insight to the evolution of the fiber orientation in the composite.

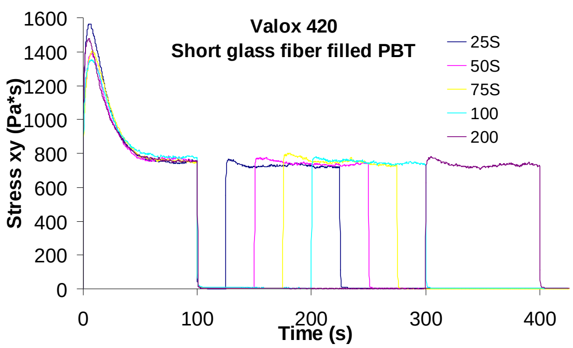

Figure 1. Intermittent stress growth/relaxation tests performed on the 30 wt% short-glass-fiber-filled PBT.

As seen in Figure 1, the initial stress overshoot is roughly double the steady-state value. This phenomenon is attributed to the random orientation of the glass fibers in the sample, which upon flow, orient themselves in the flow direction where a steady-state value is reached. An interesting observation is that this large peak does not reappear after the composite is allowed to relax, even after long periods of time. This is attributed to the fibers holding their position and staying oriented. As a note, it is believed with a highly viscoelastic polymer matrix, the recoiling of the polymer chain upon relaxation of flow could slightly affect the fiber orientation, but this has yet to be confirmed.

Model Development

To capture both the effects of the fiber and the non-Newtonian suspending medium in an approach where the flow is coupled with the fiber orientation, we propose an additive scheme, where the total extra stress is equal to a sum of contributions from the fiber and the suspending medium. In the model, the contribution of the fiber is calculated using a special form of the Doi theory for concentrated rigid-rod molecules. As a note, because the Doi theory was developed for rigid rods, we will synonymously use the term "rods" to refer to glass fibers in our real system. The contribution from the suspending medium is captured using a multi-mode viscoelastic constitutive relation.

We begin with the simple framework that the total extra stress is equal to the sum of the contribution to the stress tensor from the rods and the matrix as follows:

$$\underline{\underline{\tau}}_{\text{total}} = \underline{\underline{\tau}}_{\text{rods}} + \underline{\underline{\tau}}_{\text{matrix}} . \qquad (1)$$

Rod contribution to the stress. The starting point for the development of the contribution of the rods to the extra stress is Doi's molecular theory for mono-disperse rod-like molecules suspended in a Newtonian fluid. The Doi theory for rod-like molecules consists of two components. The first calculates the rod-orientation distribution and its evolution under external forces. The second post calculates the stress tensor which is a function of the rod orientation. In both, the quadratic-closure approximation is used. The rod orientation within the system is characterized by the deviatoric form of the orientation order parameter tensor ($\underline{\underline{S}}$), and is defined as

$$\underline{\underline{S}} = \left\langle \underline{u}\underline{u} - \frac{1}{3}\underline{\underline{\delta}} \right\rangle \qquad (2)$$

where $\underline{u}$ is a unit vector parallel to the axis of a rod, $\underline{\underline{\delta}}$ is the unit tensor, and the brackets $\langle\text{--}\rangle$ represent the ensemble average over the distribution function.

In simple shear flow, the time evolution of $\underline{\underline{S}}$ is equal to the contributions from Brownian motion, $\underline{\underline{F}}(\underline{\underline{S}})$, plus the contribution from the macroscopic flow field, $\underline{\underline{G}}(\nabla\underline{v}, \underline{\underline{S}})$:

$$\frac{\partial \underline{\underline{S}}}{\partial t} = \underline{\underline{F}}\left(\underline{\underline{S}}\right) + \underline{\underline{G}}\left(\underline{\nabla v}, \underline{\underline{S}}\right) \quad . \tag{3}$$

The Brownian motion contribution is dominant in the case of rod-like molecules or in the case where the rods are on the length scale where the effect of Brownian motion is a contributing factor and is defined by:

$$\underline{\underline{F}}\left(\underline{\underline{S}}\right) = -6\overline{D}_r\left[\left(1-\frac{U}{3}\right)\underline{\underline{S}} - U\left(\underline{\underline{S}}\cdot\underline{\underline{S}} - \frac{\underline{\underline{\delta}}}{3}\underline{\underline{S}}:\underline{\underline{S}}\right) + U\underline{\underline{S}}\left(\underline{\underline{S}}:\underline{\underline{S}}\right)\right] \tag{4}$$

where U is a phenomenological parameter representing the interaction potential of the system, and $\overline{D}_r$ is the average rotational diffusivity. The $\underline{\underline{F}}\left(\underline{\underline{S}}\right)$ quantity acts as a randomizing potential and is most easily understood by using the model to predict interrupted stress growth behavior. During stress relaxation, $\underline{\underline{F}}\left(\underline{\underline{S}}\right)$ causes the rod orientation to relax or randomize, as one would expect for suspensions of rod-like molecules. For systems of glass fibers, the $\underline{\underline{F}}\left(\underline{\underline{S}}\right)$ term is very small and can be neglected. The $\underline{\underline{G}}\left(\underline{\nabla v}, \underline{\underline{S}}\right)$ component is defined by

$$\underline{\underline{G}}\left(\underline{\nabla v}, \underline{\underline{S}}\right) = \frac{1}{3}\left[\underline{\nabla v} + \left(\underline{\nabla v}\right)^t\right] + \left[\underline{\nabla v}\cdot\underline{\underline{S}} + \left(\underline{\nabla v}\cdot\underline{\underline{S}}\right)^t - \frac{2}{3}\underline{\underline{\delta}}\,\underline{\nabla v}:\underline{\underline{S}}\right] - 2\left(\underline{\nabla v}:\underline{\underline{S}}\right)\underline{\underline{S}} \tag{5}$$

where $\underline{\nabla v}$ is the velocity gradient. Equations (3, 5) represent six coupled ordinary differential equations that can be solved numerically for the time evolution of orientation for a known velocity profile.

The Doi theory states that the stress contribution from the rods is equal to the sum of an elastic component ($\underline{\underline{\tau}}_E$) and a viscous component ($\underline{\underline{\tau}}_V$):

$$\underline{\underline{\tau}}_{rods} = \underline{\underline{\tau}}_E + \underline{\underline{\tau}}_V \quad . \tag{6}$$

$\underline{\underline{\tau}}_E$ comes entirely from the Brownian potential and the contribution to the stress from the rods is very small. The viscous dissipation of energy of the rods is given by

$$\underline{\underline{\tau}}_{rods} = \underline{\underline{\tau}}_V = -A\left(\underline{\nabla v}\cdot\underline{\underline{S}}\right)\left(\underline{\underline{S}} + \frac{\underline{\underline{\delta}}}{3}\right) \quad . \tag{7}$$

A is a constant theoretically equal to $ck_bT/2D_r$, where *c* is the concentration of rods, k_b is Boltzman's constant, and *T* is temperature in Kelvin. For modeling purposes, we choose to fit the parameter *A* to transient-stress growth data.

Matrix contribution to the stress: A key concept behind the model is that the contribution from the rods to the stress primarily occurs while the rods are changing their orientation. After the rods have reached a steady-state in their orientation, their contribution to the stress is at a minimum. However, the enhanced steady-state rheology and the viscoelastic properties can be predicted by superimposing the rod contribution onto a viscoelastic constitutive relation fit to the bulk steady-state rheology. In this approach the contribution to the extra stress of the matrix is captured using a multi-mode viscoelastic constitutive relation. For the model predictions in the paper, we chose to use the Phan-Thien Tanner equation (PTT).

Model Prediction

The Doi theory equations that make up the rod contribution to the total extra stress (equations 3, 5, and 7) are similar in structure and in what they predict to Dinh and Armstrong. The model predicts $\underline{\underline{\tau}}_{rods} \to 0$ at long times or at steady-state. However, the model predicts a transient stress contribution when the initial orientation of $\underline{\underline{S}}$ is different from the steady-state value of $\underline{\underline{S}}$. This can be seen graphically in Fig. 2, for a random initial $\underline{\underline{S}}$ at a shear rate of 1 s^{-1}.

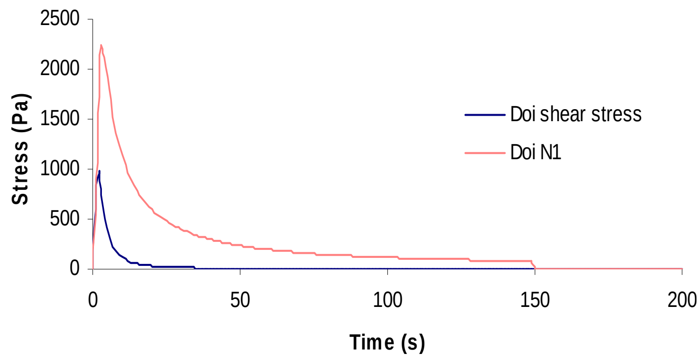

Figure 2. Modified Doi theory prediction for the contribution of the rods to the extra stress. Prediction is for a shear rate of $1s^{-1}$.

The model predicts the steady-state shear rheology to the degree of accuracy of the multi-mode PTT model. The ability of the model to predict the transient shear rheology of a suspension is generally summarized in Figure 3. Figure 3 is a graph of the experimental data for the short glass fiber filled PP in an interrupted stress growth test. Beginning with an isotropic fiber orientation, the sample was subject to a constant rate of deformation, 1 s^{-1}. After 150 seconds the flow was stopped and the stresses were allowed to relax. After another 75 seconds the flow was reapplied and the stresses were recorded. As expected, initially the sample exhibited a large stress overshoot that decayed to a steady state. As previously mentioned, this is believed to be a result of the rods rotating to align themselves in the principle flow direction. Subsequent to the overshoot , a steady state in the stresses was reached which is believed to coincide with a steady state in the rod orientation. When the flow is removed, the stresses relax. However, when the flow is reapplied at the same shear rate, the overshoot does not reoccur. This is a typical result where particles, for which Brownian motion can be neglected, are suspended in a fluid in which particle sedimentation is negligible. It is believed to be a result of the rods maintaining their orientation during the stress relaxation. Hence, when the flow is reapplied, the stress immediately grows to its previous value because the rod orientation has not changed. When the model is set to the same test conditions, i.e., initial random fiber orientation subject to interrupted stress growth shear flow, it predicts the transient response fairly well. First, it can predict the magnitude of the stress overshoot but slightly under-predicts the breadth of time the overshoot takes to decay. The steady-state plateau and the

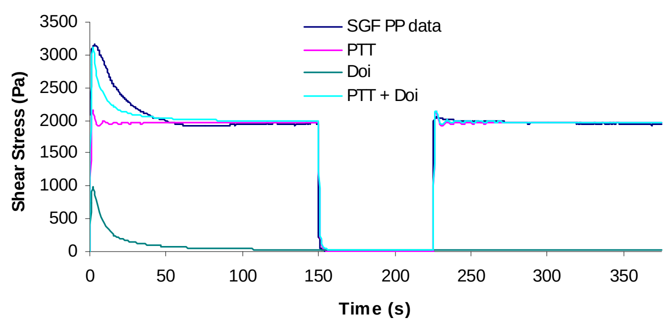

Figure 3. The shear stress vs. time for an interrupted stress growth test. Short-glass-fiber (SGF) PP data is the experimental data for a short-glass-fiber-filled PP. PTT and Doi are the separate model predictions for the 7-mode PPT and the modified Doi theory respectively. The PTT+Doi is the addition of the three stress contributions. Prediction is for a shear rate of $1s^{-1}$.

relaxation dynamics are dominated by the multi-mode PTT model resulting in a good model prediction. Interestingly, when the flow is reapplied in the model, it also does not predict a reoccurring overshoot.

The primary normal stress difference (N_1) exhibits a similar behavior to the shear stress. The model is capable of predicting the steady-state N_1 to the degree of accuracy of the multi-mode PTT model. The model prediction of the transient shear stress can be seen in Figure 4, which is graph of N_1 vs. time for the short-glass-fiber PP suspension at a shear rate of $1s^{-1}$. N_1 initially exhibits a large overshoot that decays to a steady-state. The model does predict an overshoot in N_1 but not of the magnitude seen experimentally.

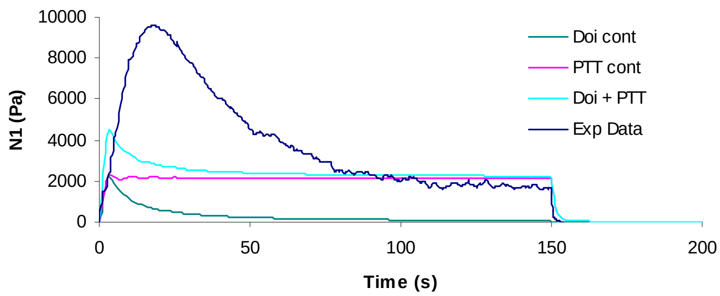

Figure 4. The primary normal stress difference vs. time for a stress growth/relaxation test. PTT and Doi are the separate model predictions for the 7-mode PPT and the modified Doi theory, respectively. The PTT+Doi is the addition of the three stress contributions. Prediction is for a shear rate of $1s^{-1}$.

The inability of the model to predict breadth of time in the shear stress overshoot and the magnitude of the first normal stress overshoot is believed to be a result of a deficiency in the equation governing rod motion. Currently, the equation is developed for dilute suspensions of rods and does not account for interaction between the fibers. We have initiated the formulation of such an equation that includes fiber interaction.

Simulation

The simulation of mold-filling in injection molding will be completed in two phases. Phase 1: a discontinuous Galerkin finite-element method code will be developed for 2-D using the Hele-Shaw approximation, which treats the flow as being dominated by shear flow. Phase 2: the code will be adapted to incorporate the kinematics of the frontal region which has been shown to be dominated by extensional flow and plays a major role in controlling fiber orientation on the part surface. It is also noted that the quadratic decoupling approximation in the Doi theory will be modified to a Bingham approximation for the frontal flow region.

Currently, Phase 1 of the computer simulation has been completed. A discontinuous Galerkin finite-element method has been implemented for multiple constitutive equations including Doi theory and various viscoelastic models. A simple and stable numerical technique to track the frontal flow in simulations of fiber-filled suspensions has been developed and implemented. The method tracks the frontal motion along spines at the moving front.

The location of the frontal surface at a new time level is obtained along spines (lines of constant height) and a particle tracking technique. At every spine, first the position of the particle is determined that arrives at the spine in a time interval Delta t. The second step of the method determines the new position in the direction of the spine. Preliminary tests have shown that the above method is stable and predicts a surface without oscillations. The accuracy of the method has been tested for a Newtonian fluid and compared with results in the literature.

Injection-Molded Samples/Fiber Orientation Analysis

Long- and short-glass-fiber samples have been injection molded into a center-gated die (thickness: .5 cm, diameter: 11 cm). A series of increasing diameter "short shots" has been completed to look at the development of the advancing front and the evolution of fiber orientation in the mold-filling process. Currently we are in contact with Vlastimil Kunc from ORNL to use x-ray tomography and the "Leeds method" to look at fiber orientation in the long glass fiber and short glass fiber samples, respectively. (See 4.I.)

Conclusions

Our research efforts to complete the project objectives correlate with the time-line for project completion. In recap of our efforts: Various short- and long-glass-fiber composite have been made. The short-glass-fiber-filled composite materials have been rheologically characterized. A sliding- plate rheometer has been designed and is under production to rheologically characterize the long-glass-fiber composite. A modified form of the Doi theory that accounts for the non-Newtonian nature of the suspending medium and the interaction between the fiber is currently being developed. Phase 1 of the computer simulation has been completed and Phase 2 has been initiated.

Presentations

1. D.G. Baird, A.P.R. Eberle, and P. Wapperom, "Transient Rheology of a Polypropylene Melt Reinforced with Long and Short Glass Fibers," 77th Annual Meeting of The Society of Rheology, October 16-20, 2005, Vancouver BC, Canada (2005).

2. A.P.R. Eberle, D.G. Baird, "Transient Rheology of a Polypropylene Melt Reinforced with Long and Short Glass Fibers," AIChE Annual Meeting, October 30-November 4, 2005, Cincinnati, OH (2005).

3. A.P.R. Eberle, D.G. Baird, and P. Wapperom, "Modeling the Transient Rheology of a Polypropylene Melt Reinforced with Long and Short Glass Fibers," SPE ANTEC Annual Meeting, May 7-10 2006, Charlotte, NC (2006).

4. A.P.R. Eberle, G.M. Velez, D.G. Baird, and P. Wapperom, "Modeling Polymer Melts Containing Long and Short Glass Fibers: Part I Transient Rheology," 78th Annual Meeting of The Society of Rheology, October 2006, Portland, Maine (2006).

5. A.P.R. Eberle, G.M. Velez, D.G. Baird, and P. Wapperom, "Modeling Polymer Melts Containing Long and Short Glass Fibers: Part I Transient Rheology," AIChE Annual Meeting, San Fransisco Ca, USA November (2006).

6. G.M. Velez, A.P.R. Eberle, D.G. Baird, and P. Wapperom, "Modeling Polymer Melts Containing Long and Short Glass Fibers: Part II the Simulation of Injection Molded Parts," AIChE Annual Meeting, San Fransisco Ca, USA November (2006).

7. P. Wapperom, G.M. Velez, A.P.R. Eberle, and D.G. Baird, "Numerical Simulation of Polymer Melts Containing Short and Long Fibers," Workshop on Numerical Methods for non-Newtonain Flows, Rhodes Greece, June (2007).

8. A.P.R. Eberle, G.M. Velez,, D.G. Baird, and P. Wapperom, "Rheology and Flow Simulation of Polymer Melts Containing Glass Fibers," European Polymer Congress (EPC) Annual Meeting, Portoroz, Slovenia, July (2007).

Publications

1. Aaron P.R. Eberle, Donald G. Baird, and Peter Wapperom, "Modeling the Transient Rheology of a Polypropylene Melt Reinforced with Long and Short Glass Fibers at Small Deformation Rates", *SPE Proceedings of the 64th Annual Technical Meeting*, 52, 2315-2319 (2006).

2. D. Baird and A. Eberle, "Modeling The Rheology And Orientation Distribution Of Short Glass Fibers Suspended In Polymeric Fluids: Simple Shear Flow", *Proceedings of the 65th Annual Technical Conference*, Cincinnati, OH,

May 6-11, Society of Plastics Society of Plastics Engrs. 2823-2827(2007).

3. A.P.E. Eberle, D.G. Baird, and P. Wapperom, "The Rheological Properties of Non-Newtonian Fluids Containing Glass Fibers: A Review of Literature", *Ind. Eng. Chem. Res.* Submitted for publication.