Modeling the Transient Rheology of a Polypropylene Melt Reinforced with Long and Short Glass Fibers

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Abstract

In this paper we investigate the transient shear rheology of a polypropylene containing long fibers (2.75 to 11 mm, L/D > 150) and short fibers (1 mm, L/D < 50). The objectives of this work are to determine the relationship between stress growth and relaxation behavior of fiber orientation and determine the feasibility of extending Doi's theory for the rheology of rod-like molecules to fiber reinforced materials.

Introduction

Adding high modulus and strength fibers to thermoplastics increases their mechanical properties including strength and stiffness [1]. However, their addition significantly changes the processing performance of the matrix. The performance is altered by the orientation of the fiber and fiber interactions, which lead to changes in the rheological properties of the matrix. In modeling the flow behavior of the composites it is desired to be able to predict the fiber orientation as a function of processing conditions; this will determine the stiffness, strength, and warpage of the final part [2-4].

Previous work on modeling fiber orientation has mostly been accomplished by using a decoupling method, where the kinematics are calculated using a purely viscous constitutive equation and then the fiber orientation is post-calculated with the known velocity field [5]. Tucker showed using scaling arguments that for simple geometries with small gaps this decoupling approximation is accurate [6]. However, Libscomb et al. showed that in complex geometries, specifically, contractions, the presence of fiber can have a major effect on the kinematics of the flow, as well as the size and strength of vortices at the contraction region [7].

The overall aim of our research is to be able to predict and compare the fiber orientation in an injection molded part using the finite element method by incorporating a constitutive equation that couples the orientation of the fiber with the velocity field of the fluid,

and includes viscoelastic effects. For this we propose to extend the molecular theory proposed by Doi [8]. The work presented in this paper investigates the ability of Doi's theory for rigid rod molecules in a concentrated solution to be extended to long (2.75-11mm), and short (1mm) glass fibers suspended in a polypropylene matrix. The model's validity will be determined by its ability to predict the transient shear rheology of the system.

Theory

Doi's molecular theory was originally formulated for a solution of isotropic rod-like polymers with a monodisperse molecular weight. He then extended the theory to concentrated systems which spontaneously become anisotropic after a critical concentration without the presence of any external fields due to excluded volume effects.

In the Doi theory for concentrated solutions the orientation order tensor $S_{\alpha\beta}$, which describes the anisotropic molecular orientation of the system, is defined as:

$$S_{\alpha\beta} = \left\langle u_\alpha u_\beta - \frac{1}{3}\delta_{\alpha\beta} \right\rangle \tag{1}$$

where u_α is the unit vector parallel to the rod back bone, $\delta_{\alpha\beta}$ is the Kronecker Delta, and the brackets represent the average over the distribution function. By using a closure approximation, the time evolution of the orientation order tensor is given by:

$$\frac{\partial S_{\alpha\beta}}{\partial t} = F_{\alpha\beta} + G_{\alpha\beta} \tag{2}$$

$F_{\alpha\beta}$ represents the contribution due to the Brownian motion and the interaction potential of the system and is defined by:

$$F_{\alpha\beta} = -6\overline{D}_r \left[\begin{array}{c} \left(1 - \dfrac{U}{3}\right) S_{\alpha\beta} \dots \\ \dots -U\left(S_{\alpha\mu}S_{\beta\mu} - \dfrac{\delta_{\alpha\beta}}{3} S_{\mu\nu}^2 \right) + US_{\alpha\beta}S_{\mu\nu}^2 \end{array} \right] \quad (3)$$

where U is the phenomenological parameter representing the interaction potential of the system, $\overline{D}_r$ is the average rotational diffusivity given by:

$$\overline{D}_r = D_r \left(1 - \dfrac{3}{2} S_{\alpha\beta}^2 \right)^{-2} \quad (4)$$

and D_r is the lumped rotational diffusivity of the system. $G_{\alpha\beta}$ represents the contributions of the macroscopic flow field and is defined by:

$$G_{\alpha\beta} = \dfrac{1}{3}\left(v_{\alpha\beta} + v_{\beta\alpha} \right) + \dots$$
$$\dots \left(v_{\alpha\mu}S_{\mu\beta} + v_{\beta\mu}S_{\mu\alpha} - \dfrac{2}{3}\delta_{\alpha\beta}v_{\mu\nu}S_{\mu\nu} \right) - 2v_{\mu\nu}S_{\mu\nu}S_{\alpha\beta} \quad (5)$$

where $v_{\alpha\beta}$ is the velocity gradient. Equations (2, 3, and 5) represent six coupled ordinary differential equations which can be solved numerically for the time evolution of orientation for a known velocity field. The stresses are then calculated using equation (6), where it is assumed that the stresses arise solely from the free energy associated with the anisotropic distribution of rods.

$$\sigma_{\alpha\beta} = 3ck_bT \left[\begin{array}{c} S_{\alpha\beta}\left(1 - \dfrac{U}{3}\right) - \dots \\ \dots U\left(S_{\alpha\mu}S_{\beta\mu} - \dfrac{1}{3}\delta_{\alpha\beta}S_{\mu\nu}^2 \right) + US_{\alpha\beta}S_{\mu\nu}^2 \end{array} \right] \quad (6)$$

In equation (6) c is the concentration of the rods, k_b is Boltzmann's constant, and T is the temperature in Kelvin. It is noted that the stress here is formulated for small deformation rates. Doraiswamy and Metzner [9] modified the equations to incorporate a solvent contribution to the stress (neglected by Doi in his derivation for small deformation rates) which becomes a significant contribution at high shear rates. The solvent contribution term which is simply added to equation (6) is $\eta_r\eta_s\left(v_{\alpha\beta} + v_{\beta\alpha}\right)$, were η_r is the ratio of the viscosity of the suspension to that of the solvent and η_s is the viscosity of the solvent. Because the suspending medium in our system is a non-Newtonian fluid, $\eta_r\eta_s$ is replaced by the Carreau-Yasuda model (equation 7):

$$\dfrac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[1 + \left(\lambda\dot{\gamma}\right)^a \right]^{\frac{(n-1)}{a}} \quad (7)$$

In this model η_0 is the zero-shear viscosity, η_∞ is infinite-shear viscosity, λ is a time constant, n is the "power-law exponent", $\dot{\gamma}$ is the shear-rate, and a is a dimensionless parameter describing the transition region between the zero-shear-rate and power-law region [10]. Parameters were found by least-square regression of a full flow curve incorporating steady shear, dynamic, and capillary measurements. The Carreau-Yasuda model constants for the short glass fiber sample was found to be $\eta_0 = 3,999$ (Pa·s), $\eta_\infty = 0$ (Pa·s), $\lambda = .903$ s, $n = .66$, $a = .41$.

Experimental Procedure

Rheology:
Two fiber filled polypropylene samples were used in this work. The first, a glass fiber filled polypropylene pellet, was formed by pultrusion and then cut into 2.75mm, 5.5mm and 11mm fiber length samples allowing for the evaluation of fiber length on rheology. The other sample, a glass fiber filled polypropylene, was prepared by melt compounding with short glass fibers and then pelletized with an average fiber length of 1mm. The two samples had different matrix viscosities due to molecular weight differences.

Rheological testing in the low shear rate region (0.1-1s^{-1}) and dynamic frequency region (0.1-100 rad/s) was performed on a Rheometrics Mechanical Spectrometer (RMS-800) fitted with parallel plate geometry (diameter 25mm), which allows for gap control. A Göttfert Rheograph 2001 capillary rheometer was used for high shear rate data (10-2000 s^{-1}). Samples were pre-formed for all parallel plate measurements (thickness ~ 1mm). A pre-shear of 1s^{-1} was performed for 40s on all the pultruded samples.

Model:
It was found that the theoretical calculation of U and D_r gave unrealistic results and, hence, for modeling purposes D_r was replaced by D, and $3ck_bT$ (term in front of stress equation 6) was replaced by A. This follows the same method used by Doraiswamy and Metzner [9], except U was also varied and not calculated   In total the model has three constants, A, U, and D.

Results and Discussion

Dynamic oscillatory measurements were used to asses the influence of fiber length on complex viscosity, and

validate the necessary step of pre-shearing ($1s^{-1}$ for 40 s) the pultruded fiber filled polypropylene samples. It was found that when no pre-shear was performed on the pultruded samples of increasing length 2.75, 5.5, and 11mm their complex viscosity overlapped, the value of which is believed to be an enhanced matrix viscosity. Figure 1 shows that after a pre-shear was performed the effect of fiber length on the complex viscosity is distinguishable, and although the steady state values of the shear measurements did oscillate over time (figure 2) the overall values were more constant and consistent after the pre-shear. It was determined that the pre-shear was necessary to disperse the fibers, which were initially concentrated at the center of the pellet. This creates a more uniform stress contribution.

Steady shear measurements were performed in parallel plate geometry (25mm diameter), allowing for gap control. The geometry added a certain degree of uncertainty in the validity of the transient experiments. The first was the varying shear rate from the center to the outside diameter of the plate. The second is the length of the fiber in the long fiber samples compared to the diameter of the plate. It appeared that the fibers tried to align themselves in the flow (theta) direction but could not, due to their large size compared to the plate radius, and in doing so protruded from the plate gap. As a note, fibers protruding from the gap were only an issue for the long fiber samples. The short fiber sample remained in the gap, and measurements were very consistent and reproducible. In the future the transient tests on the long fibers will be reproduced and validated with a sliding plate rheometer where these complications should not be an issue. Because of the uncertainties in the experimental data, in this paper we only investigate some of the interesting transient response to shear of fiber filled systems to see if Doi's theory can predict the same trends.

Figure 2 represents transient steady shear data for all samples. The short fiber sample exhibited a large stress overshoot which relaxed over a time period of roughly 60s, at which steady state was reached. At time t = 450s the steady shear was removed and the stresses relaxed completely in about 10s. The large stress overshoot is attributed to the initial random orientation of the small fibers in the sample, which aligned in the flow direction over a time period proportional to the relaxation time of the stress overshoot. The long fiber samples were subject to a pre shear, allowed to relax for 100s, and then subject to a constant shear of $1s^{-1}$. No stress overshoot was observed for these samples. This was attributed to all the fibers being in the plane parallel to the rheometer plates, and being unable to align themselves completely in the flow direction, moving from a higher stress state to a lower one. At time t = 450s, the constant shear was removed and the stresses relaxed over a much larger time period than the short fiber sample to some asymptotic value, resulting in a residual stress.

The model's prediction of transient stress response to constant shear with varying D can be seen in figure 3. The values for the model parameters ($A = 30,000$ Pa, $U = 3.2$) where chosen to give steady state stress predictions of the same magnitude as the experimental results. The initial conditions for $S_{\alpha\beta}$ were set equal to zero, representing a random orientation state. From the graph one can see that the model does predict stress overshoot that relaxes to a steady state value over a much shorter time than is seen experimentally. When steady shear is removed, the model does predict a certain relaxation time, and by varying the different model constants, specifically D, a large range of relaxation times can be accomplished

Doi theory was originally developed for small deformation rates; the applicable range seems to be proportional to D. At higher shear rates the stresses saturate, and plateau. As previously mentioned, by incorporating a term for the solvent contribution one can predict a full shear rate range. Figure 4 shows the model prediction both for Doi's original theory and with the solvent contribution term. Model parameters and conditions were held constant at $A = 30,000$ Pa, $U = 3.2$, and $D = .1s^{-1}$, while varying the shear rate.

Summary

The Doi theory for rigid rods in a Newtonian solution in its original form was able to predict some of the interesting phenomena exhibited by glass fiber filled polypropylene systems. This includes stress overshoot, which is dependent on the initial fiber orientation of the system that relaxes to some steady state value, and a relaxation spectrum that can be controlled to include residual stresses. By including a solvent contribution term, as shown by Doraiswamy and Metzner, the theory was able to hold over a large shear rate range.

Acknowledgements

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Key Words

Polypropylene, long and short glass fiber, transient rheology, Doi Theory
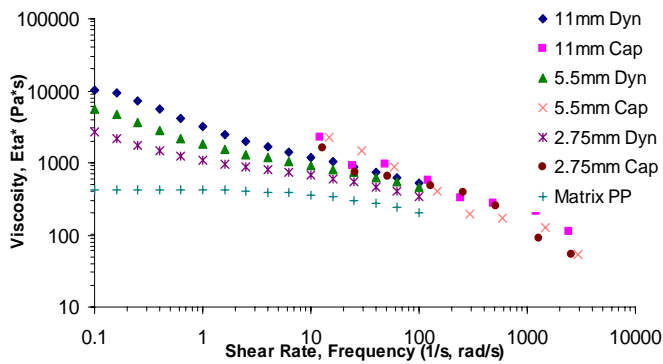
Figure 1. Dynamic oscillatory (after pre-shear) and capillary rheology master curve of glass fiber filled polypropylene, and polypropylene matrix.
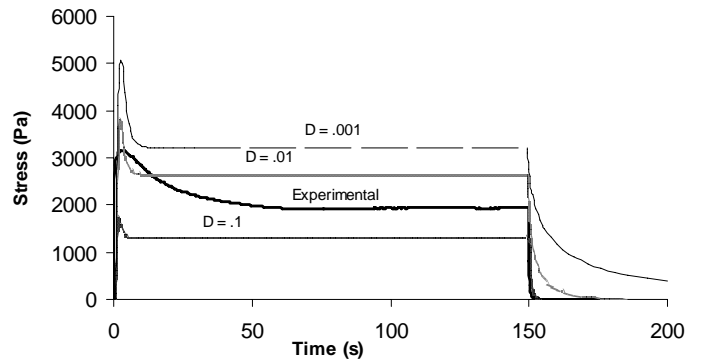
Figure 3. Model's prediction of the transient stress, compared to experimental result. Model parameters and conditions were held constant at shear rate = $1s^{-1}$, A = 30,000 Pa, and U = 3.2, while varying D (representative value of D_r).
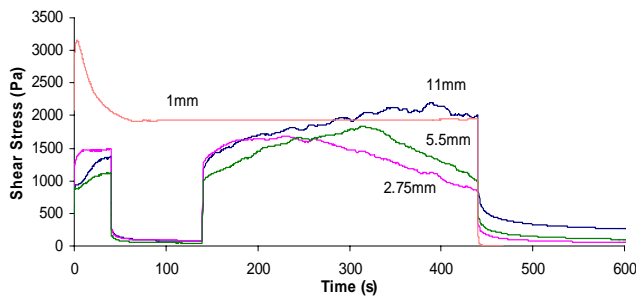
Figure 2. Transient stress of the four different glass filled polypropylene systems at a steady shear rate of $1s^{-1}$. Long fiber samples were pre-sheared at $1s^{-1}$ for 40s.
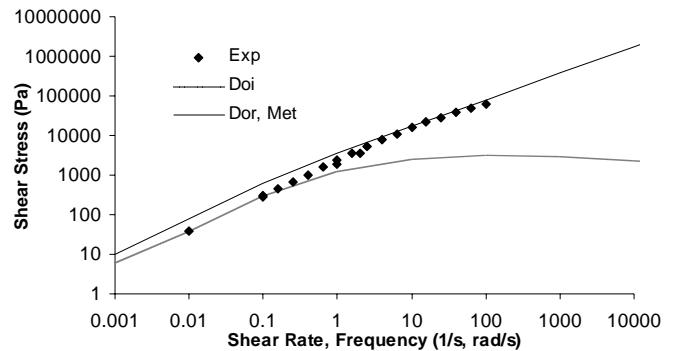
Figure 4. Pure Doi theory model, and Doraiswamy Metzner modified model prediction of steady state stress compared to experimental results for the short glass fiber system. Model parameters and conditions were held constant at A = 30,000 Pa, U = 3.2, and D = $.1s^{-1}$, while varying the shear rate.