APPLICATION OF A CONSTITUTIVE MODEL TO EXTENSIONAL AND SHEAR RHEOLOGY OF POLYSTYRENE CARBON NANOFIBER COMPOSITES

Undergraduate Research Thesis

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Abstract

This research focuses on improving an existing constitutive model to predict the rheology of polystyrene-carbon nanofiber (CNF) composites and examining the differences between two nanocomposite preparation techniques and two types of nanofibers. The constitutive model is a set of equations adapted to predict the dynamic behavior of polymer nanocomposites and the orientation evolution of nanofibers. The equations in the model are functions of time, type of flow, stress, deformation, nanofiber orientation, and flow history due to the polymer's viscoelasticity. Important parameters in the model include: polymer relaxation time, polymer viscosity, mobility factor, polymer-particle interaction, particle-particle interaction, and aspect ratio. Three flow fields were examined: small-amplitude oscillatory shear, transient shear, and transient extensional flows. The two preparation techniques examined are commonly used in preparing polymer composites: melt-blending and solvent casting. The nanofibers examined were as received from the manufacturer with some undergoing additional high-heat treating. This research resulted in the development of an accurate model for the composites for all three flow fields. Values of parameters in the model have given insight into the physical behavior of the composite due to polymer-particle and particle-particle interactions and due to agglomeration. An accurate model of a polymer-CNF composite would be beneficial to industry, as the manufacturing processes such as extrusion, flow through dies, or spraying alter the orientation and consequently the mechanical, electrical, thermal, and optical properties of the composite. This model can provide a way to understand these effects would improve the optimization of properties.

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Publications

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Field of Study

Major Field: Chemical Engineering

Minor Field: Mathematics

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Chapter 1: Introduction

Particles are classified as nanoparticles if at least one dimension is in the nanometer scale. Common examples are single-walled (SWNT) and multi-walled carbon nanotubes (MWNT), carbon nanofibers (CNFs), and nanoclays. Interest in nanoparticles has been sparked in industry because nanoparticles are capable of increasing the mechanical strength of composites at lower loadings than conventional macroscopic particles such as carbon black. Thermal and electrical properties of poor conducting media such as polymers may also be improved with the addition of nanoparticles [1]. Such materials are called nanocomposites, combining at least two distinct materials [2].

Single-walled carbon nanotubes are formed of graphite sheets rolled into a tube with a diameter of approximately 1 nm, displaying either zig-zag or armchair conformations [3]. These conformations can be seen below in Figure 1: **Single-walled nanotube conformations (a) zig-zag (b) armchair**Figure 1.

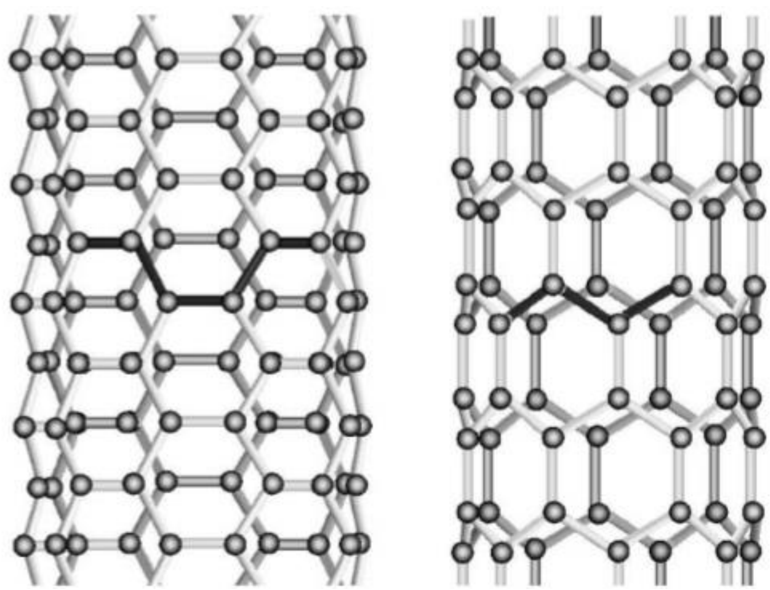

Figure 1: Single-walled nanotube conformations (a) zig-zag (b) armchair [3]

Multi-walled nanotubes are made of concentric single-walled nanotubes with diameters around 10-20 nm. Both of these carbon nanotubes (CNTs) can be 10-100 times stronger than steel at a lower weight [4]. Electrons are able to move along the carbon lattice giving them their good electrical properties [5]. However, the current limitation of their use is their high cost.

CNFs are also tube-like structures, but are much larger than CNTs with diameters of 50-200nm and lengths into the micron range. The structure of nanofibers is also different, displaying graphitized stacked cups structure as can be seen in Figure 2.

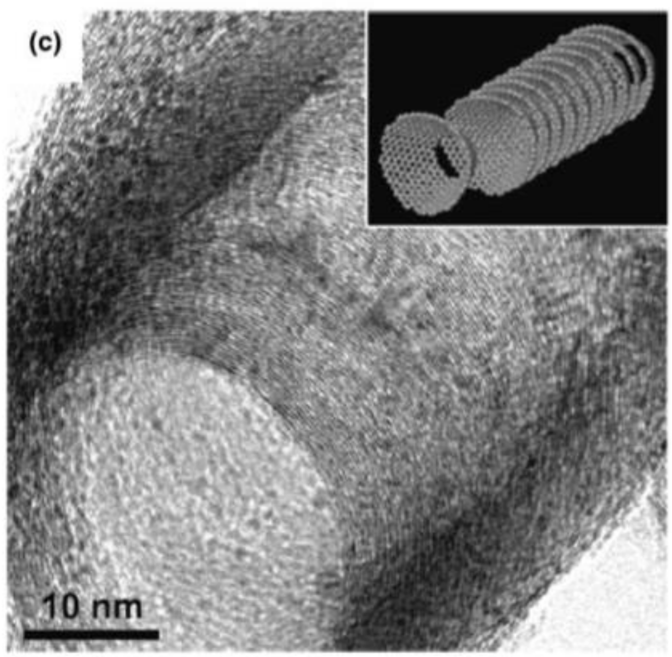

Figure 2: Stacked cup structure of CNFs (angled view) [6]

This structure is not as ordered as CNTs so the mechanical properties of CNTs are better than CNFs; however, CNFs still have very good mechanical properties. Additionally, the edges of

CNFs have improved physical bonding with other materials such as polymers [1]. The advantage to CNFs over CNTs is their availability at 1/500 of the cost [8]. Therefore, since they also display many of the properties of nanotubes, they have a strong potential for use in industry.

One of the common ways of making CNTs and CNFs is chemical vapor decomposition. Organic vapors are heated to high temperatures and in the presence of metal catalysts, the vapors decompose into SWNTs, MWNTs, and CNFs, [7]. These particles can then be further treated to purify them. Methods include high heat treatment and washing with an acid. Particularly with CNFs, both techniques can shorten fiber length and affect how the CNFs interact with each other and with a polymer [1].

One problem for the use of CNTs and CNFs in composites is achieving a high level of dispersion. SWNT tend to clump into ropes, and MWNT and CNFs are often tangled [4]. This is of concern when the nanoparticles are placed in a matrix such as a polymer, where dispersion is desired for optimal mechanical properties [5]. The three common techniques used to improve dispersion with a polymer are melt blending, solution processing, and *in-situ* polymerization [2]. Melt blending involves melting a polymer, and then mechanically mixing in the nanoparticles and allowing the diffusing of polymer chains between the nanoparticles [11]. One negative effect of melt blending when using CNFs is a breakdown of CNF length due to the mechanical mixing; however, melt-blending generally achieves good dispersion of nanoparticles. In solvent casting, a polymer is dissolved in a solvent, the nanoparticles are mixed in by sonication, and then the solvent is evaporated off, forming the composite [12]. Solvent casting preserves the original length of CNFs which is longer than in melt-blending but may not disperse the particles as well. The final method, i*n-situ* polymerization, involves sonicating the nanoparticles in a monomer solution which is then polymerized to give the composite [13].

Another important detail is the dependence of the properties of nanocomposites with the orientation of the CNTs or CNFs. Mechanical and electrical properties are strong along the length of the CNTs and CNFs but are weak in the perpendicular direction [14]. Therefore, properties can be optimized in a particular direction by orienting the particles in that direction. One way to orient the particles in a matrix, such as a polymer, is to flow the melted composite. The degree of alignment is different under different flow fields as can be seen in Figure 3.

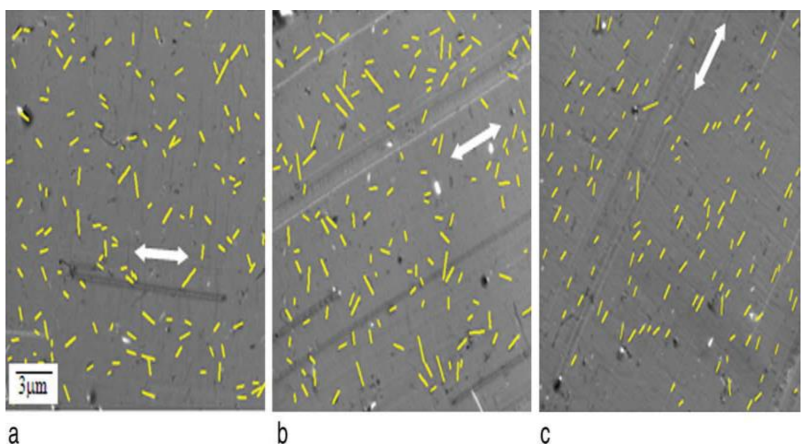

Figure 3: Aligning of CNFs under shear and extensional flow (a) before deformation (random alignment) (b) undergoing shear flow (c) undergoing extensional flow (highly aligned) [14]

Additionally, industrial processes involving nanocomposites could also affect the orientation of the nanoparticles, thus affecting the properties of the final product. Extrusion, injection molding, spraying, and fiber spinning are examples of such processes. To be able to understand these effects, the rheology of polymer nanocomposites is of interest.

There has been a great interest in researching polymer-CNT composites, with far less research devoted to polymer-CNF composites [15-19]. The research that has described the rheology of polymer-CNF composites for various polymer systems such as polyethylene [20], polypropylene [21-29], polycarbonate [21, 30-32], polyester [33], polyamide [34, 35], poly(methyl methacrylate) [36, 37], and polystyrene [38]. Additionally, these focus only on shear rheology, excluding extensional rheology and the evolution of fiber orientation [14].

Previous research in Koelling's group has addressed some of these deficiencies by researching both shear and extensional rheology of CNFs in polystyrene. A constitutive model for both flow fields was developed by Kagarise [10]. This model was then applied to the shear rheology during forward and reverse flows by Murch and Kremer [39, 40].

This research is focused on improving the accuracy of the model, incorporating shear, extensional, and small-amplitude oscillatory shear experiments. Within the constitutive model is a parameter that can couple the stress of the polymer to the stress due to CNFs. Kagarise did not use this coupling parameter in his studies of shear and extensional flows [10], and neither did Murch in his shear flow reversal experiments [39]. Kremer did allow the coupling effect in his flow reversal and small-amplitude oscillatory shear experiments and found an improvement in the accuracy of the model [40]. One of the improvements in this research is now applying that coupling also to extensional flows, with the goal of optimizing one set of parameters for the constitutive model to describe shear, extensional, and small-amplitude oscillatory shear flows. Two preparation methods, melt-blending and solvent casting described above, were examined and modeled to characterize differences in the rheology between the two methods. Rheological differences between two types of CNFs, one as received from the manufacturer and one high heat treated for purification, were also examined.

Chapter 2: Materials and Methodology

A polymer – CNF composite system was examined for all the experiments which had been previously conducted in this lab [41]. The polymer used was polystyrene (PS) as received from the Chevron Phillips Chemical Company LP (MC3600, specific gravity: 1.03, MFI: 13.0 g/ 10 min at 200^{o}C), chosen for its well-characterized rheology, lack of crystallinity, and affinity for CNFs due to the aromatic group in the repeated polymer unit [14].

The two types of CNFs used were as received in powder form from Applied Science with the first being ordinary CNFs (Pyrograf III, type PR-24-PS) denoted O-CNF, and the second being high heat treated to 3000^{o}C (Pyrograf III, type PR-24-XT-HHT) denoted HHT-CNF. O-CNFs have been pyrolytically stripped, meaning polyaromatic hydrocarbons have been removed from the surface of the fibers, whereas the high heat treating in HHT-CNFs graphitizes carbon on the surface, creating the most graphitic CNF offered by Applied Science and having reduced concentrations of iron catalyst in the CNFs. Since the high heat treating improves conductivity, HHT-CNFs would be useful for electronic and thermal applications, and O-CNFs for mechanical and electrical. The chemical vapor deposition process produces entangled fibers in both instances [42].

Two preparation methods for the samples were examined: melt-blending (MB), and solvent casting (SC). MB samples were prepared by adding PS pellets and CNF powder to a DACA twin screw microcompounder, heating to 200^{o}C, and mixing for 5 minutes at 250 rpm. These conditions allowed good dispersion of CNFs without degrading the PS. Samples were prepared at 0wt% and 2wt%. Once mixed, the composite was extruded through a 2mm die and cut into 2-3mm length pellets [14].

SC samples were prepared by dissolving 19.6g PS in 200 mL tetrahydrofuran (THF), stirring for 12h, and adding CNFs. CNFs were added in 0wt% and 2wt%. The composite was ice-cooled while being sonicated at 20 kHz for 15 min using a Sonic Dismembrator (Fisher Scientific, Model: 550; probe: 1") at a power level of 550 WL^{-1}. The composite was then film cast at room temperature, dried in a vacuum oven at 65°C, broken by an Analytical Mill (IKA) into 0.5-1mm diameter chips, and dried in a vaccum oven at 65°C for an additional 5 days to remove all THF [14].

Test samples for both preparation methods were created by compression molding of the pellets/chips into 25mm diameter and 0.9-1.2mm thick discs for shear flow tests and 52mm x 7mm x 1.55mm rectangular bars for extensional flow tests. The compression molding was done by melting the pellets/chips at 200°C for 15 min, quickly pressurizing and releasing pressure four times to remove air bubbles, pressurisizing for an additional 10 min, turning off the pressure and heat, and removing samples once cooled. Storage of test samples in a vacuum oven for 24 hours at 65°C before rheological measurements was done to prevent absorption of air or moisture [14].

The nanometer-scale diameters of CNFs were measured using a FEI Technai G2 Spirit transmission electron microscope (TEM) at 100keV and 4800 x magnification, and the micron-scale lengths were measured with a Zeiss Axioskop optical microscope at 400 x magnification. The lengths of CNFs after test sample preparation were examined to characterize differences in aspect ratio between the different preparation methods. Figure 4 shows the distribution of lengths. Table 1 shows the average diameters, number average lengths, weight average lengths, aspect ratios, and polydispersity of average lengths [41].

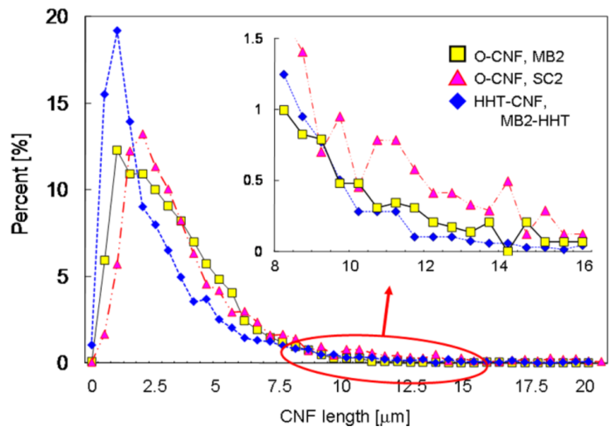

Figure 4: Distribution of CNF length [41]

Table 1: Analysis of CNF length after preparation of PS/CNF composites [41]

Specimens	Diameter [µm]	L_N [µm]*1	L_W [µm]*2	% of long CNFs*3	Aspect ratio*4	Polydispersity
O-CNF, MB	0.065± 17	3.43	4.78	1.56	53	1.39
HHT-CNF, MB	0.066± 18	2.92	4.64	3.06	44	1.59
O-CNF, SC	0.065± 17	4.46	8.01	7.86	69	1.80

*1: Number average length of CNFs

*2: Weight average length of CNFs

*3: Total percentage of CNFs longer than 10 µm

*4: L_N /Diameter of CNF

*5: L_W/L_N

Of note, the CNFs in the SC composites have the longest lengths and aspect ratios. CNFs in MB and MB-HHT are more comparable, with CNFs in MB being longer than MB-HHT. L_N, number average length, was used in the calculation of all aspect ratios.

Linear viscoelastic behavior was characterized with SAOS. A strain-controlled rheometer, ARES LS2 from TA Instruments, with a torque transducer (0.02-2000 g cm) and a normal force transducer (2-2000 g) was used. Parallel plate geometry with 25mm diameter and 0.9-1.2mm gap distance was used. Molded test samples were placed on the plates, heated to 160^{o}C, allowed to rest for 15 min to relax the polymer. Each test sample was measured at maximum strains of 0.5 and frequencies from 0.01-100 s^{-1}. The storage (G') and loss (G") moduli were then measured.

Transient shear rheology was also characterized using the ARES LS2 with the same geometry and sample heating as with SAOS tests. Five shear rates were tested: 0.01, 0.1, 0.3, 1, and 3 s^{-1}. New test samples were used for each shear rate.

Extensional rheology was characterized using a Rheometrics Melt Extensiometer (RME) from Rheometetrics Scienctific. Test samples were heated to 160^{o}C , allowed to rest for 15 min, and tested at one of five extension rates: 0.01, 0.03, 0.1, 0.3, 1 s^{-1}. New test samples were used for each extension rate.

Orientation evolution of CNFs in extensional flows were characterized by stretching test samples to total strains of 0, 0.1, 0.3, 1, or 3 at constant extension rates of 0.01, 0.1, or 1 s^{-1}. The samples were cut with a ultra-microtome to 200nm thickness at a 20^o angle relative to the stretching direction, previously determined to be optimum [43]. A TEM microscope was used to view and characterize the average orientation of CNFs.

Chapter 3: Description of Constitutive Model

The constitutive model is composed of the following four equations:

$$\tau_{ij}^{c} = -p\delta_{ij} + 2\eta_s D_{ij} + \tau_{ij}^{p} + \tau_{ij}^{CNF} \tag{1}$$

$$\sigma\tau_{ij,m}^{p} + \lambda_m \frac{D\tau_{ij,m}^{p}}{Dt} + \frac{\alpha_m \lambda_m}{\eta_{p,m}}\left(\tau_{ik,m}^{p}\tau_{kj,m}^{p}\right) + \frac{3(1-\sigma)}{2}\left(a_{ik}\tau_{kj,m}^{p} + \tau_{ik,m}^{p}a_{kj}\right) = 2\eta_{p,m}D_{ij} \tag{2}$$

$$\tau_{ij}^{CNF} = 2[\eta_s + \eta]\varphi[AD_{kl}a_{ijkl} + B\left(D_{ik}a_{kl} + a_{ik}D_{kj}\right) + CD_{ij} + 2Fa_{ij}D_r] \tag{3}$$

$$\frac{da_{ij}}{dt} = \left(W_{ik}a_{kj} - a_{ik}W_{kj}\right) + \chi\left(D_{ik}a_{kj} + a_{ik}D_{kj} - 2D_{kl}a_{ijkl}\right) + 4C_I \Pi_D^{1/2}(\delta_{ij} - 3a_{ij}) \tag{4}$$

Equation (1) expresses the total stress in the composite. Equation (2) is the mulit-mode Giesekus model which predicts the flow induced stress in the polymer, and Equation (3) expresses the flow induced stress from the CNFs. Equation (4) describes the evolution of CNF orientation during flow.

Equation (1), proposed by Azaiez [44] for fiber suspensions in viscoelastic media, expresses the total stress (τ_{ij}^{c}) in the composite as a sum of the pressure maintaining incompressibility (p), the stress from a Newtonian solvent ($2\eta_s D_{ij}$), from the polymer (τ_{ij}^{p}), and from the CNFs (τ_{ij}^{CNF}). Since no solvent was used during rheological testing in the PS/CNF composites studied, there is no solvent contribution. Transient shear viscosity is defined as

$$\eta^{+} = \frac{\tau_{12}}{\dot{\gamma}}, \tag{5}$$

where $\dot{\gamma}$ is the shear rate, and extensional viscosity is

$$\eta_E^+ = \frac{\tau_{11}-\tau_{22}}{\dot{\varepsilon}}, \tag{6}$$

where $\dot{\varepsilon}$ is the extension rate.

Equation (2) is a mulit-mode version of the model proposed by Giesekus [45] which predicts the flow induced stress in the polymer as a sum of the stresses of all the modes

$$\tau_{ij}^p = \sum_{m=1}^{N} \tau_{ij,m}^p, \tag{7}$$

where N is the number of modes. The upper convected derivative of τ_{ij}^p is given as

$$\frac{D\tau_{ij}^p}{Dt} = \frac{d}{dt}\tau_{ij}^p - W_{ik}\tau_{kj}^p + \tau_{ik}^p W_{kj} - D_{ik}\tau_{kj}^p - \tau_{ik}^p D_{kj}, \tag{8}$$

where W_{ij} is the skew part and D_{ij} is the symmetric part of the Eulerian velocity gradient. For shear flow,

$$W_{ij} = \begin{bmatrix} 0 & \dot{\gamma}/2 & 0 \\ -\dot{\gamma}/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad D_{ij} = \begin{bmatrix} 0 & \dot{\gamma}/2 & 0 \\ \dot{\gamma}/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \tau_{ij} = \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix}, \tag{9}$$

and for extensional flow,

$$W_{ij} = 0, \quad D_{ij} = \begin{bmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon}/2 & 0 \\ 0 & 0 & -\dot{\varepsilon}/2 \end{bmatrix}, \quad \tau_{ij} = \begin{bmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix}. \tag{10}$$

The remaining parameters, $\sigma, \eta_{p,m}, \lambda_m$, and α_m, are fitting parameters that describe the polymer-particle interaction and the zero strain rate viscosity of the polymer, relaxation time, and mobility factor for each mode, respectively. Of note, the appearance σ in this equation allows the coupling of τ_{ij}^p and τ_{ij}^{CNF} when $\sigma < 1$, or this coupling can be turned off by setting $\sigma = 1$. These are discussed in more detail in the following sections.

Equation (3), proposed by Tucker [46], expresses the flow induced stress contribution from the CNFs due to the traction of the polymer on the surface of the particles, averaged over all particle orientations. In this equation, η is the viscosity of the polymer. φ is the volume fraction of CNFs. A, B, C, and F are shape factors which are defined below in Table 2 for various particle loading and orientation regimes where r is the aspect ratio of the CNFs given as $r = length/diameter$.

Table 2: Shape Factors for Various Concentration Regimes

Shape Factor	**Dilute** [47]	**Semidilute Aligned** [48]	**Semidilute Aligned** [49]	**Semidilute Isotropic** [49]
A	A_1	A_2	A_3	A_4
B	$\frac{6\ln(2r)-11}{r^2}$	0	0	0
C	2	0	0	0
F	$\frac{3r^2}{\ln(2r)-0.5}$	0	0	0

$$A_1 = \frac{r^2}{2[\ln(2r)-1.5]} \qquad A_2 = \frac{r^2}{3\ln\left(\sqrt{\left(\frac{\pi}{\phi}\right)}\right)}$$

$$A_3 = \frac{16r^2}{3\ln\left(\frac{1}{\phi}\right)}\left[1-\frac{\ln\ln\left(\frac{1}{\phi}\right)}{\ln\left(\frac{1}{\phi}\right)}+\frac{0.6344}{\ln\left(\frac{1}{\phi}\right)}\right] \qquad \mathrm{A}_4 = \frac{16r^2}{3[\ln\left(\frac{1}{\phi}\right)+\ln\ln\left(\frac{1}{\phi}\right)+1.4389]}$$

The semi-dilute regime is defined as volume fractions within the range specified as

$$r^{-2} < \phi < r^{-1} \tag{11}$$

a_{ij} and a_{ijkl} are the second and fourth order orientation tensors that capture the average orientation of the CNFs in three-dimensions. These tensors are derived from a probability distribution of individual fiber orientations. An individual fiber can be described by a vector **p** in three dimensional space in spherical coordinates as described by

$$\boldsymbol{p} = (p_1, p_2, p_3) = (\cos\phi\sin\theta, \sin\phi\sin\theta, \cos\theta) \tag{12}$$

Figure 5 demonstrates such a vector and coordinate system.

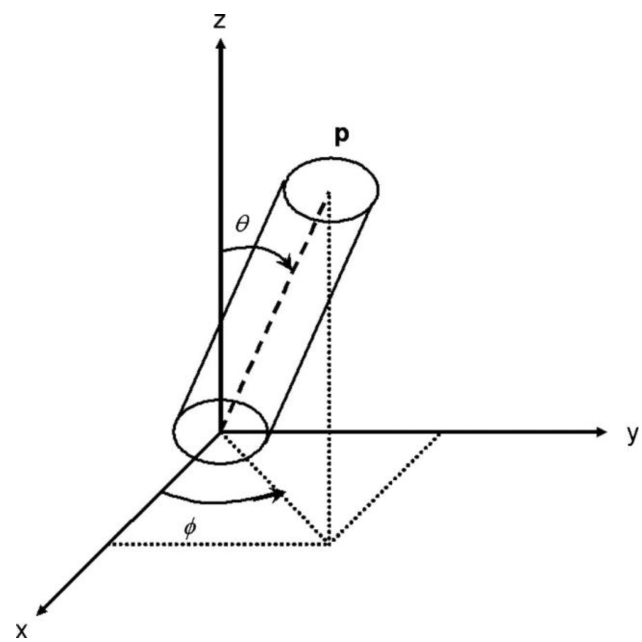

Figure 5: Coordinate System for Orientation of Single Nanofiber [10]

A probability distribution function, $\psi(\theta, \phi)$, can describe the probability, P, of finding a fiber oriented between θ_1 and $(\theta_1 + d\theta)$ and between ϕ_1 and $(\phi_1 + d\phi)$, given as [50]

$$P(\theta_i \leq \theta \leq \theta_i + d\theta, \phi_i \leq \phi \leq \phi + d\phi) = \psi(\theta, \phi) \sin \theta_i d\theta d\phi \tag{13}$$

with each fiber described by a (θ, ϕ) existing on the surface of a unit sphere and with [50]

$$\oint \psi(p)dp = \int_0^{2\pi}\int_0^{2\pi} \psi(\theta,\phi)\sin\theta \, d\theta d\phi = 1. \tag{14}$$

The orientation tensors can then be described over the orientation space by [50]

$$a_{ij} = \int p_i p_j \psi(p)dp \tag{15}$$

$$a_{ijkl} = \int p_i p_j p_k p_l \psi(p)dp \tag{16}$$

and by the definition of p from Equation 12,

$$a_{ij} = \begin{bmatrix} \cos^2\theta & \sin\theta\cos\theta\sin\phi & \sin\theta\cos\theta\cos\phi \\ \sin\theta\cos\theta\sin\phi & \sin^2\phi\sin^2\theta & \sin^2\theta\sin\phi\cos\phi \\ \sin\theta\cos\theta\cos\phi & \sin^2\theta\sin\phi\cos\phi & \cos^2\phi\sin^2\theta \end{bmatrix}. \tag{17}$$

By averaging over a sufficiently large number of nanofibers, the second order orientation tensor can be calculated [51].

The calculation of the fourth order orientation tensor requires an approximation in terms of the second order orientation tensor. There are three common choices for this approximation: the linear closure approximation for non-aligned fibers given by [52]

$$\hat{a}_{ijkl} = -\frac{1}{35}\left(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\right) + \frac{1}{7}(a_{ij}\delta_{kl} + a_{ik}\delta_{jl} + a_{kl}\delta_{ij} + a_{jl}\delta_{ik} + a_{jk}\delta_{il} + a_{il}\delta_{jk}) \tag{18}$$

the quadratic closure approximation for aligned fibers given by [52]

$$\tilde{a}_{ijkl} = a_{ij}a_{kl} \tag{19}$$

and the hybrid closure approximation, combining linear and quadratic closure approximations for the entire range of non-aligned and aligned fibers given by [52]

$$a_{ijkl} = (1-f)\,\hat{a}_{ijkl} + f\tilde{a}_{ijkl},\ \ f = 1 - 27\det(a_{ij}) \tag{20}$$

The hybrid closure approximation was chosen for this research as the experiments consist of flows that orient the CNFs from a random orientation initially to an oriented state by the end of the experiment, including high degrees of orientation for extensional flows.

D_r is the rotary diffusivity due to Brownian motion defined as

$$D_r = 2C_I \Pi_D^{1/2} \tag{21}$$

where C_I is a fitting parameter describing the hydrodynamic particle-particle interaction and is discussed in more detail in the composite parameter fitting section, and Π_D is the second invariant of the symmetric part of the velocity gradient equal to $\frac{\dot{\gamma}^2}{4}$ for shear flow and $\frac{3\dot{\varepsilon}^2}{4}$ for extensional flows.

The final equation in the model is Equation (4) suggested by Folgar and Tucker [53] and used by Advani and Tucker to describe the evolution of CNF orientation during flow. χ is a shape factor described by the aspect ratio as

$$\chi = \frac{r^2-1}{r^2+1}\,. \tag{22}$$

Chapter 4: Optimizing the Model

Parameter fitting for pure polymer

Three of the parameters discussed above, $\eta_{p,m}, \lambda_m$, and α_m, describe only the polymer and so could be fit to pure polymer samples. This was done by fitting the model to experimental data from pure polystyrene for transient shear and transient extensional data as well as fitting the storage and loss moduli to small-amplitude oscillatory shear (SAOS) data. The overhead program used to optimize these parameters can be found in the appendix under the "Pure Polymer: Overhead Parameter Optimization" section. From previous experimental data, it was shown that there was no difference between MB-0wt% and SC-0wt%, so the MB-0wt% was used for pure-polymer parameter fitting [14]. The storage and loss moduli were modeled with the mulit-mode general linear viscoelastic model using the following equations:

$$G'(\omega) = \sum_{m=1}^{N} \frac{\eta_{p,m}\lambda_m\omega^2}{1+(\lambda_m\omega)^2} \tag{23}$$

$$G"(\omega) = \sum_{m=1}^{N} \frac{\eta_{p,m}\omega}{1+(\lambda_m\omega)^2} \quad . \tag{24}$$

where ω is the frequency of the oscillation. Many frequencies are tested to capture the behavior of the moduli over a range of oscillation frequencies. The model predictions were compared to SAOS experimental moduli data through the following error calculation:

$$E_{SAOS} = \sum_{m=1}^{N}\{ [\log_{10} G'_{exp}(\omega_i) - \log_{10} G'(\omega_i)]^2 + [\log_{10} G^{"}_{exp}(\omega_i) - \log_{10} G"(\omega_i)]^2\} \tag{25}$$

The program developed to optimize $\eta_{p,m}, \lambda_m$, and α_m for SAOS flows can be found in the appendix under "Pure Polymer: SAOS Flows".

Model predictions for shear and extensional flows were likewise compared to experimental viscosity data through the following error calculation:

$$E = \sum_{j=1}^{N} [\log_{10} \eta_{exp}(t_j) - \log_{10} \eta_{model}(t_j)]^2 \quad (26)$$

where N is the number of experimental data points and t_j is the time of the j-th point. The total error was then

$$E_{total} = E_{Extensional} + y * E_{Shear} + z * E_{SAOS} \quad (27)$$

where y and z can change the relative weighting of errors so that the error in the model's prediction of shear and SAOS are the same order of magnitude as the error in extensional predictions. Balancing the order of magnitudes of the errors yields accurate model predictions for all three flows. The programs used for transient shear and extensional flows in a pure polymer can be found in the appendix under "Pure Polymer: Transient Shear Flow" and "Pure Polymer: Transient Extensional Flow", respectively. Additionally, the sub-programs that solved the constitutive model for these two flow fields can be found under "Constitutive Model Solver: Extensional Flow" and "Constitutive Model Solver: Shear Flow".

Since shear viscosity vs. time is typically plotted on a log-log plot, any time delay in the start-up of an experiment would be noticeable in the plot. This was accounted for by examining the experimental data on a log-log plot to see when data appeared to approach the time axis at short times. From this, it was determined that the rheometer used had a time delay of approximately 0.0095 s. By shifting all of the time data points back by this factor, a more accurate plot of experimental data at short times could be observed and compared to model predictions, both through the error minimization program and visually.

In extensional flows at low extension rates and short times, the strain is so low that large inaccuracies can occur in the experimental data due to transducer insensitivity. At these low extension rates and strains, it is known that extensional viscosity follows the linear viscoelastic plateau so these inaccuracies can be correctly labeled as transducer error. However, when fitting a model to this data, these large deviations make minimizing the error between model and experimental data more difficult, and can even lead away from optimal parameter values. Thus, the experimental data for the two lowest strain rates were truncated at short times, leaving the experimental data at higher times which was free of these large inaccuracies. This gave a smoother curve fit the model to and resulted in a far more accurate optimization of model parameters.

A program was written in MATLAB to solve the model, and through the use of a constrained minimization function, "fmincon", minimize the error between experiment and model for all three flow fields by changing $\eta_{p,m}, \lambda_m,$ and α_m. Fmincon is a MATLAB function that finds the minimum of a contrained nonlinear multivariable function, in this case, the error between nonlinear functions and experimental data. The parameter design space was examined by the minimization function through the use of the "Interior-point" algorithm. This algorithm is the standard one used by MATLAB and is useful for large, sparse problems and small, dense problems. Additionally, this algorithm is capable of recovering from divergent results, and all constraints are satisfied with each iteration [54]. The number of modes was incrementally increased from one until the model could accurately capture the behavior of the polymer and additional modes provided no significant improvements.

Parameter fitting for composite

The remaining two parameters, σ and C_I, describe effects due to nanofibers in a composite and thus were fit to experimental composite data. A similar approach to fitting these parameters using error analysis as described for the pure polymer was initially employed but did not yield ideal results due to a gross over-prediction of viscosity. This had been observed in this model before by Kagarise [10], and the only solution to bring the model prediction within the range of experimental data was to scale the experimentally measured aspect ratio, thus making an “effective” aspect ratio. An additional motivation behind this scaling factor was that an agglomerate of fibers would have a reduced aspect ratio below that of a single fiber. Therefore, this scaling factor might be able to capture the amount of agglomeration in the composites.

In this research, effective aspect ratio was made into another fitting parameter for composite data defined as

$$r_{effective} = r_{exp}/h \qquad (28)$$

where h is the scaling factor. However, introducing this parameter now caused the optimization of aspect ratio to dominate the optimization process and mask the effect σ and C_I. Therefore, a new method for optimizing these three parameters was created.

Since C_I is the only parameter that appears in the Equation 4, the orientation evolution of nanofibers, it can be fit to the steady-state orientation of nanofibers, as suggested by Kagarise [10]. Steady-state orientation was measured only for extensional flows at four strains since a high degree of orientation is achieved in this type of flow. Equation 4 was set to zero, and the error between experimental data at three strain rates

(0.01, 0.1, and 1 s^{-1}) and model predictions for the component of the orientation tensor in the direction of flow, a_{11}, given by

$$E_{a_{11}} = \left[a_{11,exp} - a_{11,model}\right]^2 \tag{29}$$

was minimized to yield the optimal value for C_I. The same function, fmincon, and algorithm, Interior-point, that were used in the pure polymer optimization were also used in this error minimization. This program can be found in the appendix under "Composite Parameter Optimization: C_I".

To fit σ and $r_{effective}$ the major effects these parameters have on model predictions needed to be examined. This was done by changing one parameter while fixing the other and minimizing the error between the resulting viscosity predictions of the model and experiment using the same algorithm as before. These results can be seen below in Figure 6 and Figure 7.

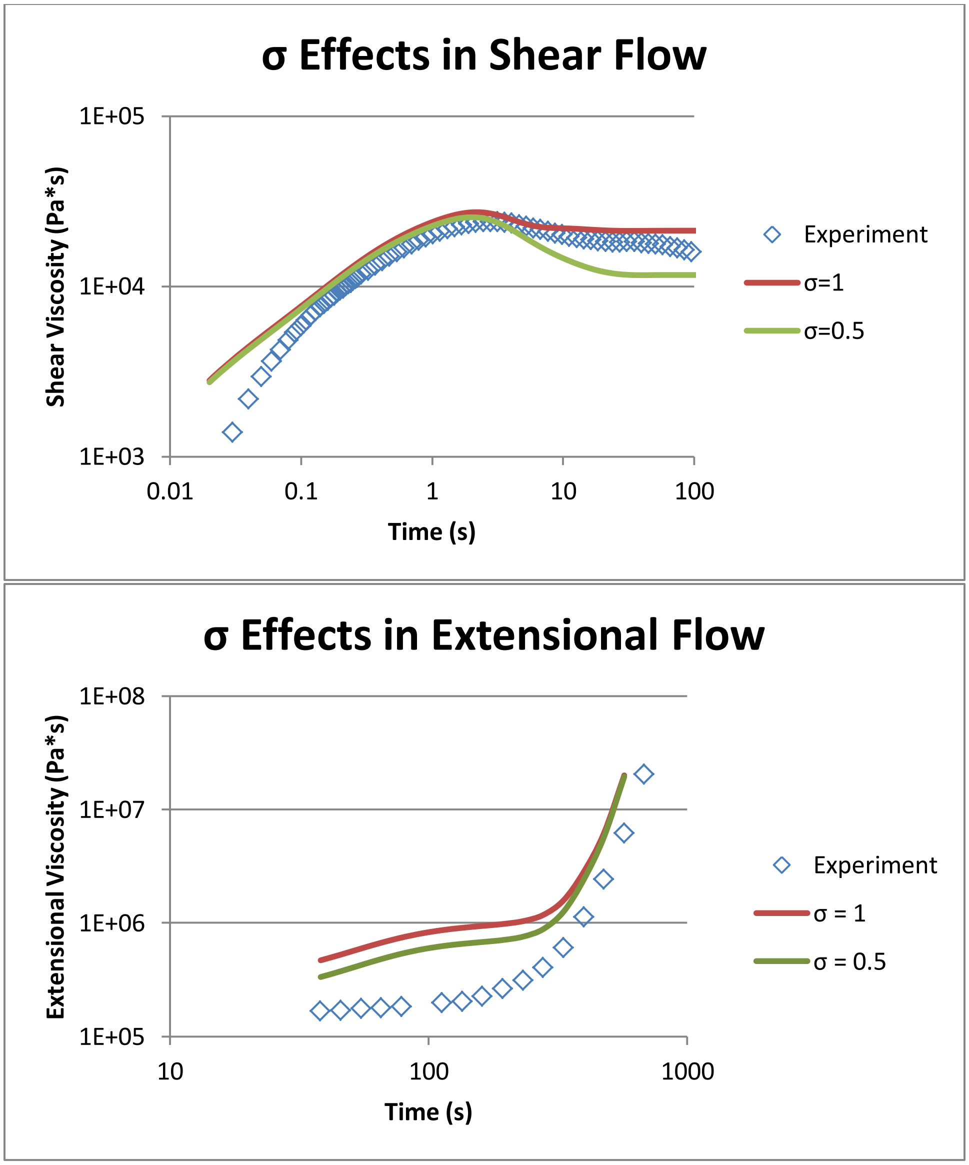

Figure 6: Effect of σ in (a) shear and (b) extensional flow; other parameters fixed:

$$C_I = 0.005, r = 40, 2wt\%$$

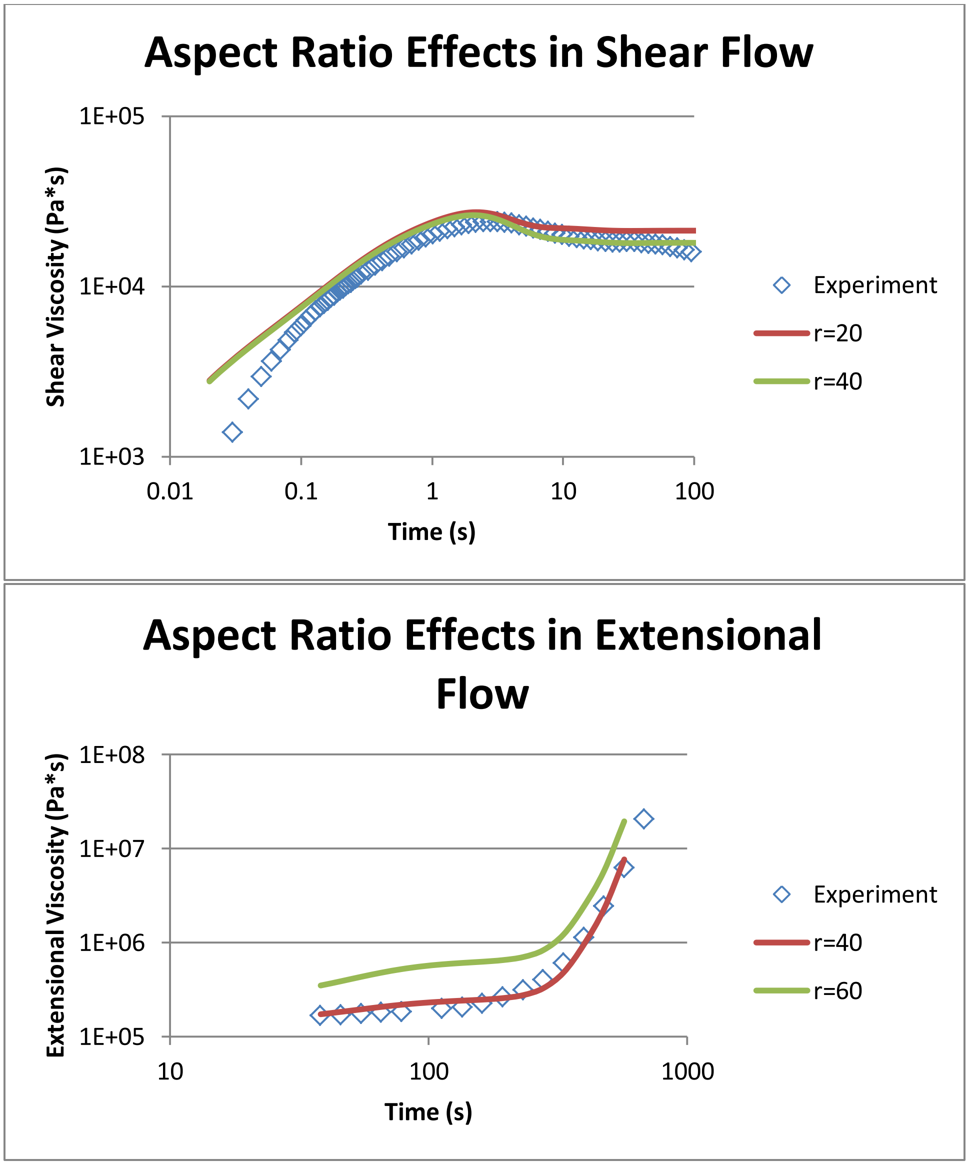

Figure 7: Effect of $r_{effective}$ in (a) shear and (b) extensional flow; other parameters fixed: $C_I = 0.005, \sigma = 0.75, 2wt\%$

From this analysis, the following optimization scheme was created. Since aspect ratio has a large effect on the order of magnitude of the viscosity prediction, the peak viscosity overshoot in experimental shear data and the linear viscoelastic plateau (LVP) in experimental extensional data from 1 to 100 seconds were defined as characteristic points to fit the model to. The error of the shear characteristic point between experiment and model as well as the error of the extensional characteristic point between experiment and model was minimized by optimizing $r_{effective}$ with the following equation

$$E = \left[\log_{10} \eta_{max,exp} - \log_{10} \eta_{max,model}\right]_{shear}^2 + z * \left[\log_{10} \eta_{LVP,exp} - \log_{10} \eta_{LVP,model}\right]_{extension}^2 \tag{30}$$

where z can change the relative weighting of shear to extensional error so that both are the same order of magnitude, thus equally weighting the contribution to error from both flows. This result was then used to optimize the value of σ. Since σ mainly affects the amount of shear thinning, the error between the experimental amount of shear thinning the model's prediction was minimized by optimizing σ with the following equation

$$E = \left[\eta_{SS,exp} - \eta_{SS,model}\right]^2 \tag{31}$$

This process was then used iteratively to converge to optimal values for $r_{effective}$ and σ. These programs can be found in the appendix under "Composite Parameter Optimization: Aspect Ratio Scaling Factor" and "Composite Parameter Optimization: σ". Once $C_I, \sigma,$ and effective aspect ratio were fit, the model predictions could be made and compared against experimental data. Programs for generating the model predictions can be found in the appendix for the three composites, all under sections starting with "Composite Model Predictions".

SAOS experimental data could also be fit by this model. Because of the addition of CNFs, the multi-mode Maxwell model for the storage and loss moduli no longer applies. However, an alternative method can be applied as suggested by Kremer [40]. The strain wave applied in SAOS experiments can be described by

$$\gamma(t) = \gamma^0 \sin \omega t \tag{32}$$

The shear rate is the derivative of the strain wave given by

$$\frac{d\gamma}{dt} = \dot{\gamma}(t) = \gamma^0 \cos \omega t \tag{33}$$

The stress wave can then be written as contributions from the in-phase and out-of-phase stresses which are functions of the storage and loss moduli, respectively. The stress wave is given by

$$\tau_{12}^{Gs} = G'(\omega)\gamma^0 \sin \omega t + G"(\omega)\gamma^0 \cos \omega t \tag{34}$$

The moduli are fit in two steps. First, the model is solved using Equation 33 in place of a constant strain rate to predict the stress wave for a given frequency. This method can be seen in the program under the section "Composite Model Predictions: Modeling the Stress Wave in SAOS Flow" in the appendix. Then using an initial guess for G' and G", Equation 34 is solved, and the error between these two stress waves is minimized where error is defined as

$$E = \sum_{j=1}^{N} \left[\tau_{12}^{c}(t_j) - \tau_{12}^{Gs}(t_j)\right]^2 \tag{35}$$

where N is the number of experimentally tested frequencies. This process is repeated for all experimentally tested frequencies giving $G'_{model}(\omega)$ and $G"_{model}(\omega)$. This can be seen in the appendix under "Composite Model Predictions: Solving the Constitutive Model for SAOS Flow" for the model solving and under "Composite Model Predictions: Fitting G' and G"" for the fitting of moduli to the oscillatory stress wave.

Divergence

Previous work by Kremer [40] found that when σ is allowed to be less than one, at certain values of λ and α the model prediction for shear viscosity would diverge to negative infinity. In this work, the same problem was also seen in extensional viscosity, but with the model prediction diverging to positive infinity. The way he dealt with this problem was to map out the design space of $\sigma, \lambda,$ and α values that lay on the boundary of the model converging/diverging by testing values of these three parameters within the following range: $0.1 \leq \alpha \leq 1$, $0.1 \leq \lambda \leq 10$, and $0.6 \leq \sigma \leq 1$. His plot can be seen below in Figure 8.

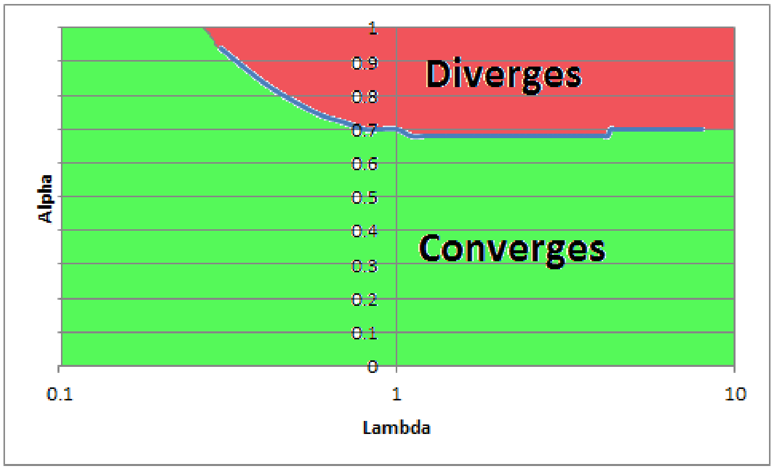

Figure 8: Convergence area for $\boldsymbol{\lambda}$ and $\boldsymbol{\alpha}$ values at $\sigma = 0.6$, 5wt% CNFs, and $\dot{\gamma} = 1s^{-1}$ [40]

As σ decreases, the diverging boundary shifts vertically downward in α. Additionally, larger CNF concentrations, aspect ratios, and strain rates increase the area of divergence. Therefore, by specifying the smallest value of σ, largest concentration of CNFs, largest aspect ratio, and largest strain rate of interest, the extreme points of the diverging boundary can be defined. Once these are defined, by limiting the error optimization program to only look in the converging area of α and λ, pure polymer parameters can be fit that will not cause the model to diverge when modeling composites in the future. A program for defining the convergence boundary can be found in the appendix under "Determining Boundary of Convergence for $\sigma, \lambda,$ and α".

Since this study was examining larger aspect ratios, lower CNF loadings, and extensional flows, this process of mapping out the area of divergence was repeated. However, the range on σ was increased 0.5 to allow for any increased polymer-particle interaction that may occur with the new preparation methods. The new convergence area used in this research can be seen in Figure 9.

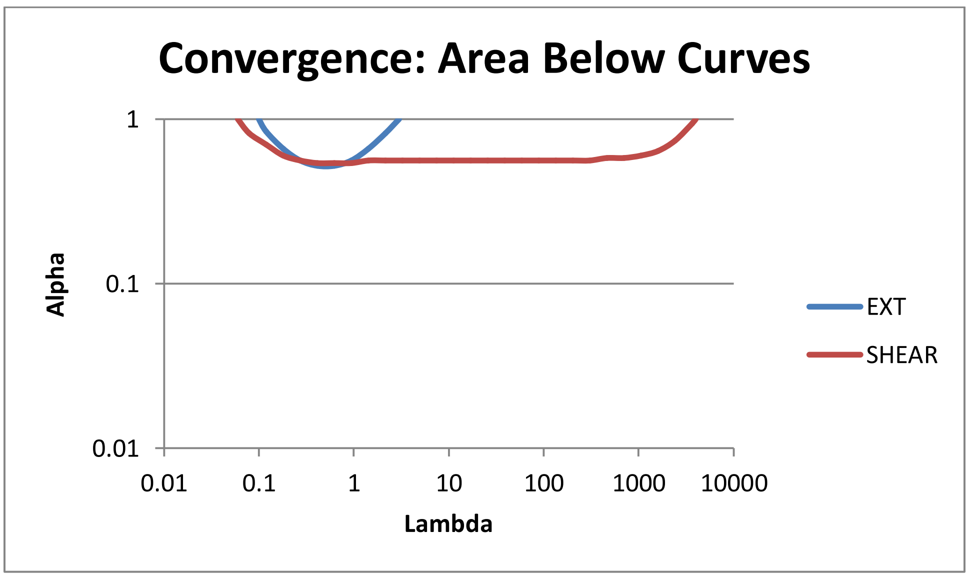

Figure 9: New convergence area for $\boldsymbol{\lambda}$ and $\boldsymbol{\alpha}$ values at $\sigma = 0.5$, 2wt% CNFs, and

$$\dot{\varepsilon} = 1s^{-1},\ \dot{\gamma} = 3s^{-1}$$

This diverging can also be displayed as a surface over the range of σ values, where the set of parameter values inside the surface diverge. Such a surface for extensional and shear flows can be seen in

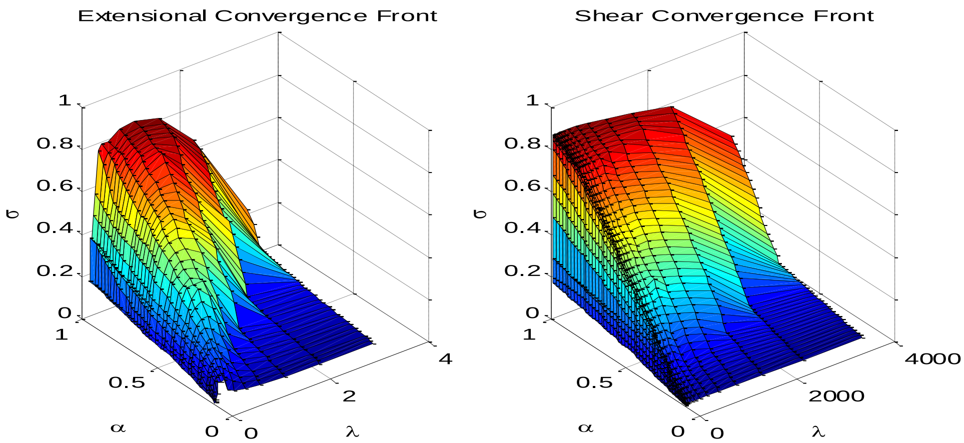

Figure 10.

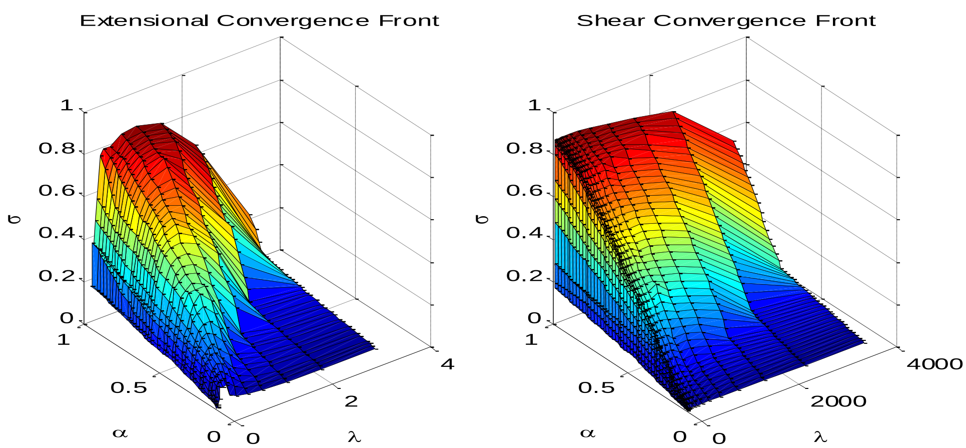

Figure 10: Divergence Surface for (a) extensional flow (b) shear flow

Chapter 5: Results and Discussion

Pure polymer

Modes and Optimized Parameters

Previous research had used 5 modes, but it was found that using 6 modes allowed the strain-hardening behavior in extensional flow, especially at low extension rates, to be captured far more accurately than with only 5 modes. Adding a seventh mode hardly increased the accuracy of the model and led to two modes having very similar relaxation times, suggesting the additional mode was not needed. Because using more modes also increases the complexity of solving the equations and optimizing the parameters, 6 modes were determined to be optimal.

The error minimization technique and program described above for pure polymers were used to optimize the values for $\eta_{p,m}$, λ_m, and α_m. These values are shown in Table 3

Table 3: Optimized Parameter Values for Pure Polymer

	Mode 1	**Mode 2**	**Mode 3**	**Mode 4**	**Mode 5**	**Mode 6**
λ_m **(sec)**	0.0146	0.236	3.21	34.4	6390	116000
$\eta_{p,m}$ **(Pa*s)**	1560	10500	30800	9860	9310	40700
α_m	0.819	0.560	0.560	0.0786	0.0252	0.00184

The error weighting parameters were found to be $y = 0.1$ for shear and $z = 100$ for SAOS so that all error contributions were of the same order of magnitude.

The values of $\boldsymbol{\lambda_m}$, the relaxation time for mode m, increase by an order of magnitude from mode to mode as is common for polymers, except for the last two modes. Constraining these modes to follow the order of magnitude pattern decreased the accuracy of results, and since a seventh mode had already been shown to not improve accuracy, it was concluded that a relaxation time of order 10^2 was unnecessary. The final relaxation time is of great interest since it is such a long relaxation time. When this value was constrained to a range with lower values, the optimization kept running up against the constrained boundary, suggesting a larger relaxation time would be optimal. These constrained optimization additionally did not provide as accurate results as the unconstrained optimal, particularly in extensional viscosity predictions at large times. Therefore, despite the abnormally large value, it was determined that this relaxation time was important to the accuracy of the model predictions.

The values of $\eta_{p,m}$, the zero strain viscosity of the polymer, are generally of order 10^4 magnitude. The first mode shows a small η_p because it is the dominant mode at short times when the viscosity of the polymer is small. The last mode is also of note, displaying the largest zero strain viscosity, and due to the large relaxation time of the mode, this zero strain viscosity is important in capturing the strain hardening behavior at long times.

The values of α_m, the mobility factor, also display a range of magnitudes. It was observed that smaller values of α lead to more abrupt changes in the viscosity during strain hardening in extensional flows. It therefore makes sense that the last mode with the longest relaxation time has a very small value of α, allowing the polymer to strain harden quickly as seen in the experimental extensional viscosity at long times. Additionally, modes 4 and 5 also have relatively smaller values of α than the first two, and these relaxation times occur near the experimental times when strain hardening occurs in the smaller extension rates (0.1, 0.03, 0.01 s^{-1}) and therefore influence the prediction of the model.

Small-Amplitude Oscillatory Flow Predictions

The model prediction for storage and loss moduli can be seen in Figure 11.

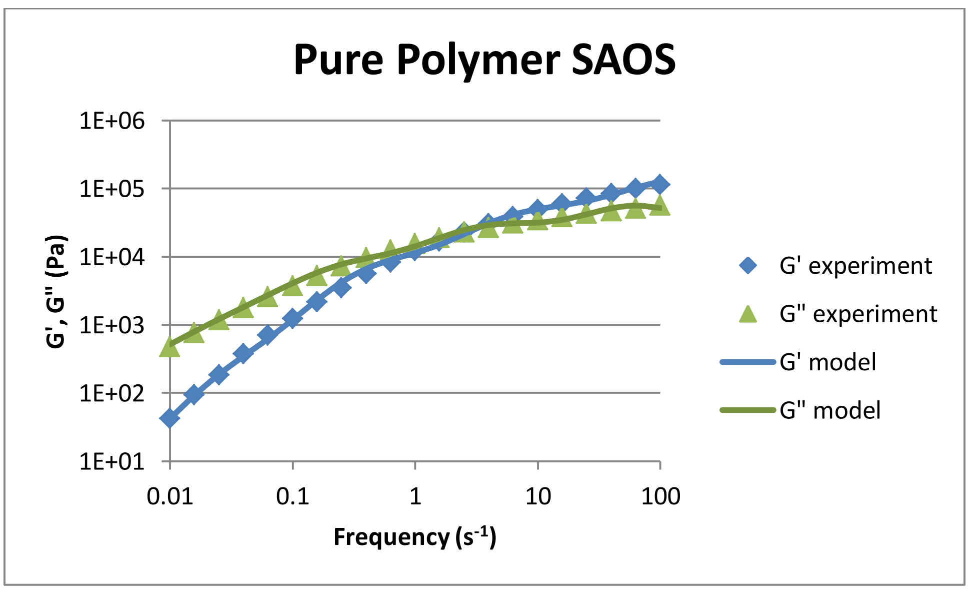

Figure 11: Pure polymer predictions for storage and loss moduli

The experimental data is accurately captured by the model. G’ and G” fitting did not have any notable difficulties. What was important in G’ and G” fitting was an appropriate value of the relative error weighting parameters, y and z, so that the error due to SAOS predictions and due to extensional and shear predictions were of the same order of magnitude. By achieving this, the optimization was equally weighted amongst all three flow fields and gave accurate predictions for all three.

Shear Flow Predictions

The model prediction for shear viscosity can be seen in Figure 12.

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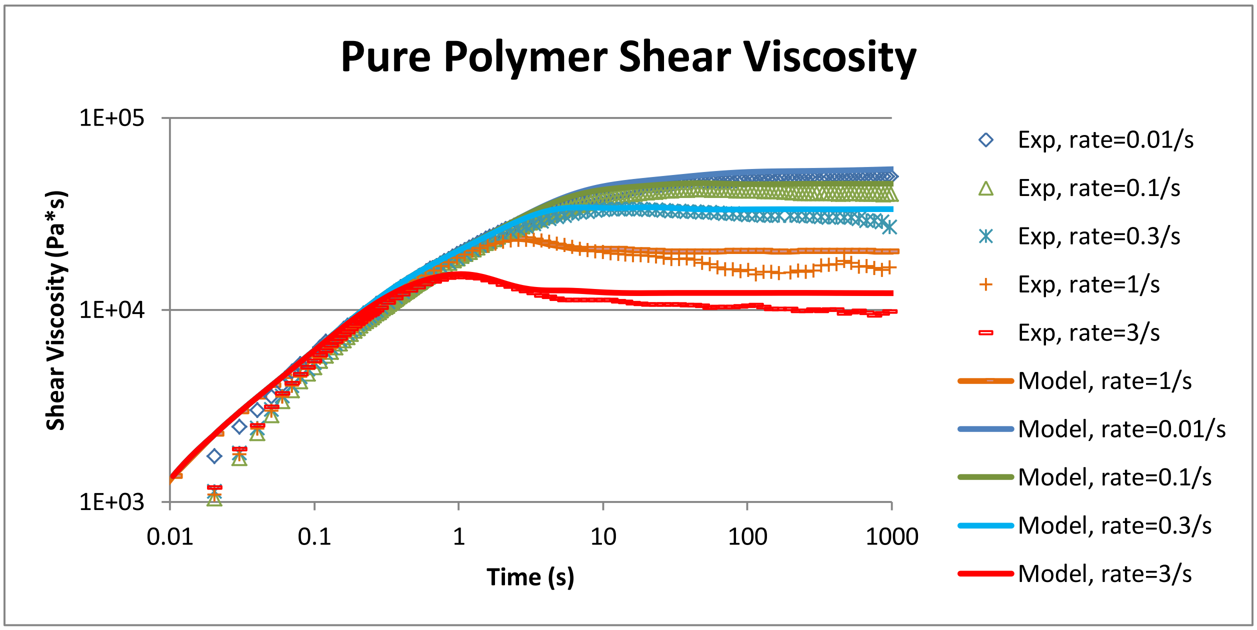


Figure 12: Pure polymer prediction for shear viscosity

Shear viscosity data was accurately fit by the model over five shear rates. A particular problem with fitting the shear data was the delay time of the rheometer. On a log-log plot, this delay time caused the experimental data to look like it was dropping to zero viscosity at a non-zero time; however, the starting point for the model was at 0 seconds and 0 Pa*s, and thus showed an over-prediction of viscosity at very short times. By shifting the experimental data by the delay time of the rheometer, 0.0095 s, this over-prediction disappeared, showing the model to be accurate even at short times.

Extensional Flow Predictions

The model prediction for extensional viscosity can be seen in Figure 13.

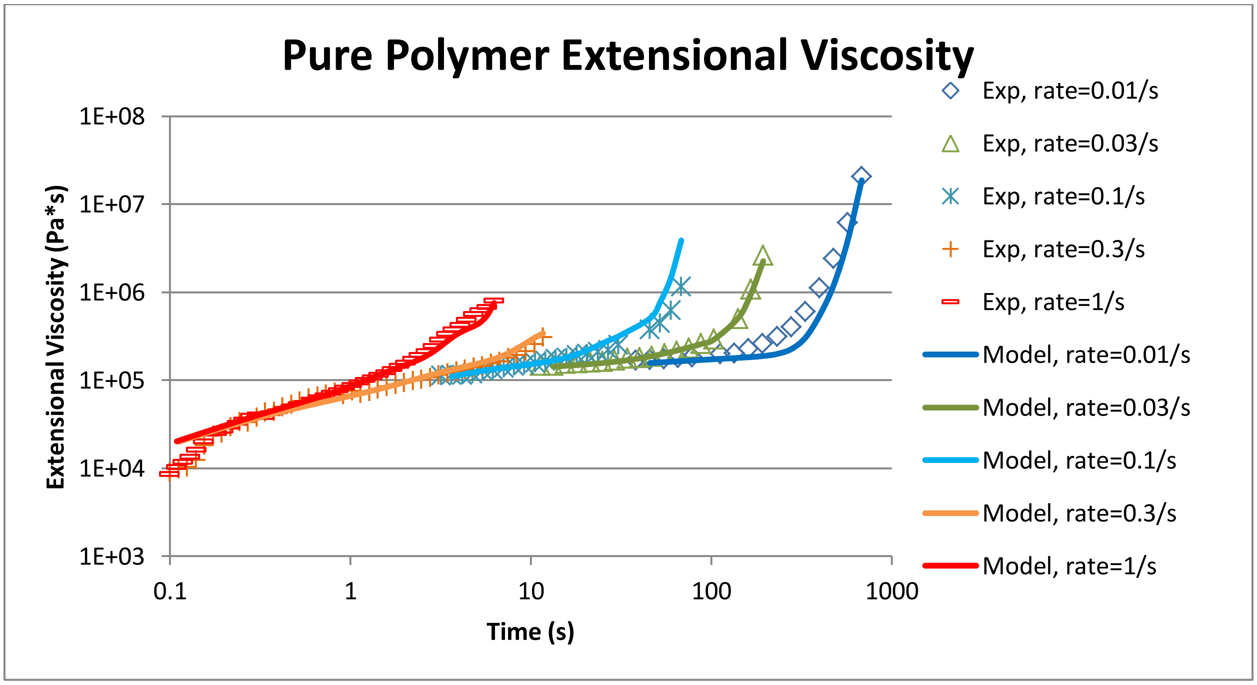


Figure 13: Pure polymer prediction for extensional viscosity

As discussed above, the range of parameter values amongst the six modes allow an accurate model prediction for extensional viscosity over all five extension rates. Especially difficult to capture was the experimental data at the smallest extension rate, 0.01 s^{-1}. This was improved over past research by allowing an additional mode with a very long relaxation time, mode 6.

Composite

Shape factor

Previous work by Kagarise found 2wt% composites to be in the semi-dilute regime and suggested the use of A_2 in the semidilute-aligned regime [10]. The three different shape factors for semidilute regimes, A_2, A_3, and A_4, were re-examined in the context of this research since an additional preparation technique and fiber type were being examined and as an attempt to improve the accuracy of the model. The predictions of both shear and extensional rheology using a range of σ and C_I values for each shape factor were compared. This comparison can be seen in Figure 14.

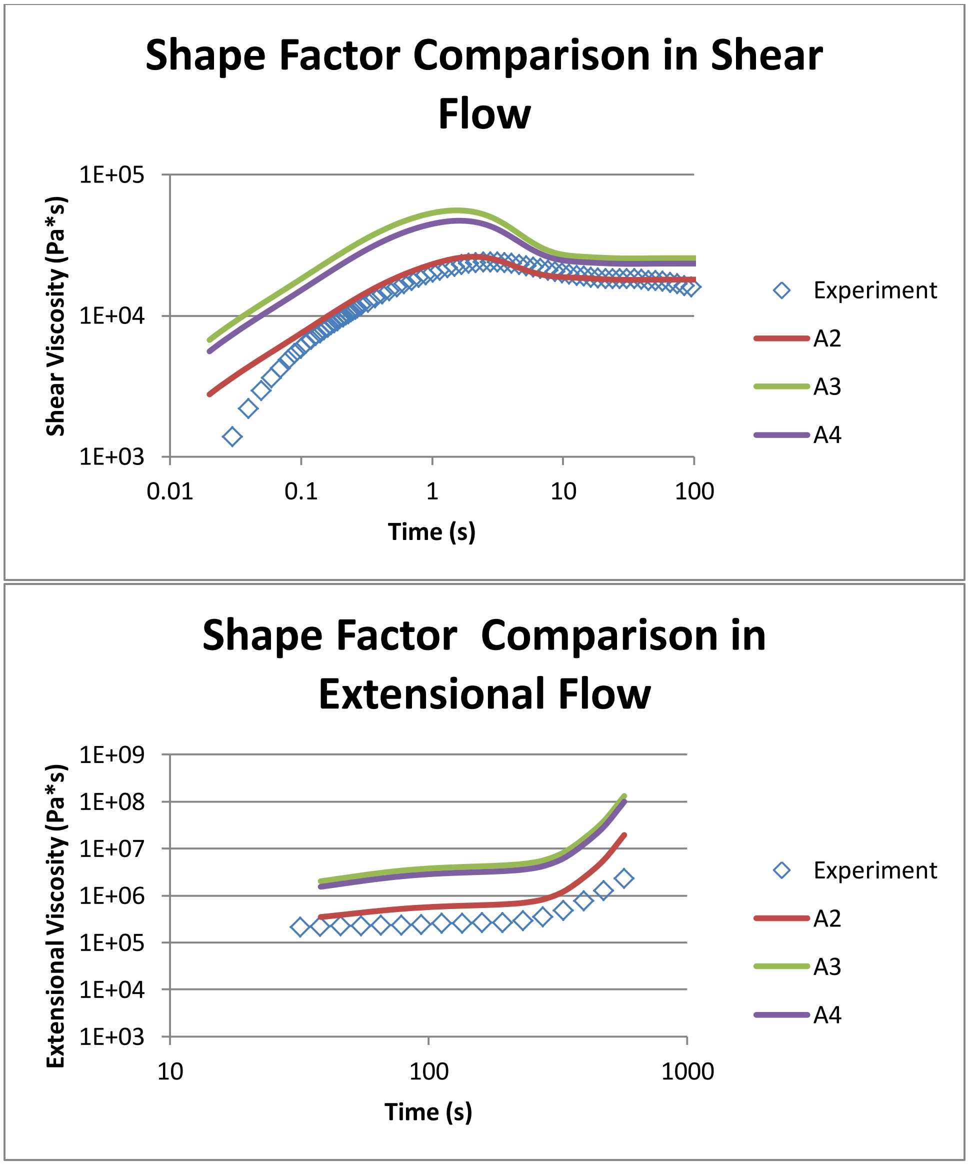


Figure 14: Shape Factor Comparison (a) shear flow (b) extensional flow

As can be seen from Figure 14, A_2 was found to be the best choice in agreement with previous studies by Kagarise of MB composites alone [10].

Optimized Parameters

The methods and programs described above for composites were used to optimize the values for σ, C_I and $r_{effective}$ for MB 2wt%, MB-HHT 2wt%, and SC 2wt% composites. The relative error weighting factor was chosen to be $z = 0.01$ so that the error contributions from shear and extensional model predictions were of the same order of magnitude. The values for the optimized parameters are shown in Table 4.

Table 4: Optimized Parameter Values for Composites

	MB 2wt%	MB-HHT 2wt%	SC 2wt%
$\boldsymbol{C_I}$	0.0306	0.0301	0.0499
$\boldsymbol{\sigma}$	0.810	0.544	0.500
$\boldsymbol{r_{effective} = r_{exp}/h}$	53 / 1.84	44 / 1.45	69 / 1.76

The effects of these parameters are discussed further in the discussion of the model predictions, but a brief overview is discussed here.

C_I, the particle-particle interaction parameter, is very similar between MB and MB-HHT composites but differs more in SC composites. A larger value of C_I suggests more interaction between the particles which makes sense since SC composites have the longest fibers. Additionally, a larger value of C_I results in a lower steady-state orientation of CNFs in extensional flows.

σ, the polymer-particle interaction parameter, ranges more broadly over the three different composites. Since $\sigma = 1$ implies no interaction, smaller values of σ signify larger interactions. These interactions likely are due to two effects: CNF surface chemistry differences and physical interaction between fibers and polymer molecules. SC composites which had the longest CNFs displays the smallest value of σ, suggesting that longer fibers interact more with polymer molecules. Such interactions could be entanglement of the fibers with polymer molecules or that longer fibers "see" more polymer molecules and can thus interact with more polymer molecules than shorter fibers. However, this trend of longer fibers having a lower value of σ is reversed when comparing MB to MB-HHT composites. This could suggest a surface chemistry difference between HHT and O CNFS. An additional study of SC-HHT composites may be able to define how values of σ capture both types of polymer-particle interactions. This research also did not characterize surface chemistry so the effect of surface chemistry differences between fibers cannot be quantitatively described with σ as found in this research. Additionally, the lower bound of tested σ values was 0.5, so further investigation into lower σ values is necessary to better define the difference between SC and MB composites. Because of the diverging issue, this would involve restricting the design space on α and λ to avoid diverging at lower σ values.

h, the effective aspect ratio scaling factor, is similar amongst all three composites. MB-HHT had the lowest value of *h* suggesting the least agglomeration of fibers. Since HHT fibers likely have a different surface chemistry as mentioned above, this may lead to less agglomeration of fibers than O-CNFs. Since σ suggests more polymer-particle interactions for the HHT-CNFs, there is likely a stronger affinity between the polymer and HHT-CNFs than with O-CNFs which would lead to a better dispersion of the HHT-CNFs than O-CNFs. Additionally, SC and MB composites displayed only a small difference in *h*, suggesting similar amounts of agglomeration with SC having slightly less. However, this result is unexpected as the solvent-casting preparation method is known to not distribute fibers as well as melt-blending; thus, in SC composites, a larger scaling factor should be expected than in MB. These results would suggest the affinity between fibers and the polymer has more of an impact on the amount of agglomeration than the preparation method; however, the amount of agglomeration in all composites should be determined experimentally to justify the use of an effective aspect ratio, to determine relative amounts of agglomeration between composites, and even to quantitatively determine what an effective aspect ratio could be by the average amount of fibers in an agglomerate.

Small-Amplitude Oscillatory Shear Flow Predictions

Model predictions for SAOS flow can be seen in Figure 15.

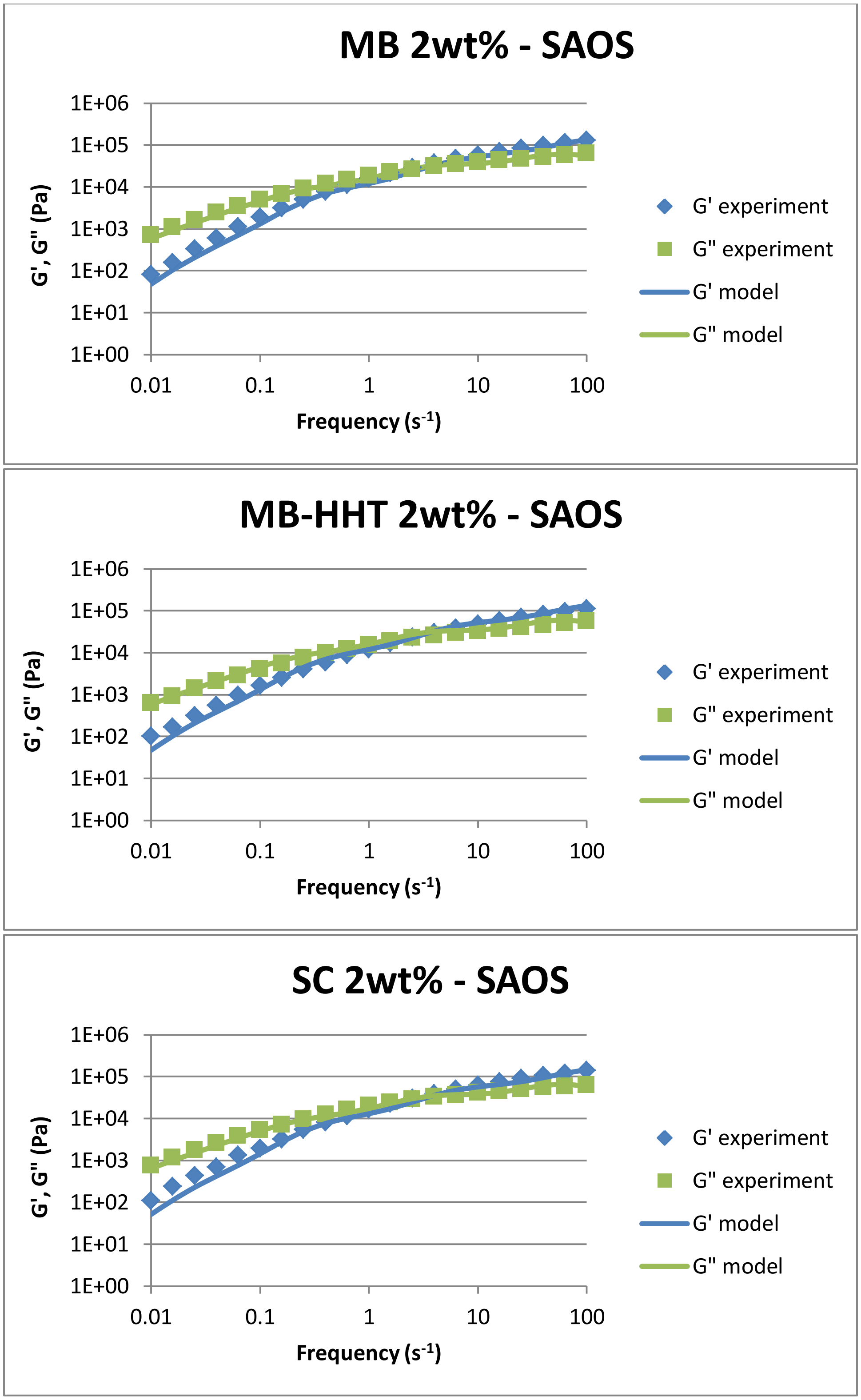
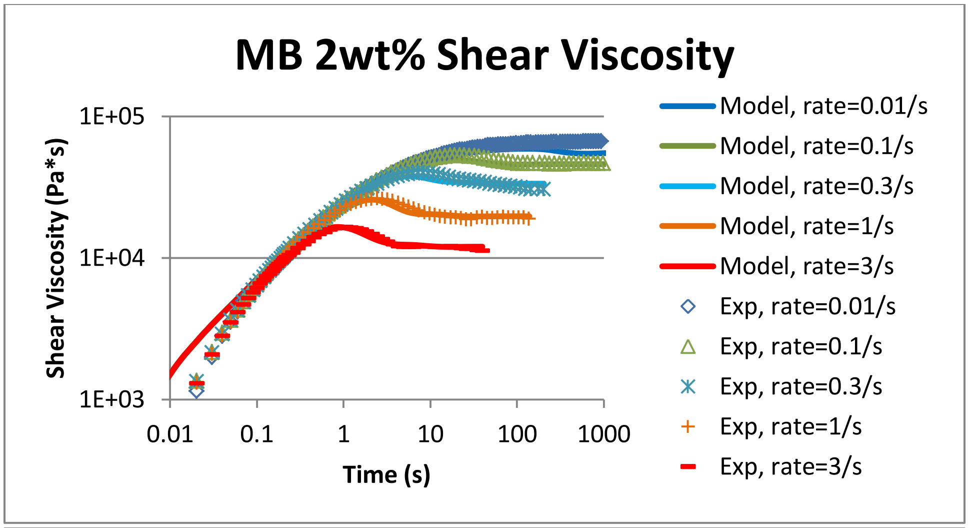


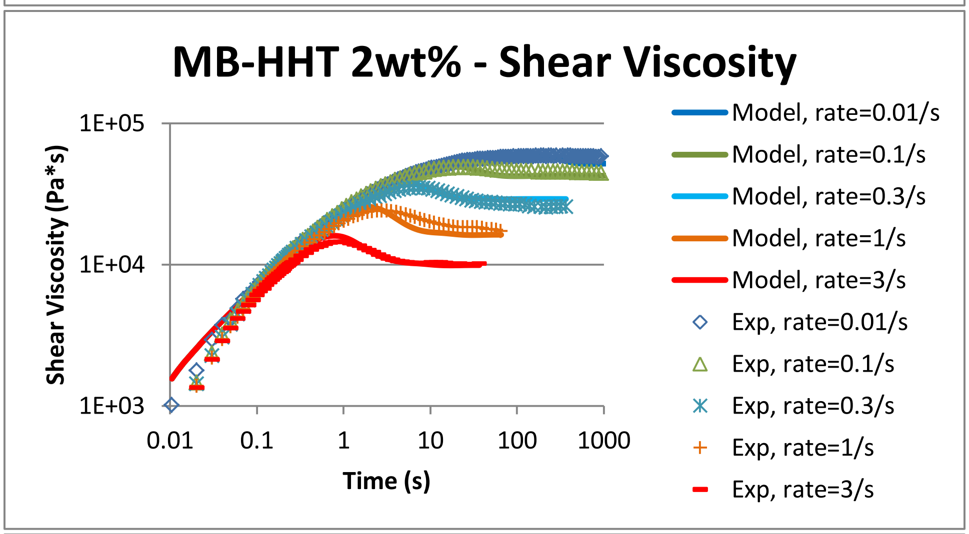
Figure 15: Moduli Predictions for: (a) MB 2wt%, (b) MB-HHT 2wt%, (c) SC 2wt%

These plots show that the model can accurately predict the moduli for all three composites. This also further verifies Kremer's method of fitting to moduli data [40].

Shear Flow Predictions

Model predictions for shear flow can be seen in Figure 16.





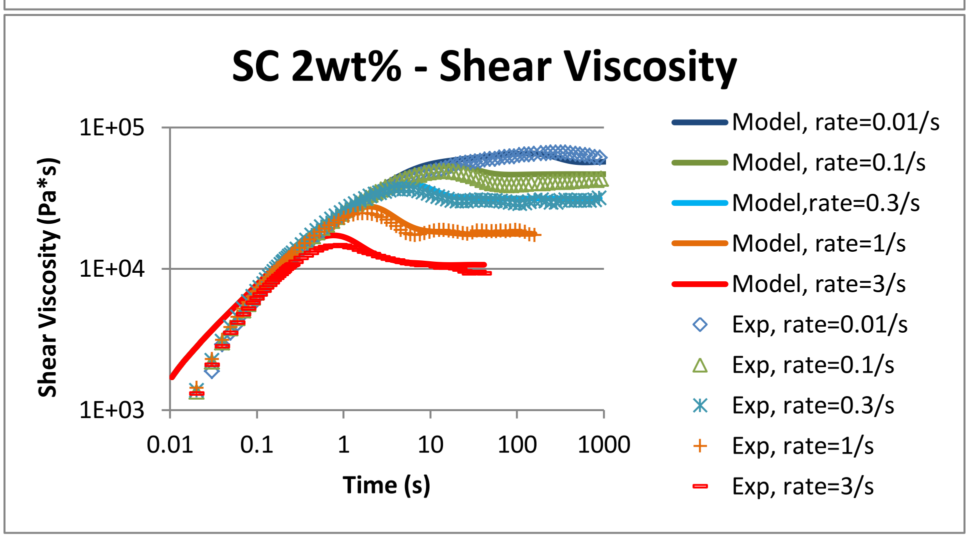


Figure 16: Shear Viscosity Predictions for: (a) MB 2wt%, (b) MB-HHT 2wt%, (c) SC 2wt%

The model accurately captures the shear viscosity behavior for all three composites. In particular, by using the parameter optimization method discussed above for h and σ, the model predictions are all of the correct order of magnitude, heavily influenced by h, and possess the proper amount of shear thinning, influenced by σ. The largest inaccuracy in the predictions is at short times, when the model slightly over-predicts the shear viscosity. Accounting for rheometer start-up delay eliminated this problem in pure polymer predictions and improved composite predictions, but a small inaccuracy is still visible particularly in MB and SC composites. The start-up time could be re-examined in the context of the composites alone to verify the delay is not larger, but since this is such a minor issue and since the model is accurate everywhere else, this is likely not necessary to improve.

Extensional Flow Predictions

Model predictions for extensional flow can be seen in Figure 17.

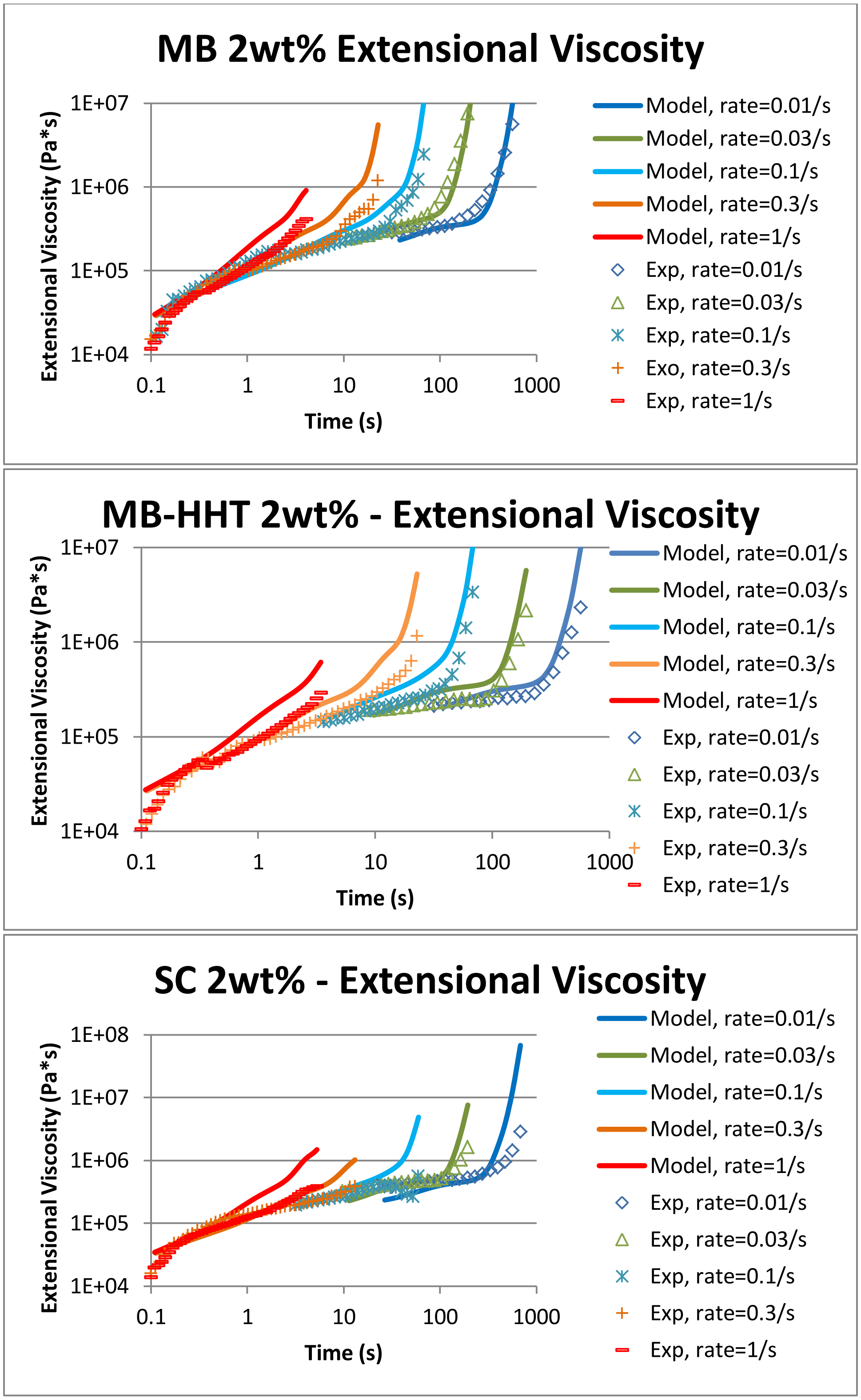


Figure 17: Extensional Viscosity Predictions for: (a) MB 2wt%, (b) MB-HHT 2wt%, (c) SC 2wt%

The model predictions are fairly accurate for extensional flows as well, especially for MB and MB-HHT composites. All composites experience a slight over-prediction in extensional viscosity at larger extension rates, but SC composites also experience an early rise in strain hardening at the lowest two extension rates. Since α is responsible for this behavior, this could suggest that the addition of CNFs somehow affects the mobility factor of the polymer molecules. Future work could examine if fiber interactions with polymer molecules could influence values of α and provide another source of coupling between polymer and CNF behavior.

Orientation Tensor Predictions

Model predictions for orientation evolution for a_{11}, the component of the orientation tensor in the direction of flow, can be seen in Figure 18.

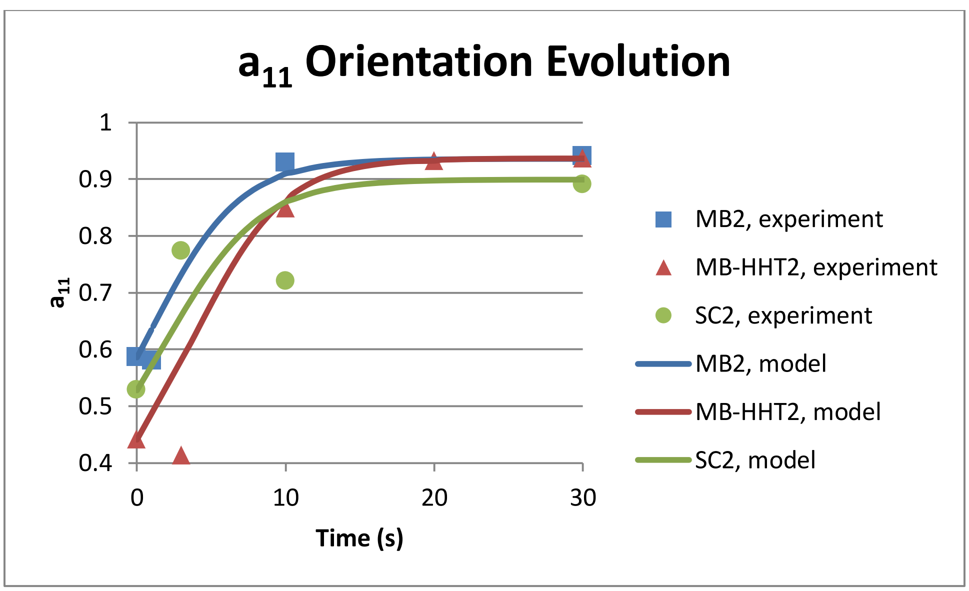


Figure 18: Orientation Evolution of a_{11}, $\dot{\varepsilon} = 0.1s^{-1}$

The model predicts the steady-state orientation of CNFs and the general trend of orientation evolution well. However, the experimental data shows significant error such as the second data point for MB-HHT2 decreasing from the first and the third data point for SC2 decreasing from the second, not to be expected experimentally as a_{11} should continuously increase to the steady-state value. Repeated experiments examining the orientation evolution more closely would allow for better comparison to the model prediction. For the purpose of steady-state orientation, though, the model is accurate, and the evolution of orientation in the model seems to be reasonable.

Chapter 6: Conclusions and Future Work

Conclusions

This research was focused on modeling the rheological behavior of polystyrene-carbon nanofiber (PS-CNF) composites. Three different flow fields, extensional, shear, and small-amplitude oscillatory shear (SAOS), were examined. The model used 6 six modes and contains 3 parameters in each mode that only describe pure polymer behavior as well as three additional parameters that are used in composite modeling.

Experiments in the three flow fields for a range of oscillatory frequencies from 0.01 to 100 s^{-1}, 5 shear rates, and 5 extension rates were examined for a pure polymer, and data from these experiments were used to fit the parameters pertaining to the behavior of the polymer: zero shear viscosities, relaxation times, and mobility factors of the polymer.

PS-CNF composites were then prepared using two different preparation methods, melt-blending and solvent-casting, as well as two different types of CNFs, regular CNFs with no treatment (O-CNFs) and high-heat treated CNFS (HHT-CNFs). Three types of composites were examined all at 2 wt% loading of CNFs: melt-blended with O-CNFs (MB), melt-blended with HHT-CNFs (MB-HHT), and solvent-casted with O-CNFs (SC). The same three flow fields as the pure polymer were examined for these composites. The remaining three parameters were fit for all three composites: particle-particle interaction parameter, polymer-particle interaction parameter, and scaling factor for effective aspect ratio. Orientation evolution of CNFs were also examined and modeled.

From these results, an accurate model prediction was obtained for PS-CNF composites at 0 and 2 wt%, prepared different ways and with different CNFs, and for three different flow fields at different strain rates. The relative values of parameters between composites can additionally give insight into the different behavior observed experimentally. Finally, a method for fitting polymer-nanoparticle composites has been further developed so that accurate models can be created.

Future Work

There is certainly room for future work. Higher loadings of CNFs have been examined by others in this research group but have not been studied as the composites in this research have. With the developments of this research and study of composites under extensional, shear, and SAOS, composites with higher CNF loadings could be studied in more detail and accuracy. In this research, an effective aspect ratio was used with the motivation that agglomerations were present in the composites. An investigation into this assumption is certainly a next step and would either verify this assumption or raise new questions into the reason for viscosity over-predictions in the model. A more detailed analysis into the evolution of the orientation tensor experimentally would also aid in verifying the accuracy of the model predictions of orientation evolution. Finally, expanding the parameter space of $\lambda, \alpha,$ and σ, to allow for model convergence at values of $\sigma < 0.5$ should be investigated. Optimization of σ for SC composites led to the boundary value of $\sigma = 0.5$ suggesting lower σ values to provide more accurate model predictions.

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Appendix A: Programs

Constitutive Model Solver: Extensional Flow

```
function [time, etac, diverge] =
extensional_pde_solver(r,mass,sigma,CI,etap,lambda,alpha,tspan,modes,re
,orientation)
% This program solves the constitutive model equations for extensional
flow

%dummy variables used to catch divergence
diverge=0; p=0;
total12=0;

chi=1.0*(re^2-1)/(re^2+1); %another form of aspect ratio
rf=1750.0; %fiber density
rs=1000.0; %polymer density

phi=rs*mass/(rf+(rs-rf)*mass);%volume fract of CNFs
Ap=re^2/(3*log(sqrt(pi/phi))); %shape factor, aka A_2

initial=[0 0 0 orientation]; %initial conditions for the differential
equation solver

for x=1:modes
    %solves differential equations
    [time, yout]=ode23tb(@modeextensionalsub,tspan,initial);

    tau11=yout(:,1);
    tau22=yout(:,2);
    tau12=(tau11-tau22); %not actually tau12, just the difference
between 11 and 22
    length_tau=length(tau12); %dummy variable for divergence

    if p==0 %in first loop to set up the length of tau when solution
converges
        total12=total12+tau12;
        converge_length=length(total12);
        if mass~=0
            a11=yout(:,4);
            a22=yout(:,5);
            a33=yout(:,6);
            a11out(:,1)=a11;
            a22out(:,1)=a22;
            a33out(:,1)=a33;
            timeout(:,1)=time;
        end
        p=p+1;
    elseif p>0 %after the first loop, this checks to see if tau's are
all same length as previous mode
        if length_tau<converge_length %if not, then the solution
diverged
            diverge=1;
            break %get out of this program because current conditions
cause divergence
        end
```

```
        total12=total12+tau12;
        converge_length=length(total12);

        if mass~=0
            a11=yout(:,4);
            a22=yout(:,5);
            a33=yout(:,6);
            a11out(:,x)=a11;
            a22out(:,x)=a22;
            a33out(:,x)=a33;
            timeout(:,x)=time;
        end
    end
end

eta=total12./r; %definition of extensional viscosity
if mass==0
    etac=eta; %viscosity of pure polymer = the viscosity from the
polymer
else
    a11_out=a11out(:,1); %the 11 component of orientation
    %stress due to cnfs
    coef=2.0.*eta*phi;
    tf12=(coef).*(Ap*r*((27.0*(a11.*a22.*a33)).*(-
3/35+(4*a11+2*a22)/7)+(1-27*(a11.*a22.*a33)).*(a11.^2+(-3.*a11.*a22-
a11.*a33+a22.^2+a22.*a33)/2)));
    etac=tf12/r+eta; %viscosity of a composite = the viscosity from the
polymer + stress/rate from the cnfs
end



function dy = modeextensionalsub(t,y)
% this sub-function includes the differential equations for polymer
stress
% and cnf orientation evolution

    %stress tensor components
    t11=y(1);
    t22=y(2);
    t33=y(3);
    %orientation tensor components
    a11=y(4);
    a22=y(5);
    a33=y(6);

    %polymer stress differential equations
    dy=zeros(6,1);
    dy(1,1)=2*r*etap(x)/lambda(x)-sigma*t11/lambda(x)-
alpha(x)/etap(x)*t11^2+2*r*t11-3*(1-sigma)*2*a11*t11/lambda(x);
    dy(2,1)=-r*etap(x)/lambda(x)-sigma*t22/lambda(x)-
alpha(x)/etap(x)*t22^2-r*t22-3*(1-sigma)*a22*t22/lambda(x);
    dy(3,1)=-r*etap(x)/lambda(x)-sigma*t33/lambda(x)-
alpha(x)/etap(x)*t33^2-r*t33-3*(1-sigma)*a33*t33/lambda(x);
```

```
    if mass~=0
        %cnf orientation evolution equations
        dy(4,1)=CI*2*3^(.5)*r*(1-3*a11)+2*chi*r*a11-
2*chi*r*(27*a11*a22*a33*(-2/35+(10*a11-a22-a33)/14)+(1-
27*a11*a22*a33)*(a11^2-(a11*a22+a11*a33)/2));
        dy(5,1)=CI*2*3^(.5)*r*(1-3*a22)-chi*r*a22-
2*chi*r*(27*a11*a22*a33*(1/35+(2*a11-5*a22-a33)/14)+(1-
27*a11*a22*a33)*(a11*a22-(a22^2+a22*a33)/2));
        dy(6,1)=CI*2*3^(.5)*r*(1-3*a33)-chi*r*a33-
2*chi*r*(27*a11*a22*a33*(1/35+(2*a11-a22-5*a33)/14)+(1-
27*a11*a22*a33)*(a11*a33-(a22*a33+a33^2)/2));
    end
end

end
```

Constitutive Model Solver: Shear Flow

```
function [time1, etacf,diverge] =
shear_pde_solver(r,mass,sigma,CI,etap,lambda,alpha,tspan,modes,re,orien
tation)
% This program solves the constitutive model equations for shear flow

%dummy variables used to catch divergence
diverge=0; p=0;
total12=0;

chi=1.0*(re^2-1)/(re^2+1); %another form of aspect ratio
rf=1750.0; %fiber density
rs=1000.0; %polymer density
phi=rs*mass/(rf+(rs-rf)*mass);  %volume fract of CNFs
Ap=re^2/(3*log(sqrt(pi/phi))); %shape factor, aka A_2

initial=[0 0 0 0 orientation]; %initial conditions for the differential
equation solver

tau_finalf=zeros(4,modes);

for x=1:modes
    [time1, yo]=ode23tb(@modeshearsub,tspan,initial);    %ode solver
for solving Equations (2) & (4) simultaneously

    length_tau=length(yo(:,1)); %dummy variable to catch divergence
    L=length(time1);

    if x==1
        tau1=zeros(L,modes);
        tau12=zeros(L,modes);
        tau2=zeros(L,modes);
        tau3=zeros(L,modes);
    end
    if p==0 %in first loop to set up the length of tau when solution
converges
        tau1(:,x)=yo(:,1);
        converge_length=length(tau1);
        tau12(:,x)=yo(:,2);
        tau2(:,x)=yo(:,3);
        tau3(:,x)=yo(:,4);
        tau_finalf(:,x) = [tau1(L,x) tau12(L,x) tau2(L,x) tau3(L,x)]';

        p=p+1;
    elseif p>0 %after the first loop, this checks to see if tau's are
all same length as previous mode
        if length_tau<converge_length %if not, then the solution
diverged
            diverge=1;
            break %get out of this program because current conditions
cause divergence
        end
        tau1(:,x)=yo(:,1);
```

```
        converge_length=length(tau1);
        tau12(:,x)=yo(:,2);
        tau2(:,x)=yo(:,3);
        tau3(:,x)=yo(:,4);

        tau_finalf(:,x) = [tau1(L,x) tau12(L,x) tau2(L,x) tau3(L,x)]';
    end
end

if diverge==0
total11f=sum(tau1,2);
total12f=sum(tau12,2);
total22f=sum(tau2,2);
total33f=sum(tau3,2);

if mass~=0
    a11f=yo(:,5);
    a12f=yo(:,6);
    a22f=yo(:,7);
    a33f=1-a11f-a22f;
    a_final = [a11f(L) a12f(L) a22f(L)]';
    a11final_shr=a11f(end);
end
T_final= [total11f(L) total12f(L) total22f(L) total33f(L)];


etaf=total12f./r; %definition of shear viscosity
coef=2.0*etaf*phi;

%%%%This section computes the fiber stress from Equation (3)
if mass==0
    etacf=etaf; %viscosity of pure polymer = the viscosity from the
polymer
else
    %stress due to cnfs
    tf12f=(2.0*phi.*total12f.*Ap).*((27.0*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(-
1.0/35.0+1.0/7.0*(a11f+a22f))+(a12f.^2).*(1-27*(a11f.*a22f.*(1-a11f-
a22f))+27.0*(a12f.^2).*(1-a11f-a22f)));
    tf11f=(2.0*phi.*total12f.*Ap).*((27.0*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(3.0/7.0*(a12f))+(a11f.*a12f).*(1-
27*(a11f.*a22f.*(1-a11f-a22f))+27.0*(a12f.^2).*(1-a11f-a22f)));
    tf22f=(2.0*phi.*total12f.*Ap).*((27.0*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(3.0/7.0*(a12f))+(a22f.*a12f).*(1-
27*(a11f.*a22f.*(1-a11f-a22f))+27.0*(a12f.^2).*(1-a11f-a22f)));
    tf33f=(2.0*phi.*total12f.*Ap).*((27.0*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(1.0/7.0*(a12f))+((1-a11f-a22f).*a12f).*(1-
27*(a11f.*a22f.*(1-a11f-a22f))+27.0*(a12f.^2).*(1-a11f-a22f)));

tauc12f=tf12f+total12f;
tauc11f=tf11f+total11f;
tauc22f=tf22f+total22f;
tauc33f=tf33f+total33f;
etacf=tauc12f./r; %viscosity of composite = the viscosity from the
polymer + stress/rate from the cnfs
```

```
end

elseif diverge==1
    etacf=0;
end

function dyo = modeshearsub(t,y)
% this sub-function includes the differential equations for polymer
stress
% and cnf orientation evolution

    %stress tensor components
    tp11=y(1);
    tp12=y(2);
    tp22=y(3);
    tp33=y(4);
    %orientation tensor components
    a11=y(5);
    a12=y(6);
    a22=y(7);
    a33=1-a11-a22;
    dyo=zeros(7,1);

    %polymer stress differential equations
    dyo(1,1)=-alpha(x)*(tp11^2+tp12^2)/etap(x)-
sigma*tp11/lambda(x)+2*r*tp12-3*(1-
sigma)*(tp11*a11+tp12*a12)/lambda(x);
    dyo(2,1)=-alpha(x)*(tp11*tp12+tp12*tp22)/etap(x)-
sigma*tp12/lambda(x)+etap(x)*r/lambda(x)+r*tp22-3*(1-
sigma)/2/lambda(x)*(a11*tp12+a12*tp22+a12*tp11+a22*tp12);
    dyo(3,1)=-alpha(x)*(tp12^2+tp22^2)/etap(x)-sigma*tp22/lambda(x)-
3*(1-sigma)/lambda(x)*(tp12*a12+tp22*a22);
    dyo(4,1)=-alpha(x)*(tp33^2)/etap(x)-tp33*sigma/lambda(x)-3*(1-
sigma)/lambda(x)*a33*tp33;

    if mass~=0
        %cnf orientation evolution equations
        dyo(5,1)=r*a12+2*CI*abs(r)*(1.0-3.0*a11)+chi*r*a12-...
            2*chi*r*(3.0/7.0*a12*(27.0*a11*a22*(1-a11-a22)...
            -27.0*(a12^2)*(1-a11-a22))+(1.0-27.0*a11*a22*(1-a11-
a22)+...
            27.0*(a12^2)*(1-a11-a22))*a11*a12);
        dyo(6,1)=1.0/2.0*r*a22-1.0/2.0*r*a11+chi*((1.0/2.0*r*a22+...
            1.0/2.0*r*a11)-(2.0*r)*((27.0*a11*a22*(1-a11-a22)-...
            27.0*(a12^2)*(1-a11-a22))*(-
1.0/35.0+1.0/7.0*a11+1.0/7.0*a22)+...
            (1.0-27.0*a11*a22*(1-a11-a22)...
            +27.0*(a12^2)*(1-a11-a22))*a12^2))-6.0*CI*abs(r)*a12;
        dyo(7,1)=-r*a12+2*CI*abs(r)*(1.0-3.0*a22)+chi*r*a12-...
            2*chi*r*(3.0/7.0*a12*(27.0*a11*a22*(1-a11-a22)-...
            27.0*(a12^2)*(1-a11-a22))+(1.0-27.0*a11*a22*(1-a11-a22)+...
            27.0*(a12^2)*(1-a11-a22))*a12*a22);
    end
end

end
```

Pure Polymer: Overhead Parameter Optimization

```
function [] = Pure_Polymer_Optimization()
% This program optimizes the pure polymer parameters (etap, lambda, and
% alpha) using transient extension, transient shear, and SAOS data.
% This program also plots model predictions for all three flows

format long g
z=.01; %relative drror scaling factor, number to divide Gerror by
y=10; %relative drror scaling factor, number to divide Serror by

modes=6; %number of modes for Giesekus model
solved=1; % =0 optimize (use fmincon), =1 already solved (don't use
fmincon)

%initial guesses for pure polymer parameters in fmincon: etap, lambda,
and alpha
Eta0=[4.068958213059190e+4   0.161814434808827e+4
0.926492125161873e+4   0.889129038018490e+4   3.023078079743952e+4
0.824206633606583e+4];
lambda=[1.162556126233308e+5   0.000000152130995e+5
0.064530255537243e+5   0.000002089102109e+5   0.000026539367359e+5
0.000302338431186e+5];
alpha=[0.001745546564408   0.851749611132819   0.027375867196483
0.799680223515555   0.471561581048678   0.072223157940858];

% Final results:
% if previously optimized, plug in results here for quick plotting
  Final=[   1563.180023 10503.23358 30793.85272 9864.433234 9310.030642
40690.01669; %eta by mode
            0.01461114  0.235979496 3.210427777 34.39722848 6390.005373
116255.5053; %lambda by mode
            0.818868357 0.56        0.56        0.078601046 0.025189799
0.001841609]; %alpha by mode

if solved==0
        options=optimset('Algorithm','interior-point'); %search
algorithm
        f0=[Eta0; lambda; alpha]; %initial guesses for fmincon

        % Note on fmincon: the two matrices passed to fmincon are the
lower
        % bounds and upper bounds on the parameters
        % (column = mode, row = eta; lambda; alpha)
        [Final, fval, exitflag]=fmincon(@FIT_0wt,f0,[],[],[],[],[ 0 0 0
0 0 0; 0 0 0 0 0 0; 0 0 0 0 0 0],[inf inf inf inf inf inf; inf inf inf
inf inf inf; 0.999 0.999 0.999 0.999 0.999 0.999],[],options);

        % Adjust Final lambda and alpha values to converging region
        % Note: this is actually what fmincon saw for values of lambdas
and
        % alphas since it was changed within its operation, but the
values
        % it returns may not be the ones it used for error
minimization,
```

```
        % hence this for-loop is needed to change the values back to
what
        % was used in the error minimization
        for q=1:modes %these convergences are based on sigma=0.5,
CI=.01
            if Final(2,q)>0.07 && Final(2,q)<=0.11 && Final(3,q)>0.7
                Final(3,q)=0.7;
            elseif Final(2,q)>0.11 && Final(2,q)<=0.18 &&
Final(3,q)>0.6
                Final(3,q)=0.6;
            elseif Final(2,q)>0.18 && Final(2,q)<=0.27 &&
Final(3,q)>0.56
                Final(3,q)=0.56;
            elseif Final(2,q)>0.27 && Final(2,q)<=0.94 &&
Final(3,q)>0.52
                Final(3,q)=0.52;
            elseif Final(2,q)>0.94 && Final(2,q)<=1.43 &&
Final(3,q)>0.54
                Final(3,q)=0.54;
            elseif Final(2,q)>1.43 && Final(2,q)<=465 &&
Final(3,q)>0.56
                Final(3,q)=0.56;
            elseif Final(2,q)>465 && Final(2,q)<=1061 &&
Final(3,q)>0.58
                Final(3,q)=0.58;
            elseif Final(2,q)>1061 && Final(2,q)<=1604 &&
Final(3,q)>0.6
                Final(3,q)=0.6;
            elseif Final(2,q)>1604 && Final(2,q)<=2425 &&
Final(3,q)>0.64
                Final(3,q)=0.64;
            elseif Final(2,q)>2425 && Final(2,q)<=3666 &&
Final(3,q)>0.74
                Final(3,q)=0.74;
            end
        end
end

% Plot model vs experiment
graph=1;
figure
[GerrorFinal]=SAOS_MB_0wt(Final,graph,modes)
figure
[TerrorFinal]=Extensional_MB_0wt(Final,graph,modes)
figure
[SerrorFinal]=Shear_MB_0wt(Final,graph,modes)

% Display final errors and values
GerrorFinal/z
TerrorFinal
SerrorFinal/y
e=TerrorFinal+GerrorFinal+SerrorFinal

etafinal=Final(1,:)'
lambdafinal=Final(2,:)'
alphafinal=Final(3,:)'
```

```
function e = FIT_0wt(para)
%this subfunction calculates the model predictions for all three flow
%fields and the error between the model predictions and experiment
    graph=0;
    Eta=para(1,:);
    Lambda=para(2,:);
    Alpha=para(3,:);

    % This for-loop constricts lambda and alpha values to the
converging region previously determined by "Parameter_Convergence"
program.
    % Note: this region is dependent on sigma, so if you want to
examine lower values of sigma in future composite fittings, you need to
refit the converging region, alter this for-loop to constrict lambdas
and
    % alphas, and refit the pure polymer.
    for g=1:modes %these convergences are based on sigma=0.5, CI=.01
        if Lambda(g)>0.07 && Lambda(g)<=0.11 && Alpha(g)>0.7
            Alpha(g)=0.7;
        elseif Lambda(g)>0.11 && Lambda(g)<=0.18 && Alpha(g)>0.6
            Alpha(g)=0.6;
        elseif Lambda(g)>0.18 && Lambda(g)<=0.27 && Alpha(g)>0.56
            Alpha(g)=0.56;
        elseif Lambda(g)>0.27 && Lambda(g)<=0.94 && Alpha(g)>0.52
            Alpha(g)=0.52;
        elseif Lambda(g)>0.94 && Lambda(g)<=1.43 && Alpha(g)>0.54
            Alpha(g)=0.54;
        elseif Lambda(g)>1.43 && Lambda(g)<=465 && Alpha(g)>0.56
            Alpha(g)=0.56;
        elseif Lambda(g)>465 && Lambda(g)<=1061 && Alpha(g)>0.58
            Alpha(g)=0.58;
        elseif Lambda(g)>1061 && Lambda(g)<=1604 && Alpha(g)>0.6
            Alpha(g)=0.6;
        elseif Lambda(g)>1604 && Lambda(g)<=2425 && Alpha(g)>0.64
            Alpha(g)=0.64;
        elseif Lambda(g)>2425 && Lambda(g)<=3666 && Alpha(g)>0.74
            Alpha(g)=0.74;
        end
    end

    para1=[Eta;Lambda;Alpha]; %new 'para' with adjusted lambdas and
alphas

[Gerror]=SAOS_MB_0wt(para1,graph,modes);
[Terror]=Extensional_MB_0wt(para1,graph,modes);
[Serror]=Shear_MB_0wt(para1,graph,modes);

Gerror=Gerror/z;
Serror=Serror/y;
e=Terror+Gerror+Serror;

end
end
```

Pure Polymer: SAOS Flow

```
function [Gerror] = SAOS_MB_0wt(para,graph,modes)
%This program calculates the error between this model prediction of
moduli
%vs frequency and the experimental data and sends it back to
%Pure_Polymer_Optimization to be used in the error minimzation for
%parameter optimization.  This program can also plot the model
%prediction of moduli given the set of pure polymer parameters

eta=para(1,:);
lambda=para(2,:);

%from excel: 0wt%SAOS and Model fitting: Fit to extension
freq=[100   63.096  39.811  25.119  15.849  10  6.3096  3.9811  2.5119
1.5849  1   0.63096 0.39811 0.25119 0.15849 0.1 0.063096    0.039811
0.025119    0.015849    0.01];
%storage modulus
Gexp=[1.15E+05  99721   85344   72157   59959   48938   39138   30504
23217   17157   12214   8405.3  5602.5  3536.2  2187.2  1252.3  701.47
378.3   185.27  93.604  42.558];
%loss modulus
GDexp=[57682    51912   47430   43100   38967   34927   30883   26877
22964   19168   15682   12477   9636    7275.6  5317.9  3783.3  2614.8
1782.6  1178.2  766.23  482.01];

%graph G'&G"
Gerror=0;
Gprime=zeros(length(freq),1);
GDprime=zeros(length(freq),1);
Gerror=0;
    %G' & G" calculation
        for j=1:length(freq)
            Gtemp=zeros(1,5);
            GDtemp=zeros(1,5);
        for i=1:modes

Gtemp(i)=eta(i)*lambda(i)*freq(j)^2/(1+(lambda(i)*freq(j))^2);
            GDtemp(i)=eta(i)*freq(j)/(1+(lambda(i)*freq(j))^2);
        end

        %calculate G' and G" as sum of modes
        Gprime(j)=sum(Gtemp);
        GDprime(j)=sum(GDtemp);
        %calculate error between model and experiment
        Gerror=Gerror+(log10(Gexp(j))-
log10(Gprime(j)))^2+(log10(GDexp(j))-log10(GDprime(j)))^2;
        end
%plot the model predictions and experimental data
if graph==1

loglog(freq,Gprime,'b',freq,Gexp,'+b',freq,GDprime,'g',freq,GDexp,'^g')
;
    title('G-Prime and GDouble-Prime MB 0wt%');
    xlabel('Frequency (rad/s)');
```

```
    ylabel('Gprime,GDprime (Pa*s)');
    legend('Model Gprime','Exp Gprime','Model GDprime','Exp GDprime',-
1);
end
end
```

Pure Polymer: Transient Shear Flow

```
function [Serror] = Shear_MB_0wt(para,graph,modes)
%This program calls on shear_pde_solver to solve the transient
%differntial equations from the constitutive model and create a model
%prediction for the transient shear viscosity vs time.  The error
%between this model prediction and the experimental data is calculated
and
%sent back to Pure_Polymer_Optimization to be used in the error
minimzation
%for parameter optimization.  This program can also plot the model
%prediction of transient shear viscosity given the set of pure polymer
%parameters

sigma=1; %no cnfs - value doesn't matter
CI=0; %no cnfs - value doesn't matter
wt=0; %no cnfs - value doesn't matter
re=0; %no cnfs - value doesn't matter
orient=[0 0 0]; %no cnfs - value doesn't matter

Serror=zeros(1,5); %initialize error variable

for w=1:5 % w designates the w-th shear rate
        if w==1
            r=.01;
            %ave data - can truncate at t= 95.28, exp= 47586
            timedata=[0 0.02    0.03    0.04    0.05    0.06    0.07
0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15    0.16
0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24    0.25
0.26    0.27    0.28    0.29    0.3 0.31    0.32    0.33    0.34
0.35    0.36    0.37    0.38    0.39    0.4 0.41    0.42    0.43
0.44    0.45    0.46    0.47    0.48    0.49    0.5 0.51    0.52
0.53    0.54    0.55    0.56    0.57    0.58    0.59    0.6 0.61
0.62    0.63    0.64    0.65    0.66    0.685   0.725   0.77    0.82
0.875   0.935   0.995   1.06    1.13    1.205   1.285   1.37    1.465
1.565   1.665   1.775   1.895   2.02    2.155   2.295   2.445   2.61
2.78    2.96    3.16    3.37    3.59    3.83    4.085   4.355   4.645
4.955   5.285   5.635   6.01    6.41    6.835   7.285   7.765   8.285
8.835   9.42    10.045  10.71   11.42   12.18   12.99   13.85   14.77
15.75   16.795  17.91   19.1    20.37   21.72   23.16   24.7    26.34
28.09   29.955  31.945  34.065  36.325  38.74   41.31   44.05   46.975
50.095  53.425  56.975  60.755  64.785  69.085  73.675  78.57   83.785
89.345  95.28   101.61  108.35  115.55  123.22  131.4   140.13  149.43
159.35  169.93  181.22  193.25  206.08  219.77  234.36  249.92  266.52
284.22  303.1   333.6   355.76  379.38  404.57  431.43  460.07  490.63
523.21  557.96  594.99  634.51  676.64  721.58  769.48  820.58  875.07
933.17  995.13  1061.2  1131.7  1206.8  1287    1372.4  1463.6  1560.7
1664.4  1774.9  1892.8  2018.4  2152.5  2295.4  2447.8  2610.4  2783.7
2968.5  3165.7  3375.9];
            expdata=[0 217  945.14  1718.2  2445.9  3001.6  3530.6
4035.4  4727    5198.9  5287.9  5707.5  6336.1  6785.1  6768.4  7095.1
7532.2  7921.6  8225.2  8373.8  8640    8774.3  9115.2  9558.7  9609.5
9786    10121   10407   10693   10571   10861   11203   11381   11647
11717   11869   12065   12414   12606   12594   12751   13024   13142
13288   13449   13671   13740   13927   14033   14050   14208   14414
```

```
14538   14678   14871   15031   15006   15119   15238   15337   15505
15823   15757   15984   16090   16315   16476   16870   17342   17833
18359   18908   19428   20005   20435   20954   21541   22141   22752
23371   23920   24414   25054   25631   26223   26748   27206   27877
28562   29154   29682   30316   30947   31437   32022   32633   33239
33829   34347   34913   35470   36032   36589   37054   37442   37888
38263   38697   39120   39486   39934   40320   40757   41061   41453
41795   42157   42737   43150   43440   43635   43756   43833   43980
44368   44750   44994   45227   45406   45355   45513   45978   46470
46466   46549   46714   46909   46765   47036   47159   46912   47238
47702   47586   47660   47749   47735   47748   48108   47970   48142
47937   48534   48367   48457   48642   48708   48621   48914   48943
48970   49099   49102   49219   49213   49142   49399   49436   49473
49477   49630   49629   49634   49657   49467   49573   49532   49449
49332   49334   49204   49068   48875   48756   48780   48845   48595
48665   48405   48407   48195   48307   48154   47951   47885   47777
47499   47408   47395];
        elseif w==2
            r=.1;
            %ave data - can truncate at t= 95.28, exp= 41663.66667
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.27    0.28    0.29    0.3 0.31    0.32    0.33
0.34    0.35    0.36    0.37    0.38    0.39    0.4 0.41    0.42
0.43    0.44    0.45    0.46    0.47    0.48    0.49    0.5 0.51
0.52    0.53    0.54    0.55    0.56    0.57    0.58    0.59    0.6
0.61    0.62    0.63    0.64    0.65    0.66    0.685   0.725   0.77
0.82    0.875   0.935   0.995   1.06    1.13    1.205   1.285   1.37
1.465   1.565   1.665   1.775   1.895   2.02    2.155   2.295   2.445
2.61    2.78    2.96    3.16    3.37    3.59    3.83    4.085   4.355
4.645   4.955   5.285   5.635   6.01    6.41    6.835   7.285   7.765
8.285   8.835   9.42    10.045  10.71   11.42   12.18   12.99   13.85
14.77   15.75   16.795  17.91   19.1    20.37   21.72   23.16   24.7
26.34   28.09   29.955  31.945  34.065  36.325  38.74   41.31   44.05
46.975  50.095  53.425  56.975  60.755  64.785  69.085  73.675  78.57
83.785  89.345  95.28   101.61  108.35  115.55  123.22  131.4   140.13
149.43  159.35  169.93  181.22  193.25  206.08  219.77  234.36  249.92
266.52  284.22  303.1   333.6   355.76  379.38  404.57  431.43  460.07
490.63  523.21  557.96  594.99  634.51  676.64  721.58  769.48  820.58
875.07  933.17  995.13  1061.2  1131.7  1206.8  1287    1372.4  1463.6
1560.7  1664.4  1774.9  1892.8  2018.4  2152.5  2295.4  2447.8  2610.4
2783.7  2968.5  3165.7  3375.9];
            expdata=[0 44.674   445.1933333 1038.633333 1678.366667
2264.7  2822.4  3330.333333 3806.566667 4234.2  4643.9  5025.1
5395.533333 5726.833333 6028.733333 6346.066667 6652.933333 6924.633333
7195.466667 7477.433333 7727.4  7978.633333 8221.6  8470.866667 8676.4
8900.6  9136.5  9330.433333 9541.4  9716.4  9923.1  10113.76667
10317.16667 10496.36667 10680.86667 10862   11040   11216.66667 11393
11565   11712.33333 11884.33333 12023.66667 12214.66667 12363
12493.66667 12650   12786   12937   13069.66667 13222.33333 13383.33333
13531.33333 13683   13810.66667 13937.66667 14077   14205.66667 14332
14443.66667 14581.66667 14684.66667 14806   14931.66667 15024.66667
15102   15272.66667 15567   16007   16492.33333 16973.66667 17496.33333
18016.66667 18500   18962.33333 19504   19993   20538.33333 21050
21640   22208.66667 22761.33333 23311.33333 23908.66667 24509.33333
25044   25588   26149.66667 26691   27190   27764.33333 28404.66667
```

```
28996.33333 29527   30056.33333 30566.66667 31120   31719   32299.66667
32764.33333 33265   33856.33333 34346.66667 34773   35272.33333
35753.66667 36167.66667 36639.33333 37008.33333 37470.66667 37817
38151   38527.66667 38897.33333 39226.66667 39526   39766.66667
40058.33333 40349.33333 40554.66667 40759.66667 40977.66667 41150.66667
41325.66667 41518.66667 41606.66667 41777.33333 41845.33333 41977.66667
42015.33333 42116.33333 42137.66667 42136.33333 42185.66667 42155.66667
42124.33333 42087   42054.66667 42014   41959.66667 41903.33333
41832.33333 41778.33333 41708.66667 41663.66667 41638.33333 41598.66667
41550   41492   41424.66667 41374   41335   41285   41201.66667
41086.33333 40944.33333 40771.33333 40616.33333 40496.66667 40428.66667
40396   40394.33333 40426.66667 40416.33333 40415   40402.33333 40282
40197.33333 40205   40252   40439.66667 40517.66667 40314.33333
40145.33333 40132   40195   40234.33333 39989   39892   40112.33333
40045.33333 39964.33333 39701.66667 39329.33333 39101.33333 38771.66667
38443.33333 37884.66667 37163.33333 36779.33333 36912   36586   36052
35758.66667 34737   33775.66667 33285   32825   31775.33333
30978.33333];
        elseif w==3
            r=.3;
            %.3(3) - can truncate at t= 90.275, exp= 31274
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.27    0.28    0.3 0.335   0.375   0.42    0.475
0.535   0.605   0.685   0.77    0.87    0.985   1.115   1.26    1.42
1.605   1.815   2.05    2.315   2.615   2.955   3.335   3.765   4.255
4.81    5.435   6.14    6.935   7.835   8.855   10.005  11.305  12.775
14.435  16.31   18.43   20.825  23.535  26.595  30.05   33.955  38.37
43.36   48.995  55.365  62.565  70.7    79.89   90.275  102.01  115.27
130.25  147.19  166.33  199.43  225.35  254.65  287.76  325.16  367.44
415.21  469.2   530.21  599.14  677.03  765.05  864.51  976.91  1103.9
1247.5  1409.6  1592.9  1800];
            expdata=[0 52.448   478.99  1133.5  1791.7  2420.8  3005.5
3543    4016.5  4470.2  4877.3  5276.1  5615.4  5991.2  6341.7  6650.9
6953.1  7268.9  7544.4  7821.5  8081.8  8344.2  8591.3  8818.4  9049.9
9282.1  9508.5  9704.7  9931    10338   10991   11662   12372   13169
13978   14883   15810   16667   17568   18476   19497   20560   21509
22470   23427   24406   25296   26267   27183   28017   28770   29596
30311   30940   31554   32044   32436   32770   33007   33208   33339
33389   33404   33326   33194   33039   32857   32667   32459   32261
32213   32138   31999   31842   31653   31466   31274   31157   31099
30875   30788   30765   30926   30888   30724   30581   30448   30265
30404   30118   30184   29777   29055   29118   28672   26800   27125
26434   25741   24756   24923];
        elseif w==4
            r=1;
            %1(2) - can truncate at t= 90.275, exp= 15891
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.27    0.28    0.3 0.335   0.375   0.42    0.475
0.535   0.605   0.685   0.77    0.87    0.985   1.115   1.26    1.42
1.605   1.815   2.05    2.315   2.615   2.955   3.335   3.765   4.255
4.81    5.435   6.14    6.935   7.835   8.855   10.005  11.305  12.775
14.435  16.31   18.43   20.825  23.535  26.595  30.05   33.955  38.37
43.36   48.995  55.365  62.565  70.7    79.89   90.275  102.01  115.27
```

```
130.25  147.19  166.33  199.43  225.35  254.65  287.76  325.16  367.44
415.21  469.2   530.21  599.14  677.03  765.05  864.51  976.91  1103.9
1247.5  1409.6  1592.9  1800];
            expdata=[0 65.549   490.9   1090.5  1764.7  2393.7  2976.9
3507.7  4000.8  4447.5  4881.1  5267.9  5634.4  5980.8  6320.5  6629
6936.4  7220    7492.1  7762.9  8023.9  8264.7  8537.8  8768.7  9012.4
9243.8  9522    9742.7  9965    10344   11064   11769   12531   13337
14182   15000   15918   16792   17643   18543   19392   20174   20862
21528   22074   22543   22862   23075   23141   23055   22863   22522
22081   21608   21144   20731   20367   20097   19882   19660   19446
19275   19245   19164   19095   18929   18594   18297   18305   18445
18175   17508   17196   16573   16211   16175   15891   16108   15234
15704   15690   15466   15594   15998   15671   15906   16899   17104
17162   17846   17468   16644   16772   16497   16022   16569   16323
16064   17184   16867   16103];
        elseif w==5
            r=3;
            %ave data - can truncate at t= 90.275, exp= 10376
            timedata=[0.01  0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.27    0.28    0.3 0.335   0.375   0.42    0.475
0.535   0.605   0.685   0.77    0.87    0.985   1.115   1.26    1.42
1.605   1.815   2.05    2.315   2.615   2.955   3.335   3.765   4.255
4.81    5.435   6.14    6.935   7.835   8.855   10.005  11.305  12.775
14.435  16.31   18.43   20.825  23.535  26.595  30.05   33.955  38.37
43.36   48.995  55.365  62.565  70.7    79.89   90.275  102.01  115.27
130.25  147.19  166.33  199.43  225.35  254.65  287.76  325.16  367.44
415.21  469.2   530.21  599.14  677.03  765.05  864.51  976.91  1103.9
1247.5  1409.6  1592.9  1800];
            expdata=[80.791 534.02  1183.7  1868.1  2498.3  3107.3
3649.5  4140    4589.9  5004.1  5402.2  5790.6  6128    6480    6793.6
7078.1  7388.7  7651.8  7926.1  8174.3  8411    8666    8901.7  9077.6
9313    9485.5  9716.8  9897.5  10246   10841   11437   12009   12622
13104   13618   14041   14366   14623   14761   14772   14695   14522
14212   13892   13525   13147   12768   12443   12152   11859   11617
11382   11214   11239   11207   11171   11208   11217   11184   11060
10992   10824   10663   10649   10602   10652   10623   10612   10545
10506   10449   10222   10274   10306   10286   10376   10438   10567
10267   10072   10103   10039   9804.6  9809.6  9994.7  9855.8  9974.2
9955.5  9543.2  9700.2  9800.7  9600.7  9304    9541    9758.7  9939.9
10043   8959.4  9158.9  9522.6];
        end

        %shift time data back to account for start up delay in
rheometer
        factor=timedata(2)-0.0005;
        timedata=timedata-factor;
        timedata(1)=0;

        %differential equation solver to get model prediction of
viscosity vs time

[t,etatemp,diverge]=shear_pde_solver(r,wt,sigma,CI,para(1,:),para(2,:),
para(3,:),timedata,modes,re,orient);
        if diverge==1 %keep track of divergence
```

```
            fprintf('Divergent Point (shear):')
            fprintf('\nLambda: %f',para(2,:))
            fprintf('\nAlpha: %f\n\n',para(3,:))
        elseif diverge==0 %if no divergence, calculate error between
model and experiment
            for k=2:length(timedata)
                Serror(w)=Serror(w) + (log10(expdata(k))-
log10(etatemp(k)))^2;
            end
        end

%plot the model predictions and experimental data
if graph==1
     if w==1
         figure
         loglog(timedata,expdata,'*',t,etatemp,'Color',[1,0,0]);
         hold on
     elseif w==2
         loglog(timedata,expdata,'*',t,etatemp,'Color',[0,1,0]);
     elseif w==3
         loglog(timedata,expdata,'*',t,etatemp,'Color',[0,0,1]);
     elseif w==4
         loglog(timedata,expdata,'*',t,etatemp,'Color',[0,0,0]);
     elseif w==5
         loglog(timedata,expdata,'*',t,etatemp,'Color',[0,1,1]);
         xlabel('Time (s)')
         ylabel('Viscosity (Pa*s)')
         title('Shear Viscosity')
         legend('Exp \gamma=0.01','Mod \gamma=0.01','Exp
\gamma=0.1','Mod \gamma=0.1','Exp \gamma=0.3','Mod \gamma=0.3','Exp
\gamma=1','Mod \gamma=1','Exp \gamma=3','Mod \gamma=3',-1);
         set(gcf,'Units','normalized',
'WindowStyle','docked','OuterPosition',[0 0 1 1]); %this places the
plot in a maximized window
         hold off
     end

end
end
    Serror=sum(Serror); %sum up error from all shear rates
end
```

Pure Polymer: Transient Extensional Flow

```
function [Terror] = Extensional_MB_0wt(para,graph,modes)
%This program calls on extensional_pde_solver to solve the transient
%differntial equations from the constitutive model and create a model
%prediction for the transient extensional viscosity vs time.  The error
%between this model prediction and the experimental data is calculated
and
%sent back to Pure_Polymer_Optimization to be used in the error
minimzation
%for parameter optimization.  This program can also plot the model
%prediction of transient extensional viscosity given the set of pure
%polymer parameters

wt=0; %mass fraction of cnfs
sigma=1; %no cnfs - value doesn't matter
CI=0; %no cnfs - value doesn't matter
re=0; %no cnfs - value doesn't matter
orient=[0 0 0]; %no cnfs - value doesn't matter

Terror=zeros(1,5); %initialize error variable

 for m=1:5 % m designates the m-th extension rate
        if m==1
            r=.01;  %extensional rate
            %data Koki used at 900s melt time 0.01(4) - TRUNCATED
            timedata= [0 38.2077    45.7507 54.7829 65.5982 78.5487
112.6245    134.8589    161.4830    193.3631    231.5372    277.2475
331.9821    397.5225    476.0019    569.9748 682.5000];
            expdata=[0 168492.5 170607.5    175964.1    179823.5
183979.9    199236.2    204547.3    226705.7    262619  314207.9
403477  602314.5    1129767 2432705 6232116 20593550];
        elseif m==2
            r=.03;
            %data Koki used at 400s melt time 0.03(4) - TRUNCATED
            timedata=[0 11.35781    13.29856    15.57092    18.23158
21.34686    24.99447    29.26535    34.26601    40.12115    46.97677
55.00384    64.40251    75.40717    88.29222    103.379 141.7268
165.9441    194.2995];
            expdata=[0 146779.5000  148095.4000 154832.9000 159295.1000
161106.7000 163667.9000 169304.2000 176864.4000 180235.5000 186648.7000
198452.5000 213460.4000 231445.1000 259906.8000 294510.1000 499871.8000
1082033.0000    2616750.0000];
        elseif m==3
            r=.1;
            %data set Koki used at 400s melt time  0.1(3)
            timedata = [0 3.190139  3.644588    4.163775    4.756922
5.434566    6.208744    7.093206    8.103663    9.258065    10.57692
12.08364    13.80501    15.77159    18.01832    20.58511    23.51755
26.86772    30.69514    45.77055    52.29077    59.73981    68.25];
            expdata = [0 113170.4000    115866.3000 115710.9000
119300.8000 128344.5000 132105.2000 139148.5000 146302.6000 151249.3000
157990.5000 165545.4000 174792.1000 182221.3000 193300.1000 200885.4000
210597.0000 222691.6000 250768.3000 380212.9000 444930.5000 626399.9000
1159610.0000];
```

```
        elseif m==4
            r=.3;
            %data set Koki used at 900s melt time 0.3(4)
            timedata = [0 0.1   0.1117125   0.1247968   0.1394135
0.1557423   0.1739836   0.1943614   0.2171259   0.2425567   0.2709661
0.3027029   0.3381569   0.3777634   0.4220089   0.4714366   0.5266534
0.5883376   0.6572464   0.7342262   0.8202223   0.9162906   1.023611
1.143501    1.277433    1.427052    1.594195    1.780915    1.989504
2.222524    2.482837    2.773638    3.0985  3.461411    3.866828
4.319729    4.825676    5.390882    6.022287    6.727646    7.51562
8.395884    9.37925 10.47779    11.705];
            expdata=[0 9063.837 9737.7  10258.08    12387.07
18360.81    23822.21    25218.44    29457.06    33695.11    33500.95
38132.72    43247.05    44498.33    49870.7 53450.51    58368.96
63280.75    66423.27    70025.27    73785.37    68276.05    75092.21
70893.91    74983.12    79406.44    84650.98    89659.12    94508.59
98780.58    103107.8    108275.5    114432  121238.7    127093.3
132984.4    140180.4    144799.7    156472.5    163388.1    180290.9
192133.9    215290.3    255532.4    310504];
        elseif m==5
            r=1;
            %data set Koki used at 400s 1.0(2)
            timedata = [0 0.1000    0.1090  0.1188  0.1295  0.1412
0.1539  0.1677  0.1828  0.1993  0.2172  0.2368  0.2581  0.2813  0.3066
0.3342  0.3643  0.3971  0.4328  0.4718  0.5143  0.5605  0.6110  0.6660
0.7259  0.7913  0.8625  0.9402  1.0248  1.1170  1.2176  1.3272  1.4466
1.5768  1.7187  1.8735  2.0421  2.2259  2.4262  2.6446  2.8827  3.1421
3.4250  3.7333  4.0693  4.4356  4.8348  5.2700  5.7444  6.2614 ];
            expdata = [0 8603.345   10275.25    11740.97    13521.02
16231.83    20042.37    24496.71    25221.1 26805.39    29678.07
33029.05    35903.96    39329.07    40819.31    38128.38    42085.04
44251.41    46737.63    49700.84    53122.45    55426.59    59770.41
63570.79    67420.58    71928.44    76829.28    82574.72    88348.64
94573.99    100835  107093.4    114905.7    123918.8    133751.8
145084.7    159288  173989.3    192173.7    212003.2    245028.6
288546.2    334680.5    379258.3    425686.6    486103.8    568304.4
626113.8    673079.6    803106.5];
        end

    %differential equation solver to get model prediction of viscosity
vs time

[t,etatemp,diverge]=extensional_pde_solver(r,wt,sigma,CI,para(1,:),para
(2,:),para(3,:),timedata,modes,re,orient); %use for calculation of
Terror
    if diverge==1 %keep track of divergence
        fprintf('Divergent Point (ext):')
        fprintf('\nLambda: %f',para(2,:))
        fprintf('\nAlpha: %f\n\n',para(3,:))
    elseif diverge==0 %if no divergence, calculate error between model
and experiment
        for k=2:length(timedata)
                Terror(m)=Terror(m) + (log10(expdata(k))-
log10(etatemp(k)))^2;
        end
    end
```

```
%plot the model predictions and experimental data
if graph==1
     if m==1
         loglog(t,etatemp,'r',timedata,expdata,'*r');
         hold on
     elseif m==2
         loglog(t,etatemp,'g',timedata,expdata,'*g');
     elseif m==3
         loglog(t,etatemp,'b',timedata,expdata,'*b');
     elseif m==4
         loglog(t,etatemp,'c',timedata,expdata,'*c');
     elseif m==5
         loglog(t,etatemp,'k',timedata,expdata,'*k');
         title('Extensional Viscosity');
         xlabel('Time (s)');
         ylabel('Viscosity (Pa*s)');
         legend('Mod \epsilon=.01','Exp \epsilon=.01','Mod
\epsilon=.03','Exp \epsilon=.03','Mod \epsilon=.1','Exp
\epsilon=.1','Mod \epsilon=.3','Exp \epsilon=.3','Mod \epsilon=1','Exp
\epsilon=1',-1);
         set(gcf,'Units','normalized',
'WindowStyle','docked','OuterPosition',[0 0 1 1]); %this places the
plot in a maximized window
         hold off
     end
end

 end
 Terror=sum(Terror); %sum up error from all extension rates
end
```

Determining Boundary of Convergence for σ, λ, and α

```
function Parameter_Convergence
%This program tests convergence of model due to alphas and lambdas for
a
%range of sigmas
%By Tim's theory:
%   tests at the most extreme: highest deformational rates, highest wt%
%   single mode
%give the boundary of the parameter convergence

warning('off','all')

%optimized pure polymer parameters
Final=[   0.961768502242416e+4   0.849997471090374e+4
0.141393472087865e+4   1.782368034425766e+4   2.400790731282941e+4;
%etap by mode
          9.789278339157816e+3   0.000189405013332e+3
0.000013348257373e+3   0.018781148809731e+3   0.001901628993121e+3;
%lambda by mode
          0.001603491662313   0.985105739933884   0.847316738754344
0.132461526978848   0.554616118726100]; %alpha by mode

%values pulled out of 'Final' matrix
eta=[0.961768502242416e+4   0.849997471090374e+4   0.141393472087865e+4
1.782368034425766e+4   2.400790731282941e+4];
lambda=[9.789278339157816e+3   0.000189405013332e+3
0.000013348257373e+3   0.018781148809731e+3   0.001901628993121e+3];
alpha=[0.001603491662313   0.985105739933884   0.847316738754344
0.132461526978848   0.554616118726100];

sigma=.1:.1:1; %range of sigmas to test at
CI=.09;
wt=.1; %highest weight percent of interest
shear_rate=3; %highest shear rate of interest
shear_time=[0 0.01  0.02    0.03    0.04    0.05    0.06    0.07
0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15    0.16
0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.25    0.285
0.325   0.37    0.425   0.49    0.565   0.65    0.75    0.865   0.995
1.145   1.315   1.51    1.74    2.005   2.31    2.66    3.06    3.525
4.06    4.675   5.38    6.195   7.135   8.215   9.46    10.895  12.545
14.445  16.635  19.155  22.06   25.41   29.265  33.7    38.81   44.695
51.475  59.285  68.275  78.63   90.555  104.29  120.11  138.32  170.54
196.39  226.18  260.49  300.01];
shear_eta=[0 128.86 1006    1343.5  3486.7  4705.7  5808.4  6804.9
7699.4  8541.3  9324.6  9990.2  10618   11210   11803   12262   12708
13230   13703   14069   14486   14777   15181   15508   16140   17072
17926   18725   19471   20077   20517   20791   20771   20384   19659
18649   17570   16732   16039   15622   15359   15062   14832   14575
14577   14929   15216   15221   15140   15024   15021   15042   14762
13992   13644   13652   13425   13484   12779   11962   11177   10332
11237   11004   9504.5  9399.4  8319    7674.5  6953    6238.7  5759.6
5584.8  5409.9  5322.7  5310.3];
ext_rate=1; %highest extension rate of interest
```

```
ext_time=[0 0.1 0.109001    0.1188123   0.1295066   0.1411636
0.1538698   0.1677197   0.1828162   0.1992716   0.2172081   0.2367591
0.2580699   0.2812989   0.3066187   0.3342176   0.3643007   0.3970916
0.432834    0.4717935   0.5142599   0.5605487   0.6110039   0.6660007
0.7259477   0.7912906   0.862515    0.9401504   1.024774    1.117014
1.217557    1.32715 1.446607    1.576817];
ext_eta=[0 20591.25 27356.84    32020.18    39944.88    49080.84
56677.08    61538.6 65226.97    70765.52    77795.37    82053.54
86141.62    93525.47    96412.62    96613.42    104997.7    108339.2
116050.4    120507.6    129031.3    134957.4    142610  150228
157416.4    164235.9    170554.6    177867.3    183905.5    187905
191496.6    196336.7    199949.9    200844.6];
p=1; q=1; conv1=zeros(100,3); conv2=zeros(100,3);

%for-loop to test the boundary at all sigma values
for i=1:10
    for j=1:8
        for k=1:100
            lambda(5)=10^(j-3);
            alpha(5)=.001*k;
            [t1
etatemp1,flag1]=ext_pde(eta,lambda,alpha,sigma(i),CI,wt,ext_rate,ext_ti
me);
            flag1
            if flag1(2)>10
                conv1(p,:)=[i j k];
                p=p+1;
            end
            eta=[0.961768502242416e+4   0.849997471090374e+4
0.141393472087865e+4   1.782368034425766e+4   2.400790731282941e+4];
            [t2
etatemp2,flag2]=shr_pde(eta,lambda,alpha,sigma(i),CI,wt,shear_rate,shea
r_time);
            flag2
            if flag2(2)>10
                conv2(q,:)=[i j k];
                q=q+1;
            end
        end
    end
end
conv1
conv2
plot(conv1(2),conv1(3))
figure
plot(conv2(2),conv2(2))

%write results to excel spreadsheet
xlswrite('ParamConverg',conv1,'Sheet1');
xlswrite('ParamConverg',conv2,'Sheet2');


function [time, etac,flag] =
ext_pde(etap,lambda,alpha,sigma,CI,mass,r,tspan)
%this subfunction is a specialized version of 'extensional_pde_solver'
that
```

```
%examines divergence.  see that program for specific details about its
%operation

x=1;
total12=0;
y=zeros(1,3);
tp=zeros(1,3);
re=44.0;
chi=1.0*(re^2-1)/(re^2+1); %another form of aspect ratio
rf=1750.0; %fiber density
rs=1000.0; %polymer density

phi=rs*mass/(rf+(rs-rf)*mass);  %volume fract of CNFs
Ap=re^2/(3*log(sqrt(pi/phi))); %shape factor, aka A_2

orientation=[.586, .207, .207];

initial=[0 0 0 orientation];
while x<6
    options=odeset('Stats','on');
    [time, yout,
flag]=ode23tb(@modeextensionalsub,tspan,initial,options);

    tau11=yout(:,1);
    tau22=yout(:,2);
    tau12=(tau11-tau22);
    asdf=size(tau12)
    if asdf==34
        total12=total12+tau12;
    elseif asdf~=34
        break
    end

    a11=yout(:,4);
    a22=yout(:,5);
    a33=yout(:,6);

    x=x+1;
end


eta=total12./r;
coef=2.0.*eta*phi;
tf12=(coef).*(Ap*r*((27.0*(a11.*a22.*a33)).*(-3/35+(4*a11+2*a22)/7)+(1-
27*(a11.*a22.*a33)).*(a11.^2+(-3.*a11.*a22-
a11.*a33+a22.^2+a22.*a33)/2)));
etac=tf12/r+eta;

    function dy = modeextensionalsub(t,y)

        t11=y(1);
        t22=y(2);
        t33=y(3);
        a11=y(4);
        a22=y(5);
```

```
        a33=y(6);

        dy=zeros(6,1);
        dy(1,1)=2*r*etap(x)/lambda(x)-sigma*t11/lambda(x)-
alpha(x)/etap(x)*t11^2+2*r*t11-3*(1-sigma)*2*a11*t11/lambda(x);
        dy(2,1)=-r*etap(x)/lambda(x)-sigma*t22/lambda(x)-
alpha(x)/etap(x)*t22^2-r*t22-3*(1-sigma)*a22*t22/lambda(x);
        dy(3,1)=-r*etap(x)/lambda(x)-sigma*t33/lambda(x)-
alpha(x)/etap(x)*t33^2-r*t33-3*(1-sigma)*a33*t33/lambda(x);



        dy(4,1)=CI*2*3^(.5)*r*(1-3*a11)+2*chi*r*a11-
2*chi*r*(27*a11*a22*a33*(-2/35+(10*a11-a22-a33)/14)+(1-
27*a11*a22*a33)*(a11^2-(a11*a22+y(1)*a33)/2));
        dy(5,1)=CI*2*3^(.5)*r*(1-3*a22)-chi*r*a22-
2*chi*r*(27*a11*a22*a33*(1/35+(2*a11-5*a22-a33)/14)+(1-
27*a11*a22*a33)*(a11*a22-(a22^2+a22*a33)/2));
        dy(6,1)=CI*2*3^(.5)*r*(1-3*a33)-chi*r*a33-
2*chi*r*(27*a11*a22*a33*(1/35+(2*a11-a22-5*a33)/14)+(1-
27*a11*a22*a33)*(a11*a33-(a22*a33+a33^2)/2));

    end

end

function [time1, etaf,flag] =
shr_pde(etap,lambda,alpha,sigma,CI,mass,r,tspan)
%this subfunction is a specialized version of 'shear_pde_solver' that
%examines divergence.  see that program for specific details about its
%operation

modes=5;
total12=0;
y=zeros(1,3);
tp=zeros(1,3);
re=44.0; %aspect ratio, aka h    %keep this value in mind

chi=1.0*(re^2-1)/(re^2+1); %another form of aspect ratio
rf=1750.0; %fiber density
rs=1000.0; %polymer density

phi=rs*mass/(rf+(rs-rf)*mass);  %volume fract of CNFs
Ap=re^2/(3*log(sqrt(pi/phi))); %shape factor, aka A_2

orientation=[.586, .207, .207];
initial=[0 0 0 0 orientation];

tau_finalf=zeros(4,5);

for x=1:modes
    initial=[0 0 0 0 orientation];  %initial conditions for ode solver

    options=odeset('Stats','on');
```

```
    [time1, yo, flag]=ode23tb(@modeshearsub,tspan,initial,options);
%ode solver for solving Equations (2) & (4) simultaneously

    L=length(time1);


        tau1=zeros(L,5);
        tau12=zeros(L,5);
        tau2=zeros(L,5);
        tau3=zeros(L,5);


    tau1(:,x)=yo(:,1);
    tau12(:,x)=yo(:,2);
    tau2(:,x)=yo(:,3);
    tau3(:,x)=yo(:,4);


    tau_finalf(:,x) = [tau1(L,x) tau12(L,x) tau2(L,x) tau3(L,x)]';

end

total11f=sum(tau1,2);
total12f=sum(tau12,2);
total22f=sum(tau2,2);
total33f=sum(tau3,2);

a11f=yo(:,5);
a12f=yo(:,6);
a22f=yo(:,7);
a33f=1-a11f-a22f;

T_final= [total11f(L) total12f(L) total22f(L) total33f(L)];

a_final = [a11f(L) a12f(L) a22f(L)]';

etaf=total12f./r;
coef=2.0*etaf*phi;

%%%%This section computes the fiber stress from Equation (3)
if r~=0
    %disp('r~=0')
    tf12f=(coef*Ap*r).*((27.0.*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(-
1.0/35.0+1.0/7.0.*(a11f+a22f))+(a12f.^2).*(1-27.*(a11f.*a22f.*(1-a11f-
a22f))+27.0.*(a12f.^2).*(1-a11f-a22f)));
    tf11f=(coef*Ap*r).*((27.0.*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(3.0/7.0.*(a12f))+(a11f.*a12f).*(1-
27*(a11f.*a22f.*(1-a11f-a22f))+27.0.*(a12f.^2).*(1-a11f-a22f)));
    tf22f=(coef*Ap*r).*((27.0.*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(3.0/7.0.*(a12f))+(a22f.*a12f).*(1-
27*(a11f.*a22f.*(1-a11f-a22f))+27.0.*(a12f.^2).*(1-a11f-a22f)));
    tf33f=(coef*Ap*r).*((27.0.*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(1.0/7.0.*(a12f))+((1-a11f-
```

```
a22f).*a12f).*(1-27.*(a11f.*a22f.*(1-a11f-a22f))+27.0.*(a12f.^2).*(1-
a11f-a22f)));
else
    %disp('r==0')
    tf12f=(2.0*phi.*total12f.*Ap).*((27.0*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(-
1.0/35.0+1.0/7.0*(a11f+a22f))+(a12f.^2).*(1-27*(a11f.*a22f.*(1-a11f-
a22f))+27.0*(a12f.^2).*(1-a11f-a22f)));
    tf11f=(2.0*phi.*total12f.*Ap).*((27.0*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(3.0/7.0*(a12f))+(a11f.*a12f).*(1-
27*(a11f.*a22f.*(1-a11f-a22f))+27.0*(a12f.^2).*(1-a11f-a22f)));
    tf22f=(2.0*phi.*total12f.*Ap).*((27.0*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(3.0/7.0*(a12f))+(a22f.*a12f).*(1-
27*(a11f.*a22f.*(1-a11f-a22f))+27.0*(a12f.^2).*(1-a11f-a22f)));
    tf33f=(2.0*phi.*total12f.*Ap).*((27.0*(a11f.*a22f.*(1-a11f-a22f)-
(a12f.^2).*(1-a11f-a22f))).*(1.0/7.0*(a12f))+((1-a11f-a22f).*a12f).*(1-
27*(a11f.*a22f.*(1-a11f-a22f))+27.0*(a12f.^2).*(1-a11f-a22f)));
end

tauc12f=tf12f+total12f;
tauc11f=tf11f+total11f;
tauc22f=tf22f+total22f;
tauc33f=tf33f+total33f;
etacf=tauc12f./r;

    function dyo = modeshearsub(t,y)

        tp11=y(1);
        tp12=y(2);
        tp22=y(3);
        tp33=y(4);
        a11=y(5);
        a12=y(6);
        a22=y(7);
        a33=1-a11-a22;
        dyo=zeros(7,1);

        dyo(1,1)=-alpha(x)*(tp11^2+tp12^2)/etap(x)-
sigma*tp11/lambda(x)+2*r*tp12-3*(1-
sigma)*(tp11*a11+tp12*a12)/lambda(x);
        dyo(2,1)=-alpha(x)*(tp11*tp12+tp12*tp22)/etap(x)-
sigma*tp12/lambda(x)+etap(x)*r/lambda(x)+r*tp22-3*(1-
sigma)/2/lambda(x)*(a11*tp12+a12*tp22+a12*tp11+a22*tp12);
        dyo(3,1)=-alpha(x)*(tp12^2+tp22^2)/etap(x)-
sigma*tp22/lambda(x)-3*(1-sigma)/lambda(x)*(tp12*a12+tp22*a22);
        dyo(4,1)=-alpha(x)*(tp33^2)/etap(x)-tp33*sigma/lambda(x)-3*(1-
sigma)/lambda(x)*a33*tp33;

        dyo(5,1)=r*a12+2*CI*abs(r)*(1.0-3.0*a11)+chi*r*a12-...
            2*chi*r*(3.0/7.0*a12*(27.0*a11*a22*(1-a11-a22)...
            -27.0*(a12^2)*(1-a11-a22))+(1.0-27.0*a11*a22*(1-a11-
a22)+...
            27.0*(a12^2)*(1-a11-a22))*a11*a12);
        dyo(6,1)=1.0/2.0*r*a22-1.0/2.0*r*a11+chi*((1.0/2.0*r*a22+...
            1.0/2.0*r*a11)-(2.0*r)*((27.0*a11*a22*(1-a11-a22)-...
```

```
            27.0*(a12^2)*(1-a11-a22))*(-
1.0/35.0+1.0/7.0*a11+1.0/7.0*a22)+...
            (1.0-27.0*a11*a22*(1-a11-a22)...
            +27.0*(a12^2)*(1-a11-a22))*a12^2))-6.0*CI*abs(r)*a12;
        dyo(7,1)=-r*a12+2*CI*abs(r)*(1.0-3.0*a22)+chi*r*a12-...
            2*chi*r*(3.0/7.0*a12*(27.0*a11*a22*(1-a11-a22)-...
            27.0*(a12^2)*(1-a11-a22))+(1.0-27.0*a11*a22*(1-a11-a22)+...
            27.0*(a12^2)*(1-a11-a22))*a12*a22);

    end

end

end
```

Composite Parameter Optimization: C_I

```
function [ci_mb2,ci_mb2hht,ci_sc2]=ci_optimization()
%This program is used for optimizing the values of CI for MB2, MB2HHT,
and
%SC2 composites using the steady state orientation of cnfs (a11
component)
%in extensional flows.  Orientation at one or two extension rates are
used

f0=[.01]; %initial guess for fmincon
options=optimset('Algorithm','interior-point'); %search algorithm

%MB2
[ci_mb2, fval,
exitflag]=fmincon(@MB2,f0,[],[],[],[],[0],[1],[],options);

    function e=MB2(ci)
    %this sub-function calculates error between model and experiment
for
    %fmincon so fmincon can optimize ci
        re=53;
        strain_rate=[.01,.1,1];
        a11_mb2_exp=[.928 .94 .94]; %experimental orientation (a11)
        a11_mb2=zeros(1,3);
        for i=1:length(strain_rate)
            t0=[0,3/strain_rate(i)];
            %calculate model prediction
            [t,a]=ode45(@orient,t0,[.586 .207 .207 re ci
strain_rate(i)]);
            a11_mb2(i)=a(end,1); %model prediction for steady-state
value
        end
        e=sum((a11_mb2_exp-a11_mb2).^2); %total error
    end

%MB2-HHT
[ci_mb2hht, fval,
exitflag]=fmincon(@MB2HHT,f0,[],[],[],[],[0],[1],[],options);

    function e=MB2HHT(ci)
    %this sub-function calculates error between model and experiment
for
    %fmincon so fmincon can optimize ci
        re=44;
        strain_rate=[.1];
        a11_mb2hht_exp=[.937]; %experimental orientation (a11)
        a11_mb2hht=zeros(1,1);
        for i=1:length(strain_rate)
            t0=[0,3/strain_rate(i)];
            %calculate model prediction
            [t,a]=ode45(@orient,t0,[.441 .2795 .2795 re ci
strain_rate(i)]);
            a11_mb2hht(i)=a(end,1); %model prediction for steady-state
value
```

```
        end
        e=sum((a11_mb2hht_exp-a11_mb2hht).^2); %total error
    end

%SC2
[ci_sc2, fval,
exitflag]=fmincon(@SC2,f0,[],[],[],[],[0],[1],[],options);

    function e=SC2(ci)
    %this sub-function calculates error between model and experiment
for
    %fmincon so fmincon can optimize ci
        re=69;
        strain_rate=[.01,.1];
        a11_sc2_exp=[.909 .89]; %experimental orientation (a11)
        a11_sc2=zeros(1,2);
        for i=1:length(strain_rate)
            t0=[0,3/strain_rate(i)];
            %calculate model prediction
            [t,a]=ode45(@orient,t0,[.528 .236 .236 re ci
strain_rate(i)]);
            a11_sc2(i)=a(end,1); %model prediction for steady-state
value
        end
        e=sum((a11_sc2_exp-a11_sc2).^2); %total error
    end

%display optimized values
ci_mb2;
ci_mb2hht;
ci_sc2;

    function dy = orient(t,y)
    %this subfunction solves the differential equation that describes
the
    %orientation evolution of cnfs
        a11e=y(1);
        a22e=y(2);
        a33e=y(3);
        chi=1.0*(y(4)^2-1)/(y(4)^2+1);
        CI=y(5);
        r=y(6);
        dy=zeros(6,1);

        %extensional orientation evolution equations
        dy(1,1)=CI*2*3^(.5)*r*(1-3*a11e)+2*chi*r*a11e-
2*chi*r*(27*a11e*a22e*a33e*(-2/35+(10*a11e-a22e-a33e)/14)+(1-
27*a11e*a22e*a33e)*(a11e^2-(a11e*a22e+a11e*a33e)/2));
        dy(2,1)=CI*2*3^(.5)*r*(1-3*a22e)-chi*r*a22e-
2*chi*r*(27*a11e*a22e*a33e*(1/35+(2*a11e-5*a22e-a33e)/14)+(1-
27*a11e*a22e*a33e)*(a11e*a22e-(a22e^2+a22e*a33e)/2));
        dy(3,1)=CI*2*3^(.5)*r*(1-3*a33e)-chi*r*a33e-
2*chi*r*(27*a11e*a22e*a33e*(1/35+(2*a11e-a22e-5*a33e)/14)+(1-
27*a11e*a22e*a33e)*(a11e*a33e-(a22e*a33e+a33e^2)/2));
    end
end
```

Composite Parameter Optimization: Aspect Ratio Scaling Factor

```
function
[scale_mb2,scale_mb2hht,scale_sc2]=aspect_ratio_optimization(z,CI)
%This function optimizes the scaling factor for aspect ratio for MB2,
%MB2HHT, and SC2 for given values of sigma.  These results can then be
used
%in "sigma_optimization" to optimize sigma for these scaling factors.
%Iteratively use these two programs until the values for the scaling
%factors and sigmas converge

sig=[.8099 .5439 .5]; %change with iterations with "sigma_optimization"

CI=[.0306,.0301,.0499]; %optimized values from "ci_optimization"
program
z=.01; %relative error scaling (make error from shear and from
extensional same order of magnitude)

%optimized parameters from pure polymer
etap=[1563.180023   10503.23358 30793.85272 9864.433234 9310.030642
40690.01669];
lambda=[0.01461114  0.235979496 3.210427777 34.39722848 6390.005373
116255.5053];
alpha=[0.818868357  0.56        0.56        0.078601046 0.025189799
0.001841609];
rate=[.1,.3,1,3]; %shear rates
wt=.02; %mass fraction of cnfs
tspan=0:100; %time span for differntial equation solver
modes=6;

f0=1; %initial guess for fmincon
options=optimset('Algorithm','interior-point'); %search algorithm

%MB2
for i=1:4
    %experimental viscosity
    if i==1
        expdata=[0 50.7945  584.48  1344.55 2156.55 2936.75 3642.3
4300.35 4916.1  5486.55 6033.9  6547.35 6989.2  7478.75 7894.65 8337.05
8711.15 9078.3  9467.1  9817.15 10128.55    10489.5 10776   11133.5
11398   11718.5 11999   12539.5 13462   14433   15452   16596   17857
19195.5 20482   21804.5 23187.5 24604   26029   27489   28942.5 30349
31871   33540   35291   36825.5 38329   39883.5 41336.5 42792   44163.5
45455.5 46928   48050   49140.5 50051.5 50998.5 51635.5 52298   52613.5
52941.5 52956   52840   52555   52109   51529   50807.5 50015   49252.5
48562.5 47945.5 47447.5 47096   46859.5 46687.5 46553   46500.5 46521.5
46502   46310   46213   46145   46097.5 46524   46700   46803   46926
46665   46758.5 46678.5 46505.5 45537.5 44098   43581   41589.5 40157.5
38101.5 36936.5 34339   32735   30810];
    elseif i==2
        expdata=[0 99.9685  604.9975    1340.875    2132.75 2901.175
3615.725    4250.8  4849.225    5396.025    5902.575    6368.925
6840.575    7264.625    7669.825    8073.225    8450.65 8810.425
9167.825    9500.225    9835.875    10147.425   10466.975   10761.575
11107.75    11687.75    12541.75    13574.25    14676   15808   17049
```

```
18279.75    19525.75    20877.5 22255   23687   25110.75    26524
27946.75    29342.75    30698   32143.5 33463.25    34690.75    35815.5
36905.75    37777   38536.75    39114.5 39512   39696.75    39695
39474.25    39051.75    38471   37797   37087.5 36418.25    35882
35513.25    35195.25    34831.25    34404.5 34004.5 33589.5 33141.75
32648.25    32318.75    32091.5 31819   31350.5 30692   30481.25
30675.25    30402.25    29974.5 29579.5 28524.75    27139.75    26114.5
24383.5 23727.25    22031.25    21686.5 20093.75    19055];
    elseif i==3
        expdata=[0 75.508   584.995 1305.55 2089.8  2826.1  3530.25
4155.5  4741.3  5265.55 5766.4  6218.95 6653.3  7066.3  7452.2  7830.9
8208.15 8569.3  8903.4  9235.3  9574    9888.8  10211.55    10576.5
11194   12001.5 12934.5 13984   15073   16183   17332   18511   19647
20766.5 21847.5 22890   23849   24647.5 25327   25832.5 26130   26237
26117.5 25766   25226.5 24509.5 23675   22860   22161   21531   20934
20404.5 20015.5 19619   19396.5 19309   19296   19082   18705   18660
19259   19385.5 19098   19093   19317.5 19446   19286.5 19275.5 19199
19171.5 18758];
    elseif i==4
        expdata=[0 78.294   584.5   1295.5  2058.9  2794.3  3467.05
4099.4  4652.75 5184.15 5693.65 6131.4  6549.8  6960.3  7353.75 7697.25
8050.75 8371.05 8697.05 8987.3  9279.05 9581.5  9843.1  10101.55
10413   10876.5 11622   12405   13143   13891.5 14622   15196.5 15731.5
16098   16360.5 16433   16367   16110   15742.5 15233.5 14640.5 14039
13493.5 12955.5 12382   12081.5 11936   11877.5 11958.5 11980.5 11993
11977   11949.5 11858.5 11969.5 11983   11825.5 11698   11571   11515
11315   11197];
    end
    maxpoints_exp(i)=max(expdata'); %max viscosity of overshoot
end

%minimize error between model and experiment
[scale_mb2, fval,
exitflag]=fmincon(@MB2,f0,[],[],[],[],[1],[4],[],options);
re_mb2=53/scale_mb2; %effective aspect ratio
scale_mb2; %scaling factor

    function e=MB2(hscale)
    %this sub-function calculates error between model and experiment
for
    %fmincon so fmincon can optimize the aspect ratio scaling factor
        orient=[.586 0 .207]; %experimental initial orientation
(a11,a12,a22)
        h=53/hscale;
        for j=1:4
            %calculate model prediction
            [t,eta,div] =
shear_pde_solver(rate(j),wt,sig(1),CI(1),etap,lambda,alpha,tspan,modes,
h,orient);
            maxpoints(j)=max(eta); %max viscosity point in shear
overshoot in model prediction
        end
            r0=0.01;
            %Linear viscoselastic plateau: used data for trouton at
0.01s^-1 (3*eta) between 1 and 100 sec
```

```
            time_trout=[0 1.125 1.28    1.455   1.655   1.885   2.145
2.44    2.775   3.155   3.59    4.085   4.645   5.285   6.015   6.845
7.79    8.865   10.085  11.475  13.06   14.865  16.915  19.245  21.9
24.92   28.355  32.265  36.715  41.78   47.545  54.105  61.565  70.055
79.72   90.72];
            exp_trout=[0 83514  88821   93177   98445   103725  108942
113946  118962  124137  129135  134151  139248  144234  149094  153879
159309  164502  168870  173403  177450  181362  184707  187107  190683
195153  198306  200370  202899  204825  205572  207951  208434  211290
212115  212574];
            orient1=[.586 .207 .207]; %experimental initial orientation
(a11,a22,a33)

            %calculate model prediction

[t,ext,div]=extensional_pde_solver(r0,wt,sig(1),CI(1),etap,lambda,alpha
,time_trout,modes,h,orient1);
            a=find(t>1 & t<100); %model prediction for linear
viscoelastic plateau
            e_trout=0; %initialize error variable
            %calculate error of model prediction of LVE plateau
            for k=2:length(a)
                e_trout=e_trout+(log10(exp_trout(k))-
log10(ext(a(k))))^2;
            end
        %calculate total error for mb2
        e=(sum((log10(maxpoints_exp)-log10(maxpoints)).^2))+z*e_trout;
    end

%MB2-HHT
for i=1:4
    %experimental viscosity
    if i==1
        expdata=[0 47.56    606.43  1449.7  2348.5  3178.3  3978.3
4677.2  5311.3  5910.9  6447.8  6956.1  7433.9  7911    8342.7  8777.3
9160.9  9561.8  9965.6  10310   10633   10989   11310   11617   11936
12170   12487   12903   13640   14766   15862   16922   18042   19203
20436   21708   23068   24427   25852   27324   28686   30031   31401
32729   34119   35448   36699   38064   39314   40295   41652   42824
43781   44732   45417   46413   47050   47539   48099   48349   48675
48741   48758   48700   48503   48247   47970   47606   47242   46890
46533   46219   45951   45749   45587   45514   45503   45427   45343
45249   45145   45181   45302   45257   45066   44909   44915   44746
44712   44278   44189   43827   43584   43794   43760   43936];
    elseif i==2
        expdata=[0 66.031   624.41  1415    2256.7  3048.4  3757.8
4418.8  5029.6  5591.8  6115.1  6603.6  7075.5  7510.8  7905.8  8311
8684.8  9049.8  9405.8  9731.3  10069   10373   10663   10960   11241
11512   11779   12170   12897   13781   14677   15656   16606   17564
18662   19842   21006   22105   23166   24286   25339   26509   27518
28569   29665   30583   31487   32281   33070   33657   34197   34532
34771   34785   34647   34332   33770   33081   32301   31465   30681
30001   29422   28873   28377   27963   27606   27475   27409   27087
26845   26816   26650   26670   26531   26342   25856   25536   25542
25261   25432   25555   25623   25484];
    elseif i==3
```

```
        expdata=[0 87.354   628.09  1384.5  2182.5  2935    3619.7
4239.6  4826.3  5366.2  5836.6  6320.1  6761.8  7166.7  7542.3  7928.6
8241.4  8592.8  8879.2  9196.6  9512.9  9765.7  10042   10323   10559
10822   11075   11311   11747   12442   13335   14168   14970   15923
16845   17730   18594   19405   20269   21011   21711   22367   22907
23391   23716   23927   24009   23952   23764   23433   23011   22523
22006   21492   20996   20534   20078   19625   19248   18957   18707
18433   18248   18210   18207   18220   18286   18058   17770   17614
17452   17137   16801   16329   15954   15278   15025   14791   14257];
    elseif i==4
        expdata=[0 82.036   606.86  1335.9  2110.6  2844.7  3506.9
4095.5  4625.8  5119.7  5589.3  6035.9  6411.6  6741.9  7117.2  7440.7
7745.2  8032.4  8299.3  8550.5  8808.2  9026.2  9261.2  9544    9730.8
9949.6  10173   10344   10786   11417   12030   12639   13152   13567
13980   14230   14400   14420   14353   14139   13851   13457   13004
12563   12119   11723   11333   11006   10731   10514   10373   10274
10158   10107   10166   10208   10270   10335   10306   10145   10120
10129   10067   10013   9953.8  9964.8  10036];
    end
    maxpoints_exp(i)=max(expdata'); %max viscosity of overshoot
end

%minimize error between model and experiment
[scale_mb2hht, fval,
exitflag]=fmincon(@MB2HHT,f0,[],[],[],[],[1],[4],[],options);
re_mb2hht=44/scale_mb2hht; %effective aspect ratio
scale_mb2hht; %scaling factor

    function e=MB2HHT(hscale)
    %this sub-function calculates error between model and experiment
for
    %fmincon so fmincon can optimize the aspect ratio scaling factor
        orient=[.441 0 .2795]; %experimental initial orientation
(a11,a12,a22)
        h=44/hscale;
        for j=1:4
            %calculate model prediction
            [t,eta,div] =
shear_pde_solver(rate(j),wt,sig(2),CI(2),etap,lambda,alpha,tspan,modes,
h,orient);
            maxpoints(j)=max(eta); %max viscosity point in shear
overshoot in model prediction
        end
            r0=0.01;
            %Linear viscoselastic plateau: used data from 0.0001s^-1
(n*eta, n=3.8) between 1 and 100 sec
            time_trout=[0 1.075 1.22    1.385   1.575   1.79    2.035
2.31    2.625   2.985   3.39    3.85    4.375   4.97    5.645   6.415
7.29    8.285   9.415   10.7    12.16   13.82   15.705  17.845  20.28
23.05   26.195  29.77   33.835  38.45   43.7    49.665  56.44   64.145
72.9    82.845  94.15];
            exp_trout=[0 113661.8   99913.4 119114.8    119525.2
116078.6    132342.6    131882.8    152311.6    159824.2    146053
163673.6    164574.2    164619.8    177631  180370.8    184212.6
181678  193792.4    197045.2    197980  212610  213875.4    218294.8
```

```
216182  219548.8    242896  232172.4    230553.6    233377  240585.6
244062.6    238058.6    243112.6    250689.8    252787.4    245324.2];
            orient1=[.441 .2795 .2795]; %experimental initial
orientation (a11,a22,a33)

            %calculate model prediction

[t,ext,div]=extensional_pde_solver(r0,wt,sig(2),CI(2),etap,lambda,alpha
,time_trout,modes,h,orient1);
            a=find(t>1 & t<100); %model prediction for linear
viscoelastic plateau
            e_trout=0; %initialize error variable
            %calculate error of model prediction of LVE plateau
            for k=2:length(a)
                e_trout=e_trout+(log10(exp_trout(k))-
log10(ext(a(k))))^2;
            end
        %calculate total error for mb2hht
        e=(sum((log10(maxpoints_exp)-log10(maxpoints)).^2))+z*e_trout;
    end

%SC2
for i=1:4
    %experimental viscosity
    if i==1
        expdata=[0 46.69    534.64  1332.6  2176.3  2964.8  3727.8
4412.9  5013.3  5591.9  6170.2  6691.2  7173.6  7642.8  8091.4  8493.5
8883.1  9289.5  9642.4  9972    10353   10704   11007   11334   11646
11934   12221   12630   13447   14563   15682   16835   17961   19139
20369   21656   22966   24300   25739   27163   28570   30014   31453
32987   34555   35976   37305   38609   40282   41632   42792   43995
45096   45865   46987   47621   48093   48491   48618   48453   48145
47535   46686   45747   44626   43371   42111   40947   40067   39452
38987   38733   38722   38947   39274   39675   39927   40047   40079
40401   40765   40633   40822   40897   41109   41582   41733   41999
42335   42222   42799   42591   42464   42640   43358   44800];
    elseif i==2
       expdata=[0 1.7318    546.57  1358.4  2224.9  3051.1  3824.1
4527.7  5180    5776.1  6333.1  6842.5  7329.9  7808.9  8244.6  8681.6
9047.8  9481.8  9860.3  10224   10572   10907   11203   11517   11832
12153   12453   12874   13704   14730   15835   17078   18362   19554
20856   22145   23421   24779   26081   27376   28694   29895   31154
32385   33357   34290   35010   35745   36162   36356   36445   36218
35860   35244   34470   33662   32841   32027   31258   30592   30145
29850   29780   29898   30123   30304   30329   30249   30213   30149
29944   29640   29198   28897   28697   28995   29499   30168   30387
29750   29243   29098   30009   30418   30073   30110   30002   30242
29961   30404   31371];
    elseif i==3
        expdata=[0 83.562   635.88  1426    2283    3094.4  3843.7
4523.4  5155.8  5733.9  6312.9  6823.6  7291.8  7762    8188    8612.7
9032.3  9384.7  9755.5  10029   10417   10735   11029   11349   11635
11933   12268   12515   13071   13947   14939   15939   16941   17989
18969   19988   20965   21849   22637   23360   23937   24322   24533
24502   24247   23711   22939   21997   20968   19850   18720   17770
17262   17162   17303   17616   18041   18401   18610   18591   18525
```

```
18315   18014   17718   17554   17912   18391   18547   18259   18296
18344   18484   18327   18469   18667   18545   18048   17298   17227
16680   15784   14849   14048   14042   14292   13739   13411   13484
14157];
    elseif i==4
        expdata=[0 71.359   585.85  1288.8  2060.1  2807    3484
4112.1  4690.9  5193.1  5668.5  6120.5  6540.9  6912.2  7291.7  7589.7
7944.7  8231.9  8528.3  8813.8  9118.9  9353.9  9592    9839.8  10067
10278   10477   10665   11086   11760   12342   12867   13415   13797
14099   14302   14417   14446   14352   14110   13858   13506   13146
12793   12486   12169   11887   11663   11463   11275   11086   10901
10753   10580   10532   10572   10461   10248   10124   10108   10275
9986.5  9727.1  9464.9  9189.8  9304.7  9346.9  9218.6  8557.1  7401.4
6479    6499.6  6478.8  6392.4  6535.5  6508.1  6727.7  6844.7  6884.1
6761.7  6629.9  6373.8  6136.3];
    end
    maxpoints_exp(i)=max(expdata'); %max viscosity of overshoot
end

%minimize error between model and experiment
[scale_sc2, fval,
exitflag]=fmincon(@SC2,f0,[],[],[],[],[1],[4],[],options);
re_SC2=69/scale_sc2; %effective aspect ratio
scale_sc2; %scaling factor

    function e=SC2(hscale)
    %this sub-function calculates error between model and experiment
for
    %fmincon so fmincon can optimize the aspect ratio scaling factor
        orient=[.528 0 .236]; %experimental initial orientation
(a11,a12,a22)
        h=69/hscale;
        for j=1:4
            %calculate model prediction
            [t,eta,div] =
shear_pde_solver(rate(j),wt,sig(3),CI(3),etap,lambda,alpha,tspan,modes,
h,orient);
            maxpoints(j)=max(eta); %max viscosity point in shear
overshoot in model prediction
        end
            r0=0.01;
            %Linear viscoselastic plateau: used data from 0.001s^-1
(n*eta, n=5.5) between 1 and 100 sec
            time_trout=[0 1.01  1.15    1.31    1.49    1.695   1.93
2.195   2.5 2.85    3.245   3.69    4.2 4.785   5.445   6.2 7.06
8.035   9.15    10.42   11.865  13.51   15.38   17.51   19.935  22.7
25.85   29.43   33.51   38.155  43.445  49.47   56.325  64.13   73.02
83.145  94.675];
            exp_trout=[0 150920 160611  171561.5    181549.5
191889.5    199160.5    210743.5    222717  233722.5    241125.5
254578.5    265589.5    274334.5    284971.5    296015.5    304942
314418.5    323306.5    333388  341660  349266.5    356438.5    363352
370507.5    376623.5    382299.5    386996.5    391968.5    396995.5
401362.5    404827.5    407539  410217.5    413693.5    416152
421635.5];
```

```
            orient1=[.528 .236 .236]; %experimental initial orientation
(a11,a22,a33)

            %calculate model prediction

[t,ext,div]=extensional_pde_solver(r0,wt,sig(3),CI(3),etap,lambda,alpha
,time_trout,modes,h,orient1);
            a=find(t>1 & t<100); %model prediction for linear
viscoelastic plateau
            e_trout=0; %initialize error variable
            %calculate error of model prediction of LVE plateau
            for k=2:length(a)
                e_trout=e_trout+(log10(exp_trout(k))-
log10(ext(a(k))))^2;
            end
        %calculate total error for sc2
        e=(sum((log10(maxpoints_exp)-log10(maxpoints)).^2))+z*e_trout;
    end

%display optimized aspect ratio scaling factors
scale_mb2
scale_mb2hht
scale_sc2

end
```

Composite Parameter Optimization: σ

```
function sigma_optimization
%This function optimizes sigma for MB2,MB2HHT, and SC2 for given values
of
%of the aspect ratio scaling factors.  These results can then be used
%in "aspect_ratio_optimization" to optimize aspect ratio scaling facotr
for
%these sigmas.
%Iteratively use these two programs until the values for the scaling
%factors and sigmas converge

hscale=[1.8443 1.4487 1.7566]; %change with iterations with
"aspect_ratio_optimization"

CI=[.0306,.0301,.0499]; %optimized values from "ci_optimization"
program

%steady-state values for shear viscosity
ss_mb2=[46446.68182 33019.95 19162.46429 11904.21429]; %averaged from
t=[103,400] for r=0.1, t=[34,105] for r=0.3, t=[19,111] for r=1,
t=[4,25] for r=3
ss_mb2hht=[44760.23529 26285.09091 18196.2 10099.5875]; %averaged from
t=[177,1391] for r=0.1, t=[57,219] for r=0.3, t=[23,39] for r=1,
t=[6,41] for r=3
ss_sc2=[39842.375 29802.24 18115 10362.5]; %averaged from t=[46,337]
for r=0.1, t=[18,417] for r=0.3, t=[21,57] for r=1, t=[7,17] for r=3

%optimized from pure polymer
etap=[1563.180023   10503.23358 30793.85272 9864.433234 9310.030642
40690.01669];
lambda=[0.01461114  0.235979496 3.210427777 34.39722848 6390.005373
116255.5053];
alpha=[0.818868357  0.56        0.56        0.078601046 0.025189799
0.001841609];
rate=[.1,.3,1,3]; %shear rates
wt=.02; %mass fraction of cnfs
modes=6;
tspan=0:100;

f0=.5; %initial guess for fmincon
options=optimset('Algorithm','interior-point'); %search algorithm

%MB2
[sigma_mb2, fval,
exitflag]=fmincon(@MB2,f0,[],[],[],[],[.5],[1],[],options);

    function e=MB2(sigm)
    %this sub-function calculates error between model and experiment
for
    %fmincon so fmincon can optimize sigma
        orient=[.586 0 .207]; %experimental orientation (a11,a12,a22)
        h=53/hscale(1); %effective aspect ratio
        ss_visc=zeros(1,4);
        for j=1:4
```

```
            %calculate model prediction
            [t,eta] =
shear_pde_solver(rate(j),wt,sigm,CI(1),etap,lambda,alpha,tspan,modes,h,
orient);
            ss_visc(j)=eta(end); %find model prediction for steady
state viscosity
        end
        e=sum((ss_mb2-ss_visc).^2); %total error from all shear rates
    end

%MB2HHT
[sigma_mb2hht, fval,
exitflag]=fmincon(@MB2HHT,f0,[],[],[],[],[.5],[1],[],options);

    function e=MB2HHT(sigm)
    %this sub-function calculates error between model and experiment
for
    %fmincon so fmincon can optimize sigma
        orient=[.441 0 .2795]; %experimental orientation (a11,a12,a22)
        h=44/hscale(2); %effective aspect ratio
        ss_visc=zeros(1,4);
        for j=1:4
            %calculate model prediction
            [t,eta] =
shear_pde_solver(rate(j),wt,sigm,CI(2),etap,lambda,alpha,tspan,modes,h,
orient);
            ss_visc(j)=eta(end); %find model prediction for steady
state viscosity
        end
        e=sum((ss_mb2hht-ss_visc).^2); %total error from all shear
rates
    end

%SC2
[sigma_sc2, fval,
exitflag]=fmincon(@SC2,f0,[],[],[],[],[.5],[1],[],options);

    function e=SC2(sigm)
    %this sub-function calculates error between model and experiment
for
    %fmincon so fmincon can optimize sigma
        orient=[.528 0 .236]; %experimental orientation (a11,a12,a22)
        h=69/hscale(3); %effective aspect ratio
        ss_visc=zeros(1,4);
        for j=1:4
            %calculate model prediction
            [t,eta] =
shear_pde_solver(rate(j),wt,sigm,CI(3),etap,lambda,alpha,tspan,modes,h,
orient);
            ss_visc(j)=eta(end); %find model prediction for steady
state viscosity
        end
        e=sum((ss_sc2-ss_visc).^2); %total error from all shear rates
    end

%display optimized values
```

```
sigma_mb2
sigma_mb2hht
sigma_sc2

end
```

Composite Model Predictions: Melt Blended with O-CNFS (MB)

```
function MB_2wt
%This program plots the viscosity for the MB 2wt% composite for
transient
%extension and transient shear as well as moduli predictions for SAOS
% given the optimized values for sigma and CI and hfactor

format long g
sigma=.809;
CI=.0306;
hfactor=1.84;

para=[   1563.180023    10503.23358 30793.85272 9864.433234 9310.030642
40690.01669; %optimized values for etap by mode
            0.01461114  0.235979496 3.210427777 34.39722848 6390.005373
116255.5053; %optimized values for lambda by mode
            0.818868357 0.56        0.56        0.078601046 0.025189799
0.001841609]; %optimized values for alpha by mode
modes=6;
wt=.02; % mass fraction of cnfs
re=53/hfactor; %53= number ave length, 74= weight ave length
orient_ext=[.586, .207, .207]; %experimentally determined initial
orientation of fibers (a11,a22,a33)
orient_shr=[.586 0 .207]; %%experimentally determined initial
orientation of fibers (a11,a12,a22)

%%
%%Part 1: Extensional plotting
terr=zeros(1,5); %error per extension rate in model predictions
tdiv=0; %keeps track of any divergences in extensional model
predictions

for m=1:5 % m designates the m-th extension rate
        if m==1
            r=.01;
            %truncated, set .01(3), time and viscosity
            timedata=[0 31.90831    38.20769    45.7507 54.78287
65.59817    78.54865    94.05583    112.6245    134.8589    161.483
193.3631    231.5372    277.2475    331.9821    397.5225    476.0019
569.9748    682.5]';
            expdata=[0  289168.7    288428.7    292556.6    294624.6
310069.7    320538.6    330746.3    343389.5    360977.1    406048.1
448489.1    530888.7    671355.9    919199.6    1431823 2544252 5630486
23059090]';
        elseif m==2
            r=.03;
            %truncated, set .03(2)
            timedata=[0 11.35781    13.29856    15.57092    18.23158
21.34686    24.99447    29.26535    34.26601    40.12115    46.97677
55.00384    64.40251    75.40717    88.29222    103.379 121.0437
141.7268    165.9441    194.2995    227.5]';
            expdata=[0  242964.2    249710.6    259360.2    265015.3
284672.8    297642.1    307550.8    325966.1    339455.4    349054.5
```

```
382981.4    422765.9    469610.8    565065.9    764341.5    1133653
1886361 3582319 7532099 14584450]';
        elseif m==3
            r=.1;
            %set .1(4)
            timedata=[0 0.1 0.1142454   0.1305202   0.1491133
0.1703552   0.194623    0.2223479   0.2540223   0.2902088   0.3315503
0.3787811   0.4327401   0.4943858   0.5648131   0.6452732   0.7371951
0.8422117   0.9621884   1.099256    1.25585 1.434751    1.639138
1.87264 2.139405    2.444173    2.792356    3.190139    3.644588
4.163775    4.756922    5.434566    6.208744    7.093206    8.103663
9.258065    10.57692    12.08364    13.80501    15.77159    18.01832
20.58511    23.51755    26.86772    30.69514    35.0678 40.06336
45.77055    52.29077    59.73981    68.25]';
            expdata=[0  6890.88 16548.34    19710.05    32912.64
44620.99    45268.02    49846.2 55173.66    60234.97    63974.17
75411.8 77752.9 79499.09    84612.06    93833.12    109072.4
108508.3    124097.4    129830.1    144399.7    152719.9    167945.9
163324.8    174523.3    151088.1    155467.1    158789.5    165107.9
176287.1    179696.5    188722.5    196268.9    206751.6    216295
223766.6    234607.3    243259.2    257513.2    263149.5    265260.4
278204.8    298160.7    331136.5    384562.6    529194.5    590804.1
684427.5    855833.6    1237321 2425558]';
        elseif m==4
            r=.3;
            %set .3(2)
            timedata=[0 0.1 0.1117125   0.1247968   0.1394135
0.1557423   0.1739836   0.1943614   0.2171259   0.2425567   0.2709661
0.3027029   0.3381569   0.3777634   0.4220089   0.4714366   0.5266534
0.5883376   0.6572464   0.7342262   0.8202223   0.9162906   1.023611
1.143501    1.277433    1.427052    1.594195    1.780915    1.989504
2.222524    2.482837    2.773638    3.0985  3.461411    3.866828
4.319729    4.825676    5.390882    6.022287    6.727646    7.51562
8.395884    9.37925 10.47779    11.705  13.07595    14.60746
16.31836    18.22964    20.36478    22.75]';
            expdata=[0  15244.8 16808.13    19480.84    24398.25
31463.05    34981.9 35769.67    43030.57    48934.49    48372.1
56862.49    59324.29    66840.18    71717.51    77075.24    79760.8
86767.66    93515.34    100470.5    102423.9    104845.2    99072.72
102442  107144.2    112945.6    119091  124251.3    130352.7
136666.7    142334.2    148959.1    156724.6    165724.5    174678.5
181392.2    189530.8    194037.3    204958.5    220579.5    237540.7
258784.2    297150.3    356699.3    410071.4    444201.3    493379.5
543629.5    541386.1    695399.3    1190882]';
        elseif m==5
            r=1;
            %set 1(3)
            timedata=[0 0.1 0.109001    0.1188123   0.1295066
0.1411636   0.1538698   0.1677197   0.1828162   0.1992716   0.2172081
0.2367591   0.2580699   0.2812989   0.3066187   0.3342176   0.3643007
0.3970916   0.432834    0.4717935   0.5142599   0.5605487   0.6110039
0.6660007   0.7259477   0.7912906   0.862515    0.9401504   1.024774
1.117014    1.217557    1.32715 1.446607    1.576817    1.718747
1.873452    2.042083    2.225892    2.426245    2.644632    2.882677
3.142148    3.424974    3.733258    4.06929]';
            expdata=[0  11681.41    13905.72    16483.72    19666.6
23990.51    28958.02    31093.06    33655.69    37375.28    41634.22
```

```
43956.18    46473.75    51156.52    54938.75    54887.86    55067.26
57913.16    61620.79    65169.65    69197.97    73716.18    78080.86
82602.3 87552.7 93346.01    99427.7 106027.7    112532.7    119715.9
127646.6    135435.2    143607.9    151167.4    159694.1    171481.5
184090.3    199013.9    219175  240814.2    268412.1    302961.1
341944.7    384204.2    409236.3]';
        end

    %differential equation solver to get model prediction of viscosity
vs time

[t,etatemp,diverge]=extensional_pde_solver(r,wt,sigma,CI,para(1,:),para
(2,:),para(3,:),timedata,modes,re,orient_ext);

    if diverge==1 %keep track of divergence
        tdiv=1;
        terr(m)=inf;
    elseif diverge==0 %if no divergence, calculate error between model
and experiment
        for k=2:length(timedata)
            terr(m)=terr(m)+(log10(expdata(k))-log10(etatemp(k)))^2;
        end
    end

    %plot the model predictions and experimental data
    if m==1
         figure
         if diverge==0
            loglog(t,etatemp,'r',timedata,expdata,'*r');
         end
         hold on
     elseif m==2
         if diverge==0
            loglog(t,etatemp,'g',timedata,expdata,'*g');
         end
     elseif m==3
         if diverge==0
            loglog(t,etatemp,'b',timedata,expdata,'*b');
         end
     elseif m==4
         if diverge==0
            loglog(t,etatemp,'c',timedata,expdata,'*c');
         end
     elseif m==5
         if diverge==0
            loglog(t,etatemp,'k',timedata,expdata,'*k');
         end

         title('Extensional Viscosity MB 2wt%');
         xlabel('Time (s)');
         ylabel('Viscosity (Pa*s)');
         legend('Mod \epsilon=.01','Exp \epsilon=.01','Mod
\epsilon=.03','Exp \epsilon=.03','Mod \epsilon=.1','Exp
\epsilon=.1','Mod \epsilon=.3','Exp \epsilon=.3','Mod \epsilon=1','Exp
\epsilon=1',-1);
```

```
        set(gcf,'Units','normalized',
'WindowStyle','docked','OuterPosition',[0 0 1 1]); %this places the
plot in a maximized window
        hold off
    end

end
Terror=sum(terr); %sum of error from all extension rates


%%
%%Part 2: Shear plotting
serr=zeros(1,5); %error per shear rate in model predictions
sdiv=0; %keeps track of any divergences in shear model predictions

for w=1:5 % w designates the w-th shear rate
        if w==1
            r=.01;
            %set .01(2)
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.27    0.28    0.29    0.3 0.31    0.32    0.33
0.34    0.35    0.36    0.37    0.38    0.39    0.4 0.41    0.42
0.43    0.44    0.45    0.46    0.47    0.48    0.49    0.5 0.51
0.52    0.53    0.54    0.55    0.56    0.57    0.58    0.59    0.6
0.61    0.62    0.65    0.7 0.75    0.8 0.855   0.915   0.975   1.04
1.115   1.195   1.28    1.37    1.465   1.565   1.675   1.795   1.92
2.05    2.19    2.345   2.51    2.685   2.875   3.08    3.295   3.525
3.77    4.03    4.315   4.62    4.94    5.285   5.655   6.05    6.475
6.93    7.42    7.94    8.495   9.09    9.725   10.41   11.14   11.92
12.755  13.65   14.61   15.63   16.725  17.9    19.155  20.495  21.93
23.47   25.115  26.875  28.76   30.775  32.935  35.245  37.715  40.36
43.19   46.22   49.46   52.925  56.635  60.61   64.86   69.405  74.27
79.48   85.055  91.02   97.4    104.22  111.53  119.36  127.73  136.68
146.27  156.52  167.5   179.24  191.82  205.26  219.65  235.06  251.54
269.18  288.06  318.7   341.04  364.96  390.55  417.94  447.24  478.61
512.17  548.08  586.52  627.64  671.66  718.76  769.16  823.09  880.82
942.58  1008.7  1079.4  1155.1  1236.1  1322.8  1415.5  1514.8  1621
1734.7  1856.3  1986.5  2125.8  2274.9  2434.4  2605.1  2787.8  2983.3
3192.5  3416.3  3655.9];
            expdata=[0  86.632  490.45  1141.1  1980.1  2802.5  3502.8
4159.4  4967    5516.4  5839.9  6362.8  6919.1  7355.4  7592.2  8024.5
8481.5  8837.5  9211.8  9629.1  9869.9  10189   10446   10878   11089
11333   11695   12074   12278   12396   12533   13057   13212   13304
13763   14040   14209   14305   14672   14909   14988   15419   15779
15709   15877   16202   16524   16356   16660   16979   17076   17326
17524   17784   17606   17773   18226   18183   18104   18535   18824
18837   18892   19368   20036   20711   21354   21923   22707   23363
24137   25027   25783   26572   27449   28141   28936   29905   30604
31397   32191   32995   33670   34543   35557   36510   37229   38016
38955   39986   40701   41471   42450   43468   44362   45178   45816
46413   47332   47849   48622   49248   49922   50602   51325   51898
52544   53100   53770   54327   54860   55603   56233   56791   57426
57845   58002   58251   58869   59389   59760   60072   60345   60468
60798   61485   62214   62142   62327   62721   62998   62871   63217
```

```
63306   63167   63867   63902   64177   63997   64257   64163   64840
64860   64796   64692   65239   65143   65213   65391   65445   65393
65843   65655   65766   65715   65890   65737   65947   65887   65831
65894   65992   66072   66268   66306   66341   66285   66326   66606
66494   66813   66754   66819   67025   67161   66853   67071   67055
66968   66602   66396   66315   65891   65984   66252   66269   66709
67091   66863   66350   65831];
        elseif w==2
            r=.1;
            %set ave of 1 and 2
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.28    0.315   0.355   0.4 0.455   0.52    0.595
0.675   0.765   0.87    0.99    1.125   1.28    1.455   1.655   1.885
2.145   2.44    2.775   3.155   3.59    4.085   4.645   5.285   6.015
6.845   7.79    8.865   10.085  11.475  13.06   14.865  16.915  19.245
21.9    24.92   28.355  32.265  36.715  41.78   47.545  54.105  61.565
70.055  79.72   90.72   103.24  117.47  133.68  152.12  184.27  209.68
238.61  271.54  308.99  351.61  400.13  455.32  518.14  589.61  670.95
763.51  868.83  988.7   1125.1  1280.3  1456.9  1657.9  1886.6  2146.9
2443    2780.1  3163.6  3600];
            expdata=[0  50.7945 584.48  1344.55 2156.55 2936.75 3642.3
4300.35 4916.1  5486.55 6033.9  6547.35 6989.2  7478.75 7894.65 8337.05
8711.15 9078.3  9467.1  9817.15 10128.55    10489.5 10776   11133.5
11398   11718.5 11999   12539.5 13462   14433   15452   16596   17857
19195.5 20482   21804.5 23187.5 24604   26029   27489   28942.5 30349
31871   33540   35291   36825.5 38329   39883.5 41336.5 42792   44163.5
45455.5 46928   48050   49140.5 50051.5 50998.5 51635.5 52298   52613.5
52941.5 52956   52840   52555   52109   51529   50807.5 50015   49252.5
48562.5 47945.5 47447.5 47096   46859.5 46687.5 46553   46500.5 46521.5
46502   46310   46213   46145   46097.5 46524   46700   46803   46926
46665   46758.5 46678.5 46505.5 45537.5 44098   43581   41589.5 40157.5
38101.5 36936.5 34339   32735   30810];
        elseif w==3
            r=.3;
            %set ave 1,2,3,4
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.255   0.285   0.325   0.37    0.425   0.49    0.56    0.64    0.735
0.84    0.96    1.1 1.26    1.44    1.645   1.885   2.16    2.475
2.835   3.245   3.715   4.255   4.875   5.585   6.4 7.33    8.395
9.62    11.02   12.625  14.465  16.57   18.98   21.74   24.905  28.535
32.69   37.45   42.905  49.15   56.31   64.51   73.905  84.67   97
111.13  127.31  145.85  178.43  204.41];
            expdata=[0  99.9685 604.9975    1340.875    2132.75
2901.175    3615.725    4250.8  4849.225    5396.025    5902.575
6368.925    6840.575    7264.625    7669.825    8073.225    8450.65
8810.425    9167.825    9500.225    9835.875    10147.425   10466.975
10761.575   11107.75    11687.75    12541.75    13574.25    14676
15808   17049   18279.75    19525.75    20877.5 22255   23687
25110.75    26524   27946.75    29342.75    30698   32143.5 33463.25
34690.75    35815.5 36905.75    37777   38536.75    39114.5 39512
39696.75    39695   39474.25    39051.75    38471   37797   37087.5
36418.25    35882   35513.25    35195.25    34831.25    34404.5 34004.5
```

```
33589.5 33141.75    32648.25    32318.75    32091.5 31819   31350.5
30692   30481.25    30675.25    30402.25];
        elseif w==4
            r=1;
            %set ave 1,2 truncated
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.245
0.27    0.305   0.35    0.405   0.465   0.535   0.615   0.705   0.81
0.93    1.07    1.23    1.41    1.62    1.86    2.135   2.455   2.82
3.24    3.725   4.285   4.925   5.66    6.505   7.475   8.59    9.87
11.345  13.04   14.985  17.225  19.8    22.755  26.15   30.055  34.545
39.705  45.635  52.45   60.285  69.295  79.65   91.545  105.22  120.94
139];
            expdata=[0  75.508  584.995 1305.55 2089.8  2826.1  3530.25
4155.5  4741.3  5265.55 5766.4  6218.95 6653.3  7066.3  7452.2  7830.9
8208.15 8569.3  8903.4  9235.3  9574    9888.8  10211.55    10576.5
11194   12001.5 12934.5 13984   15073   16183   17332   18511   19647
20766.5 21847.5 22890   23849   24647.5 25327   25832.5 26130   26237
26117.5 25766   25226.5 24509.5 23675   22860   22161   21531   20934
20404.5 20015.5 19619   19396.5 19309   19296   19082   18705   18660
19259   19385.5 19098   19093   19317.5 19446   19286.5 19275.5 19199
19171.5 18758];
        elseif w==5
            r=3;
            %set ave 1,2 truncated
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.245
0.27    0.31    0.355   0.405   0.465   0.535   0.615   0.705   0.81
0.93    1.07    1.23    1.415   1.625   1.865   2.145   2.465   2.83
3.255   3.745   4.3 4.94    5.68    6.53    7.505   8.625   9.91
11.39   13.095  15.05   17.3    19.885  22.855  26.27   30.195  34.71
39.9];
            expdata=[0  78.294  584.5   1295.5  2058.9  2794.3  3467.05
4099.4  4652.75 5184.15 5693.65 6131.4  6549.8  6960.3  7353.75 7697.25
8050.75 8371.05 8697.05 8987.3  9279.05 9581.5  9843.1  10101.55
10413   10876.5 11622   12405   13143   13891.5 14622   15196.5 15731.5
16098   16360.5 16433   16367   16110   15742.5 15233.5 14640.5 14039
13493.5 12955.5 12382   12081.5 11936   11877.5 11958.5 11980.5 11993
11977   11949.5 11858.5 11969.5 11983   11825.5 11698   11571   11515
11315   11197];
        end
            %shift time data back to account for start up delay in
rheometer
            factor=timedata(2)-0.0005;
            timedata=timedata-factor;
            timedata(1)=0;

        %differential equation solver to get model prediction of
viscosity vs time

[t,etatemp,diverge]=shear_pde_solver(r,wt,sigma,CI,para(1,:),para(2,:),
para(3,:),timedata,modes,re,orient_shr);

        if diverge==1 %keep track of divergence
```

```
            sdiv=1;
            serr(w)=inf;
        elseif diverge==0 %if no divergence, calculate error between
model and experiment
            for k=2:length(timedata)
                serr(w)=serr(w)+(log10(expdata(k))-
log10(etatemp(k)))^2;
            end
        end

     %plot the model predictions and experimental data
     if w==1
         figure
         if diverge==0
            loglog(timedata,expdata,'*',t,etatemp,'Color',[0,0,1]);
         end
         hold on
     elseif w==2
         if diverge==0
            loglog(timedata,expdata,'*',t,etatemp,'Color',[0,0,0]);
         end
     elseif w==3
         if diverge==0
            loglog(timedata,expdata,'*',t,etatemp,'Color',[0,1,1]);
         end
     elseif w==4
         if diverge==0
            loglog(timedata,expdata,'*',t,etatemp,'Color',[.6,0,.9]);
         end
     elseif w==5
         if diverge==0
            loglog(timedata,expdata,'*',t,etatemp,'Color',[.7,.9,.3]);
         end

         xlabel('Time (s)')
         ylabel('Viscosity (Pa*s)')
         title('Shear Viscosity MB 2wt%')
         legend('Exp \gamma=0.01','Mod \gamma=0.01','Exp
\gamma=0.1','Mod \gamma=0.1','Exp \gamma=.3','Mod \gamma=.3','Exp
\gamma=1','Mod \gamma=1','Exp \gamma=3','Mod \gamma=3',-1);
         set(gcf,'Units','normalized',
'WindowStyle','docked','OuterPosition',[0 0 1 1]);
         hold off
     end
end
Serror=sum(serr); %sum of error from all shear rates


%%
%%PART 3: SAOS plotting
%read in sigma and CI values to be sent to other programs
%call SAOSModeling variant to calc experimental stress.
%call SAOSFittingGpGdp variant to calc model prediction.
%find error between the two and send back as Gerror

%NOTE: diverging probably kills the programs this subfunction calls
```

```
Gerror=0; %error in SAOS model predictions
gdiv=0; %keeps track of any divergences in SAOS model predictions

%data from Koki Data
freq=[100   63.096  39.811  25.119  15.849  10   6.3096   3.9811   2.5119
1.5849  1   0.63096 0.39811 0.25119 0.15849 0.1  0.063096    0.039811
0.025119    0.015849    0.01 ];
%storage modulus
GpExp=[130960   114830  98906   84285   70796   58502   47372   37583
29009   21859   15970   11238   7708.9  5039.8  3136.6  1919.4  1121.7
600.49  329.64  157.37  81.182];
%loss modulus
GdpExp=[63437   57164   52141   47527   43278   39018   34902   30717
26605   22503   18723   15144   11977   9210.6  6844.8  5003.9  3512.5
2444.1  1647    1089.6  704.4];


% this commented-out section calls on 'SAOSOModeling' which calculates
and
% plots the stress wave from SAOS flow. Uncomment if you desire to see
% this, but only use every third point from the experimental data;
% otherwise, the computations are way too many and tedious and MATLAB
struggles
%          [export] =
SAOSModeling(para,sigma,CI,freq,GpExp,GdpExp,modes,graph);
%          time=export(:,1);
%          tauc12=export(:,2);
%          pred=export(:,3);

        graph=0; %=0 for no plotting in SAOSFittingGpGdp, =1 for
plotting
        %fit G' G" of composite to SAOS stress wave
        [GpGdp,diverge] =
SAOSFittingGpGdp(para,sigma,CI,freq,GpExp,GdpExp,wt,modes,graph,re,orie
nt_shr);
        GpMod=GpGdp(:,1);
        GdpMod=GpGdp(:,2);

        if diverge==0 %if no divergence, calculate error between model
and experiment
            for j=1:length(freq)
                Gerror=Gerror+(log10(GpExp(j))-
log10(GpMod(j)))^2+(log10(GdpExp(j))-log10(GdpMod(j)))^2;
            end
            %plot model predictions and experimental data
            figure

loglog(freq,GpExp,'b*',freq,GdpExp,'g*',freq,GpMod,'b',freq,GdpMod,'g')
            legend('GpExp','GdpExp','GpMod','GdpMod',-1)
            title('SAOS MB 2wt%')
        else %keep track of divergence
            Gerror=inf;
            gdiv=1;
        end
```

```
%%
% uncomment to check errors and divergences if interested
% Terror
% Serror
% Gerror
% tdiv
% sdiv
% gdiv
end
```

Composite Model Predictions: Melt Blended with HHT-CNFs (MBHHT)

```
function MBHHT_2wt
%This program plots the viscosity for the MB-HHT 2wt% composite for
transient
%extension and transient shear as well as moduli predictions for SAOS
% given the optimized values for sigma and CI and hfactor

format long g

sigma=.544;
CI=.0301;
hfactor=1.45;

para=[   1563.180023    10503.23358 30793.85272 9864.433234 9310.030642
40690.01669; %optimized values for etap by mode
            0.01461114  0.235979496 3.210427777 34.39722848 6390.005373
116255.5053; %optimized values for lambda by mode
            0.818868357 0.56        0.56        0.078601046 0.025189799
0.001841609]; %optimized values for alpha by mode
modes=6;
wt=.02; %mass fraction of cnfs
re=44/hfactor; %44= number ave length, 70= weight ave length
orient_ext=[.441 .2795 .2795]; %experimentally determined initial
orientation of fibers (a11,a22,a33)
orient_shr=[.441 0 .2795]; %experimentally determined initial
orientation of fibers (a11,a12,a22)



%%
%%Part 1: Extensional plotting
terr=zeros(1,5); %error per extension rate in model predictions
tdiv=0; %keeps track of any divergences in extensional model
predictions

for m=1:5 % m designates the m-th extension rate
        if m==1
            r=.01;
            %set .01(2) from HHT truncated
            timedata=[0 31.90831    38.20769    45.7507 54.78287
65.59817    78.54865    94.05583    112.6245    134.8589    161.483
193.3631    231.5372    277.2475    331.9821    397.5225    476.0019
569.9748]';
            expdata=[0  210335.3    219691  226971.8    229421.2
234941.7    236315.3    242302.8    254875.7    253289.3    261135.1
267509.6    286954.2    349713.8    472989.1    757980.2    1256944
2316228]';
        elseif m==2
            r=.03;
            %set .03(2) from HHT truncated
            timedata=[0 8.284668    9.700294    11.35781    13.29856
15.57092    18.23158    21.34686    24.99447    29.26535    34.26601
40.12115    46.97677    55.00384    64.40251    75.40717    88.29222
103.379 121.0437    141.7268    165.9441    194.2995]';
```

```
            expdata=[0  190341.9    190633.6    193699  196175
201475.2    205108.4    212185.2    219170.7    225653.7    230200.8
235710.5    244995.5    250231.8    248900.3    240684.8    253282.5
304421.8    390583.3    593847.9    1056209 2144129]';
        elseif m==3
            r=.1;
            %set .1(2) from HHT truncated
            timedata=[0 3.644588    4.163775    4.756922    5.434566
6.208744    7.093206    8.103663    9.258065    10.57692    12.08364
13.80501    15.77159    18.01832    20.58511    23.51755    26.86772
30.69514    35.0678 40.06336    45.77055    52.29077    59.73981
68.25]';
            expdata=[0  142596.5    147838  156105.2    157534.9
165326.7    170982.4    186709.8    194717.8    199831.1    204846.9
215419.2    226120.8    237852.2    249579.6    255556  274173.5
301182.8    318106.8    354322.3    451478  668521.6    1408449
3373191]';
        elseif m==4
            r=.3;
            %set .3(3) from HHT
            timedata=[0 0.1 0.1117125   0.1247968   0.1394135
0.1557423   0.1739836   0.1943614   0.2171259   0.2425567   0.2709661
0.3027029   0.3381569   0.3777634   0.4220089   0.4714366   0.5266534
0.5883376   0.6572464   0.7342262   0.8202223   0.9162906   1.023611
1.143501    1.277433    1.427052    1.594195    1.780915    1.989504
2.222524    2.482837    2.773638    3.0985  3.461411    3.866828
4.319729    4.825676    5.390882    6.022287    6.727646    7.51562
8.395884    9.37925 10.47779    11.705  13.07595    14.60746
16.31836    18.22964    20.36478    22.75]';
            expdata=[0  8633.724    11790.94    15199.42    18997.25
23847.63    27551.82    29358.34    35422.57    44593.52    42772.54
49858.95    59421.91    57570.51    53920.42    53526.64    65837.6
71856.54    79041.58    83939.48    83833.5 90149.65    96295.93
91846   94179.86    99715.19    106030.4    111699.3    117268.3
123649.4    130450.6    138892.3    146197.4    153980.6    163027.9
173915.2    184254.8    195853.7    205960.2    216452.4    240066.3
250082.8    264790.7    291294.8    322962.1    355202.6    397853.6
432315.8    493080.9    626274.2    1159989]';
        elseif m==5
            r=1;
            %set 1(1) from HHT
            timedata=[0 0.1 0.109001    0.1188123   0.1295066
0.1411636   0.1538698   0.1677197   0.1828162   0.1992716   0.2172081
0.2367591   0.2580699   0.2812989   0.3066187   0.3342176   0.3643007
0.3970916   0.432834    0.4717935   0.5142599   0.5605487   0.6110039
0.6660007   0.7259477   0.7912906   0.862515    0.9401504   1.024774
1.117014    1.217557    1.32715 1.446607    1.576817    1.718747
1.873452    2.042083    2.225892    2.426245    2.644632    2.882677
3.142148    3.424974]';
            expdata=[0  10425.37    12723.77    16399.96    17158.68
20517.69    25343.61    30538.38    34726.26    37314.98    39768.33
43790.19    47506.67    49910.75    55692.83    56281.4 46442.42
52572.11    52047.22    57894.11    57611.62    64044.35    65610.49
68344.34    73008.01    78265   83632.1 88987.9 94336.64    99972.76
106802.6    114539  123166.9    131871  141309.6    153551.4
165299.4    175279.9    187812.7    200590.6    220207.4    251397
289119.8]';
```

```
        end

    %differential equation solver to get model prediction of viscosity
vs time

[t,etatemp,diverge]=extensional_pde_solver(r,wt,sigma,CI,para(1,:),para
(2,:),para(3,:),timedata,modes,re,orient_ext);

    if diverge==1 %keep track of divergence
        tdiv=1;
        terr(m)=inf;
    elseif diverge==0 %if no divergence, calculate error between model
and experiment
        for k=2:length(timedata)
            terr(m)=terr(m)+(log10(expdata(k))-log10(etatemp(k)))^2;
        end
    end

    %plot the model predictions and experimental data
    if m==1
         figure
         if diverge==0
            loglog(t,etatemp,'r',timedata,expdata,'*r');
         end
         hold on
     elseif m==2
         if diverge==0
            loglog(t,etatemp,'g',timedata,expdata,'*g');
         end
     elseif m==3
         if diverge==0
            loglog(t,etatemp,'b',timedata,expdata,'*b');
         end
     elseif m==4
         if diverge==0
            loglog(t,etatemp,'c',timedata,expdata,'*c');
         end
     elseif m==5
         if diverge==0
            loglog(t,etatemp,'k',timedata,expdata,'*k');
         end

         title('Extensional Viscosity HHT 2wt%');
         xlabel('Time (s)');
         ylabel('Viscosity (Pa*s)');
         legend('Mod \epsilon=.01','Exp \epsilon=.01','Mod
\epsilon=.03','Exp \epsilon=.03','Mod \epsilon=.1','Exp
\epsilon=.1','Mod \epsilon=.3','Exp \epsilon=.3','Mod \epsilon=1','Exp
\epsilon=1',-1);
         set(gcf,'Units','normalized',
'WindowStyle','docked','OuterPosition',[0 0 1 1]);
         hold off
    end
end
Terror=sum(terr); %sum up error from all extension rates
```

```
%%
%%Part 2: Shear plotting
serr=zeros(1,5); %error per shear rate in model predictions
sdiv=0; %keeps track of any divergences in shear model predictions

for w=1:5  % w designates the w-th shear rate
        if w==1
            r=.01;
            %set .01(1)
            timedata=[0 0.02    0.03    0.04    0.05    0.06    0.07
0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15    0.16
0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24    0.25
0.26    0.27    0.28    0.29    0.3 0.31    0.32    0.33    0.34
0.35    0.36    0.37    0.38    0.39    0.4 0.41    0.42    0.43
0.44    0.45    0.46    0.47    0.48    0.49    0.5 0.51    0.52
0.53    0.54    0.55    0.56    0.57    0.58    0.59    0.6 0.61
0.62    0.65    0.7 0.75    0.8 0.855   0.915   0.975   1.04    1.115
1.195   1.28    1.37    1.465   1.565   1.675   1.795   1.92    2.05
2.19    2.345   2.51    2.685   2.875   3.08    3.295   3.525   3.77
4.03    4.315   4.62    4.94    5.285   5.655   6.05    6.475   6.93
7.42    7.94    8.495   9.09    9.725   10.41   11.14   11.92   12.755
13.65   14.61   15.63   16.725  17.9    19.155  20.495  21.93   23.47
25.115  26.875  28.76   30.775  32.935  35.245  37.715  40.36   43.19
46.22   49.46   52.925  56.635  60.61   64.86   69.405  74.27   79.48
85.055  91.02   97.4    104.22  111.53  119.36  127.73  136.68  146.27
156.52  167.5   179.24  191.82  205.26  219.65  235.06  251.54  269.18
288.06  318.7   341.04  364.96  390.55  417.94  447.24  478.61  512.17
548.08  586.52  627.64  671.66  718.76  769.16  823.09  880.82  942.58
1008.7  1079.4  1155.1  1236.1  1322.8  1415.5  1514.8  1621    1734.7
1856.3  1986.5  2125.8  2274.9  2434.4  2605.1  2787.8  2983.3  3192.5
3416.3  3655.9  3912.3  4186.6  4480.2  4794.3  5130.5  5490.3  5875.3
6287.3  6728.2  7200];
            expdata=[0  442.64  1012.6  1768.6  2905    3693.3  4019.2
4837.7  5707.1  6051.3  6424    6934.2  7417.4  7639.1  8243.1  8756.5
8951.2  9213.4  9683.1  10026   10196   10692   11106   11223   11343
12047   12375   12229   12497   13078   13134   13283   13768   14100
13909   14075   14593   14733   14758   15145   15393   15522   15706
15976   16100   16236   16487   16822   16940   17219   17450   17269
17178   17706   18079   18081   18052   18307   18582   18720   18925
19368   19545   20145   20880   21524   22221   22951   23539   24236
24983   25724   26478   27178   27925   28723   29389   30215   30926
31721   32379   33212   33891   34669   35378   36193   36878   37659
38397   39094   39824   40522   41229   41905   42581   43234   43880
44549   45106   45687   46292   46859   47401   47898   48191   48606
49024   49518   50068   50641   51214   51859   52474   53114   53550
53781   54085   54345   54495   54668   55090   55401   55627   55698
55979   56407   56502   56358   56159   56863   57508   57383   57255
57510   57540   57767   57349   58001   58283   58119   58154   58100
58251   58316   58445   58237   58426   58546   58330   58434   58483
58326   58528   58243   58567   58359   58451   58369   57997   58063
58251   57987   57875   57986   57889   57863   57985   57750   57731
58025   57827   57892   58248   58222   58181   58610   58435   58570
58417   58520   58417   58313   58573   58589   58580   58899   58822
59262   59322   59461   59233   58792   58723   58762   58858   59021
58702   58253   58316   58514];
```

```
        elseif w==2
            r=.1;
            %set .1(3)
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.275   0.305   0.35    0.4 0.455   0.515   0.585
0.665   0.755   0.86    0.975   1.105   1.255   1.425   1.62    1.845
2.1 2.39    2.715   3.085   3.51    3.99    4.54    5.165   5.87
6.675   7.595   8.635   9.82    11.17   12.7    14.445  16.43   18.685
21.255  24.175  27.495  31.275  35.57   40.455  46.01   52.33   59.52
67.695  76.995  87.575  99.605  113.28  128.85  146.55  177.4   201.77
229.49  261.01  296.88  337.66  384.05  436.82  496.82  565.08  642.71
731.01  831.43  945.66  1075.6  1223.4  1391.4  1582.6  1800];
            expdata=[0  47.56   606.43  1449.7  2348.5  3178.3  3978.3
4677.2  5311.3  5910.9  6447.8  6956.1  7433.9  7911    8342.7  8777.3
9160.9  9561.8  9965.6  10310   10633   10989   11310   11617   11936
12170   12487   12903   13640   14766   15862   16922   18042   19203
20436   21708   23068   24427   25852   27324   28686   30031   31401
32729   34119   35448   36699   38064   39314   40295   41652   42824
43781   44732   45417   46413   47050   47539   48099   48349   48675
48741   48758   48700   48503   48247   47970   47606   47242   46890
46533   46219   45951   45749   45587   45514   45503   45427   45343
45249   45145   45181   45302   45257   45066   44909   44915   44746
44712   44278   44189   43827   43584   43794   43760   43936];
        elseif w==3
            r=.3;
            %set .3(3)
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.275   0.305   0.345   0.39    0.445   0.505   0.57
0.65    0.74    0.84    0.955   1.085   1.23    1.395   1.59    1.81
2.055   2.335   2.65    3.01    3.425   3.89    4.42    5.025   5.71
6.49    7.38    8.39    9.535   10.835  12.315  14  15.915  18.09
20.56   23.375  26.575  30.205  34.335  39.03   44.365  50.43   57.325
65.165  74.075  84.205  95.72   108.81  123.69  140.6   159.83  193.32
219.75  249.8   283.96  322.79  366.93];
            expdata=[0  66.031  624.41  1415    2256.7  3048.4  3757.8
4418.8  5029.6  5591.8  6115.1  6603.6  7075.5  7510.8  7905.8  8311
8684.8  9049.8  9405.8  9731.3  10069   10373   10663   10960   11241
11512   11779   12170   12897   13781   14677   15656   16606   17564
18662   19842   21006   22105   23166   24286   25339   26509   27518
28569   29665   30583   31487   32281   33070   33657   34197   34532
34771   34785   34647   34332   33770   33081   32301   31465   30681
30001   29422   28873   28377   27963   27606   27475   27409   27087
26845   26816   26650   26670   26531   26342   25856   25536   25542
25261   25432   25555   25623   25484];
        elseif w==4
            r=1;
            %set 1(1)
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.27    0.29    0.325   0.37    0.42    0.475   0.54
0.615   0.7 0.795   0.9 1.02    1.155   1.31    1.485   1.685   1.915
2.17    2.46    2.79    3.165   3.59    4.075   4.625   5.245   5.95
```

```
6.755   7.665   8.695   9.87    11.2    12.71   14.425  16.365  18.57
21.075  23.915  27.135  30.79   34.94   39.65   44.995  51.06   57.945
65.755];
            expdata=[0  87.354  628.09  1384.5  2182.5  2935    3619.7
4239.6  4826.3  5366.2  5836.6  6320.1  6761.8  7166.7  7542.3  7928.6
8241.4  8592.8  8879.2  9196.6  9512.9  9765.7  10042   10323   10559
10822   11075   11311   11747   12442   13335   14168   14970   15923
16845   17730   18594   19405   20269   21011   21711   22367   22907
23391   23716   23927   24009   23952   23764   23433   23011   22523
22006   21492   20996   20534   20078   19625   19248   18957   18707
18433   18248   18210   18207   18220   18286   18058   17770   17614
17452   17137];
        elseif w==5
            r=3;
            %set 3(3)
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.27    0.295   0.335   0.38    0.435   0.495   0.56
0.635   0.72    0.815   0.925   1.05    1.19    1.35    1.535   1.745
1.98    2.245   2.545   2.89    3.285   3.73    4.235   4.81    5.46
6.2 7.045   8   9.08    10.315  11.715  13.3    15.105  17.155  19.485
22.13   25.135  28.545  32.415  36.815];
            expdata=[0  82.036  606.86  1335.9  2110.6  2844.7  3506.9
4095.5  4625.8  5119.7  5589.3  6035.9  6411.6  6741.9  7117.2  7440.7
7745.2  8032.4  8299.3  8550.5  8808.2  9026.2  9261.2  9544    9730.8
9949.6  10173   10344   10786   11417   12030   12639   13152   13567
13980   14230   14400   14420   14353   14139   13851   13457   13004
12563   12119   11723   11333   11006   10731   10514   10373   10274
10158   10107   10166   10208   10270   10335   10306   10145   10120
10129   10067   10013   9953.8  9964.8  10036];
        end
            %shift time data back to account for start up delay in
rheometer
            factor=timedata(2)-0.0005;
            timedata=timedata-factor;
            timedata(1)=0;
        %differential equation solver to get model prediction of
viscosity vs time

[t,etatemp,diverge]=shear_pde_solver(r,wt,sigma,CI,para(1,:),para(2,:),
para(3,:),timedata,modes,re,orient_shr);

        if diverge==1 %keep track of divergence
            sdiv=1;
            serr(w)=inf;
        elseif diverge==0 %if no divergence, calculate error between
model and experiment
            for k=2:length(timedata)
                serr(w)=serr(w)+(log10(expdata(k))-
log10(etatemp(k)))^2;
            end
        end

     %plot the model predictions and experimental data
     if w==1
```

```
        figure
        if diverge==0
           loglog(timedata,expdata,'*',t,etatemp,'Color',[0,0,1]);
        end
        hold on
    elseif w==2
        if diverge==0
           loglog(timedata,expdata,'*',t,etatemp,'Color',[0,0,0]);
        end
    elseif w==3
        if diverge==0
           loglog(timedata,expdata,'*',t,etatemp,'Color',[0,1,1]);
        end
    elseif w==4
        if diverge==0
           loglog(timedata,expdata,'*',t,etatemp,'Color',[.6,0,.9]);
        end
    elseif w==5
        if diverge==0
           loglog(timedata,expdata,'*',t,etatemp,'Color',[.7,.9,.3]);
        end

        xlabel('Time (s)')
        ylabel('Viscosity (Pa*s)')
        title('Shear Viscosity HHT 2wt%')
        legend('Exp \gamma=0.01','Mod \gamma=0.01','Exp
\gamma=0.1','Mod \gamma=0.1','Exp \gamma=.3','Mod \gamma=.3','Exp
\gamma=1','Mod \gamma=1','Exp \gamma=3','Mod \gamma=3',-1);
        set(gcf,'Units','normalized',
'WindowStyle','docked','OuterPosition',[0 0 1 1]); %this places the
plot in a maximized window
        hold off
    end
end
Serror=sum(serr); %sum up error from all shear rates


%%
%%PART 3: SAOS plotting
%read in sigma and CI values to be sent to other programs
%call SAOSModeling variant to calc experimental stress.
%call SAOSFittingGpGdp variant to calc model prediction.
%find error between the two and send back as Gerror

%NOTE: diverging probably kills the programs this subfunction calls

Gerror=0; %error in SAOS model predictions
gdiv=0; %keeps track of any divergences in SAOS model predictions

%data from Koki Data_Solvent Casting
freq=[ 100      63.096   39.811  25.119  15.849  10      6.3096  3.9811
2.5119  1.5849  1       0.63096 0.39811 0.25119 0.15849 0.1
0.063096    0.039811    0.025119    0.015849    0.01];
%storage modulus
```

```
GpExp=[109980   95781   82077   69679   58066   47737   38316   30197
23154   17170   12300   8915.7  5835.3  4025.7  2576.3  1613.8  967.34
549.9       310.61      167.18      102.05];
%loss modulus
GdpExp=[55997   50642   45518   41323   37171   33418   29749   25877
22421   18612   15694   12371   9995.4  7626.9  5584.5  4093.9  2849.3
2075.2      1420.2      903.06      619.69];

% this commented-out section calls on 'SAOSOModeling' which calculates
and
% plots the stress wave from SAOS flow. Uncomment if you desire to see
% this, but only use every third point from the experimental data;
% otherwise, the computations are way too many and tedious and MATLAB
struggles
%          [export] =
SAOSModeling(para,sigma,CI,freq,GpExp,GdpExp,modes,graph);
%          time=export(:,1);
%          tauc12=export(:,2);
%          pred=export(:,3);

        graph=0; %=0 for no plotting in SAOSFittingGpGdp, =1 for
plotting
        %fit G' G" of composite to SAOS stress wave
        [GpGdp,diverge] =
SAOSFittingGpGdp(para,sigma,CI,freq,GpExp,GdpExp,wt,modes,graph,re,orie
nt_shr);
        GpMod=GpGdp(:,1);
        GdpMod=GpGdp(:,2);

        if diverge==0 %if no divergence, calculate error between model
and experiment
            for j=1:length(freq)
                Gerror=Gerror+(log10(GpExp(j))-
log10(GpMod(j)))^2+(log10(GdpExp(j))-log10(GdpMod(j)))^2;
            end
            %plot the model predictions and experimental data
            figure

loglog(freq,GpExp,'b*',freq,GdpExp,'g*',freq,GpMod,'b',freq,GdpMod,'g')
            legend('GpExp','GdpExp','GpMod','GdpMod',-1)
            title('SAOS HHT 2wt%')
        else %keep track of divergence
            Gerror=inf;
            gdiv=1;
        end

%%
% uncomment to check errors and divergences if interested
% Terror
% Serror
% Gerror
% tdiv
% sdiv
% gdiv

end
```

Composite Model Predictions: Solvent Cast with O-CNFs (SC)

```
function SC_2wt
%This program plots the viscosity for the SC 2wt% composite for
transient
%extension and transient shear as well as moduli predictions for SAOS
% given the optimized values for sigma and CI and hfactor

sigma=.5;
CI=.0499;
hfactor=1.76;

para=[   1563.180023    10503.23358 30793.85272 9864.433234 9310.030642
40690.01669; %optimized values for etap by mode
            0.01461114  0.235979496 3.210427777 34.39722848 6390.005373
116255.5053; %optimized values for lambda by mode
            0.818868357 0.56        0.56        0.078601046 0.025189799
0.001841609]; %optimized values for alpha by mode
modes=6;
wt=.02; %mass fraction of cnfs
re=69/hfactor; %69= number ave length, 124= weight ave length
orient_ext=[.528 .236 .236]; %experimentally determined initial
orientation of fibers (a11,a22,a33)
orient_shr=[.528 0 .236]; %experimentally determined initial
orientation of fibers (a11,a12,a22)

%%
%%Part 1: Extensional plotting
terr=zeros(1,5); %error per extension rate in model predictions
tdiv=0; %keeps track of any divergences in extensional model
predictions

for m=1:5 % m designates the m-th extension rate
        % see data for poster for all sets which have been truncated
        if m==1
            r=.01;
            %set .01(1) slight trunc at beginning
            timedata=[0 22.25409    26.64752    31.90831    38.20769
45.7507 54.78287    65.59817    78.54865    94.05583    112.6245
134.8589    161.483 193.3631    231.5372    277.2475    331.9821
397.5225    476.0019    569.9748    682.5]';
            expdata=[0  387843.5    377964.3    376909.3    400561.4
416749.4    430228.8    446005.1    453425.2    464266.9    480019.8
481094.1    496619.5    525034.7    549660.1    602283.9    686062.9
759297.2    943786.7    1428359 2798893]';
        elseif m==2
            r=.03;
            %set .03(1) trunc
            timedata=[0 9.700294    11.35781    13.29856    15.57092
18.23158    21.34686    24.99447    29.26535    34.26601    40.12115
46.97677    55.00384    64.40251    75.40717    88.29222    103.379
121.0437    141.7268    165.9441    194.2995]';
            expdata=[0  318799.5    322584.2    331946.3    351364.5
369053  384363.7    395667.4    412336.7    428658.5    443033.7
```

```
447931.5    464958.8    467193.4    474136.4    481202.3    510103.9
600216.2    745073.8    1025986 1601637]';
        elseif m==3
            r=.1;
            %set .1(2)
            timedata=[0 3.190139    3.644588    4.163775    4.756922
5.434566    6.208744    7.093206    8.103663    9.258065    10.57692
12.08364    13.80501    15.77159    18.01832    20.58511    23.51755
26.86772    30.69514    35.0678 40.06336    45.77055    52.29077
59.73981]';
            expdata=[0  193777.5    206943.7    212962.1    220398.4
230104.9    238061.3    247736.3    258577.8    262897.8    268821.3
288701.6    313619.3    334114.8    360457.6    375016.1    392091.5
395367.7    401158  363448.8    307047.8    284038.5    260705.1
551346.6]';
        elseif m==4
            r=.3;
            %set .3(4)
            timedata=[0 0.1 0.1117125   0.1247968   0.1394135
0.1557423   0.1739836   0.1943614   0.2171259   0.2425567   0.2709661
0.3027029   0.3381569   0.3777634   0.4220089   0.4714366   0.5266534
0.5883376   0.6572464   0.7342262   0.8202223   0.9162906   1.023611
1.143501    1.277433    1.427052    1.594195    1.780915    1.989504
2.222524    2.482837    2.773638    3.0985  3.461411    3.866828
4.319729    4.825676    5.390882    6.022287    6.727646    7.51562
8.395884    9.37925 10.47779    11.705  13.07595]';
            expdata=[0  15703.5 19405.89    23630.79    30351.06
39551.26    47271.38    48617.73    55422.28    63423.53    67141.63
76307.47    79001.23    87821.25    95223.06    102599.8    109690.8
115282.6    121508.2    126849.7    130611.6    134323.6    138513.3
143107.4    149151.3    155482.3    161784.5    165403.1    170278.8
176591.8    183432.5    188674.6    190785.9    197256.5    203240.9
215745.1    221730.9    226618.8    240972.5    242744.7    265836.2
274835.6    300677.2    319750  377306.3    380382.5]';
        elseif m==5
            r=1;
            %set 1(2)
            timedata=[0 0.1 0.109001    0.1188123   0.1295066
0.1411636   0.1538698   0.1677197   0.1828162   0.1992716   0.2172081
0.2367591   0.2580699   0.2812989   0.3066187   0.3342176   0.3643007
0.3970916   0.432834    0.4717935   0.5142599   0.5605487   0.6110039
0.6660007   0.7259477   0.7912906   0.862515    0.9401504   1.024774
1.117014    1.217557    1.32715 1.446607    1.576817    1.718747
1.873452    2.042083    2.225892    2.426245    2.644632    2.882677
3.142148    3.424974    3.733258    4.06929 4.435569    4.834816
5.27]';
            expdata=[0  13700.15    19522.7 21038.07    23982.51
28076.44    33713.48    39973.21    44765.05    47850.18    51608.97
56171.65    60023.85    63253.41    66884.19    69822.2 73230.11
76699.03    79586.54    83821.8 87150.84    90598.12    95051.02
99202.08    103614.5    108540.6    113448  118565.5    124469.2
128392.1    132122.8    141084.5    146724.3    150072.6    157853.2
171811.9    181501  193433.8    209473.4    221650.6    238442
257288.8    284907.1    311394.4    335601.6    344309.1    364330
383190.8]';
        end
```

```
    %differential equation solver to get model prediction of viscosity
vs time

[t,etatemp,diverge]=extensional_pde_solver(r,wt,sigma,CI,para(1,:),para
(2,:),para(3,:),timedata,modes,re,orient_ext);

    if diverge==1 %keep track of divergence
        tdiv=1;
        terr(m)=inf;
    elseif diverge==0 %if no divergence, calculate error between model
and experiment
        for k=2:length(timedata)
            terr(m)=terr(m)+(log10(expdata(k))-log10(etatemp(k)))^2;
        end
    end

    %plot the model predictions and experimental data
    if m==1
         figure
         if diverge==0
            loglog(t,etatemp,'r',timedata,expdata,'*r');
         end
         hold on
     elseif m==2
         if diverge==0
            loglog(t,etatemp,'g',timedata,expdata,'*g');
         end
     elseif m==3
         if diverge==0
            loglog(t,etatemp,'b',timedata,expdata,'*b');
         end
     elseif m==4
         if diverge==0
            loglog(t,etatemp,'c',timedata,expdata,'*c');
         end
     elseif m==5
         if diverge==0
            loglog(t,etatemp,'k',timedata,expdata,'*k');
         end

         title('Extensional Viscosity SC 2wt%');
         xlabel('Time (s)');
         ylabel('Viscosity (Pa*s)');
         legend('Mod \epsilon=.01','Exp \epsilon=.01','Mod
\epsilon=.03','Exp \epsilon=.03','Mod \epsilon=.1','Exp
\epsilon=.1','Mod \epsilon=.3','Exp \epsilon=.3','Mod \epsilon=1','Exp
\epsilon=1',-1);
         set(gcf,'Units','normalized',
'WindowStyle','docked','OuterPosition',[0 0 1 1]); %this places the
plot in a maximized window
         hold off
    end
end
Terror=sum(terr); %sum up error from all extension rates
```

```
%%
%%Part 2: Shear plotting
serr=zeros(1,7); %error per shear rate in model predictions
sdiv=0; %keeps track of any divergences in shear model predictions

for w=1:5 % w designates the w-th shear rate
        if w==1
            r=.01;
            %set .01(1)
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.28    0.315   0.36    0.41    0.465   0.53    0.6
0.68    0.775   0.885   1.01    1.145   1.3 1.48    1.685   1.92
2.185   2.485   2.83    3.22    3.665   4.175   4.75    5.405   6.155
7.005   7.975   9.08    10.335  11.765  13.39   15.245  17.36   19.76
22.495  25.61   29.155  33.19   37.785  43.02   48.975  55.755  63.475
72.26   82.265  93.655  106.62  121.38  138.19  157.33  190.71  217.11
247.17  281.4   320.36  364.73  415.22  472.72  538.18  612.7   697.53
794.13  904.08  1029.3  1171.8  1334    1518.8  1729.1  1968.5  2241
2551.4  2904.6  3306.8  3764.7  4286    4879.5  5555.1  6324.3];
            expdata=[0  60.133  453.29  966.59  1866.4  2873    3489.5
4050.3  4782.7  5327.9  5575.5  6204.6  6852.1  7106.4  7438.6  8003.8
8383    8588.7  9011.8  9586.3  9829.8  10029   10495   10881   10928
11278   11680   12102   13014   14059   15124   16204   17375   18522
19719   20984   22344   23705   25013   26405   27851   29307   30754
32264   33690   35183   36643   38133   39581   40968   42309   43617
44910   46120   47255   48228   49075   50146   51379   52774   54190
54938   55641   56217   57085   57696   58585   58978   59304   60680
60866   61582   61777   62925   63440   63962   64578   65040   65442
65784   66052   65968   65853   65292   64631   64033   63405   62448
61320   60616   59885   59125   58773   58508   58161   57946   57719
57776   58681   59166   60205   60529   60855   60054   60654];
        elseif w==2
            r=.1;
            %set .1(2)
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.275   0.305   0.35    0.4 0.455   0.515   0.585
0.665   0.755   0.86    0.975   1.105   1.255   1.425   1.62    1.845
2.1 2.39    2.715   3.085   3.51    3.99    4.54    5.165   5.87
6.675   7.595   8.635   9.82    11.17   12.7    14.445  16.43   18.685
21.255  24.175  27.495  31.275  35.57   40.455  46.01   52.33   59.52
67.695  76.995  87.575  99.605  113.28  128.85  146.55  177.4   201.77
229.49  261.01  296.88  337.66  384.05  436.82  496.82  565.08  642.71
731.01  831.43  945.66  1075.6  1223.4  1391.4  1582.6  1800];
            expdata=[0  46.69   534.64  1332.6  2176.3  2964.8  3727.8
4412.9  5013.3  5591.9  6170.2  6691.2  7173.6  7642.8  8091.4  8493.5
8883.1  9289.5  9642.4  9972    10353   10704   11007   11334   11646
11934   12221   12630   13447   14563   15682   16835   17961   19139
20369   21656   22966   24300   25739   27163   28570   30014   31453
32987   34555   35976   37305   38609   40282   41632   42792   43995
45096   45865   46987   47621   48093   48491   48618   48453   48145
47535   46686   45747   44626   43371   42111   40947   40067   39452
38987   38733   38722   38947   39274   39675   39927   40047   40079
```

```
40401   40765   40633   40822   40897   41109   41582   41733   41999
42335   42222   42799   42591   42464   42640   43358   44800];
        elseif w==3
            r=.3;
            %set .3(1)
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.275   0.305   0.345   0.39    0.445   0.505   0.57
0.65    0.74    0.84    0.955   1.085   1.23    1.395   1.59    1.81
2.055   2.335   2.65    3.01    3.425   3.89    4.42    5.025   5.71
6.49    7.38    8.39    9.535   10.835  12.315  14  15.915  18.09
20.56   23.375  26.575  30.205  34.335  39.03   44.365  50.43   57.325
65.165  74.075  84.205  95.72   108.81  123.69  140.6   159.83  193.32
219.75  249.8   283.96  322.79  366.93  417.11  474.15  538.99  612.7
696.48  791.73  900.01];
            expdata=[0  1.7318  546.57  1358.4  2224.9  3051.1  3824.1
4527.7  5180    5776.1  6333.1  6842.5  7329.9  7808.9  8244.6  8681.6
9047.8  9481.8  9860.3  10224   10572   10907   11203   11517   11832
12153   12453   12874   13704   14730   15835   17078   18362   19554
20856   22145   23421   24779   26081   27376   28694   29895   31154
32385   33357   34290   35010   35745   36162   36356   36445   36218
35860   35244   34470   33662   32841   32027   31258   30592   30145
29850   29780   29898   30123   30304   30329   30249   30213   30149
29944   29640   29198   28897   28697   28995   29499   30168   30387
29750   29243   29098   30009   30418   30073   30110   30002   30242
29961   30404   31371];
        elseif w==4
            r=1;
            %set 1(1)
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.27    0.29    0.325   0.37    0.42    0.475   0.54
0.615   0.7 0.795   0.9 1.02    1.155   1.31    1.485   1.685   1.915
2.17    2.46    2.79    3.165   3.59    4.075   4.625   5.245   5.95
6.755   7.665   8.695   9.87    11.2    12.71   14.425  16.365  18.57
21.075  23.915  27.135  30.79   34.94   39.65   44.995  51.06   57.945
65.755  74.62   84.68   96.09   109.04  123.74  140.43  159.35];
            expdata=[0  83.562  635.88  1426    2283    3094.4  3843.7
4523.4  5155.8  5733.9  6312.9  6823.6  7291.8  7762    8188    8612.7
9032.3  9384.7  9755.5  10029   10417   10735   11029   11349   11635
11933   12268   12515   13071   13947   14939   15939   16941   17989
18969   19988   20965   21849   22637   23360   23937   24322   24533
24502   24247   23711   22939   21997   20968   19850   18720   17770
17262   17162   17303   17616   18041   18401   18610   18591   18525
18315   18014   17718   17554   17912   18391   18547   18259   18296
18344   18484   18327   18469   18667   18545   18048   17298   17227];
        elseif w==5
            r=3;
            %set 3(2)
            timedata=[0 0.01    0.02    0.03    0.04    0.05    0.06
0.07    0.08    0.09    0.1 0.11    0.12    0.13    0.14    0.15
0.16    0.17    0.18    0.19    0.2 0.21    0.22    0.23    0.24
0.25    0.26    0.27    0.295   0.335   0.38    0.435   0.495   0.56
0.635   0.72    0.815   0.925   1.05    1.19    1.35    1.535   1.745
1.98    2.245   2.545   2.89    3.285   3.73    4.235   4.81    5.46
```

```
6.2 7.045   8   9.08    10.315  11.715  13.3    15.105  17.155  19.485
22.13   25.135  28.545  32.415  36.815  41.815];
            expdata=[0  71.359  585.85  1288.8  2060.1  2807    3484
4112.1  4690.9  5193.1  5668.5  6120.5  6540.9  6912.2  7291.7  7589.7
7944.7  8231.9  8528.3  8813.8  9118.9  9353.9  9592    9839.8  10067
10278   10477   10665   11086   11760   12342   12867   13415   13797
14099   14302   14417   14446   14352   14110   13858   13506   13146
12793   12486   12169   11887   11663   11463   11275   11086   10901
10753   10580   10532   10572   10461   10248   10124   10108   10275
9986.5  9727.1  9464.9  9189.8  9304.7  9346.9  9218.6];
        end
            %shift time data back to account for start up delay in
rheometer
            factor=timedata(2)-0.0005;
            timedata=timedata-factor;
            timedata(1)=0;
        %differential equation solver to get model prediction of
viscosity vs time

[t,etatemp,diverge]=shear_pde_solver(r,wt,sigma,CI,para(1,:),para(2,:),
para(3,:),timedata,modes,re,orient_shr);

        if diverge==1 %keep track of divergence
            sdiv=1;
            serr(w)=inf;
        elseif diverge==0 %if no divergence, calculate error between
model and experiment
            for k=2:length(timedata)
                serr(w)=serr(w)+(log10(expdata(k))-
log10(etatemp(k)))^2;
            end
        end

     %plot the model predictions and experimental data
     if w==1
         figure
         if diverge==0
            loglog(timedata,expdata,'*',t,etatemp,'Color',[0,0,1]);
         end
         hold on
     elseif w==2
         if diverge==0
            loglog(timedata,expdata,'*',t,etatemp,'Color',[0,0,0]);
         end
     elseif w==3
         if diverge==0
            loglog(timedata,expdata,'*',t,etatemp,'Color',[0,1,1]);
         end
     elseif w==4
         if diverge==0
            loglog(timedata,expdata,'*',t,etatemp,'Color',[.6,0,.9]);
         end
     elseif w==5
         if diverge==0
            loglog(timedata,expdata,'*',t,etatemp,'Color',[.7,.9,.3]);
         end
```

```
        xlabel('Time (s)')
        ylabel('Viscosity (Pa*s)')
        title('Shear Viscosity SC 2wt%')
        legend('Exp \gamma=0.01','Mod \gamma=0.01','Exp
\gamma=0.1','Mod \gamma=0.1','Exp \gamma=.3','Mod \gamma=.3','Exp
\gamma=1','Mod \gamma=1','Exp \gamma=3','Mod \gamma=3',-1);
        set(gcf,'Units','normalized',
'WindowStyle','docked','OuterPosition',[0 0 1 1]);
        hold off
    end
end
Serror=sum(serr); %sum up error from all shear rates


%%
%%PART 3: SAOS
%read in sigma and CI values to be sent to other programs
%call SAOSModeling variant to calc experimental stress.
%call SAOSFittingGpGdp variant to calc model prediction.
%find error between the two and send back as Gerror

%NOTE: diverging probably kills the programs this subfunction calls

Gerror=0; %error in SAOS model predictions
div=0; %keeps track of any divergences in SAOS model predictions

%data from Koki Data_Solvent Casting
freq=[100   63.096  39.811  25.119  15.849  10  6.3096  3.9811  2.5119
1.5849  1   0.63096 0.39811 0.25119 0.15849 0.1 0.063096    0.039811
0.025119    0.015849    0.01 ];
%storage modulus
GpExp=[137280   119870  103510  88257   74226   60987   49437   38805
30013   22372   16364   11517   8185.3  5409.5  3205.8  1938.1  1320.8
689.58  421.55  236.35  109.48];
%loss modulus
GdpExp=[62302   57776   53664   49458   45444   40648   36617   32468
28097   23851   19700   16027   12551   9515.1  7175.4  5241.3  3768.1
2639.6  1749.3  1157.1  757.66];

% this commented-out section calls on 'SAOSOModeling' which calculates
and
% plots the stress wave from SAOS flow. Uncomment if you desire to see
% this, but only use every third point from the experimental data;
% otherwise, the computations are way too many and tedious and MATLAB
struggles
%          [export] =
SAOSModeling(para,sigma,CI,freq,GpExp,GdpExp,modes,graph);
%          time=export(:,1);
%          tauc12=export(:,2);
%          pred=export(:,3);

        graph=0; %=0 for no plotting in SAOSFittingGpGdp, =1 for
plotting
        %fit G' G" of composite to SAOS stress wave
```

```
        [GpGdp,diverge] =
SAOSFittingGpGdp(para,sigma,CI,freq,GpExp,GdpExp,wt,modes,graph,re,orie
nt_shr);
        GpMod=GpGdp(:,1);
        GdpMod=GpGdp(:,2);

        if diverge==0 %if no divergence, calculate error between model
and experiment
            for j=1:length(freq)
                Gerror=Gerror+(log10(GpExp(j))-
log10(GpMod(j)))^2+(log10(GdpExp(j))-log10(GdpMod(j)))^2;
            end
            %plot the model predictions and experimental data
            figure

loglog(freq,GpExp,'b*',freq,GdpExp,'g*',freq,GpMod,'b',freq,GdpMod,'g')
            legend('GpExp','GdpExp','GpMod','GdpMod',-1)
            title('SAOS SC 2wt%')
        else %keep track of divergence
            Gerror=inf;
            gdiv=1;
        end

%%
% uncomment to check errors and divergences if interested
% Terror
% Serror
% Gerror
% tdiv
% sdiv
% gdiv
end
```

Composite Model Predictions: Fitting G' and G"

```
function [GpGdp,div] =
SAOSFittingGpGdp(para,sigma,CI,freq,Gpo,Gdpo,wt,modes,graph,re,orient)
%This program models the stress wave from a small amplitude oscillatory
%shear flow and fits the optimum values of G' and G" to this stress
wave
%   calls on SAOSimulGsfit to calc composite stress wave

%From Tim Kremer: see his thesis for details on this program

format long

%initial guess of G' and G"
guess=[0 35.06125   118.77715   218.069 403.069 731.4956667 1295.72
2281.803333 3723.183333 5670.693333 8656.983333 12385.93333 17431.8
23216.63333 30205.2 38639.13333 47962.26667 58520.46667 70267.56667
82679.76667 96278.46667;
    0 532.1383333   799.4886667 1259.376667 1859.03 2733.77 3907.66
5450.736667 7393.43 9767.963333 12548.53333 15681.63333 19139.5 22729.5
26576.8 30379.83333 34434.86667 38387.86667 42793.26667 47297.4
52348.03333];

LB=zeros(2,1); %lower boundary

UB=[]; %upper boundary

div=zeros(1,length(freq)); %divergence variable

for x=1:length(freq)

    x;
    %calculate model's prediction
    [stresst tspant
diverge]=SAOSSimulGsfit(freq(x),wt,sigma,CI,para,modes,re,orient);

%     if diverge==1
%         div(x)=1;
%         continue
%     end

    temp=find(tspant>=4*pi/freq(x),1);

    stress{x}=stresst(temp:end);
    tspan{x}=tspant(temp:end);

%options=optimset('Algorithm','interior-point');

[parameters fval exitflag] = fmincon(@Fitting,[guess(1,x)
guess(2,x)],[],[],[],[],LB,UB,[]);%,options);

Gpf(x)=parameters(1);
Gdpf(x)=parameters(2);
```

```
end

Gp;
Gdp;

%model predictions for stress wave
predfinal=Gpf(x)*0.5*sin(freq(x)*tspan{x})+Gdpf(x)*0.5*cos(freq(x)*tspa
n{x});
predo=Gpo(x)*0.5*sin(freq(x)*tspan{x})+Gdpo(x)*0.5*cos(freq(x)*tspan{x}
);

%plotting
if graph ==1
figure
plot(tspan{x},predfinal,tspan{x},stress{x},tspan{x},predo)
legend('Gprime Gdoubleprime','stress','original Gs')
size(predfinal)
size(stress{x})

%calculate r^2 value (regression coefficient) with stress as value
being compared to
C = corrcoef(stress{x},predfinal);
rsq1 = C(1,2).^2;

title(['Stress Wave, r^2 = ',num2str(rsq1)])
end

GpGdp=[Gpf' Gdpf'];

finaler=sum(er);

function error = Fitting(para)
%this subfunction calculates the error between model prediction and
%experiment

Gp=para(1);
Gdp=para(2);

error=0;

 pred=Gp*0.5*sin(freq(x)*tspan{x})+Gdp*0.5*cos(freq(x)*tspan{x});
    for i=1:length(tspan{x})
        error= error + (stress{x}(i)-pred(i))^2; %calculate error
    end
    er(x)=error;

end

end
```

Composite Model Predictions: Solving the Constitutive Model for SAOS

Flow

```
function [tauc12,tspan,diverge] =
SAOSSimulGsfit(w,mass,sigma,CI,para,modes,re,orientation)
%This program solves the constitutive model equations for oscillatory
shear
%flow and outputs composite stress wave in 12 direction.  This is a
%specialized version of 'shear_pde_solver.  See'shear_pde_solver' for
more
%specific details

%From Tim Kremer: see his thesis for details on this program


p=0;
x=1;

r0=0.5; %percent

if mass==0
    sigma=1;
end

% re=33.0; %aspect ratio

chi=1.0*(re^2-1)/(re^2+1); %another form of aspect ratio
rf=1750.0; %fiber density
rs=1000.0; %polymer density

etap=para(1,:);
lambda=para(2,:);
alpha=para(3,:);

% modes=5;

tspan=0:1/6/w:8*pi/w;

phi=1.0*rs*mass/(rf+(rs-rf)*mass);  %volume fraction
Ap=1.0*re^2/(3*log(sqrt(1.0*pi/phi)));  %A2, shape factor

tau_final=zeros(3,modes);
diverge=0;

for x=1:modes
    initial=[0 0 0 0 orientation];
    [time, yo]=ode23tb(@modepolymersub,tspan,initial);

    asdf=length(yo(:,1));
    L=length(time);

    if x==1
        tau1=zeros(L,modes);
```

```
        tau12=zeros(L,modes);
        tau2=zeros(L,modes);
        tau3=zeros(L,modes);
    end

    if p==0
        tau1(:,x)=yo(:,1);
        fdsa=length(tau1);
        tau12(:,x)=yo(:,2);
        tau2(:,x)=yo(:,3);
        tau3(:,x)=yo(:,4);

        r=r0*w*cos(w*time);
%         tau_final(:,x) = [tau1(L,x) tau12(L,x) tau2(L,x) tau3(L,x)]';

        p=p+1;
    elseif p>0
%         if asdf<fdsa
%             diverge=1;
%             break
%         end
        tau1(:,x)=yo(:,1);
        fdsa=length(tau1);
        tau12(:,x)=yo(:,2);
        tau2(:,x)=yo(:,3);
        tau3(:,x)=yo(:,4);

        r=r0*w*cos(w*time);
%         tau_final(:,x) = [tau1(L,x) tau12(L,x) tau2(L,x) tau3(L,x)]';
    end
end

total11=sum(tau12,2);
total12=sum(tau12,2);
total22=sum(tau12,2);
total33=sum(tau12,2);

a11=yo(:,5);
a12=yo(:,6);
a22=yo(:,7);
a33=1-a11-a22;

eta=total12./r;
coef=2.0*eta*phi;

if r~=0
    %disp('r~=0')
    tf12=(coef.*Ap.*r).*((27.0.*(a11.*a22.*(1-a11-a22)-(a12.^2).*(1-
a11-a22))).*(-1.0/35.0+1.0/7.0.*(a11+a22))+(a12.^2).*(1-
27.*(a11.*a22.*(1-a11-a22))+27.0.*(a12.^2).*(1-a11-a22)));
    tf11=(coef.*Ap.*r).*((27.0.*(a11.*a22.*(1-a11-a22)-(a12.^2).*(1-
a11-a22))).*(3.0/7.0.*(a12))+(a11.*a12).*(1-27*(a11.*a22.*(1-a11-
a22))+27.0.*(a12.^2).*(1-a11-a22)));
```

```
    tf22=(coef.*Ap.*r).*((27.0.*(a11.*a22.*(1-a11-a22)-(a12.^2).*(1-
a11-a22))).*(3.0/7.0.*(a12))+(a22.*a12).*(1-27*(a11.*a22.*(1-a11-
a22))+27.0.*(a12.^2).*(1-a11-a22)));
    tf33=(coef.*Ap.*r).*((27.0.*(a11.*a22.*(1-a11-a22)-(a12.^2).*(1-
a11-a22))).*(1.0/7.0.*(a12))+((1-a11-a22).*a12).*(1-27.*(a11.*a22.*(1-
a11-a22))+27.0.*(a12.^2).*(1-a11-a22)));
else
    %disp('r==0')
    tf12=(2.0*phi.*total12.*Ap).*((27.0*(a11.*a22.*(1-a11-a22)-
(a12.^2).*(1-a11-a22))).*(-1.0/35.0+1.0/7.0*(a11+a22))+(a12.^2).*(1-
27*(a11.*a22.*(1-a11-a22))+27.0*(a12.^2).*(1-a11-a22)));
    tf11=(2.0*phi.*total12.*Ap).*((27.0*(a11.*a22.*(1-a11-a22)-
(a12.^2).*(1-a11-a22))).*(3.0/7.0*(a12))+(a11.*a12).*(1-
27*(a11.*a22.*(1-a11-a22))+27.0*(a12.^2).*(1-a11-a22)));
    tf22=(2.0*phi.*total12.*Ap).*((27.0*(a11.*a22.*(1-a11-a22)-
(a12.^2).*(1-a11-a22))).*(3.0/7.0*(a12))+(a22.*a12).*(1-
27*(a11.*a22.*(1-a11-a22))+27.0*(a12.^2).*(1-a11-a22)));
    tf33=(2.0*phi.*total12.*Ap).*((27.0*(a11.*a22.*(1-a11-a22)-
(a12.^2).*(1-a11-a22))).*(1.0/7.0*(a12))+((1-a11-a22).*a12).*(1-
27*(a11.*a22.*(1-a11-a22))+27.0*(a12.^2).*(1-a11-a22)));
end

tauc12=tf12+total12;
tauc11=tf11+total11;
tauc22=tf22+total22;
tauc33=tf33+total33;
etac=tauc12./r;
N1c=tauc11-tauc22;
N2c=tauc22-tauc33;
aijkl12=((27.0.*(a11.*a22.*(1-a11-a22)-(a12.^2).*(1-a11-a22))).*(-
1.0/35.0+1.0/7.0.*(a11+a22))+(a12.^2).*(1-27.*(a11.*a22.*(1-a11-
a22))+27.0.*(a12.^2).*(1-a11-a22)));

    function dyo = modepolymersub(t,y)

        tp11=y(1);
        tp12=y(2);
        tp22=y(3);
        tp33=y(4);
        a11=y(5);
        a12=y(6);
        a22=y(7);
        a33=1-a11-a22;
        dyo=zeros(7,1);

        dyo(1,1)=-alpha(x)*(tp11^2+tp12^2)/etap(x)-
sigma*tp11/lambda(x)+2*r0*w*cos(w*t)*tp12-3*(1-
sigma)*(tp11*a11+tp12*a12)/lambda(x);
        dyo(2,1)=-alpha(x)*(tp11*tp12+tp12*tp22)/etap(x)-
sigma*tp12/lambda(x)+etap(x)*r0*w*cos(w*t)/lambda(x)+r0*w*cos(w*t)*tp22
-3*(1-sigma)/2/lambda(x)*(a11*tp12+a12*tp22+a12*tp11+a22*tp12);
        dyo(3,1)=-alpha(x)*(tp12^2+tp22^2)/etap(x)-
sigma*tp22/lambda(x)-3*(1-sigma)/lambda(x)*(tp12*a12+tp22*a22);
        dyo(4,1)=-alpha(x)*(tp33^2)/etap(x)-tp33*sigma/lambda(x)-3*(1-
sigma)/lambda(x)*a33*tp33;
```

```
        dyo(5,1)=r0*w*cos(w*t)*a12+2*CI*abs(r0*w*cos(w*t))*(1.0-
3.0*a11)+chi*r0*w*cos(w*t)*a12-...
            2*chi*r0*w*cos(w*t)*(3.0/7.0*a12*(27.0*a11*a22*(1-a11-
a22)...
            -27.0*(a12^2)*(1-a11-a22))+(1.0-27.0*a11*a22*(1-a11-
a22)+...
            27.0*(a12^2)*(1-a11-a22))*a11*a12);
        dyo(6,1)=1.0/2.0*r0*w*cos(w*t)*a22-
1.0/2.0*r0*w*cos(w*t)*a11+chi*((1.0/2.0*r0*w*cos(w*t)*a22+...
            1.0/2.0*r0*w*cos(w*t)*a11)-
(2.0*r0*w*cos(w*t))*((27.0*a11*a22*(1-a11-a22)-...
            27.0*(a12^2)*(1-a11-a22))*(-
1.0/35.0+1.0/7.0*a11+1.0/7.0*a22)+...
            (1.0-27.0*a11*a22*(1-a11-a22)...
            +27.0*(a12^2)*(1-a11-a22))*a12^2))-
6.0*CI*abs(r0*w*cos(w*t))*a12;
        dyo(7,1)=-r0*w*cos(w*t)*a12+2*CI*abs(r0*w*cos(w*t))*(1.0-
3.0*a22)+chi*r0*w*cos(w*t)*a12-...
            2*chi*r0*w*cos(w*t)*(3.0/7.0*a12*(27.0*a11*a22*(1-a11-a22)-
...
            27.0*(a12^2)*(1-a11-a22))+(1.0-27.0*a11*a22*(1-a11-a22)+...
            27.0*(a12^2)*(1-a11-a22))*a12*a22);

    end

end
```

Composite Model Predictions: Modeling the Stress Wave in SAOS Flow

```
function [export] = SAOSModeling(para,sigma,CI,freq,Gp,Gdp,modes,graph)
%This program models a small amplitude oscillatory shear (SAOS) flow
and
%graphs the resulting stress wave.  Not needed in the calculation of
the
%model prediction for SAOS flow, but can be examined to verify the
accuracy
%of Kremer's method of fitting to the stress wave in SAOS flow

%From Tim Kremer: see his thesis for details on this program

x=1;
r0=0.5; %percent

c=1; %wt% CNFs, 1=2%, 2=5%, 3=10%, 4=0%

ref=10;    %index for frequencys
w=freq(ref);    %index for frequency

re=70.0; %aspect ratio

chi=1.0*(re^2-1)/(re^2+1); %another form of aspect ratio

%%% CHECK - this is same as ext_pde
rf=1750.0; %fiber density
%%% CHECK - this is same as ext_pde
rs=1000.0; %polymer density


etap=para(1,:);
lambda=para(2,:);
alpha=para(3,:);

tspan=0:1/10/w:10*pi/w;

mass=[2.0/100.0, 5.0/100.0, 10.0/100.0, 0.0];

% modes=5;
%tspan=0:0.01:shear_time;


phi=1.0*rs*mass(c)/(rf+(rs-rf)*mass(c));  %volume fraction
Ap=1.0*re^2/(3*log(sqrt(1.0*pi/phi)));  %A2, shape factor

orientation=[0.333, 0.0, 0.333];

tau_final=zeros(3,modes);


while x<modes+1
    initial=[0 0 0 0 orientation];
```

```
    [time, yo]=ode45(@modepolymersub,tspan,initial);
    export = [' mode ' num2str(x) ' calculation done'];
    disp(export)

    L=length(time);

    if x==1
        tau1=zeros(L,modes);
        tau12=zeros(L,modes);
        tau2=zeros(L,modes);
        tau3=zeros(L,modes);
    end

    tau1(:,x)=yo(:,1);
    tau12(:,x)=yo(:,2);
    tau2(:,x)=yo(:,3);
    tau3(:,x)=yo(:,4);

    r=r0*w*cos(w*time);

    if graph==1
    figure
    subplot(1,3,1)
    plot(time,tau12)
    title('Stress - Individual Modes')

    hold on
    end

    tau_final(:,x) = [tau1(L,x) tau12(L,x) tau2(L,x)]';

x=x+1;

end

total11=sum(tau1,2);
total12=sum(tau12,2);
total22=sum(tau2,2);
total33=sum(tau3,2);

a11=yo(:,5);
a12=yo(:,6);
a22=yo(:,7);
a33=1-a11-a22;

eta=total12./r;
coef=2.0*eta*phi;

if r~=0
    disp('r~=0')
    tf12=(coef.*Ap.*r).*((27.0.*(a11.*a22.*(1-a11-a22)-(a12.^2).*(1-
a11-a22))).*(-1.0/35.0+1.0/7.0.*(a11+a22))+(a12.^2).*(1-
27.*(a11.*a22.*(1-a11-a22))+27.0.*(a12.^2).*(1-a11-a22)));
```

```
    tf11=(coef.*Ap.*r).*((27.0.*(a11.*a22.*(1-a11-a22)-(a12.^2).*(1-
a11-a22))).*(3.0/7.0.*(a12))+(a11.*a12).*(1-27*(a11.*a22.*(1-a11-
a22))+27.0.*(a12.^2).*(1-a11-a22)));
    tf22=(coef.*Ap.*r).*((27.0.*(a11.*a22.*(1-a11-a22)-(a12.^2).*(1-
a11-a22))).*(3.0/7.0.*(a12))+(a22.*a12).*(1-27*(a11.*a22.*(1-a11-
a22))+27.0.*(a12.^2).*(1-a11-a22)));
    tf33=(coef.*Ap.*r).*((27.0.*(a11.*a22.*(1-a11-a22)-(a12.^2).*(1-
a11-a22))).*(1.0/7.0.*(a12))+((1-a11-a22).*a12).*(1-27.*(a11.*a22.*(1-
a11-a22))+27.0.*(a12.^2).*(1-a11-a22)));
else
    disp('r==0')
    tf12=(2.0*phi.*total12.*Ap).*((27.0*(a11.*a22.*(1-a11-a22)-
(a12.^2).*(1-a11-a22))).*(-1.0/35.0+1.0/7.0*(a11+a22))+(a12.^2).*(1-
27*(a11.*a22.*(1-a11-a22))+27.0*(a12.^2).*(1-a11-a22)));
    tf11=(2.0*phi.*total12.*Ap).*((27.0*(a11.*a22.*(1-a11-a22)-
(a12.^2).*(1-a11-a22))).*(3.0/7.0*(a12))+(a11.*a12).*(1-
27*(a11.*a22.*(1-a11-a22))+27.0*(a12.^2).*(1-a11-a22)));
    tf22=(2.0*phi.*total12.*Ap).*((27.0*(a11.*a22.*(1-a11-a22)-
(a12.^2).*(1-a11-a22))).*(3.0/7.0*(a12))+(a22.*a12).*(1-
27*(a11.*a22.*(1-a11-a22))+27.0*(a12.^2).*(1-a11-a22)));
    tf33=(2.0*phi.*total12.*Ap).*((27.0*(a11.*a22.*(1-a11-a22)-
(a12.^2).*(1-a11-a22))).*(1.0/7.0*(a12))+((1-a11-a22).*a12).*(1-
27*(a11.*a22.*(1-a11-a22))+27.0*(a12.^2).*(1-a11-a22)));
end

tauc12=tf12+total12;
tauc11=tf11+total11;
tauc22=tf22+total22;
tauc33=tf33+total33;
etac=tauc12./r;
N1c=tauc11-tauc22;
N2c=tauc22-tauc33;
aijkl12=((27.0.*(a11.*a22.*(1-a11-a22)-(a12.^2).*(1-a11-a22))).*(-
1.0/35.0+1.0/7.0.*(a11+a22))+(a12.^2).*(1-27.*(a11.*a22.*(1-a11-
a22))+27.0.*(a12.^2).*(1-a11-a22)));

export=[time tauc12];

pred=Gp(ref)*0.5*sin(freq(ref)*tspan)+Gdp(ref)*0.5*cos(freq(ref)*tspan)
;

export=[time tauc12 pred'];

if graph==1
subplot(1,3,2)
if c==4
    plot(tspan,pred,tspan,total12)
else
    plot(tspan,pred,tspan,tauc12)
end
exp=['frequency= ' num2str(w)];
legend('Gprime Gdoubleprime','stress')
title(exp)
    grid on
    grid minor
hold on
```

```
subplot(1,3,3)
plot(tspan,a11,tspan,a12,tspan,a22)
legend('a11','a12','a22')
title('Orientation Evolution')
    grid on
    grid minor
end
    function dyo = modepolymersub(t,y)

        tp11=y(1);
        tp12=y(2);
        tp22=y(3);
        tp33=y(4);
        a11=y(5);
        a12=y(6);
        a22=y(7);
        a33=1-a11-a22;
        dyo=zeros(7,1);

        dyo(1,1)=-alpha(x)*(tp11^2+tp12^2)/etap(x)-
sigma*tp11/lambda(x)+2*r0*w*cos(w*t)*tp12-3*(1-
sigma)*(tp11*a11+tp12*a12)/lambda(x);
        dyo(2,1)=-alpha(x)*(tp11*tp12+tp12*tp22)/etap(x)-
sigma*tp12/lambda(x)+etap(x)*r0*w*cos(w*t)/lambda(x)+r0*w*cos(w*t)*tp22
-3*(1-sigma)/2/lambda(x)*(a11*tp12+a12*tp22+a12*tp11+a22*tp12);
        dyo(3,1)=-alpha(x)*(tp12^2+tp22^2)/etap(x)-
sigma*tp22/lambda(x)-3*(1-sigma)/lambda(x)*(tp12*a12+tp22*a22);
        dyo(4,1)=-alpha(x)*(tp33^2)/etap(x)-tp33*sigma/lambda(x)-3*(1-
sigma)/lambda(x)*a33*tp33;

        dyo(5,1)=r0*w*cos(w*t)*a12+2*CI*abs(r0*w*cos(w*t))*(1.0-
3.0*a11)+chi*r0*w*cos(w*t)*a12-...
            2*chi*r0*w*cos(w*t)*(3.0/7.0*a12*(27.0*a11*a22*(1-a11-
a22)...
            -27.0*(a12^2)*(1-a11-a22))+(1.0-27.0*a11*a22*(1-a11-
a22)+...
            27.0*(a12^2)*(1-a11-a22))*a11*a12);
        dyo(6,1)=1.0/2.0*r0*w*cos(w*t)*a22-
1.0/2.0*r0*w*cos(w*t)*a11+chi*((1.0/2.0*r0*w*cos(w*t)*a22+...
            1.0/2.0*r0*w*cos(w*t)*a11)-
(2.0*r0*w*cos(w*t))*((27.0*a11*a22*(1-a11-a22)-...
            27.0*(a12^2)*(1-a11-a22))*(-
1.0/35.0+1.0/7.0*a11+1.0/7.0*a22)+...
            (1.0-27.0*a11*a22*(1-a11-a22)...
            +27.0*(a12^2)*(1-a11-a22))*a12^2))-
6.0*CI*abs(r0*w*cos(w*t))*a12;
        dyo(7,1)=-r0*w*cos(w*t)*a12+2*CI*abs(r0*w*cos(w*t))*(1.0-
3.0*a22)+chi*r0*w*cos(w*t)*a12-...
            2*chi*r0*w*cos(w*t)*(3.0/7.0*a12*(27.0*a11*a22*(1-a11-a22)-
...
            27.0*(a12^2)*(1-a11-a22))+(1.0-27.0*a11*a22*(1-a11-a22)+...
            27.0*(a12^2)*(1-a11-a22))*a12*a22);
     end
end
```