# Modeling the Rheology and Orientation Distribution of Short Glass Fibers Suspended in Polymeric Fluids: Simple Shear Flow

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## Abstract

In this paper we present a constitutive relation for predicting the rheology of short glass fibers suspended in a polymeric matrix. The performance of the model is assessed through its ability to predict the steady-state and transient shear rheology as well as qualitatively predict the fiber orientation distribution of a short glass fiber (0.5 mm, L/D < 30) filled polypropylene. In this approach the total extra stress is equal to the sum of the contributions from the fibers (modified Doi theory), the polymer and the rod-polymer interaction (multi-mode viscoelastic constitutive relation).

## Introduction

Adding high modulus and strength fibers to thermoplastics can significantly increase the mechanical properties of the neat matrix, especially when the fibers are aligned in the direction of mechanical interest [1]. Therefore it is desirable to be able to predict the fiber orientation as a function of processing conditions to optimize mold design to maximize mechanical properties of the final part [2]. The overall goal of our research is to be able to accurately predict the fiber orientation in injection molded parts using a finite element analysis. The goal of this paper is to present a constitutive relation for modeling the suspension rheology and predicting the fiber orientation distribution in simple shear flows.

The presence of fibers can significantly affect the rheology of the neat matrix, especially at the high fiber concentrations, and aspect ratio of industrial interest. The composite rheology is thought to be influenced by the fiber orientation distribution, concentration, and aspect ratio of the fiber, the viscoelastic nature of the suspending medium, and the degree of fiber-matrix interaction [3]. Due to the brief nature of this paper, our analysis and discussion will be limited to the general effect fiber and its orientation distribution has on the steady-state and transient rheology of polymer melts and the model's ability to qualitatively predict the rheological behavior.

Preceding the introduction of modeling glass fiber suspensions we believe it is pertinent to make a few general comments on the rheological behavior of fiber suspensions as it will aid in the explanation of the model development. The first is regarding the steady-state rheology and the second regarding the transient rheology. Generally speaking, the steady-state viscosity vs. shear rate curve is similar in nature to what one would expect from a neat polymer. 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 [4]. Point being, 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 principle flow direction. Once aligned the stresses reach a steady-state [3]. Hence, the transient rheological behavior is coupled with the fiber orientation and being able to model the evolution of orientation is imperative to correctly predicting the rheology.

Nearly all theoretical work on modeling the flow of fiber suspensions starts with the work of Jeffery [5] who investigated the motion of a single elliptically shaped particle in a Newtonian suspending medium. Effort has been made in extending the idea of a single particle to that of a distribution of fiber orientations in a suspension [6, 7]. Further work has been done to extend the theory into more concentrated fiber regimes where hydrodynamic interaction becomes an increasing factor [8, 9]. However, these theories are all based on Newtonian suspensions and, therefore, are, in general, incapable of capturing the non-Newtonian behavior of polymeric suspensions. With respect to modeling the fiber orientation in an injection molded part, the majority of work has been accomplished by using an approach that decouples the fiber orientation with the flow field. Hence the rheology of the suspension is taken as that of a generalized Newtonian fluid to predict the flow field and then a modified Jefferey's equation is used to post calculate the fiber orientation [10].

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, the suspending medium and the interaction between 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 viscoelastic constitutive relation, and the interaction between the fiber and the polymer is captured by expanding the viscoelastic constitutive relation into its multi-mode form and fitting the long relaxation times of the suspension, which is believed to be influenced by the presence of the fiber.

## Theory

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

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

**Rod contribution:**

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 theory begins with the dilute solution case where a rod is free to rotate and translate without interacting with other rods. It was then extended to concentrated systems which spontaneously become anisotropic after a critical concentration without the presence of any external fields due to excluded volume effects [11].

The Doi theory for rod-like molecules consists of two components. The first, calculating the rod orientation distribution and its evolution under external forces. The second, post calculating 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:

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

where $\underline{u}$ is a unit vector parallel to the axis of a rod, $\underline{\underline{\delta}}$ is the unit tensor, and the brackets $\langle \bullet \rangle$ 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, $\underline{\underline{G}}(\nabla\underline{v}, \underline{\underline{S}})$:

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

The Brownian motion contribution is prevalent 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:

$$\underline{\underline{F}}(\underline{\underline{S}}) = -6\overline{D}_r \begin{bmatrix} \left(1 - \frac{U}{3}\right)\underline{\underline{S}} \ldots \\ \ldots - U\left(\underline{\underline{S}} \cdot \underline{\underline{S}} - \frac{\underline{\underline{\delta}}}{3}\underline{\underline{S}} : \underline{\underline{S}}\right) + U\underline{\underline{S}}\left(\underline{\underline{S}} : \underline{\underline{S}}\right) \end{bmatrix} \quad (4)$$

where $U$ is a phenomenological parameter representing the interaction potential of the system, and $\overline{D}_r$ is the average rotational diffusivity. The $\underline{\underline{F}}(\underline{\underline{S}})$ quantity acts as a randomizing potential and is most easily understood by using the model to predict interrupted stress growth behavior. During stress relaxation $\underline{\underline{F}}(\underline{\underline{S}})$ causes the rod orientation to relax or randomize, as one would expect for suspensions of rod-like molecules. However, recent studies suggest that fibers retain their orientation during stress relaxation. Our first modification manifests itself here because the Brownian motion contribution to glass fibers in polymeric suspensions of interest (L > .25 mm) is small in an absolute sense. This can be easily verified by calculating the rotary Peclet number, which is on the order of magnitude of $10^{14}$ in the case of our short glass fiber, and is defined as the ratio of the shear rate to the rotational diffusivity [12]. Also, $\overline{D}_r$ α $1/L^3$, so the relative magnitude of $\underline{\underline{F}}(\underline{\underline{S}})$ decreases with increasing fiber length. For these reasons we neglect the Brownian motion contribution such that:

$$\frac{\partial \underline{\underline{S}}}{\partial t} = \underline{\underline{G}}(\nabla\underline{v}, \underline{\underline{S}}) \quad (5)$$

The $\underline{\underline{G}}(\nabla\underline{v}, \underline{\underline{S}})$ component is defined by:

$$\underline{\underline{G}}\left(\underline{\nabla v},\underline{\underline{S}}\right)=\frac{1}{3}\left[\underline{\nabla v}+\left(\underline{\nabla v}\right)^t\right]+...$$
$$...\left[\underline{\nabla v}\cdot\underline{\underline{S}}+\left(\underline{\nabla v}\cdot\underline{\underline{S}}\right)^t-\frac{2}{3}\underline{\underline{\delta}}\underline{\nabla v}:\underline{\underline{S}}\right]-2\left(\underline{\nabla v}:\underline{\underline{S}}\right)\underline{\underline{S}} \quad (6)$$

where $\underline{\nabla v}$ is the velocity gradient. Equations (5, 6) 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 ($\underline{\underline{\tau}}_V$):

$$\underline{\underline{\tau}}_{rods}=\underline{\underline{\tau}}_E+\underline{\underline{\tau}}_V \quad (7)$$

$\underline{\underline{\tau}}_E$ comes entirely from the Brownian potential and leads us to our second modification. Using the same arguments stated previously for neglecting the $\underline{\underline{F}}\left(\underline{\underline{S}}\right)$ term in computing the evolution of orientation we neglect $\underline{\underline{\tau}}_E$. We are left with the total rod contribution to the stress equal to the viscous dissipation of energy of the rods; given by:

$$\underline{\underline{\tau}}_{rods}=\underline{\underline{\tau}}_V=-A\left(\underline{\nabla v}\cdot\underline{\underline{S}}\right)\left(\underline{\underline{S}}+\frac{\underline{\underline{\delta}}}{3}\right) \quad (8)$$

$A$ 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.

**Contribution of the matrix and rod-matrix interaction:**

The 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 predict 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 and the rod-matrix interaction 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) [13]. The ability to indirectly capture the rod-matrix interaction is based on the presence of the fiber retarding the long relaxation times of the matrix. Currently, we are unable to make the profound statement that this is always true but our preliminary results allude to this behavior. The enhanced relaxation times are then captured by fitting the multi-mode constitutive equation to the suspension steady-state shear rheology including the low shear rates.

## Experimental Procedure

**Rheology:**

All tests were performed on a short glass fiber (L ~ 0.5mm), 30 wt% filled polypropylene (PP). Rheological tests in the low shear rate region (0.001-1 $s^{-1}$) were performed on a Rheometrics Mechanical Spectrometer (RMS-800) fitted with cone and plate geometry (diameter 25mm) to supply a constant shear rate within the gap. As a note, we must mention that some level of boundary effect was likely using the cone and plate geometry. These effects would have been most prevalent in the transient experiments where there is an evolving fiber orientation whose characteristic length changes depending on its orientation state. For this reason, we make the statement that any analysis is purely qualitative. In the future we hope to resolve this issue using a sliding plate rheometer. In the low shear rate region two tests were performed, steady shear flow and transient interrupted stress growth. For a further explanation of the test the reader is referred to Bird et. al. [14]. For high steady shear rate analysis (10-2000 $s^{-1}$) a Göttfert Rheograph 2001 capillary rheometer was used.

**Model:**

With respect to the rod contribution to the extra stress, Gears implicit predictor-corrector method for stiff differential equations was used to solve Equations 5 and 6 for the evolution of fiber orientation at a constant velocity gradient. The stress tensor was then post calculated using a value of *A=12,000* that best fit the transient stress growth overshoot (see Results and Discussion). The matrix and rod-matrix interaction contribution to the extra stress was accomplished by fitting a 7-mode PPT to the bulk steady-state rheology from 0.001-2000 $s^{-1}$ as can be seen in Figure 1. The fit was accomplished using non-linear least squared regression in Matlab resulting in parameter values of $\varepsilon$ = 0 (exponential factor), $\xi$ = 1.48 and $\lambda_i$ and $\eta_i$ can be found in Table 1.

## Results and Discussion

**Rod contribution to stress:**

The modified Doi theory equations that make up the rod contribution to the total extra stress (equations 5, 6, and 8) are similar in structure and in what they predict to Dinh and Armstrong [9]. The model predicts $\underline{\underline{\tau}}_{rods}\rightarrow 0$ 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 Figure 2, for a random initial $\underline{\underline{S}}$ at a shear rate of 1 $s^{-1}$.

**Suspension rheology vs. model prediction:**

The model predicts the steady-state shear rheology to the degree of accuracy of the multi-mode PTT model. This is an obvious result of fitting the multi-mode PTT to the bulk viscosity vs. shear rate data. Figure 1 is a graph of the 7 mode PTT fit to the steady shear viscosity vs. shear rate flow curve.

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 [3]. 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 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. This is because during the stress relaxation there is no driving force to randomize the rod orientation that is found in models containing a Brownian or Brownian-like term.

The normal stress differences, specifically, 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 1$s^{-1}$. $N_1$ 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.

## Summary

Glass fiber suspensions cannot be characterized by their steady-state shear rheology alone. Their transient rheology must also be characterized. Similarly, fiber suspension models must be able to predict both the steady-state and transient rheology of fiber suspensions. Our scheme to modeling the rheology and rod orientation distribution involves an additive approach where the total extra stress is the sum of the contributions from the rods (modified Doi theory), the matrix and rod-matrix interaction (multi-mode viscoelastic constitutive equation). Using this approach we are able to, at least qualitatively predict the steady-state and transient shear stress of a short glass fiber filled PP. We are unable to predict the large primary normal stress growth overshoot exhibited by the suspension.

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## Key Words

glass fiber, fiber orientation, transient rheology, Doi theory, suspension

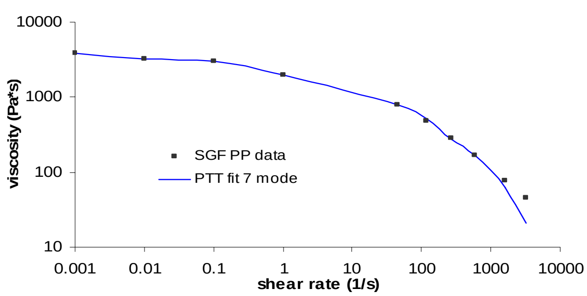


**Figure 1.** 7 mode PTT model fit to the bulk steady-state viscosity vs. shear rate curve of a short glass fiber filled PP. Rheological tests were performed at 200 C.

**Table 1.** The multi-mode PTT fit parameters lamda ($\lambda_i$) and eta ($\eta_i$).

| Mode | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| $\lambda_i$ | 0.001 | 0.01 | 0.1 | 1.0 | 10 | 100 | 1000 |
| $\eta_i$ | 181.5 | 691.0 | 74.6 | 1776.6 | 514.7 | 0 | 1036.9 |

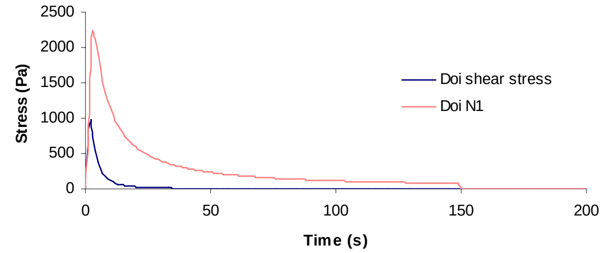


**Figure 2.** Modified Doi theory prediction for the contribution of the rods to the extra stress. Prediction is for a shear rate of $1s^{-1}$.

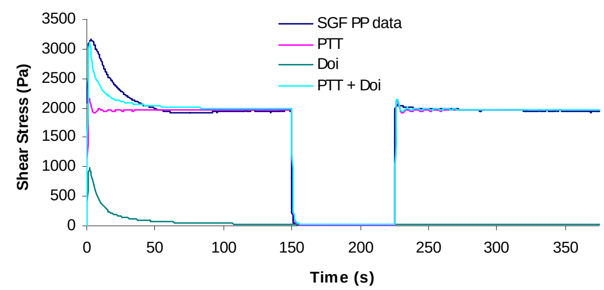


**Figure 3**. The shear stress vs. time for an interrupted stress growth test. SGF PP data is the experimental data for a short glass fiber filled PP. PTT and Doi are the separate model predictions for the 7-mode PPT and the modified Doi theory respectively. The PTT+Doi is the addition of the three stress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

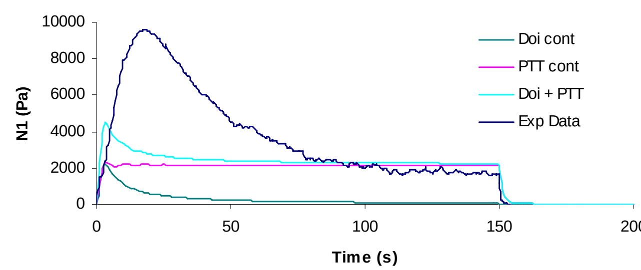


**Figure 4.** The primary normal stress difference vs. time for a stress growth/relaxation test. PTT and Doi are the separate model predictions for the 7-mode PPT and the modified Doi theory respectively. The PTT+Doi is the addition of the three stress contributions. Prediction is for a shear rate of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