MODELING OF POLYMER MELT/NANOPARTICLE COMPOSITES AND MAGNETO-RHEOLOGICAL FLUIDS

DISSERTATION

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ABSTRACT

Polymers composed with carbon nanofibers, carbon nanotubes, and nanoclays show remarkable promise for enhancements of mechanical, electrical, and thermal properties of polymeric materials. This research work describes an experimental and modeling study of nanoparticle/polymer composite systems in their melt processing and performance phases. The goal is to create a predictive understanding of the coupling of processing to the development of the performance properties of the composite, focusing on the measuring and modeling of nano- and mesoscale features, and how they dictate macroscale behavior.

Nanostructurally-based constitutive models are developed to describe the comprehensive characterization of rheology, flow/particle interaction, and structure development of aqueous nanofiber suspensions and polymer nanocomposites. The aqueous nanofiber suspensions are modeled as elastic/rigid dumbbells suspended in a Newtonian solvent, where the bulk rheological properties are deduced from the microstructural measurements and all but one coefficients in the constitutive equations are specified not by a fit to macroscale experimental flow measurements, but rather in terms of primitive measurements of particle microstructure, carrier fluid viscosity and density, and temperature.
The rheological behavior of carbon nanofiber/polystyrene (CNF/PS) composites in their melt phase has been characterized as rigid rods in a viscoelastic fluid matrix: the nanofibers are described by rigid rod model and the modified Giesekus model is employed to describe the polymer behavior. The constitutive models, which include the strain-rate-dependent inter-fiber interaction parameter and polymer-fiber interaction parameter, successfully capture the transient and steady shear behavior of the CNF/PS composites and correctly predict the nanofiber orientations.

Based on the successes of microstructurally based models for CNF suspensions, kinetic theory-based models of MR fluids are developed by incorporating a magnetic force. The model characterizes the 3-D MR response of the composite system to mechanical and magnetic inputs in terms of primitive measurements of the carrier fluid and microstructural characterization of the metallic particles. This fundamental, 3-D, microstructurally based model will replace the inherent empiricism of the current modeling with a fundamental understanding of the mechanical and magnetic coupling in the fluid at the particle level.

All these models are validated through comparison of model predictions to experimental measurements of nano-/macro-scale behavior.
Dedicated to my beloved parents and husband, Shanhu Li.
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CHAPTER 1

INTRODUCTION

1.1 Polymer Melt/Nanoparticle Composites

Polymers composed with carbon nanoparticles, carbon nanotubes, and nanoclays show remarkable promise for enhancements of mechanical, electrical, thermal, and barrier properties of polymeric materials. Properties of polymer/carbon nanotube (CNT) composites have been extensively studied and numerous papers have been published on the mechanical, thermal and electrical properties of composites of CNT in both thermoset and thermoplastic polymers, and promising results have been found. However, low volume of production and high cost of the CNT greatly limit development and application. Carbon nanofibers (CNF), which have diameters of 100-200 nm and lengths of 1-100 microns, may serve as a substitute for the carbon nanotubes. Recent researchers have found that CNF/polymer composites have similar properties as CNT/polymer composites\textsuperscript{1-3}. The CNF/polymer composites exhibit reduced uniform surface electrical conductivity, while maintaining mechanical properties of matrix polymers. They can be used to make conductive paints, coatings, films, tubes, sheets, and parts for electrostatic painting, electro-magnetic interference (EMI) and electro-static discharge (ESD)
applications. In addition, these composites also provide improved strength, stiffness, dimensional stability and thermal conductivity, etc. This behavior makes CNF/polymer composites very promising materials for a wide range of applications in automotive, aerospace, electronic and chemical industries.

The addition of nanoparticles to the flow in processing of these nanocomposites complicates the rheology, flow, and evolving microstructure, and affects the processing as well as the final properties of the composite material. In this research work, the rheology of both the CNF aqueous suspensions and the carbon nanofiber/polystyrene (CNF/PS) melt composites are discussed. We study the rheology of CNF suspensions starting from Newtonian solvents, which has merits in the aspect of both industrial application and fundamental understanding of the rheology as a function of fiber properties since any non-Newtonian behavior of the suspensions can be attributed to interaction with the particles. Also theoretically selecting a Newtonian solvent greatly reduces the complexity of stress the analysis.

In experiments it has been found that at low fiber concentrations, the suspensions still exhibit Newtonian shear viscosity. The viscosity increases with the fiber concentration. Ganani and Powell\(^4\) showed that the glass fiber suspensions are Newtonian in dilute and semi-dilute regime. Chaouche and Koch\(^5\) found the same results with their nylon fibers in Newtonian fluids at semi-dilute regime. At higher fiber concentrations, the viscosity of the suspensions becomes shear rate dependent. This dependence becomes more obvious with increasing fiber loadings\(^6\). Chaouche and Koch\(^5\) studied nylon fibers in several Newtonian fluids and found that the suspensions were generally Newtonian but showed shear thinning at low shear rates. The shear thinning was stronger at higher fiber
concentrations and weaker at lower solvent viscosity. They attributed the shear thinning to the formation of flocs under flow which was hold by the adhesion force. Under flow, the flocs were broken by the shear stress, therefore showing shear thinning behavior.

Numerous researchers are working on developing models to predict the CNF/PS composites behavior. In the dilute regime, the Jeffery equation can give satisfactory results. However, beyond the dilute regime, the fibers cannot rotate freely without touching other fibers and therefore the fiber-fiber interactions come into play. The neighboring fibers confine the movement of a fiber. Batchelor\textsuperscript{7} studied rod-like particles in non-dilute regime under extension flow, where the fiber interactions were assumed to be hydrodynamic and Brownian effects were neglected. An equation relating elongational viscosity to the size of particle and shear viscosity was derived and was shown to have good agreements with experimental results\textsuperscript{8}. Folger and Tucker\textsuperscript{9} claimed that the interactions between fibers tend to randomize the fiber orientation. By assuming that these interactions will cause fibers to re-orientate independently, as analogous to the concept of Brownian motion, the authors set up a phenomenological equation to account for the interactions which contains a coefficient that has to be determined through experiments. Dinh and Armstrong\textsuperscript{10} developed a rheological model for semi-concentrated rigid-rod suspensions. They assumed that physical contacts between fibers were rare and therefore most of the interactions were hydrodynamic. Starting from analyzing the stress on a single fiber, they modeled the fiber interactions as relative “slippage” between each other along the axis and estimated the drag coefficient based on Batchelor’s cell model\textsuperscript{7}. Effects of hydrodynamic interactions have also been studied by Mackaplow and Shaqfeh\textsuperscript{11}. A set of integral equations was set up to solve for the hydrodynamic
interaction of a large number of fibers. These equations were applicable to suspensions up to simidilute regime and were shown to be able to reproduce published shear and extensional viscosity data. Phan-Thien and Graham\textsuperscript{12} developed a phenomenological constitutive equation based on experimental results that effective specific viscosity increases with increasing fiber volume fraction at high fiber loadings. Although the Jeffery’s model is based on dilute regime where fibers can rotate without contacting other fibers, Koch and Shaqfeh\textsuperscript{13} calculated the distance between the fibers and showed that the model can be applied to semi-dilute regime with good approximation.

Efforts have been made to extend the models to non-Newtonian solvents. Grmela et al\textsuperscript{14} modeled the viscoelastic matrix as dumbbells and extended the Jeffery’s equation to the application of suspensions with viscoelastic solvents. Following Grmela’s idea, Ramazani et al\textsuperscript{15} modified the Jeffery equation for the fiber using a Hookean energy model for the non-Newtonian matrix. Quantitative agreement between model prediction and experimental results was obtained. The Doi-type models are also based on Newtonian solvents. Becraft and Metzner\textsuperscript{16} added a viscous dissipation term with which the shear thinning effects of the solvents were taken into consideration. The modified Doi model was found to agree well with steady shear viscosity of the glass fiber filled polypropylene.

All the models we have discussed up to now are based on straight fibers. In reality the fibers are sometimes not strictly straight (see Figure 2.2). One can expect that the behavior of a suspension containing straight fibers should be different from that containing curved ones. Experimental results suggest that curved/flexible fibers may cause higher suspensions viscosity than straight fibers\textsuperscript{17-19}. The effects of fiber curvature
have been studied by Joung et al.\textsuperscript{20,21} through direct simulation. The curved fiber was modeled on the concept of chain and beads described by Bird et al.\textsuperscript{22} Short range interactions between fibers and solvents were assumed to be lubrication forces as proposed by Yamane et al.\textsuperscript{23}, and long range interactions were assumed to be hydrodynamic effects. The simulation results showed that curved fibers would cause marked increase in the suspension viscosity. Goto et al.'s claim was confirmed that suspension viscosity was inversely dependent on the fiber stiffness\textsuperscript{19}.

1.2 Fiber orientation

Since the nanoparticle orientation pattern is the dominant structural feature of the composite microstructure, and the rheological behavior of the nanoparticle/polymer composite is sensitive to nanoparticle orientation, accurate rheological models must account for this internal structure and its time evolution. Therefore it is desirable that constitutive equations be derived that couple rheology (both bulk and mesoscale) with particle orientation. The central topic of the proposed research on nanoparticle/polymer composite systems is to develop sets of constitutive equations that can predict the macroscopic and mesoscopic rheological properties based on a microscopic knowledge of the composite system, including size, volume concentration, and orientation of the particles, and properties of the suspending fluid.

The particle orientation is the vector along the particle. This vector can be a dimensionless unit vector (which we denote by $\mathbf{p}$, see Figure 1.1) or be dimensional, with magnitude equal to the length of the particle (which we denote by $\mathbf{q}$, see Figure 1.2).

There are different ways to treat the particle orientation for a system of particles. The choice of the description used to represent particle orientation affects the accuracy
and efficiency of the calculation of model predictions. One possible representation is a probability distribution function $\psi(\theta, \phi)$ (PDF) for particle orientation. In this representation, it is assumed that the particles are cylinders, uniform in length and diameter. The orientation of a single particle can be described by the angles $(\theta, \phi)$ shown in Figure 1.1. The orientation state at a point is determined by $\psi(\theta, \phi)$, with the probability of finding a particle between $\theta_i$ and $\theta_i + d\theta$, and $\phi_i$ and $\phi_i + d\phi$, given by 25, 26.

$$P(\theta_i \leq \theta \leq \theta_i + d\theta, \phi_{i} \leq \phi \leq \phi_{i} + d\phi) = \psi(\theta_i, \phi_i) \sin \theta_i d\theta d\phi.$$  (1.1)

The distribution function $\psi$ is periodic and normalized. The evolution equation

$$\frac{D\psi}{Dt} = -\frac{\partial}{\partial \theta}(\theta \psi) - \frac{1}{\sin \theta} \frac{\partial}{\partial \phi}(\phi \psi)$$  (1.2)

describes the change of $\psi$ with time when the particles are changing orientation. Solving this equation in a numerical simulation is cumbersome. Therefore, although the orientation distribution function is a complete, unambiguous description of the particle orientation state, it is only practical in some simple problems9,25,27. Another possibility to describe the particle orientation is orientation parameters28,29. A set of four orientation parameters was developed and in this development, the distribution function is assumed to have symmetries such that:

$$\psi(\theta, \phi) = \psi(-\theta, \phi), \quad \psi(\theta, \phi) = \psi(\theta, -\phi).$$  (1.3)

In addition, $\psi$ is assumed to be separable into a product of functions of $\theta$ and $\psi$:

$$\psi(\theta, \phi) = \varphi(\theta) \cdot \psi(\phi).$$  (1.4)

The orientation parameters are defined as:
where

\begin{align}
    f_p &= 2\langle \cos^2 \phi \rangle - 1 \\
    g_p &= \frac{1}{5} \left[ 8\langle \cos^4 \phi \rangle - 3 \right] \\
    f_a &= \frac{1}{2} \left[ 3\langle \cos^2 \theta \rangle - 1 \right] \\
    g_a &= \frac{1}{4} \left[ 5\langle \cos^4 \theta \rangle - 1 \right]
\end{align}

(1.5)

This description of the orientation state is compact, requiring only four scalar parameters to specify three-dimensional orientation. The parameters \( f_p \) and \( g_p \) describe the orientation in the 1-2 plane and \( f_a \) and \( g_a \) describe the axial orientation around the 3-axis. The values of \( f_p \) and \( g_p \) range from zero to unity; values of zero indicate a random distribution in the 1-2 plane, and the values of unity indicate a totally aligned distribution. The values of \( f_a \) range from -1/2 to 1, and \( g_a \) varies between -1/4 to 1. The case of \( f_a = -1/2 \) and \( g_a = -1/4 \) corresponds to all the particles perpendicular to the 3-axis, i.e., lying in the 1-2 plane. The physical interpretation for \( f_a = g_a = 0 \) and \( f_a = g_a = 1 \) are random and totally aligned distributions along the 3-axis, respectively\(^{30}\).

Although the orientation parameters in equation (1.5) provide concise interpretation of orientation state, they rely on assumptions about the symmetries of the probability distribution function. This is not reasonable for all situations. Also the definitions involve the use of the distribution function, which precludes any advantage to be gained from the compactness of the orientation parameter description\(^{30}\).
We need a description of particle orientation which is both general (like the distribution function, e.g. no symmetry assumptions) and concise (easy to compute, like the orientation parameters). This requirement is fulfilled by orientation tensors.

Orientation tensors are typically used as intermediate results which summarize the influence of the orientation state on the stress tensor. When formulating constitutive equations it is common to eliminate the orientation information from the equations if at all possible\textsuperscript{22}. In the work of Hinch and Lea\textsuperscript{31} on suspension rheology and the work of Doi\textsuperscript{32} and Grema\textsuperscript{33} on liquid crystal rheology, the orientation tensors replace the probability distribution function and are used as state variables to describe the instantaneous structure of the material. The orientation tensors are free from assumptions about the symmetry of the probability distribution function.

The second order orientation tensor \( a_2 \) of the nanoparticle is defined as the dyadic product of \( p \) averaged over orientation space:

\[
a_{ij} = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} p_i p_j \psi(\phi, \theta) \sin \theta d\theta d\phi, \tag{1.7}
\]

or, in direct notation,

\[
a_2 = \int (p \otimes p) \psi(p) dp, \tag{1.8}
\]

where \( \psi(\theta, \phi) \) (or \( \psi(p) \)) is the probability distribution function. \( p \) is a unit vector denoting the orientation of a particle, as shown in Figure 1. The components of \( p \) are related to the angles \( \theta \) and \( \phi \):

\[
\begin{align*}
p_1 &= \sin \theta \cos \phi \\
p_2 &= \sin \theta \sin \phi \\
p_3 &= \cos \theta
\end{align*}
\tag{1.9}
\]

Since \( p.p = 1 \), the set of all possible directions of \( p \) corresponds to the unit sphere.
The orientation tensor has a convenient physical interpretation. The diagonal elements of a second orientation tensor $a_{11}; a_{22}; a_{33}$ measure the degree of alignment in the 1, 2, and 3 directions respectively, and off-diagonal elements $a_{12}; a_{13}; a_{23}$ are measures of the skewness in the 1-2, 1-3, and 2-3 planes, respectively. For a random distribution, all off-diagonal tensor components $a_{ij}$ are equal to zero, and the distribution function is equal to the constant $1/4\pi^{26,30}$.

Compared with hundreds of discretizations of $\theta$ and $\phi$ when calculating the PDF (equation (1.2)), the compact nature of the orientation tensor makes computation relatively efficient: due to symmetry ($a_{ij}=a_{ji}$) and normalization ($a_{ii}=1$), a second-order orientation tensor needs only two independent components ($a_{11}; a_{12}$) for a planar problem and five ($a_{11}; a_{12}; a_{13}; a_{22}; a_{23}$) for a three dimensional problem to describe the average nanoparticle orientation at each point. When an appropriate closure approximation is employed, the orientation tensor is adequate to recover the actual probability distribution function$^{25}$.

Polymer/nanoparticle composites are characterized in terms of the number $n$ of particles per unit volume, particle length $L$, and particle diameter $D$ as being either dilute ($nL^3 << 1$), semidilute ($nL^3 >> 1; nL^2D << 1$), or concentrated ($nL^3 >> 1; nL^2D >> 1$). $nL^3$ is the number of interacting particles in a volume swept by a single particle, and $nL^2D$ is an excluded volume of interacting particles due to a line approximation of a particle. In the dilute regime, the nanoparticles can freely rotate in any direction without touching other particles. A composite system is called semi-dilute when the distance between two neighboring particles is greater than the diameter but less than the length of the particle. In the semi-dilute regime, a new particle can be randomly inserted into the system with
negligible probability of it intersecting with other particles. Since there is little correlation between the orientations of neighboring particles, particles can be thought of as lines with zero volume. In the concentrated regime, the distance between two neighboring particles is less than the diameter, such that the particles in the fluids become aligned and particle/particle interactions come into play. The rotational, end-over-end motion of each particle is restricted, as well as the translational motion perpendicular to the particle axis. The entanglement constraint determines that the particle cannot pass through each other.

My research objectives are to develop modeling capabilities of nanoparticle/polymer solution and nanoparticle/polymer melt composites to include viscoelasticity of the polymer matrix, interparticle interaction, particle/polymer matrix interaction of the particles. Interparticle interaction will be included in the evolution equation of the particle orientation, and the particle/polymer matrix interactions will be introduced through a friction factor that depends on the nanoparticle orientation. Models will be created for both the semi-dilute and concentrated regimes.

1.3 Magnetorheological Fluids

Magnetorheological (MR) fluids, which consist of micron-sized ferrous particles suspended in viscous oil and are subjected to coupled effects of mechanical forces and a magnetic field, are a class of smart materials whose threshold stress for initiating flow changes significantly when an external magnetic field is applied. The variable yield stress, low power requirements for control, and fast response of MR fluids make them attractive in force feedback systems for telerobotic minimally invasive cardio-thoracoscopic (MICT) surgery. The state of the art for MICT surgery is a telerobotic surgical system where the surgeon sits at a workstation and controls a robot, which conducts the surgery (Figure 1.3)
Some of the benefits of using telerobotic MICT surgery are reduced body trauma, less anesthesia, lower risk of infection, less scarring, improved cosmesis, and a reduction in recovery time of at least a factor of 5. These benefits arise because MICT surgery requires only three small (2-3 inch) incisions and stopping the heart is optional, unlike in conventional open-heart surgery where the surgeons must saw the breastbone, pry open the rib cage, and stop the heart from beating while they repair its valves or supporting blood vessels.

Currently, the surgeon has only visual feedback from a camera (scope) inserted in the patient. The lack of force feedback has been cited by surgeons as one of the main reasons for limited adoption of telerobotic machines. By synergistically combining novel magnetorheological (MR) fluid devices with fully 3-D dimensional microstructural analysis and control system design, the capabilities of modern force feedback systems could be improved to be employed in MICT surgery. Using the force feedback system the slave would receive motion commands from the master and transmit force from the external object back to the master, thereby allowing the surgeon to “feel” the object.

MR devices have been under development since Rabinow employed them in the late 1940s. Researchers have utilized the controllable variation in yield stress to develop various smart devices, such as vibration dampers, transmission clutches and brakes. Carlson have recently developed MR sponge based dampers to solve vibration-related problems in high-performance washing machines. Recently, researchers have explored providing force feedback using electrorheological (ER) fluid devices. MR fluids have advantages over their ER counterparts, including an order of magnitude higher yield stress, broader operating temperature range, and low sensitivity to impurities.
These significant advantages make MR fluid more attractive in force feedback applications.

To date, all MR models are 1-D and empirical. Measurements of the bulk response of MR fluids reveal the existence of an apparent yield stress which varies with an applied magnetic field \( H \). This characteristic phenomenological behavior is typically modeled by Bingham's visco-plasticity equation\(^{44,46}\),

\[
\tau = \tau_y(H) + \eta \dot{\gamma},
\]

where \( \tau \) is the shear stress, \( \tau_y \) is the yield stress (a function only of magnetic field), \( \eta \) is the effective bulk viscosity of composite system (assumed constant), \( H \) is the magnetic field, and \( \dot{\gamma} \) is the shear rate of the flow. Since MR fluid exhibits shear thinning behavior, the Herschel-Bulkley viscoplastic model\(^{56}\) can be employed to accommodate this effect. In Herschel-Bulkley model, the constant viscosity is replaced with a power law term dependent on the shear strain rate,

\[
\tau = \left[ \tau_y(H) + K \left| \dot{\gamma} \right|^m \right] \text{sgn}(\dot{\gamma}),
\]

where \( m, K \) are fluid parameters with \( m > 0 \) and \( K > 0 \). Equation (1.11) describes the fluid shear thinning behavior when \( m > 1 \) and fluid shear thickening effect when \( m < 1 \). These formula, which combine empiricism with features appropriated from the form of the solution for the shear flow of a Newtonian fluid, have no fundamental, explicit connection to the microstructure of an MR fluid. For the 2-D and 3-D devices, Bingham plastic/Herschel-Buckley-type models are lacking in three specific areas: (i) they only model 1-D simple shear flow with a transverse applied magnetic field. (ii) Bingham plastic/Herschel-Buckley-type models are largely phenomenological, with no explicit
connection to the fundamental principles governing the mechanical and magnetic
coupling in the fluid at the particle level. (iii) because the models predict no flow for small
values of shear stress, the models are inaccurate at low values of shear stress. These low
values of shear are very important to haptic systems especially at low levels of touch.

In order to realize the conceptual vision of MR fluid-based force feedback device,
fundamental (as opposed to empirical), 3-D, microstructurally based models of MR fluid
are required, which characterize the full 3-D magneto-rheological response of the
composite system to mechanical and magnetic inputs in terms of primitive measurements
of the carrier fluid and microstructural characterization of the metallic particles. The use
of these microstructurally based models will replace the inherent empiricism of the
current modeling with a fundamental understanding of the mechanical and magnetic
coupling in the fluid at the particle level. It is envisioned that a more fundamental
understanding will provide fidelity over a wide range, importantly to low shear rate
movements corresponding to touch. In doing so, we will produce for the first time force-
feedback capability in telerobotic minimally invasive cardio-thoracoscopic surgery. This
capability will be a significant advance in MICT surgery, leading to more widespread
adoption of this surgery instead of open-heart surgery, with the attendant saving in
reduced recovery time, inpatient care, medical complications, and malpractice lawsuits.

The goal of my research on MR fluids is to develop, validate, and exploit
microstructurally based, fundamental models for MR fluid devices, which build on the
success in prior research developing microstructurally based models for composite
systems of carbon nanofibers (CNFs) suspended in a Newtonian fluid. The model MR
fluids will be modeled as micron-sized ferrous particles in a Newtonian carrier fluid,
subjected to magnetic forces. The models in this research reduce to forms similar to Bingham’s model in a simple shear flow, but with coefficients which arise from fundamental electromagnetic considerations and microstructural features such as geometrical, magnetic and mechanical characterization of the particles, quantities measured primitively from the carrier fluid, magnetic field and temperature.

1.4 Outline of the dissertation

Chapter 1 is a general description of the research background and literature review of carbon nanofiber suspensions, carbon nanofiber/polystyrene melt composites, fiber orientation, and MR fluids. The research motivations are stated and the objectives of the research work are declared. Chapter 2 and Chapter 3 describe the experimental apparatus, sample preparations, experiments performed, and the constitutive models (elastic dumbbell model for CNF/PS suspensions and rigid rod model for CNF/PS melt composites) developed to predict the system behavior of the carbon nanofiber/polystyrene suspensions and carbon nanofiber/polystyrene melt composites at steady state, respectively. Chapter 4 focuses on experimental measurements and model predictions of the start-up simple shear flow rheology of the carbon nanofiber/polystyrene melt composites. We also discuss the experimental measurements of 3-D fiber orientation in Chapter 4. The changes of fiber orientation with respect to time at each shear rate during the start-up period are predicted by the constitutive models. Based on the success of developing microstructurally based models for carbon nanofiber/polystyrene suspensions in Chapter 2, the 3-D fundamental models of Magnetorheological Fluids is presented in Chapter 5.
Figure 1.1. Coordinate system of a particle

Figure 1.2. Dumbbell Model
Figure 1.3. OSU’s Telerobotic MICT Surgical System.
CHAPTER 2

RHEOLOGY OF CARBON NANOFIBER SUSPENSIONS

2.1 Introduction

Carbon nanotubes have been of great interest since their discovery in 1991 by Iijima\textsuperscript{56}, due to their excellent electrical, mechanical, and thermal properties. Intensive studies have been conducted on polymer/carbon nanotube composites and some exciting results have been found\textsuperscript{57-66}. However, due to their limited availability and hence the prohibitive price, it seems unlikely that carbon nanotubes will be widely used in the near future. As an alternative, vapor-grown carbon nanofibers, which have average diameters of about 100 to 200 nm, can be used to produce polymer reinforced nanocomposites. Since nanofibers and nanotubes have similar structures and physical properties, polymer composites filled with carbon nanofibers may have similar properties as those filled with carbon nanotubes. Therefore, studies on the nanofibers will directly facilitate their applications. Moreover, these nanofibers can be produced in large quantity at an affordable price, making them amenable for industrial scale applications.
With their extraordinary physical properties, the carbon nanofibers are promising candidates for reinforcing or conducting fillers. Kennel et al.\textsuperscript{67} reported that although the structure of carbon nanofibers is not as regular as that of nanotubes, and hence nanofibers have relatively inferior mechanical properties, yet they still possess impressive mechanical characteristics\textsuperscript{62-66}. The nanofibers have graphene edge planes, which improve physical bonding with other materials. This property may lead to successful applications in the development of polymer/carbon nanofiber composites. Carbon nanofibers used as reinforcement and conducting agents in polymer matrices have been studied by Lozano and Barrera\textsuperscript{1} and Lozano et al.\textsuperscript{68}. They compounded up to 15wt% carbon nanofiber into polypropylene using a twin-screw extruder and discovered that agglomerates are eliminated by the high shear in the extruder. The tensile strength of the composite remained unaltered from polystyrene, but the dynamic modulus increased 350%. In addition, a percolation threshold for electrical conduction of 9-18% was found. Thermal behavior was not significantly changed due to the chemical treatment of the nanofibers. Ma et al.\textsuperscript{2} studied Poly (ethylene terephthalate) resin compounded with 5wt% carbon nanofiber (Pyrograf III) using different methods, including ball milling, high shear mixing in the melt, and twin screw extruding. They found no significant reinforcement in the tensile strength but considerable increase in compressive strength and torsional modulus.

In contrast to the abundant literature on polymer/carbon nanotube composites, far less work has been published for polymer/carbon nanofiber composites\textsuperscript{62-66}. Further, most of the published works concentrate on the mechanical and electrical properties; none concentrate on the rheology of carbon nanofiber suspensions in low viscosity solvents.
The objective of this research is to study the morphology and rheology of nanofibers suspended in a Newtonian solvent. A Newtonian solvent has been selected so that any non-Newtonian properties of the suspensions can be attributed solely to the addition of the carbon nanofibers (CNFs). The CNFs as delivered have a strong tendency to clump into mm-sized agglomerates. Different methods are employed to disperse the large agglomerates, and the resulting dispersion effects and the rheology of the suspensions are carefully studied.

2.2 Materials and Preparation of Suspensions

The CNFs used in this study was Pyrograf® III (type PR-24-PS) made by Applied Sciences, Inc. It is produced by decomposing organic vapors at elevated temperature in the presence of metal catalysts. These nanofibers have a tree-ring structure with a hollow core. The nanofibers obtained were not pelletized and were in powdered form. Large agglomerates of a centimeter in diameter were observed, but most of the agglomerates were less than 1 mm in diameter. The as-received powders were sieved through #60 standard sieve (mesh size 0.25mm) before preparing suspensions.

In order to improve dispersion, the surfaces of some of the nanofibers were treated using a technique similar to that described by Esumi et al. Acidic functional groups were added to the nanofiber surface so that the nanofibers would be more chemically compatible with hydrophilic solvents. 10g of the nanofiber was refluxed with 200 ml of a concentrated sulfuric acid-nitric acid mixture (1:3 by volume of 96.1% sulfuric acid and 70.4% nitric acid). The reaction mixture was heated at a constant temperature of 140°C for one hour. A combination of two water condensers in series, additionally cooled by ice, was used to cool the acid vapors. After cooling the reaction
mixture, it was diluted with water. Exploiting the difference of densities between the acid mixture and the aqueous fiber solution, centrifugation of the mixture was used to remove a greater part of the acid as supernatant. The fibers were neutralized further by repeated dilution with water and centrifugation. However, centrifugation became ineffective once the fiber-water solution density was comparable to the acidic mixture. The nanofibers were washed with more water to neutralize the any remaining acid and vacuum filtered (polycarbonate membrane, 5 µm pore diameter). Finally, after removing the residue from the filter membrane, the resultant treated nanofibers were dried in vacuum at 80°C. About 55-60% yield in the treatment was obtained, with the only losses occurring during the filtration process, wherein the polycarbonate filter was unable to retain some of the smaller fibers.

The solvent used to prepare nanofiber suspensions was a 90wt% glycerol in water solution made by mixing 99.5wt% pure glycerol with distilled water. Both sieved untreated and treated carbon nanofibers were used to prepare suspensions, so that the effects of treatment on the dispersion and rheology could be studied.

The sieved untreated nanofibers were weighed and added into the solvent and then the suspensions were sonicated using an ultrasonic bath (100W) for 3 hours. The sonication time was selected based on previous experience that longer sonication would not provide better dispersion. Six untreated sonicated nanofiber suspension samples were prepared with concentration varying from 0.5wt% to 5wt%. Six sonicated suspensions of treated nanofibers were prepared using the same procedures. A 1wt% suspension sample was made by mixing treated nanofibers with the solvent with mechanical stirring for 36 hours without sonication. In total, 13 suspensions were prepared, six untreated sonicated
suspensions of different concentrations from 0.5wt% to 5wt%, six treated sonicated suspensions in the same concentrations, and one treated unsonicated suspension of 1wt%. The size of all the samples for shear rheology was about 40 ml. The sample size for extensional rheology was about 300 ml.

2.3 Morphological Characterization

The suspension morphology was characterized using a Philips XL 30 scanning electron microscope equipped with secondary and back-scatter detectors operating at 30 kV. Magnifications were in the range of 10,000 to 12,000 times. For the as-received nanofibers, conductive glue was used to fix the powder to the SEM stub. For the suspensions, the SEM samples were prepared using the following procedure: One drop of the suspension from the 1wt% suspensions was diluted with about 2ml distilled water. Care was taken so that this drop contained fibers that were representative of the whole sample. Then several drops of the diluted suspensions were dropped onto aluminum SEM stubs and were left in open air for overnight. As the liquid on the stubs contained glycerol, the stubs were put in vacuum oven at 60°C for an hour to completely dry. A thin film of dried nanofibers was formed on each stub surface. The dilution of the suspensions and the drying speed were carefully controlled such that an optimum film thickness of nanofibers was formed. If the suspensions were not sufficiently diluted then the dried film contained too many nanofibers and no individual nanofibers could be identified. Too high a drying rate caused the liquid to contract and eventually form a small dried spot on the stub in which the nanofiber were too tightly compacted to be clearly observed. The stubs were then sputter coated with platinum at 18mA for 60 seconds using a Pelco Model 3 sputter coater. Although carbon nanofibers are conductive, the sputtered SEM
samples gave sharper images. The dispersion of nanofibers in the suspensions was also examined using optical microscopes, with the magnification in the range of 4 to 400 times.

The as-received nanofibers, purified by the supplier, were found using scanning electron microscopy to contain highly entangled aggregates but no visible impurities (Figure 2.1a and Figure 2.2a). Almost all the individual nanofibers were not straight, forming clumps with a characteristic size of 20 by 50 µm. These clumps were often clustered to form larger weakly bound agglomerates with diameters up to millimeters or even centimeters. The diameter of the nanofibers was rather uniform, in the range of 100-200 nm. Nanofiber length, however, was in a wide range from several µm up to 100 µm. As the nanofibers were so entangled, it was usually difficult to find both ends of a single nanofiber, so that an accurate distribution of the length was impossible to obtain. After analyzing many SEM micrographs, it was estimated that more than half of the as-received nanofibers were about 5-20 µm in length.

The dispersion of carbon nanofibers and nanotubes in any solvent is known to be difficult. Therefore it is important to explore the effect of dispersion of the suspension on rheological properties. Figure 2.1 and Figure 2.2 show the difference in dispersion between the as-received nanofibers and the suspensions prepared by the three different methods discussed in section II. The untreated sonicated sample (Figure 2.1b) contains many nanofiber clumps and some partially dispersed individual nanofibers, but no large agglomerates. The representative size of the clumps is 20 by 40 µm, similar to those in the as-received nanofibers. These clumps either directly touch each other, or more often are connected by the dispersed nanofibers. We conclude that the sonication disintegrates
most of the large agglomerates and some of the clumps. Both treated unsonicated suspensions (Figure 2.1c) and treated sonicated suspensions (Figure 2.1d) contain no nanofiber clumps. Some individual fibers and small clusters can be seen in the treated unsonicated suspension while there are few clusters in the treated sonicated suspension. This clearly verifies that the acid treatment greatly improves the dispersion of the nanofibers.

More details can be seen in the higher magnification of Figure 2.2. In the untreated sonicated suspension (Figure 2.2b), the length of the individual nanofibers is observed to be about 5-15 µm. Comparing with the as-received nanofibers (Figure 2.2a), no obvious fiber shortening due to sonication has been found. The treated unsonicated suspension (Figure 2.2c) contains more uniformly dispersed fibers than that in the untreated sonicated suspension (Figure 2.2b). The long fibers still entangle with each other but they are not as tightly compacted. In addition, there are some short fibers with the length of less than 1 µm. It is deduced that the acid treatment not only separates the existing less-than-1-µm fibers from long fibers, but also shortens some long fibers and thus creates more short fibers. When the treated fibers are sonicated using an ultrasonic bath, it is apparent that the suspension contains almost exclusively less-than-5-µm short fibers (Figure 2.2d). Long fibers with length of 5-10 µm exist but they are much less in number. In this case, the sonication greatly shortens the nanofibers.
The strong acid treatment of a carbon surface is not new. Herrick\textsuperscript{70} and Herrick et al.\textsuperscript{71} oxidized the surface of carbon fibers using nitric acid and observed increased surface area and surface functionality. Recently, Esumi et al.\textsuperscript{69} used a mixture of concentrated nitric acid and sulfuric acid to treat carbon nanotubes in order to obtain a better dispersion. Increased dispersion has been attributed to the fact that acidic groups were added to the nanotubes and they readily disperse in polar solvents and form well-dispersed suspensions. Esumi et al did not report any damage to the nanotubes.

Mechanical damage of carbon nanotubes caused by ultrasound was first reported by Lu et al.\textsuperscript{72}. They observed that the ultrasound caused bending and buckling, and with longer time of sonication, the outer layer of the nanotubes were stripped off to form amorphous graphite. More powerful ultrasound and long sonication time cause more damage to the nanotubes. However, the damage to the carbon nanofibers caused by the ultrasonication bath in this study is different. The nanofibers are shortened while the diameters remain unchanged. The nanofiber surface is still smooth with no amorphous graphite observed in the sample. Further analysis of the as-received nanofibers at higher magnification shows that many contain bends and other curvatures, and some have bamboo-like structures with the distance between joints of about 500 nm. Most of the nanofibers are not perfectly straight, leading to structurally weak points. These weak points were attacked by the strong acid and thus become weaker and subsequent sonication caused the nanofibers to break. Liu et al.\textsuperscript{73} sonicated single-walled carbon nanotubes in the presence of a mixture of concentrated sulfuric and nitric acid (3:1) and reduced the tubes from “endless” to several hundred nanometers.
The analysis clearly shows that sonication of the as-received nanofibers does not lead to fiber damage. After being treated with strong acid, these nanofibers become much weaker and the subsequent sonication breaks most of the nanofibers. The acid treatment followed by sonication not only opens the nanofiber clumps and disperses individual fibers, but also breaks most of them.

It should be noted that in preparing the SEM samples of the suspensions, it is difficult to guarantee that in each micrograph there are the same amount of nanofibers. Even if same amount of fibers were put on the SEM stubs, it was difficult to ensure the formation of a homogeneous film of uniform thickness. The SEM micrographs are employed in this study to reveal the important features of nanofiber length, radius, and the conclusions discussed above based not only on the SEM micrographs shown in Figure 2.1 and Figure 2.2, but also on hundreds of additional SEM micrographs.

Optical microscopy was used to study the dispersion on a larger scale. Figure 2.3 shows the micrographs for the untreated sonicated suspension and treated sonicated suspension. In the treated sonicated suspension (Figure 2.3b), the nanofibers are uniformly dispersed with only a few small clumps visible. These observations reflect the same trends as the SEM micrographs. Although the individual nanofibers are too small to be seen with optical microscopy, at this magnification (100x), in Figure 2.3a (untreated sonicated suspensions) we observe unbroken nanofiber clumps and clouds with partially dispersed nanofibers.

2.4 Rheological Characterization

Shear rheological measurements were made using a Rheometrics Fluid Spectrometer (RFS II) from Rheometrics, Inc. A Couette geometry (bob diameter 32mm,
bob length 33.3mm, cup diameter 34mm) with water bath was used for all measurements. For steady shear viscosity, the shear rate range was from 0.02 to 500s\(^{-1}\). For small amplitude oscillatory shear, the strain sweep was done first to determine the linear viscoelastic regime. The frequency was from 0.1 to 15 Hz. The first normal stress difference was measured using a Rheometrics Mechanical Spectrometer (RMS) 800. Cone and plate (50mm diameter, 0.04 radian cone angle) geometry was used. Unless otherwise specified, all the measurements were done at 25°C.

The extensional rheology was characterized using the Rheometrics RFX extensional rheometer. A 250ml suspension was put in the test beaker and jets with different diameters were used to cover the extensional rate from 2 to 2000s\(^{-1}\); 1mm diameter jets were used for extensional rate from 100 to 2000s\(^{-1}\), and 2mm jets were for 2 to 200s\(^{-1}\). The separation distance is the same as the diameter of the jets.

2.4.1 Steady state shear measurements

The steady state shear viscosity measurements of the six untreated sonicated samples are plotted in Figure 2.4a. The viscosity of the suspensions increases monotonically with the nanofiber concentration by 3 orders of magnitude at low shear rates when concentration changes from 0.5wt% to 5wt%. The suspensions exhibit strong shear thinning behavior. For example, the low shear viscosity of 5wt% untreated sonicated suspensions increases 3 orders of magnitude and the high shear viscosity increases by a factor of 8. Beyond 5wt% we found that the suspensions are too viscous to be effectively mixed by sonication.
Figure 2.6a displays the steady state shear viscosity for four treated sonicated samples. These samples show almost constant viscosity over a wide range of shear rates, increasing with the nanofiber concentration. The viscosity of the 5wt% treated sonicated suspensions is less than twice as much as that of solvent. The amount of the viscosity increases was much less than that of the untreated sonicated suspensions.

As the solvent is Newtonian, all non-Newtonian behavior of the suspensions is due to the addition of the nanofibers. We conjecture that in the untreated sonicated suspensions, the nanofiber clumps and the dispersed individual fibers entangle with each other, causing the viscosity to increase. The entanglement is relatively strong at small shear rates and becomes weaker at high shear rates due to alignment of some fibers to the flow. Hence the untreated sonicated suspension exhibits shear thinning. Ganani and Powell\textsuperscript{4} proposed a mechanism that the shear exerted on some parts of the suspensions was higher than other parts, and this might lead to a drift of low shear Newtonian plateau to lower shear rates. This non-uniform shear theory works as well for the untreated nanofibers suspensions. The shear stress is transported through both the continuous solvent phase as well as the nanofiber networks, and both mechanisms may have comparable strengths. However, the networks may break and become aligned to the flow under stress, so the total stress cannot be transported uniformly, leading to shear thinning in the suspensions.

By plotting the shear viscosity versus stress, the apparent yield stress of the suspensions can be examined. Flocculated suspensions are known to have yield stresses at high particle loadings when interactions between the particles are high enough to form continuous 3-D network structures. The untreated sonicated nanofiber suspensions in this
study are of this fluid type. They show no zero-shear viscosity but an apparent yield stress. Figure 2.5 shows that the apparent yield stress starts to become obvious when the nanofiber loading is 1wt%. At 2, 3, 4, and 5wt% the suspensions have clearly defined yield stresses of 1, 3, 6, and 9 Pa respectively. Therefore it is reasonable to conclude here that the interactions between the nanofibers are large enough in most of the untreated sonicated suspensions such that continuous 3-D network structures exist and generate yield stresses.

We attempted to measure the first normal stress coefficient for all of the suspensions, but the normal force was too small for the rheometer to detect. Start up of steady shear tests were performed and the shear stress reached steady state almost immediately after the onset of the shear, showing little time dependent behavior. Results from thixotropic loop experiments revealed no obvious thixotropic behavior.

For the treated sonicated suspensions, the situations are different than with the untreated sonicated suspensions. As the treated sonicated suspensions contain no nanofiber clumps, they have more individual particles in a unit volume. One may expect that more individual particles will have more surface area, so that the viscosity would be higher than the untreated sonicated suspensions if there were no interactions between particles. However, this is not the case. As analyzed in the morphology section, the major differences between the treated sonicated and untreated sonicated suspensions are that the latter contain nanofiber clumps and partially dispersed nanofibers which form network interactions. The interactions are so strong that they overrule the effects from the increase of the surface area. Further proof of the interaction is described in the linear viscoelasticity section. The treated sonicated suspensions are mainly composed of sub-
micron nanofibers and the average aspect ratio is less than 10. As these short fibers are also well dispersed due to the effect of acid treatment, the interactions between them are small even at high concentrations.

As seen from the SEM micrographs (Figure 2.1 and Figure 2.2), although the treated unsonicated suspensions contain many more long (5-20μm) nanofibers and therefore more entanglements between the nanofibers than do the treated sonicated suspensions, the effects of the entanglements in treated unsonicated suspensions to the viscosity can be neglected at low nanofiber concentrations. Experimentally, we observe that the treated sonicated and treated unsonicated suspensions at 1wt% exhibit about the same viscosity to within experimental error (Figure 2.7a). Figure 2.7a also shows that the viscosity of both suspensions have little strain rate dependence. The nearly Newtonian viscosity may be due to the small aspect ratio which reduces shear rate dependence of viscosity. Brenner\textsuperscript{74} showed that for suspensions of oblate and prolate spheroids the shear thinning behavior diminished when the aspect ratio decreased to unity. As a result, the traditional theory for the dilute suspensions might be a good approximation.

Many researchers have found that particle size does not necessarily affect the viscosity of suspensions. For spherical filler systems, Krieger’s\textsuperscript{75} investigation of monodisperse suspensions shows that the complex viscosity is not a function of the size of the filler. This result holds even for concentrated systems\textsuperscript{76}. Choi and Krieger\textsuperscript{77} studied sterically stabilized monodisperse systems and found that the relative viscosity is independent of the particle size. Therefore introducing more surface area does not necessarily increase the viscosity. Miles et al.\textsuperscript{78} studied the apparent viscosities of glass fiber/sucrose suspensions using a capillary viscometer and found that the viscosity is
dependent on the fiber volume fraction but is independent of the fiber length and shear rate. Some semi-empirical models predict higher viscosity with larger fiber aspect ratio and it might be the result of increased fiber interactions.

For dilute suspensions, the Einstein equation can be used to predict the viscosity. Bachelor\textsuperscript{79} modified the equation by adding a second order correction to account for hydrodynamic interactions,

\[ \frac{\eta}{\eta_s} = 1 + 2.5\phi + 6.2\phi^2 \]  \hspace{1cm} (2.1)

In equation (2.1), \( \eta \) and \( \eta_s \) are the viscosities of suspension and the solvent, respectively, and \( \phi \) is volume fraction of the filler. Krieger and Dougherty\textsuperscript{80} put forward a semi-empirical equation that can be used for concentrated suspensions:

\[ \frac{\eta}{\eta_s} = \left( \frac{1}{1 - \frac{\phi}{\phi_m}} \right)^{\phi/[\eta]} \]  \hspace{1cm} (2.2)

where \( \phi_m \) is the maximum packing fraction and \([\eta]\) is the intrinsic viscosity. Other equations\textsuperscript{81} also utilize \( \phi_m \), which takes values between 0.5 and 0.75 for monodispersed hard spheres. The relative viscosities of treated and untreated suspensions at high shear range (100s\(^{-1}\)) are plotted as a function of nanofiber volume fractions in Figure 2.8. It is clear that the Einstein and Bachelor equations are not able to accurately predict the viscosities. This may be due to interactions between some long fibers in the suspensions neglected in equation (2.1). When the Krieger-Dougherty model is used to fit the data, satisfactory fitting is obtained with the \( \phi_m=0.2, [\eta]=12 \) for treated sonicated suspensions, and \( \phi_m=0.05, [\eta]=30 \) for untreated sonicated suspensions. These \( \phi_m \) values are low as compared to 0.5-0.75 for spheres, and hence lose the original physical meanings as a maximum packing factor. Giesekus\textsuperscript{82} found that \( \phi_m \) ranges from 0.2 to 0.4 for glass fibers.
Harzallah and Dupuis\textsuperscript{83} studied the rheology of TiO\textsubscript{2} particles in polymer solutions and obtained low values of $\phi_m$ ranging from 0.07 to 0.22 from fitting the experimental data to the Krieger-Dougherty equation (equation (2.2)). Although the TiO\textsubscript{2} particles formed irregular shape of clusters, the authors did not relate the morphology to the low $\phi_m$ nor gave other explanations. Here we propose that this low $\phi_m$ is the result of particle interactions and aspect ratio.

### 2.4.2 Small amplitude oscillatory shear measurements

The linear viscoelasticity of each suspension was studied to investigate the effect of microstructures formed by the carbon nanofibers. Strain sweep measurements were performed to determine the extent of the linear viscoelastic regime. For the untreated sonicated suspensions, it was found that the maximum strain limit for the linear regime decreases with the increase of nanofiber loading, from 10\% strain at 1wt\% loading to 0.1\% strain at 5wt\% loading. This phenomenon was also observed by Aral and Kalyon\textsuperscript{84} in 40 vol\% spherical suspensions. From results of flow visualization, they suggested that this is due to internal slip of the particles. This idea is similar to the non-uniform shear theory proposed by Ganani and Powell\textsuperscript{4} to explain shear thinning. Figure 2.9a,b show the elastic modulus $G'$ and the viscous modulus $G''$ versus the dynamic frequency. Both moduli increase with more nanofiber loading, and $G'$ becomes higher than $G''$ at all frequencies studied when the suspension contains 3wt\% or more. The fact that $G'$ is greater than $G''$ is an indication of solidlike behavior, as defined in rheology textbooks (see, for example, Macosko\textsuperscript{85}). Further, the low-frequency plateau of the moduli in $G'$ is also a sign of solidlike behavior. A possible explanation for this solidlike behavior is that the nanofibers form a network microstructure. This microstructure can be easily broken.
down by deformation and rebuilt quickly when the deformation is removed. Therefore the suspensions are shear thinning but not thixotropic. At low concentrations, the microstructure is weak so the solvent dominates the rheology and the suspensions still show liquidlike behavior. Beyond a critical concentration, which is 3 wt% for the system studied here, the network structure becomes stronger and hence elastic solidlike behavior is observed. This type of microstructure is verified from the morphology study, which shows that the dispersed nanofibers are entangled with each other and also with the nanofiber clumps.

Non-terminal low-frequency rheological behavior has been widely observed in polymer/nanoclay systems, ordered block copolymers and smectic liquid crystalline small molecules. Conventional filled polymer composites also exhibit this behavior and the accepted reason is that the filler and the polymer strongly interact such that large domains are formed. Larson studied the smectic liquid crystals and suggested that the non-terminal low-frequency rheological behavior is due to the long-range domain structure and the presence of defects. Krishnamoorti and Giannelis argued that in the end-tethered polymer layered silicate nanocomposites, the presence of silicate layers and the lack of complete relaxation of the confined polymer chains cause the solidlike response at low frequencies. Solomon’s results from the polypropylene/clay hybrid materials suggested that the low frequency plateau was the result of network structure and not the orientational relaxation of individual platelets.

Interestingly, the low-frequency plateau in $G'$ presented in the untreated sonicated suspensions, also appears in the treated sonicated suspensions (Figure 2.10a). There is a wide spread of elastic modulus at low frequencies while the elastic modulus $G'$ becomes
less dependent on the fiber suspension at high frequencies. The elastic modulus generally increases with fiber loading. The viscous modulus $G''$ monotonically increases with the fiber concentration at all frequencies (Figure 2.11a). As there are no nanofiber clumps and many of the fibers have been shortened to less than $1\mu$m, the above-mentioned network structure should not exist. From the size of the particles, it is suggested the Brownian motion and colloidal forces come into play. The Brownian effects become important when the particle size is less than $500\text{nm}^{91}$. A measure of the Brownian effect is the rotary diffusivity ($D_r$), which is the rate at which a particle reorients through Brownian motion. Using the formula in Larson$^{92}$, the rotary diffusivity of the treated suspensions is calculated to be about $0.04\text{s}^{-1}$. When the external deformation rate is small, the Brownian motion tends to make the suspensions liquid-like and the colloidal forces tend to make the suspensions solid-like. Since acid groups are added to the nanofibers during the surface treatment, electrostatic forces exist in the suspensions. That act like springs and cause elastic effects$^{85}$. The Brownian and colloidal forces compete with each other, and at low frequencies the latter dominates, causing the plateau in the elastic modulus.

The untreated sonicated nanofiber suspensions were found to roughly obey the Cox-Merz rule, especially at high nanofiber concentrations. The empirical Cox-Merz rule states that the complex viscosity ($\eta^*$) versus the dynamic frequency obtained from small amplitude oscillatory shear is numerically equal to the steady shear viscosity ($\eta$) versus the shear rate. Although there is no general explanation for such a relationship, it is widely accepted and used for isotropic polymeric solutions and polymer melts. Figure 2.16 shows that at $1\text{wt\%}$, the Cox-Merz rule holds well except for the low shear region
(less than 5s\(^{-1}\)). However, for 5wt% suspensions, the complex viscosity is about an order of magnitude higher than the steady shear viscosity but the degree of shear thinning is about the same. Therefore, the Cox-Merz rule holds only for low nanofiber concentration suspensions. Kinloch et al.\(^9\) showed that for concentrated aqueous nanotube dispersions, complex viscosity was about 5 orders of magnitude greater than the steady shear viscosity.

### 2.4.3 Measurements of temperature effects

Temperature effects on the steady shear and relative viscosities of 2wt% untreated sonicated suspensions are plotted in Figure 2.12a-d and Figure 2.13a-d. The steady shear viscosity decreases as the temperature increases over the entire range of shear rates (Figure 2.12a). The difference between viscosities at different temperatures is smaller at low shear rates than that at high shear rates. Figure 2.12c shows the relative viscosity (ratio of suspension viscosity to solvent viscosity) as a function of shear rate at different temperatures. There is a clear trend that the relative viscosity is higher at lower temperatures except for the first few low shear rate points at 35°C and 45°C, implying that the contribution of the nanofibers to the viscosity of the suspension is relatively larger than that of solvent at higher temperatures. The solvent viscosity decreases rapidly while the interactions between the nanofibers might remain the same, making the latter more important. At high shear rates, the relative viscosities at all temperatures plateau at the same value. This suggests that the microstructures are rather weak and can be broken down to approximately the same extent at high shear rates. High shear rate viscosities (at 200s\(^{-1}\)) of the suspension and the solvent as a function of temperature are plotted in the Arrhenius plot in Figure 2.13c. The fact that the two curves are almost parallel indicates
that the solvent dominates the high shear viscosity. This is reasonable, as the microstructures have been broken down by the shear.

The apparent yield stress $\sigma_{ay}$ decreases as temperature increases (Figure 2.13a), implying that the strength of network microstructures comes from both particle-particle contact/entanglement and particle-solvent interaction. When temperature increases, while the particle-particle contact presumably stays the same, the particle-solvent interaction becomes weaker due to the decreased solvent viscosity, causing $\sigma_{ay}$ to decrease. The loss tangent $G''/G'$ decreases from above 1 to about 0.2 with increasing temperature (Figure 2.13d) and this is another indication that the suspension becomes more solidlike at higher temperatures.

2.4.4 Extensional rheology

The results of the extensional rheology of 1wt% untreated sonicated suspension are shown in Figure 2.14. The suspension exhibits extension rate thinning behavior over the range of extension rate examined (the apparent extensional viscosity decreases with increasing extension rate). It is clear that the untreated nanofibers cause a dramatic change in the extensional rheology. The extension rate thinning is not surprising because the breakup of the network structure decreases the viscosity, a mechanism similar to the shear thinning. The usual extension thickening (also called strain hardening) of polymer melts is a phenomenon that at a certain constant extension rate, the transient extensional viscosity increases with strain. If steady state can be reached, even some polymer melts exhibit extension rate thinning. Extension rate thickening is also seen in the literature. Eastman et al. found that the aqueous solutions of polyvinylpyrrolidone (PVP) containing sodium dodecylsulphate (SDS) were extension rate thickening and they
suggested that it was due to the increase in the dimensions of PVP/SDS complexes because of the repulsion between SDS aggregates.

The comparison of extensional and shear viscosity is through the calculation of the Trouton ratio, \( Tr \), defined as

\[
Tr = \frac{\eta_e(\dot{\varepsilon})}{\eta(\dot{\gamma})},
\]  

(2.3)

where \( \eta_e \) is the extensional viscosity at the extensional rate of \( \dot{\varepsilon} \) and \( \eta \) is the steady shear viscosity at the shear rate of \( \dot{\gamma} \). Jones et al.\(^96\) proposed that \( \dot{\gamma} = \sqrt{3}\dot{\varepsilon} \) should be used to calculate the \( Tr \). This method has been adopted by Meadows\(^97\) and Viebke et al.\(^98\). The \( Tr \) has been theoretically predicted to be 3 for Newtonian fluids and some researchers observed this value experimentally\(^99\)-\(^100\). However, Eastman\(^95\) reported that the \( Tr \) for Newtonian fluid was about 4.3 using the Rheometrics RFX. The observation for the 90wt% glycerol water solution is about 4.0. The deviation from the theoretical value of 3 may be due to the inertia of the fluid, when being pulled into or pushed from the opposing jets. The \( Tr \) of 1wt% untreated sonicated suspension calculated by both standard method (\( \dot{\gamma} = \dot{\varepsilon} \)) and Jones method (\( \dot{\gamma} = \sqrt{3}\dot{\varepsilon} \)) is plotted in Figure 2.15. The \( Tr \) decreases with extension rate from 80 using Jones method or 50 using standard method to 10, which is the same using either method. For Newtonian fluids, the Trouton ratio is 3, which has been observed experimentally and proved theoretically. The large \( Tr \) as seen here indicates strong non-Newtonian behavior. Bachelor\(^7\) studied the stress in a non-dilute suspension of elongated particles subjected to extensional flow. He found that when the average lateral distance of particles was between the diameter and length of the elongated particle, the extensional viscosity was sensitive to the length, due to the hydrodynamic effects between the aligned particles. The \( Tr \) is calculated using
Bachelor’s equation\textsuperscript{101} to vary from 5 to 35 for different fiber lengths in the untreated sonicated suspension, which falls in the range of experimental results. This implies that the hydrodynamic effects play an important role in the extensional flow. However, Bachelor’s equation cannot predict the extension rate thinning behavior. We propose that the extension rate thinning behavior may be the results of physical contacts of the nanofibers and the formation of network microstructure. Under extensional stress, the network breaks down and the nanofibers orient to the flow and thus cause the viscosity to decrease. In other words, it is due to the yield stress of the suspension. Cohu and Magnin\textsuperscript{102} studied fully formulated coil-coating paints which are dispersions of mineral or organic pigments in organic solvents with polymeric binders. They found that these paints were extension rate thinning with decreasing $Tr$ from about 20-30 to the Newtonian range 3-7. They attributed this observation to the existence of yield stress of the paints. Anklam et al.\textsuperscript{103} made a similar observation with water-in-oil emulsions. They argued that the yield stress of the emulsions dominates the force on the nozzle arm and concluded that fluids with high yield stress should not be measured using opposed nozzle rheometers.

Extension rate thinning has also been found by Viebke et al.\textsuperscript{98} in their concentrated latex dispersions. They also found that the $Tr$ was independent of the extension rate. Meadows et al.\textsuperscript{97} found that hydroxyethylcellulose solutions exhibits slight strain thinning and that it maybe attributed to the “stiffer” conformation of the cellulose polymer and thus hindered the stretch of the coils. Another possible mechanism proposed by the authors is that the breakup of overlapped coils offsets the strain-hardening coil stretch of individual polymer molecules. Kapoor et al.\textsuperscript{104} found that the
waxy corn starch solution was also extension rate thinning and they cited Dontula et al.’s argument that the instrument effects on the measured extensional viscosities using opposed nozzle rheometers are significant, hence only limited conclusion could be drawn from the data.

In order to further probe the particle interactions, the stability of the suspension after long time stretching at high extension rate was examined for 1wt% untreated sonicated suspension. After the extensional viscosity measurement was done for the fresh suspension using 2mm jets, the sample was then stretched at 600s⁻¹ extension rate for 13 hours. The “mix-cycle” function provided by the rheometer was utilized to pull the liquid into the jets and then push them out. In each mix-cycle, 40ml suspension was stretched. In the 13 hours, the total amount of suspensions that had been stretched was about 81250 ml, which was equivalent to 325 times of the amount of the sample. The extensional viscosity was measured again and was found to be identical to the fresh sample data. Then 1mm jets were used and the viscosity was measured at higher extensional rate. After that, the sample was further stretched at 4000s⁻¹ extensional rate for 2 hours, which is equivalent to 20 times of the amount of the sample, and the measured extensional viscosity did not change. Therefore it is concluded that the untreated sonicated sample is very stable under extension. The morphology of the fresh and stretched suspension was studied using optical microscopy, and the results showed no difference. The high extension rate did not change the length or interactions between the nanofibers.
2.5 Modeling

2.5.1 Kinetic Theory Models

In this chapter we develop models for the carbon nanofiber suspensions from SEM measurements of their morphology, and through these models deduce the bulk rheological properties of the composite systems from the microstructural measurements. We chose to model the nanofiber suspensions with kinetic theory-based elastic and rigid dumbbell models\textsuperscript{22,92,106,107}.

Dumbbell models are of appropriate complexity for a first attempt at microstructurally based modeling of the treated sonicated nanofiber suspensions. In the dumbbell models the carbon nanofiber suspended in a Newtonian solvent is idealized as a pair of beads joined by either a massless elastic spring connector (elastic dumbbell) or massless rigid connector (rigid dumbbell) with orientation along the vector $p$. The dumbbell models assume the solution is dilute, i.e. the dumbbells are assumed to move independently. Such models are customarily applied to polymer solutions, where the dumbbells idealize the polymer molecules; here we investigate their ability to describe nanofiber suspensions. Importantly, in the model all material coefficients in the governing equations are specified directly in terms of separate, independent primitive measurements of the constituents (the characteristic length and radius of the nanofibers measured in the morphology study, density of the nanofibers, and density and viscosity of the solvent), as well as the mass concentration of the fibers in the suspension and absolute temperature.

For the isolated nanofiber in the glycerol/water solvent, the two salient physical features of the particle/solvent interaction are the force on the fiber from the solvent,
distributed over the surface of the fiber, and the possible elasticity of the fiber (its ability
to stretch or bend under load and then return to its original configuration when the load is
removed). The dumbbell as applied here is an idealization of the fiber in which the
distributed load on the fiber and mass of the fiber are localized in the two beads, and the
elasticity of the fiber both in stretching or bending, if present, is modeled as a linear
spring. We consider the spring in the elastic dumbbell to be Hookean, i.e. the tension in
the spring is proportional to the bead separation. The relation between the length and
radius of the nanofibers and connector length and bead radius of their dumbbell
idealization must be calibrated.

The forces assumed acting on the beads are Brownian forces, intramolecular force,
and hydrodynamic drag force; external forces such as gravitational and electrical forces
are neglected. For the elastic dumbbell model, the intramolecular force is modeled as
spring force acting on the bead. For the rigid dumbbell model, the intramolecular force is
the constraint force in the rigid rod. Hydrodynamic drag force $F^{(h)}$ is the force of
resistance experienced by the bead as it moves through the solution:

$$F^{(h)} = \zeta \cdot \left[ \left[ \dot{r}_b \right] - \left( \mathbf{v} + \mathbf{v}' \right) \right],$$

(2.4)

where $\left[ \dot{r}_b \right]$ is the average bead velocity, $\mathbf{v}$ the imposed homogeneous flow field of the
solvent at the bead, $\mathbf{v}'$ the perturbation of the flow field due to the motion of the bead at
the other end of the dumbbell, and $\zeta$ the friction tensor.

We pursue six different dumbbell models of the nanofiber suspensions:

- the elastic dumbbell with isotropic hydrodynamic drag (friction tensor $\zeta = \zeta I$), as
given by Stokes’s law with friction coefficient $\zeta = 6\pi \eta_r r$, where $\eta_r$ is the solvent
viscosity and \( r \) the bead radius) without hydrodynamic interaction (\( v' \) zero in equations(2.4))\(^{22,92,106,107}\);

- the elastic dumbbell with isotropic hydrodynamic drag and with hydrodynamic interaction (\( v' \) nonzero in equations(2.4))\(^{22,108}\);

- the elastic dumbbell without hydrodynamic interaction but with anisotropic hydrodynamic drag (\( \zeta^{-1} = \xi^{-1} \left( I - \frac{\alpha}{nkT} T^p \right) \), where \( T^p \) is the particle contribution to the stress, \( n \) the number of fibers per unit volume, \( k = 1.3807 \times 10^{-23} \, J/K \) the Boltzmann constant, \( T \) absolute temperature, and \( \alpha \) the mobility factor)\(^{22,106}\);

- the elastic dumbbell with anisotropic hydrodynamic drag with hydrodynamic interaction\(^{22,106}\),

- the rigid dumbbell with isotropic hydrodynamic drag without hydrodynamic interaction\(^{22,92,106,107}\);

- the rigid dumbbell with isotropic hydrodynamic drag with hydrodynamic interaction\(^{22,92,106,107}\).

The questions we answer in this study are:

- How effective is the dumbbell idealization in modeling the nanofiber suspensions?
- Are the carbon nanofibers better modeled as rigid or elastic dumbbells?
- Should anisotropic hydrodynamic drag be included in the elastic dumbbell models?
- Should hydrodynamic interaction be included in the elastic or rigid dumbbell models?

The primitive microstructural parameters in the dumbbell models of the nanofiber/Newtonian solvent suspensions are:
\( a \) = length of the spring link (for elastic dumbbells) or length of rigid rod (for rigid dumbbells) (m),

\( r \) = radius of the beads (m),

\( \rho_f \) = density of the nanofibers (kg/m³),

\( \rho_s \) = density of the solvent (kg/m³),

\( c \) = mass concentration of the suspension (dimensionless),

\( T \) = absolute temperature (K),

\( \eta_s(T) \) = Newtonian solvent viscosity (Pa·s),

\( \alpha \) = mobility factor, only for the elastic dumbbells with anisotropic hydrodynamic drag (dimensionless).

In the kinetic theory the constitutive equation for the suspension is produced by integrating over a representative volume of dumbbells and solvent yielding that the Cauchy stress \( T \) is a superposition of a solvent contribution \( 2\eta_s D \) and a particle contribution \( T^p \):

\[
T = 2\eta_s D + T^p, \quad D = \frac{1}{2} \left( \nabla v + (\nabla v)^T \right).
\] (2.6)

For the rigid dumbbell models, the particle contribution to the stress \( T^p \) is \(^{22}\):

without hydrodynamic interaction:

\[
T^p = 3nkT \lambda \frac{D}{Dt} \langle pp \rangle, \tag{2.7}
\]

with hydrodynamic interaction:

\[
T^p = 3nkT \lambda_2^{(2)} \frac{D}{Dt} \langle pp \rangle - \left[ 1 - \frac{\lambda_2^{(2)}}{\lambda_2^{(1)}} \right] (3nkT \langle pp \rangle - nkTT), \tag{2.8}
\]
where \( \langle \mathbf{p p} \rangle = \int \int f(\mathbf{p}, t) d\theta d\phi \) is the phase-space average of the second order orientation tensor, with \( f(\mathbf{p}, t) \) the orientation distribution function, and

\[
\frac{D}{Dt} (\bullet) = \left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right)(\bullet) + (\bullet)W - W(\bullet) - (\bullet)D - D(\bullet),
\]

\[
W = \frac{1}{2} (\nabla \mathbf{v} - (\nabla \mathbf{v})^T),
D = \frac{1}{2} (\nabla \mathbf{v} + (\nabla \mathbf{v})^T).
\]

For the elastic dumbbell models, the orientation tensor \( \langle \mathbf{p p} \rangle \) can be mathematically eliminated, producing the following closed-form constitutive equations\(^\text{22}\):

with isotropic hydrodynamic drag:

\[
T^p + \lambda \frac{D}{Dt} T^p = 2\eta_p D, \tag{2.9}
\]

with anisotropic hydrodynamic drag:

\[
T^p + \lambda \frac{D}{Dt} T^p + \frac{\lambda}{\eta_p} (T^p \cdot T^p) = 2\eta_p D. \tag{2.10}
\]

The Hookean elastic dumbbell model with isotropic hydrodynamic drag, equation (2.9), is referred to as the Oldroyd fluid-B model, and the Hookean elastic dumbbell model with anisotropic hydrodynamic drag, equation (2.10), is referred to as the Giesekus model.

The material constants \( \eta, \lambda, \eta_p, \lambda_2 \) etc. in the constitutive equations (2.6)-(2.10) are expressed in terms of the primitive parameters in list (2.5)\(^\text{22,109}\):

\[
\phi = \text{volume fraction} = \frac{\rho_f c}{\rho_f + c(\rho_s - \rho_f)},
\]

\[
n = \text{number of fibers per unit volume} = \frac{\phi}{\pi r^2 a} = \frac{\rho_f c}{\rho_f + c(\rho_s - \rho_f)} \frac{1}{\pi r^2 a};
\]

for the elastic dumbbell models with hydrodynamic interaction:
\( h = \text{hydrodynamic interaction parameter} = \frac{r}{a} \), (\( h = 0 \) if neglect hydrodynamic interaction),

\[
\lambda = \text{relaxation time} = \frac{\pi \eta ra^2}{2kT \left(1 - h \sqrt{\frac{6}{\pi}}\right)},
\]

\( \eta_p = \text{particle contribution to the viscosity} \)

\[
\eta_p = \frac{n k T \lambda}{\rho_f + c (\rho_s - \rho_f)} \frac{\eta a}{2r} \frac{1}{1 - h \sqrt{\frac{6}{\pi}}},
\]

for the rigid dumbbell models with hydrodynamic interaction:

\[
\lambda = \text{relaxation time} = \frac{\pi \eta ra^2}{2kT}, \quad (2.11)
\]

\( h = \text{hydrodynamic interaction parameter} = \frac{3r}{4a} \), (\( h = 0 \) if neglect hydrodynamic interaction),

\[
\lambda_h = \frac{\lambda}{1 - h} = \frac{1}{1 - h} \frac{\pi \eta ra^2}{2kT} ,
\]

\[
\lambda_2^{(1)} = \lambda \left[1 - h \left(1 + \frac{1}{6} \left(\frac{2r}{a}\right)^2\right)\right]^{-1} = \frac{\pi \eta ra^2}{2kT} \left[1 - h \left(1 + \frac{1}{6} \left(\frac{2r}{a}\right)^2\right)\right]^{-1}.
\]

\[
\lambda_2^{(2)} = \lambda \left[1 - 2h \left(1 - \frac{1}{6} \left(\frac{2r}{a}\right)^2\right)\right]^{-1} = \frac{\pi \eta ra^2}{2kT} \left[1 - 2h \left(1 - \frac{1}{6} \left(\frac{2r}{a}\right)^2\right)\right]^{-1}.
\]

In this chapter we retain the microstructural basis of the dumbbell models: the characteristic lengths \( a \) and radii \( r \) of the model dumbbell are inferred from the morphological SEM measurements, independent of rheological measurements apart from...
a single calibration. The relaxation time $\lambda$ and particle viscosity $\eta_p$ are then deduced from $a$ and $r$, and measurements of densities $\rho_s$ and $\rho_f$, mass concentration $c$, temperature $T$, and solvent viscosity $\eta_s$, also independent of rheological measurements; see equations (2.11). Only the mobility factor $a$ of elastic dumbbell models with anisotropic hydrodynamic drag is deduced from a fit to rheological measurements.

### 2.5.2 Modeling predictions for treated sonicated nanofiber suspensions

Recall from the morphological characterization given in section 2.3 that the treated sonicated suspensions contain well-dispersed fibers with radii in the range 100 to 200nm and lengths mostly in the range of 1 to 5$\mu$m, with few fibers of length 5 to 10$\mu$m and essentially no clumps. Because of the absence of clumps, it is physically reasonable to model the treated sonicated suspensions with the kinetic theory model of dumbbells in a viscous solvent. The representative fiber length $a_f$ and radius $r_f$ are measured from the SEM images (Figure 2.2d and hundreds of others analyzed) to be $a_f=2\mu$m and the radius $r_f=100$nm. According to Doi-Edwards theory$^{31,92}$, fiber suspensions are divided into dilute, semidilute and concentrated regimes as follows: when $n a_f^3 < 1$, the suspension is said to be dilute, when $1 < n a_f^3 < \frac{a_f}{2r_f}$, the solution is semidilute, and when $n a_f^3 > \frac{a_f}{2r_f}$, the solution is concentrated. The number of fibers per unit volume $n$ is given by $n = \frac{\rho_s c}{\rho_f + c(\rho_s - \rho_f)} \cdot \frac{1}{\pi r^2 a_f}$. For the treated sonicated suspensions, the transition $\frac{a_f}{2r_f}=10$, and $n a_f^3 = 0.5, 0.9, 1.8,$ and $4.5$ for $c=0.5, 1, 2,$ and $5$wt%, respectively. Hence, according to Doi-Edwards classification, the 0.5wt% and 1wt% treated sonicated suspensions are dilute, and the suspensions are semidilute for weight percent 2 to 5wt%.
The relation between the length \(a_f\) and radius \(r_f\) of the physical nanofiber and the connector length \(a\) and bead radius \(r\) in its dumbbell idealization must be calibrated. We assume that the relation between \((a, r)\) and \((a_f, r_f)\) for the treated sonicated fibers is the same at all concentrations in all flows, and therefore the calibration utilizes only one experiment. This protocol is consistent with dilute suspensions where entanglements do not alter the effective spring constant. We choose to calibrate with the 2wt\% concentration small amplitude oscillatory shear experiment: a small amplitude oscillatory shear experiment so as not to involve the parameter \(\alpha\), and 2wt\% so as to avoid the possible inertia effects at lower concentrations and possible particle interaction at higher concentrations. We perform the calibration as follows.

### 2.5.2.1 Elastic dumbbell models

For the elastic dumbbell models, the linear viscoelastic material functions \(G', G''\) and \(\eta', \eta''\) are:\(^{22}\):

\[
\begin{align*}
G'(\omega) &= \omega \eta''(\omega) = \omega \left( \frac{nkT\lambda^2 \omega}{1 + (\lambda \omega)^2} \right), \\
G''(\omega) &= \omega \eta'(\omega) = \omega \left( \eta_s + \frac{nkT\lambda}{1 + (\lambda \omega)^2} \right).
\end{align*}
\]

(2.12)

In terms of the primitive microstructural parameters of list (2.5) these become
where \( h = 0 \) without hydrodynamic interaction and \( h = \frac{r}{a} \) with hydrodynamic interaction.

Notice that these forms do not contain the primitive parameter \( \alpha \), so that \( \alpha \) will not interfere with the calibration relating \( a \) and \( r \) to the microstructure measurements \( a_f \) and \( r_f \).

The parameters of list (2.5) that appear in equation (2.13) besides \( a \) and \( r \) are measured independently of the small amplitude oscillatory shear experiments: temperature \( T = 25^\circ C \), solvent viscosity at \( 25^\circ C \) \( \eta_s = 0.154 \) Pa·s, fiber density \( \rho_f = 1750 \) kg/m\(^3\), solvent density \( \rho_s = 1236 \) kg/m\(^3\), and fiber concentration \( c = 0.5, 1, 2, 3, 4, \) and \( 5\)wt\%. The characterization relating \( a \) and \( r \) to the measured fiber length \( a_f \) and radius \( r_f \) are obtained by selecting \( a \) and \( r \) to minimize the error

\[
\delta = \sum_{i=1}^{N} \left[ \log_{10} \eta'_\text{exp} (\omega_i) - \log_{10} \left( \eta_s + \frac{n k T \lambda}{1 + (\lambda \omega_i)^2} \right) \right]^2 + \left[ \log_{10} \eta''\text{exp} (\omega_i) - \log_{10} \left( \frac{n k T \lambda^2 \omega_i}{1 + (\lambda \omega_i)^2} \right) \right]^2
\]  

(2.14)

and comparing to \( a_f \) and radius \( r_f \). In equation (2.14) \( \eta'_\text{exp} (\omega_i) \) and \( \eta''\text{exp} (\omega_i) \) are the experimental measured values of \( \eta' \) and \( \eta'' \) at the \( N \) discrete frequencies \( \omega_i \) for a particular concentration \( c \). The fitting results using the experimental data at \( c = 2\)wt\%
(for which $N = 22$) are $a = 0.23 \mu m$, $r = 10.5 \text{nm}$ for the elastic dumbbell models without hydrodynamic interaction and $a = 0.22 \mu m$, $r = 10.7 \text{nm}$ for the elastic dumbbell models with hydrodynamic interaction.

For the elastic dumbbell models with or without hydrodynamic interaction, the ratio of the fiber radius to the fiber length is small ($h = \frac{r}{a} \approx 0.04$). Therefore for the treated sonicated suspensions, the predictions of the elastic dumbbell models without hydrodynamic interaction are essentially the same as the elastic dumbbell models with hydrodynamic interaction.

Compared with the representative fiber length $a_f = 2 \mu m$ and the radius $r_f = 100 \text{nm}$ measured from the SEM images of the treated sonicated suspensions (Figure 2.2d), we see that the model length $a$ of the spring link and the model radius $r$ of the beads are proportional to the measured $a_f$ and $r_f$ by essentially the same factor 0.11. This factor, obtained from oscillatory shear data for the 2wt% concentration, is employed at all concentrations and in both oscillatory and steady shear with no refitting, since the characteristic fiber length and radius are the same at all concentrations, in either type of shear flow.

Applying the fiber length $a = 0.23 \mu m$, radius $r = 10.5 \text{nm}$ and different mass concentration $c$ to small amplitude oscillatory shear equation (2.13), the elastic dumbbell models predict the elastic modulus $G'$ and viscous modulus $G''$ of the treated sonicated suspensions shown in Figure 2.10b and Figure 2.11b. Comparing these predicted moduli to the corresponding measured moduli displayed in Figure 2.10a and Figure 2.11a, we see that the elastic dumbbell models are successful in capturing the trends exhibited in the
measured response: The elastic dumbbell models predict that the addition of the particles into the Newtonian solvent creates an elasticity in the composite suspension, as verified in the experiments; note from the right hand side of equation (2.13) that the predicted elastic modulus $G'$ is zero when the concentration $c$ is zero, but nonzero for nonzero $c$. In agreement with the small amplitude oscillatory shear measurements, both elastic modulus $G'$ and viscous modulus $G''$ in the elastic dumbbell predictions monotonically increase with nanofiber concentration. The slopes and orders of magnitude of $G'$ and $G''$ predicted by the elastic dumbbell models are also consistent with the experimental data; the models overpredict the separation of $G'$ at high frequencies. As the elastic dumbbell models do not take colloidal forces into account, the plateau in the elastic modulus $G'$ observed in the suspensions at low frequencies could not be captured by the models.

In the simulation of steady shear, the elastic dumbbell model with isotropic hydrodynamic drag (i.e. the Oldroyd fluid-B model) predicts a constant viscosity

$$\eta(\dot{\gamma}) = \eta_s + \eta_p = \eta_s + \frac{n \pi \eta_r a^2}{2 \left(1 - h \sqrt{\frac{6}{\pi}}\right)}, \quad (2.15)$$

independent of the shear rate $\dot{\gamma}$, and the elastic dumbbell model with anisotropic hydrodynamic drag (the Giesekus model) predicts shear-rate dependent non-constant viscosity$^{22,106}$:

$$\eta(\dot{\gamma}) = \eta_s + \eta_p \frac{(1-\psi)^2}{1 + (1-2\alpha)\psi} = \eta_s + \frac{n \pi \eta_r a^2}{2 \left(1 - h \sqrt{\frac{6}{\pi}}\right)} \frac{(1-\psi)^2}{1 + (1-2\alpha)\psi}, \quad (2.16)$$

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where

\[
\psi = \frac{1 - \chi}{1 + (1 - 2\alpha)\chi},
\]

\[
\chi = \sqrt{\frac{1 + 16\alpha(1 - 2\alpha)(\gamma \lambda)^2}{8\alpha(1 - 2\alpha)(\gamma \lambda)^2} - 1} = \sqrt{\frac{1 + 16\alpha(1 - 2\alpha)\left(\frac{\pi \eta_r a^2}{2kT}\right)^2}{8\alpha(1 - 2\alpha)\left(\frac{\pi \eta_r a^2}{2kT}\right)^2} - 1}.
\]

The same microstructural parameters \(a=0.23\) µm and \(r=10.5\) nm inferred from the SEM morphological study that were found to be successful in predicting the small amplitude oscillatory shear behavior of the treated sonicated suspensions at all concentrations also are successful in predicting their steady shear behavior: when we insert \(a=0.23\) µm and \(r=10.5\) nm into equation (2.16) and fit to the experimental data of Figure 2.6a, we deduce \(\alpha = 2.50 \times 10^{-11}, 6.40 \times 10^{-11}, 6.40 \times 10^{-11}, 2.40 \times 10^{-11}\) for \(c=5\)wt%, 2wt%, 1wt%, and 0.5wt%, respectively, reflecting the slight shear thinning behavior of the treated sonicated suspensions. Because these values of \(\alpha\) are very close to zero, the predictions of the Giesekus model are essentially the same as those of the Oldroyd fluid-B model (Figure 2.6b). Comparing Figure 2.6a and Figure 2.6b, we note that the elastic dumbbell models with \(a\) and \(r\) deduced from microstructural morphology correctly predict the magnitude of the steady shear viscosity of the treated sonicated suspensions, as well as its dependence on fiber concentration.
2.5.2.2 Rigid dumbbell models

The linear viscoelastic material functions $G'$, $G''$ and $\eta'$, $\eta''$ predicted from the rigid dumbbell models are ($h = 0$ without hydrodynamic interaction, $h = \frac{3r}{4a}$ with hydrodynamic interaction):

$$G'(\omega) = \omega \eta''(\omega) = \omega \left( \frac{3}{5} \frac{1}{1-2h} \frac{n k T \lambda_a^2 \omega}{1+\left(\lambda_a \omega\right)^2} \right) = \frac{3}{5} \frac{1}{1-2h} \frac{n k T}{1+\left(1-h\right)^2 \left(\frac{2kT}{\pi \eta r a^2 \omega}\right)^2}. \tag{2.17}$$

$$G''(\omega) = \omega \eta'(\omega) = \omega \left( \eta_a + nkT \lambda_a \left[ \frac{1}{1-2h} \frac{1}{\left(1-2h\right)} \frac{1}{\left(1-h\right)^2} \left(\frac{2kT}{\pi \eta r a^2 \omega}\right)^2 \right] \right)$$
$$= \eta_a + \frac{n \pi \eta r a^2 \omega}{2} \left[ \frac{1}{1-2h} \frac{1}{1-2h} \frac{1}{1+\left(1-h\right)^2} \left(\frac{2kT}{\pi \eta r a^2 \omega}\right)^2 \right] \tag{2.18}.$$

As with the elastic dumbbell models, the constants of proportionality of $a$ and $r$ to $a_i$ and $r_i$ are also obtained from a fit to 2wt% small amplitude oscillatory shear experiment by selecting $a$ and $r$ to minimize the error:

$$\delta = \sum_{i=1}^{N} \left( \log_{10} \eta_{i, \text{exp}}' (\omega_i) - \log_{10} \left( \eta_a + nkT \lambda_a \left[ \frac{1}{1-2h} \frac{1}{1+\left(1-h\right)^2} \left(\frac{2kT}{\pi \eta r a^2 \omega}\right)^2 \right] \right) \right)^2 + \left( \log_{10} \eta_{i, \text{exp}}'' (\omega_i) - \log_{10} \left( \frac{3}{5} \frac{1}{1-2h} \frac{nk T \lambda_a^2 \omega}{1+\left(\lambda_a \omega\right)^2} \right) \right)^2. \tag{2.18}$$
The best fit to the small amplitude oscillatory experimental data for the 2wt% suspension is obtained with \( a = 0.50 \) µm and \( r = 45.8 \) nm for rigid dumbbell model without hydrodynamic interaction and \( a = 0.49 \) µm and \( r = 48.2 \) nm for rigid dumbbell model with hydrodynamic interaction. Because the results of these two models are so close, the hydrodynamic interaction can be ignored. Compared with the representative fiber length \( a_f = 2 \) µm and the radius \( r_f = 100 \) nm measured from the SEM images of the treated sonicated suspensions (Figure 2.2d), we see that the model length of rigid rod \( a = 0.25 a_f \); the model radius of the beads \( r = 0.46 r_f \).

Applying the fiber length \( a = 0.50 \) µm, radius \( r = 45.8 \) nm and different mass concentration \( c \) to small amplitude oscillatory shear equationss (2.17), the rigid dumbbell models predict the elastic modulus \( G' \) and viscous modulus \( G'' \) of the treated sonicated suspensions shown in Figure 2.10c and Figure 2.11c. A comparison with the experimental measurements of Figure 2.10a and Figure 2.11a indicates that the rigid dumbbell models correctly predict the creation of elasticity with the addition of the nanofibers, but fail to capture the magnitude and increasing trends of elastic modulus \( G' \) at high frequencies, and accurately predict the magnitude of viscous modulus \( G'' \), but underpredict its dependence on nanofiber concentration.

In the simulation of steady shear flow, the rigid dumbbell models predict the following shear-rate dependent viscosities, without hydrodynamic interaction\(^{22}\):

\[
\eta = \eta_s + nkT\lambda \left[ 1 - \frac{18}{35}(\lambda\dot{\gamma})^2 + \frac{1326}{1925}(\lambda\dot{\gamma})^4 - \cdots \right] \quad (\lambda\dot{\gamma} \leq 0.46) \tag{2.19}
\]

\[
\eta \approx \eta_s + 0.678nkT\lambda(\lambda\dot{\gamma})^{1/3} \quad (\lambda\dot{\gamma} > 0.46)
\]

with hydrodynamic interaction\(^{22,107}\).
\[
\eta = \eta_s + nkT\lambda_n \left\{ \left( \frac{1-h}{1-2h} \right) \left[ \frac{18}{35} (\lambda_n \dot{\gamma})^2 + \frac{1326}{1925} (\lambda_n \dot{\gamma})^4 + \ldots \right] \right\} \quad (\lambda \dot{\gamma} \leq 0.46)
\]

\[
\eta \approx \eta_s + 0.678nkT\lambda_n \left( \frac{1-h}{1-2h} \right) (\lambda_n \dot{\gamma})^{4/3} \quad (\lambda \dot{\gamma} > 0.46)
\]

We insert the microstructural parameters \( a = 0.50 \ \mu \text{m} \) and \( r = 45.8 \ \text{nm} \) inferred from small amplitude oscillatory shear experiment of 2wt% suspension into equations (2.19), (2.20) and evaluate at the different concentrations \( c \). The two rigid dumbbell models give essentially the same predictions which are shown in Figure 2.6c. A comparison with the experimental measurements shown in Figure 2.6a reveals that the rigid dumbbell models with and without hydrodynamic interaction are in agreement with experiment in their prediction of a nearly constant viscosity, but both of them underpredict the magnitude of viscosity at high nanofiber concentration.

Comparing Figure 2.6, Figure 2.10, and Figure 2.11, we conclude that the single-mode elastic dumbbell models based on microstructural measurements successfully model the behavior of treated sonicated suspensions over the range of nanofiber concentrations except at 5wt%, which is in the semidilute regime, whereas the rigid dumbbell models based on microstructural measurements are less successful. We surmise that the success of the dumbbell models is due to the similarity of the physical system to assumptions of the models, namely a dilute suspension of particles in a Newtonian solvent, and that the elastic dumbbell models are more successful than the rigid dumbbell models since, although the actual nanofibers are rigid in extension, they exhibit a recoverable tendency to bend or unbend that must be incorporated in the model.
2.5.2.3 Modeling predictions for treated unsonicated nanofiber suspensions

Unlike the treated sonicated suspensions, on which we performed small amplitude oscillatory shear and steady shear experiments at concentrations of 0.5, 1, 2, 3, 4, and 5wt%, for the treated unsonicated suspensions we performed these shear experiments only at the single concentration 1wt%. We recall that comparing the SEM images of the treated sonicated suspensions (Figure 2.2d) and the treated unsonicated suspensions (Figure 2.2c), the treated unsonicated suspension has longer fibers and a number small clusters. The characteristic length of the treated unsonicated fibers required for a single-mode model is five times longer than that of the treated sonicated fibers, while the fiber radius is unchanged by the sonication. Based on this observation, we insert $a_{\text{unsonicated}} = 5a_{\text{sonicated}}$, $r_{\text{unsonicated}} = r_{\text{sonicated}}$ into the response functions $G'(\omega)$, $G''(\omega)$, and $\eta(\gamma)$ predicted by the six dumbbell models (equations (2.12)-(2.13), (2.15)-(2.17), and (2.19)-(2.20)) at 1wt% fiber concentration. We ignore the presence of the small clusters. Figure 2.7b and Figure 2.7c display the predictions of steady shear viscosity given by the elastic and rigid dumbbell models, respectively, for both the treated sonicated and treated unsonicated suspensions. The mobility factor $\alpha$ of the Giesekus model is close to zero ($\alpha = 9.00 \times 10^{-12}$ for $c = 1\text{wt\%}$) so that the effect of the anisotropic hydrodynamic drag is small. Therefore the predictions of elastic dumbbell models with isotropic hydrodynamic drag (Oldroyd fluid-B model) are the same as those of the elastic dumbbell models with anisotropic hydrodynamic drag (Giesekus model). The ratio of particle radius to length $\left( h = \frac{r}{a} = 0.008 \right)$ is small, so that the effect of hydrodynamic interaction could be ignored. Therefore, the predictions of the four elastic dumbbell models with or without hydrodynamic interaction are same and the predictions of the two rigid dumbbell models...
with or without hydrodynamic interaction are also essentially the same. Figure 2.7b shows that the elastic dumbbell models for the treated unsonicated suspension overpredict the difference of viscosity between the two suspensions. Figure 2.7c shows the prediction of the rigid dumbbell models with or without hydrodynamic interaction is in agreement with the experiment. We caution that this behavior is for one experimental point at relatively low nanofiber concentration.

### 2.5.2.4 Modeling predictions for untreated sonicated nanofiber suspensions

Recall the morphological study of the untreated sonicated suspensions revealed the presence of clumps of entangled fibers. A theory of aggregated structures which accounts for both disperse fibers and fiber clumps in a Newtonian solvent would be desirable to model the untreated sonicated nanofiber suspensions, but at present, a theory taking into account the different length scales of the disperse fibers and aggregates does not exist. In the absence of such a theory, we instead introduce the concept of “effective length” into the dumbbell models, combing the disperse fibers and fiber clumps into a single length scale.

The effective spring length $a_{\text{untreated}} = 21.7 \, \mu m$ of the Oldroyd fluid-B model for the untreated sonicated suspensions is obtained by keeping $r = 10.5 \, nm$ unchanged and selecting $a_{\text{untreated}}$ to minimize the error

$$\delta = \sum_{i=1}^{N} \left[ \log_{10} \eta_{\exp} (\dot{\gamma}) - \log_{10} \left( \eta_{s} + nkT \lambda \right) \right]^2 .$$

We insert this effective length into equations (2.15) to obtain the steady shear viscosity predicted by the Oldroyd fluid-B model for the untreated sonicated suspensions, shown in Figure 2.4b; the Oldroyd fluid-B model cannot capture the shear thinning behavior of the
suspensions. The effective spring length \( a_{untreated} = 345 \, \mu m \) of the Giesekus model for the untreated sonicated suspensions is obtained by keeping \( r = 10.5 \, nm \) unchanged and minimizing the error

\[
\delta = \sum_{i=1}^{N} \left[ \log_{10} \eta_{exp} (\dot{\gamma}) - \log_{10} \left( \eta_s + n k T \lambda \frac{(1-\psi)^2}{1+(1-2\alpha)\psi} \right) \right]^2.
\] (2.22)

Inserting this effective length into equations (2.16) produces the prediction of steady shear viscosity of the untreated sonicated suspensions shown in Figure 2.4c. Comparing with the experimental measurements (Figure 2.4a), we see that despite its debatable physical basis, the effective length modeling approach in the Giesekus model (elastic dumbbells with anisotropic drag) captures the steady shear behavior of the untreated sonicated suspensions: the orders of magnitude of steady viscosity predicted by the Giesekus model are consistent with the experimental data, the Giesekus model correctly predicts that the viscosity of the suspensions increases with the nanofiber concentration and it captures the significant shear thinning behavior (\( \alpha = 1.82 \times 10^{-9}, 4.89 \times 10^{-9}, 2.13 \times 10^{-8}, 4.51 \times 10^{-8}, 4.23 \times 10^{-7}, \) and \( 9.00 \times 10^{-7} \) for \( c=5\text{wt\%}, 4\text{wt\%}, 3\text{wt\%}, 2\text{wt\%}, 1\text{wt\%}, \) and \( 0.5\text{wt\%} \), respectively). Comparing Figure 2.5a, Figure 2.5b, and Figure 2.5c, we note that the Giesekus model incorporating effective length predicts the correct dependence of viscosity on shear stress, except at low shear rates. In the above elastic dumbbell models, the ratio of particle radius to length \( \frac{r}{a} \) is so small that the influence of the hydrodynamic interaction on the relaxation time is miniscule.
The effective rigid rod length $a_{\text{untreated}} = 33.49$ m for the rigid dumbbell model of untreated sonicated suspensions is obtained by keeping $r_{\text{asonicated}} = 45.8$ nm unchanged and selecting $a_{\text{untreated}}$ to minimize the error:

$$\delta = \sum_{i=1}^{N} \left[ \log_{10} \eta_{\text{eq}}(\dot{\gamma}) - \log_{10} \left( \eta_{s} + nkT\lambda \left[ \frac{1}{1-2h} \left[ 1 - \frac{18}{35} (\lambda \dot{\gamma})^2 + \frac{1326}{1925} (\lambda \dot{\gamma})^4 - \cdots \right] \right] \right) \right]^2 \quad (\lambda \dot{\gamma} \leq 0.46), \quad (2.23)$$

$$\delta = \sum_{i=1}^{N} \left[ \log_{10} \eta_{\text{eq}}(\dot{\gamma}) - \log_{10} \left( \eta_{s} + 0.678 nkT\lambda (\lambda \dot{\gamma})^{1/3} \right) \right]^2 \quad (\lambda \dot{\gamma} > 0.46).$$

We apply this effective length into equation (2.19) or equation (2.20) to obtain the rigid dumbbell model prediction of the steady shear viscosity of the untreated sonicated suspensions, shown in Figure 2.4d. We note that the model captures the steady shear behavior of the untreated sonicated suspensions qualitatively, predicting the shear thinning behavior of the suspensions and the dependence of viscosity on the mass concentration but failing to predict the magnitude of the steady shear viscosity at high mass concentration.

Recall from equations (2.11) that in the microstructurally based forms of the dumbbell models the relaxation time $\lambda$ and the particle contribution to the viscosity $\eta_p$ are explicit functions of temperature; no calibration or fitting is allowed aside from experimentally measuring solvent viscosity as a function of temperature. We insert $T = 5^\circ C, 15^\circ C, 25^\circ C, 35^\circ C,$ and $45^\circ C$ and $c = 2\text{wt}\%$ into Equations (2.16), and note that the model accurately captures the measured temperature dependence of the untreated sonicated suspensions in shear (Figure 2.12).
All six dumbbell models with the effective length concept fail to capture the observed behavior of the untreated sonicated suspensions in small amplitude oscillatory shear.

2.6 Conclusions

The morphology and rheology of carbon nanofiber suspensions were studied. The as-received nanofibers contained millimeter and centimeter size agglomerates, with most nanofibers entangled with each other. The diameter was rather uniform, in the range 100-200 nm, and the length was estimated to be from 5 to 20 µm. Dispersion of the as-received nanofibers was difficult. Sonication could only disperse part of the nanofiber agglomerates, and many nanofiber clumps of the size of 20 by 50 µm remained in the suspensions. Surface treatment with a concentrated acid mixture improved overall dispersion greatly by opening the nanofiber clumps and possibly shortening some fibers. The nanofibers, weakened by the treatment, were shortened by subsequent sonication to less than 1 µm in length.

The untreated sonicated suspensions exhibited extreme shear thinning behavior and the viscosities increased monotonically with fiber loading. The untreated suspensions possessed apparent yield stress at the nanofiber loading above 2wt%. We suggest that this is caused by the network structures formed from the partially dispersed nanofibers and nanofiber clumps. The treated sonicated and treated unsonicated suspensions exhibited a nearly constant shear viscosity as a function of shear rate and the viscosities gradually increased with fiber concentration. At 1wt% fiber concentration, the treated sonicated and treated unsonicated suspensions had about the same viscosities, although the average length of the nanofibers was different. When the Krieger-Dougherty model was applied
to the suspensions, good fits were obtained for viscosities at high shear rates. However, the maximum packing coefficient, $\phi_m$, was small compared to that for spherical particles. This is believed to be the effects of particle aspect ratio and of interactions between particles. Small amplitude shear studies showed that for the untreated sonicated suspensions there was a critical concentration of 3wt% above which the suspensions showed solidlike behavior. $G'$ was greater than $G''$ at all frequencies studied and a low-frequency plateau was observed. This could be attributed to the continuous 3-D network structures between the nanofibers. The appearance of low-frequency plateau in $G'$ in the treated sonicated suspensions, which do not have network structures, is the result of the colloidal forces between the treated nanofibers.

Study of temperature effects on the rheology of the 2wt% untreated sonicated suspension showed that the suspension became more solidlike ($G'/G''$ increased) at higher temperatures although the overall shear viscosity decreased. This is because as temperature rises, the viscosity of the solvent decreases greatly while the interaction between the nanofibers remains about the same, inducing a solid-like behavior. At high shear rates, the shear viscosity was dominated by the solvent that follows the Arrhenius law. The extensional viscosity of 1wt% untreated sonicated suspensions was observed to be extension rate thinning, with a decreasing Trouton ratio due to the breakup of the network structure and nanofiber alignment to the flow.

We investigated the ability of elastic and rigid dumbbell models to describe the rheological behavior of the aqueous nanofiber suspensions. We retained the microstructural basis of the elastic dumbbell models and rigid dumbbell models by inferring the connector length and bead radius in the models from SEM measurements of
the suspensions, and from these and measurements of densities, concentration, and solvent viscosity, computed the relaxation time and particle viscosity in the models. We found that the elastic dumbbell models successfully capture both the small amplitude oscillatory shear and steady shear behavior of the treated sonicated suspensions, while the rigid dumbbell models fail to capture the increasing trends of the elastic modulus $G'$ at high frequency. We conjecture that the success of the dumbbell models is due to the similarity of the physical system to assumptions of the models, and that the elastic dumbbell models are more successful than the rigid dumbbell models since, although the actual nanofibers are rigid in extension, they exhibit a recoverable tendency to bend or unbend that must be incorporated in the model. Because of the small ratio of radius to length $\frac{r}{a}$ of the carbon nanofibers, the predictions of the elastic and rigid dumbbell models with or without hydrodynamic interaction are indistinguishable.

The elastic dumbbell models and the rigid dumbbell models based on SEM measurements of microstructure for treated unsonicated suspensions which ignore the small clumps present in these suspensions overpredict the difference of the treated unsonicated suspension’s viscosity and that of the treated sonicated suspension at the one concentration for which we have an experimental comparison.

The elastic dumbbell models with anisotropic hydrodynamic drag with or without hydrodynamic interaction correctly predict the observed steady shear behavior of the untreated sonicated suspensions if we introduce the concept of an effective dumbbell length to account for the presence of large agglomerates. The rigid dumbbell models predict the shear thinning behavior of the untreated sonicated suspensions but fail to predict the magnitude of the steady shear viscosity. The elastic dumbbell model with
isotropic hydrodynamic drag incorporating effective length fails to predict the strongly shear thinning behavior of the untreated sonicated suspensions. All six dumbbell models fail to capture the observed small amplitude oscillatory shear behavior of the untreated sonicated suspensions.
Figure 2.1. SEM micrographs of (a) as-received, (b) untreated sonicated, (c) treated unsonicated, and (d) treated sonicated carbon nanofibers (scale bar: 50 µm).
Figure 2.2. SEM micrographs of (a) as-received, (b) untreated sonicated, (c) treated unsonicated, and (d) treated sonicated carbon nanofibers (scale bar: 10 µm).
Figure 2.3. Optical microscopy photos of (a) 0.5wt% untreated sonicated and (b) 0.5wt% treated sonicated carbon nanofiber suspensions (scale bar: 100 µm).
Figure 2.4. Steady shear viscosity of untreated sonicated suspensions: (a) experimental measurements, (b) predictions of elastic dumbbell models with isotropic hydrodynamic drag with or without hydrodynamic interaction, (c) predictions of elastic dumbbell models with anisotropic hydrodynamic drag with or without hydrodynamic interaction, (d) predictions of rigid dumbbell models with isotropic hydrodynamic drag with or without hydrodynamic interaction.
Figure 2.5. Shear viscosity as a function of shear stress of the untreated sonicated suspensions: (a) experimental measurements, (b) predictions of elastic dumbbell models with anisotropic hydrodynamic drag with or without hydrodynamic interaction, (c) predictions of rigid dumbbell models with isotropic hydrodynamic drag with or without hydrodynamic interaction.
Figure 2.6. Steady shear viscosity of treated sonicated suspensions: (a) experimental measurements, (b) elastic dumbbell model predictions, (c) rigid dumbbell model predictions.
Figure 2.7. Steady shear viscosity of treated unsonicated suspensions: (a) experimental measurements, (b) elastic dumbbell model prediction, (c) rigid dumbbell model predictions.
Figure 2.8. Relative viscosity of treated sonicated and untreated sonicated suspensions as a function of fiber volume fraction.

Figure 2.9. Linear viscoelasticity of untreated sonicated nanofiber suspensions.
Figure 2.10. Elastic modulus $G'$ of treated sonicated suspensions: (a) experimental measurements, (b) elastic dumbbell model predictions, (c) rigid dumbbell predictions.
Figure 2.11. Viscous modulus $G''$ of treated sonicated suspensions: (a) experimental measurements, (b) elastic dumbbell model predictions, (c) rigid dumbbell model predictions.
Figure 2.12. Effects of temperature on 2wt% untreated sonicated suspensions: (a) experimental measurements of the steady shear viscosity, (b) elastic dumbbell model predictions of the steady shear viscosity, (c) experimental measurements of the relative viscosity, (d) elastic dumbbell model predictions of the relative viscosity.
Figure 2.13. Effects of temperature on 2wt% untreated sonicated suspensions: (a) experimental measurements of the apparent yield stress, (b) elastic dumbbell model predictions of the apparent yield stress, (c) Arrhenius plot, (d) linear viscoelasticity.
Figure 2.14. Extensional and shear viscosity of 1wt% untreated sonicated suspension. Fresh sample was measured using 2mm jets, and then the sample was stretched at 600 s$^{-1}$ for 13 hours. After that, the sample was measured again using 2mm jets followed by measured by 1mm jets. Then the sample was stretched at 2000 s$^{-1}$ for another 2 hours. It was measured again using 1mm jets. Temperature 28 °C.
Figure 2.15. Trouton ratio, $Tr = \frac{\eta_\epsilon(\dot{\gamma})}{\eta(\dot{\gamma})}$, of 2wt% untreated sonicated suspension calculated by the standard method ($\dot{\gamma} = \dot{\varepsilon}$) and Jones method ($\dot{\gamma} = \sqrt{3}\dot{\varepsilon}$).

Figure 2.16. Comparison of complex viscosities ($\eta^*$) and steady shear viscosities ($\eta$) of 1wt% and 5wt% untreated sonicated nanofiber suspensions. At 1wt% the Cox-Merz rule holds.
CHAPTER 3

DYNAMIC AND STEADY SHEAR OF POLYSTYRENE/CARBON
NANOFIBER COMPOSITES

3.1 Introduction

Graphitic carbon nanofilaments have been of great research interest since the discovery of the single wall carbon nanotube (SWNT) in 1991\textsuperscript{56}. Due to their extraordinary mechanical, electrical, and thermal properties, the SWNTs seem to have promising future serving as reinforcement fillers in composite systems, or improving the thermal and electrical conductivities of the composite. Experimental results so far have confirmed enhanced performance in these applications. However, due to the high cost of production, the price of SWNTs is often prohibitive.

Carbon nanofibers (CNF) are a low cost alternative to SWNTs. Typically made by decomposing organic vapor in the presence of metal catalyst (e.g. iron) at high temperature\textsuperscript{110-115}, CNFs are roughly 100 times larger than SWNTs in both diameter and length, and 1/500 the cost. Due to their excellent thermal\textsuperscript{116}, electrical\textsuperscript{117}, and mechanical properties\textsuperscript{118}, CNFs have been incorporated into a variety of thermoplastic and thermoset polymers to make polymer nanocomposites. These thermoplastic polymers include
polycarbonate$^{119-122}$, polyethylene$^{123}$, polypropylene$^{1,68,120,124-129}$, poly (ethyleneterephthalate)$^{130-131}$, nylon 6$^{125}$, nylon 66$^{126,129}$, and polyphenylene sulfide$^{125,132}$. For thermoset matrix, epoxy has been mostly used$^{125,132-136}$. Electrical and thermal conductivities of the polymer/CNF composites increase markedly with only a small amount of CNFs (less than 10wt%)$^{125}$. Applications of polymer/CNF composites include electrostatic dissipation (ESD) and electromagnetic interference (EMI) shielding. Mechanical strength also increases with the addition of CNFs into the polymer, which could lead to smaller and lighter parts in a variety of applications$^{126}$.

However, the enhancement of performance properties by the addition of CNFs to polymers is accompanied by changes, often negative, in processing properties, and equipment used to process a pure polymers may incapable of processing the same polymers filled with CNFs. Rheological studies of the polymer/CNF composites must be performed in order to evaluate the effect of carbon nanofibers on processing. Compared to the above abundant literature on the properties of the solidified polymer/CNF composites, far less can be found on the rheological properties of these composite systems in their molten processing phase$^{68,123,127,137}$. Linear viscoelasticity and steady shear viscosity of composites with different polymer matrices have been measured, but none explicitly relate rheological measurements to morphology of the composites.

This chapter addresses these deficiencies: The results of this work include the preparation of polymer/CNF composites with uniform dispersion by two different techniques (melt blending and solvent casting), comparing the damage done to the CNFs by these processing techniques to the as-received CNFs, investigation of the effect of dispersion and size of CNFs on the composite rheology, construction of mathematical
models that deduce the rheology of the melt composites and connect this rheology and process conditions to the development of CNF nanostructure, providing a tool for predicting enhanced performance properties of parts with process flow induced CNF orientation.

3.2 Experimental procedures

3.2.1 Materials

The polystyrene used in this study is Fina (CX5197) produced by Atofina. It has a density of 1000g/m³, Mₙ of approximately 200,000g/mol, and polydispersity index of 2.4. Polystyrene was chosen as our thermoplastic polymer matrix because its rheology has been well characterized, so that any deviation caused by the addition of the CNFs can be readily identified, and further its molecular structure is simple, with no crystalline structure present in solid phase, so that the nanostructure of the CNFs developed during flow in its molten phase can be preserved when cooled to its solid phase.

The carbon nanofibers used in this study are Pyrograf® III (type PR-24-PS) made by Applied Sciences, Inc. They are produced by decomposing organic vapors at elevated temperature in the presence of metal catalysts. These nanofibers have a tree-ring structure with a hollow core. The nanofibers we obtained were in powdered form consisting largely of fiber agglomerates. Large agglomerates of a centimeter in diameter were observed, but most of the agglomerates were less than 1 mm in diameter. The as-received CNFs in these agglomerates were characterized using scanning electron microscopy to have diameters of 100 to 200 nm and lengths of 1 to 50 microns.
3.2.2 Composite sample preparation

In this study, two methods have been used to prepare CNF/PS composites: melt blending and solvent casting. The composites made by melt blending are referred to here as MB composites, and composites made by solvent casting as SC composites.

In the melt blending process, CNF powder and PS pellets are fed into a DACA microcompounder, a small twin-screw extruder in which the compounding time, temperature and screw speed can be controlled. Typically five minutes compounding time at 180°C and 150 rpm achieves the best CNF dispersion with the least polymer degradation (i.e. breaking of polymer chains). Longer compounding time does not generate better CNF dispersion, but can lead to more polymer degradation. The composite is extruded through a 1mm die and then cut into pellets with approximate length of 2mm. Composites containing 2, 5, and 10wt% CNF were prepared using the melt blending process for this study.

In the solvent casting process, PS pellets are dissolved in tetrohydrofuran (THF), and the CNFs are added. The resulting 90% THF suspension is then sonicated for 0.5 hour using a Sonic Dismembrator (Fisher Scientific) at 20 kHz and power level of 760 watts per liter. After sonication, the suspensions are heated to drive off most of the solvent. The residual material, still containing about 5wt% THF solvent, is broken into powder using a blender and then further dried in a vacuum oven at 80°C for 7 days to remove the remaining THF. The dried powder is heated to 200°C and compressed through a 1mm diameter die, and the resulting rod is cut into pellets with approximate length of 2mm. This pelletization avoids the trapped air that would be present in the compression molding of the power to make disks, described below, resulting in the
growth if bubbles in the sample. Composites containing 2, 5, and 10 wt% CNF were prepared using the solvent casting method.

Both the MB and SC composite pellets were compression molded into disks of 25 mm diameter and 0.6-1 mm thickness using a hot press at 190°C. These disks served as specimens for the rheometers (described in the next subsection) employed to characterize the composites’ melt behavior. Although the CNFs in the pellets were oriented in the flow direction through the 1 mm die, the orientation of the pellets in the compressed disks was random. The disks were stored in a vacuum oven at 70°C prior to the measurement, to prevent the absorption of moisture or air; if stored in open air, bubbles would be generated during the re-melting in the rheometer, which would corrupt the rheological measurements. Two pure PS control samples were prepared one processed using the melt blending method, and the other using the solvent casting method.

Shear rheology of the melt composites was measured using a strain controlled rheometer from TA Instruments (ARES LS2) with both torque transducer (0.02g.cm to 2000g.cm) and normal force transducer (2g to 2000g). Parallel plates of 25 mm diameter were used for all measurements. The gap distance was kept in the range 0.5-0.9 mm for all tests. The molded disks were allowed to rest at the temperature of the measurement (200°C unless otherwise stated) for 15 min to relax the residue stress introduced by the compression molding process.

A transmission electron microscope (Philips CM 12 at 120 kV) was used to observe the nanometer-scale CNF dispersion and structure in the composites, and a scanning electron microscope (Philips XL 30 equipped with secondary and back-scatter detectors, operated at 30 kV) was used to characterize the as-received CNFs. An optical
microscope (Olympus BH-2) was used to study the CNF dispersion at a larger scale. The glass transition temperatures ($T_g$) of all the composites were measured using a Differential Scanning Calorimetry (TA Instrument 2920).

### 3.3 Experimental Results

In this section, we present and relate our nanoscale measurements of CNF morphology and dispersion in the PS matrix, and our mesoscale measurements of the bulk rheology of the melt phase of the CNF/PS composites in small amplitude oscillatory shear, steady state shear, and transient shear flows. In section IV these measurements are used to benchmark and validate a nanostructurally based thermo-mechanical model for the melt composites.

#### 3.3.1 Morphology and Dispersion of CNFs in the Polymer Matrix

The morphology and dispersion of CNF in composites prepared by the two methods has been characterized using both optical microscopy and transmission electron microscopy (TEM). The combination of complementary length scales of these two studies results in comprehensive measurements, with some features accessible through TEM, and others through the optical microscope.

The CNFs used in this study have diameters ranging from 100 to 200 nanometers. Since the smallest object that can be observed by optical microscopes is about 200nm, determined by the wavelength of the visible light, only those CNFs in the largest range of diameters can be observed with an optical microscope. In contrast, TEM can capture all of the CNFs, from largest to smallest, and hence TEM images are used for the measurement of the nanoscale dispersion and structure in the composites. However, TEM requires thin slices of sample, with typical thicknesses of the order of 100nm, depending
on the capability of the TEM. With our system the maximum thickness was found to be 800nm, beyond which the images are not clear. With even these thickest slices, most of the CNFs in the TEM samples will be cut during the sectioning, especially the longer fibers. Thus, TEM cannot capture the true length of the CNFs. Therefore measurement of the length of the CNFs after being processed through either melt blending or solvent casting is accomplished with optical microscopy; the CNF/PS composite is dissolved in the solvent THF, with composite to solvent ratio of about 8:100 by weight, and a thin film of the resulting THF/CNF/PS suspension is viewed through an optical microscope.

Figure 3.1 shows photographs through an optical microscope of 5wt% MB and SC composites suspended in THF. We observe in these images, and many others not shown of MB and SC composites in all CNF concentrations, that the CNFs in MB composites have lengths in the range 1-20 micron, while in SC composites the range is 4-60 microns. The diameters of the CNFs in both MB and SC composites were measured in TEM images to be in the same 100–200 nm range measured in the as-received fibers. Combining the length and diameter measurements of 800 to 1000 fibers of each composite system, we find that a representative aspect ratio for the MB composites is 40, and for the SC composites is 160; these weight-average aspect ratios of the CNFs were computed in a similar way as weight-average molecular weights for polymers are computed. We comment that in our rheological study we subjected samples to multiple runs and measured no significant change in rheology. Further, we examined the samples before and after the reruns using optical and TEM microscopy and observed no change in fiber length.
From the TEM images of sections of solidified MB and SC composites shown in Figure 3.2 and many others in all CNF concentrations, we learn that in the micron scale the CNFs are uniformly dispersed in MB composites. In contrast we observed micron-scale regions almost devoid of CNFs in SC composites, mostly due to CNF settling during the drying process; on a millimeter scale, the SC composites exhibit good uniformity.

Summarizing, our optical and TEM images of the CNF/PS composites reveal that the CNFs are well dispersed in the composites created by either melt blending or solvent casting, at least to millimeter scale, compared with the large, tightly packed CNF agglomerates in the as-received form. However, it is noticeable from both TEM and optical micrographs that the CNFs in MB composites are shorter than that in SC composites. It is likely that the CNFs in melt blended composites were severely sheared during compounding, achieving uniform dispersion in the micron scale at the cost of damage to the CNFs. In contrast, the sonication in the solvent casting process successfully dispersed, at least to the millimeter scale, most of the agglomerates in the as-received CNFs, while largely preserving the original length of the CNFs.

Fiber suspensions can be divided into three concentration regimes based on the number of fibers per unit volume $n$, fiber length $L$, and fiber diameter $D$. The suspension is said to be in dilute when the $nL^3 << 1$. In this regime, the fibers can rotate freely without touching the neighboring fibers. When $1 << nL^3 << L/D$, the suspension is in the semi-dilute regime, in which the fibers collide other fibers during rotation. For $nL^3 >> L/D$ the suspension is in the concentrated regime, with frequent physical contact between fibers. Table 3.1 summaries the measurements of our TEM and optical microscopy
studies, which include all of the properties necessary to determine the concentration regime for each composite. In our labeling scheme, MB2 is the 2wt% melt blended composite, SC5 is the 5wt% solvent cast composite, etc. Using our measurements of composite systems and their CNF and PS constituents, we compute that the melt blended composite MB2 with CNF concentration of 2wt% is in the semi-dilute regime, and the MB composites with higher CNF concentrations, and all SC composites, are in the concentrated regime. In particular, the SC5 and SC10 composites have much higher $nL^3$ values, leading us to expect that interparticle forces will play a significant role on their rheological behavior.

3.3.2 Linear Viscoelasticity

In our linear viscoelastic characterization of the response of the CNF/PS melt composites to small amplitude oscillatory shear, we first determined the boundaries of the linear regime over which elastic modulus $G'$ and viscous modulus $G''$ are independent of amplitude by running strain amplitude sweeps from 0.01% to 10% at different frequencies on each sample. We found that the boundary of the linear regime is 1% strain for the MB2, MB5, and SC2 composites, and 0.1% strain for the MB10, SC5, and SC10 composites, so that higher CNF concentration and/or longer CNF lengths reduces the linear domain of viscoelasticity. This may be evidence that any structure formed by the CNFs is weak: even a small strain may alter the structure and make the response non-linear.

Figure 3.3 shows the master curves of elastic modulus $G'$ of the MB and SC composites, as well as samples of pure polystyrene which have undergone the same mixing process as the melt blended composites (denoted MB0) and the solvent casting
process (denoted SC0). The small amplitude oscillatory shear experiments were performed over the temperature range of 140 – 220°C. The master curves were generated by shifting the measured data to 200°C following the principles of time-temperature superposition; the shift factors ($a_T$) of all the MB and SC composites as well as the pure polymer control samples are plotted in Figure 3.4. Our measurements show marked effects of the CNFs on the linear viscoelastic moduli, especially at the low frequencies (see Figure 3.3 and Figure 3.4). For both melt blended and solvent cast composites, the elastic modulus $G'$ increases monotonically with increasing CNF concentration. The amount of increase in the SC composites is larger than that in the MB composites for a given CNF concentration, an effect of aspect ratio of the CNFs.

At low frequencies, homogeneous polymers typically exhibit the terminal behavior of $G' \propto \omega^2$ and $G'' \propto \omega$, so that the slopes of log $G'$ vs. log $\omega$ and log $G''$ vs. log $\omega$ at low frequencies are near 2 and 1, respectively. Table 3.2 lists the low-frequency slopes of $d(\log G')/d(\log \omega)$ and $d(\log G'')/d(\log \omega)$ deduced from our small amplitude oscillatory shear measurements on the MB and SC composites and pure PS samples. Both the pure polymer sample that underwent the melt blending process (MB0) and the pure polymer sample that underwent solvent casting process (SC0) exhibit the terminal behavior typical of homogeneous polymers, with slopes near 2 and 1, but both the melt blended and solvent cast CNF/PS melt composites do not, with deviation of the slopes from 2 and 1 increasing with CNF concentration. Further, at any CNF concentration the slopes of $G'$ and $G''$ for SC composites are smaller than those of MB composites, indicating that the longer fibers in the SC composites have a greater influence on the viscoelasticity of the composites.
Non-terminal behavior is an indication of solid-like, elastic response, with a long relaxation time, and is also typical of physical gelation as described by other researchers: Larson et al\textsuperscript{90} studied smectic liquid crystals and suggested that non-terminal low-frequency rheological behavior is due to long-range domain structure and the presence of defects. This shows that the addition of rod-like particles is enough to produce non-terminal behavior, without the requirement of entanglement. However, Krishnamoorti\textsuperscript{139} showed that typical terminal behavior is observed in poly(dimethylsiloxane) clay composites in which the ends of polymer chains are not chemically bonded to the clay surface. In later work, Krishnamoorti and Giannelis\textsuperscript{88} argued that in end-tethered polymer layered silicate nanocomposites, the inclusion of silicate layers and the lack of complete relaxation of the confined polymer chains cause the solid-like response at low frequencies. Solomon’s results\textsuperscript{87} from the polypropylene/clay hybrid materials suggested that the low frequency plateau was the result of non-Brownian network structure formed by the individual clay platelets. Pötschke et al\textsuperscript{140} studied multi-walled carbon nanotube (MWNT)/polycarbonate systems and found that a low-frequency plateau in $G'$ occurs when the MWNT loading is 2wt% or higher. They suggested that the MWNTs form interconnected structures and dominate the rheological behavior at low frequencies. Liu et al\textsuperscript{141} further analyzed Pötschke’s data\textsuperscript{140} and showed a gellation point of about 1.6wt% for their composites. It is likely that during flow of our CNF/PS melt composites (especially those in the concentrated regime; see Table 3.1) the CNFs interact with each other. We conjecture, based on the degree of non-terminal behavior fro the different melt composites, that the shorter CNFs in MB composites interact with each other is less than the longer CNFs in the SC composites. Continuing this conjecture, the shortness of the
CNFs in the MB melt composites renders them essentially rigid rods that can be confined by their neighboring CNFs such that they cannot rotate freely, but for which fiber entanglement is almost impossible. In contrast, the longer CNFs in the SC composites can more readily entangle with each other to form network structure based on physical contact. At the higher CNF concentrations and lower frequencies these structures respond at longer time scales than the composites without CNF structure, producing solid-like behavior. As a result, decrease in the slope of $G'$ and $G''$ of SC composites is more dramatic than that of MB composites. We discovered similar non-terminal behavior is for CNFs suspended in glycerol/water solvents\textsuperscript{142}. In those systems the Newtonian solvent does not contribute any viscoelastic behavior, and the non-terminal behavior is generated entirely by interactions between the CNFs.

The linear viscoelastic response of the CNF/PS melts was measured at the temperature range of $140^\circ C$ to $220^\circ C$, and time-temperature superposition was used to generate master curves in Figure 3.3. It is found that the temperature shift factors of Figure 3.4 are independent of the CNF concentration and length, and the same as those of the pure polystyrene. The theoretical foundation of time-temperature superposition is that the relaxation times of the polymer chains have the same temperature dependence\textsuperscript{143}. In the light of this statement, and noting that the addition of CNFs to the polystyrene does not alter the shift factors, it seems that the mobility of the polymer chains are not constrained by the CNFs. (Polymer nanoclay composites\textsuperscript{87-88} are similar systems in which inorganic particles are observed to have marked effects on $G'$ and $G''$, but not on the shift factors of time-temperature superposition.) The mobility of the polymer chains was further probed by measuring the glass transition temperature ($T_g$) as a function of mass.
concentration. We did not detect apparent change of $T_g$ from pure PS to composites with up to 10wt% CNFs (data not shown here). By definition, $T_g$ is the temperature above which the polymer chains are mobile. Thus, the lack of change in $T_g$ of all composites also suggests that presence of CNFs does not effect the mobility of the polymer chains.

The composites are further investigated by examining the shift of the cross over point of $G'$ and $G''$ curves vs. frequency. For polymer melts the inverse of the frequency at the cross over point can be defined as a characteristic relaxation time\(^{109}\). Figure 3.5a and Figure 3.5b exhibit the cross over points of $G'$ and $G''$ for the melt composites and polymer control samples. In Figure 3.5a, the crossover point for MB composites shifts slightly to the left with increasing CNF concentration, corresponding to a slight increase of the characteristic relaxation time with CNF concentration, if we extend the above concept for polymer melts to our composite systems. In SC composites (Figure 3.5b) the crossover point also shifts only slightly to the left when the CNF concentration is 2wt%, but shifts more than a decade to the left in 10wt% composite. Adopting the common interpretation from polymer melts, this shift of crossover point indicates that at low CNF concentrations the characteristic relaxation times in SC composites behave like those in MB composites, increasing slightly with CNF concentration. However at high CNF concentrations the crossover behavior of the SC composite departs from that of the corresponding MB composite, with for example the characteristic relaxation time for the 10wt% SC composite defined as the reciprocal of crossover point being nine times the relaxation time of pure polystyrene melt, compared to one and half times for the 10wt% MB composite. Summarizing, the MB composites gradually become more elastic as the CNF concentration increases up to 10wt%; the SC composites behave similarly at CNF
concentrations up to 2 wt%, but become significantly more elastic at 10 wt%. The gradual increase of $G'$ and $G''$ with CNF concentration observed in Figure 3.5 for the MB composites and the low-concentration SC composites is likely the result of fiber-matrix interactions, while the dramatic changes exhibited by the SC10 composite is likely caused by the entanglements of the CNFs, since the CNFs in SC composites are much longer than that in MB composites. These structures make the composite more elastic.

### 3.3.3 Start-up of steady shear

Before displaying the transient shear viscosity $\eta^+$ of the MB and SC melt composites, we show in Figure 3.6 the transient shear viscosity of the pure PS in the start-up of steady shear, for rates from 0.0001 to 10 s$^{-1}$. The $\eta^+$ curves at shear rates 0.01 s$^{-1}$ and smaller fall on top of each other in the figure. It can be seen that for the pure PS, at small shear rates the transient viscosity $\eta^+$ gradually approaches steady state from below, but at large shear rates overshoots the steady state value and then approaches steady state from above.

Figure 3.7 shows the transient shear viscosity $\eta^+$ and primary normal force difference $N_1$ of the SC10 composite over the same range of shear rates. Comparing Figure 3.6 and Figure 3.7a, the $\eta^+$ of SC10 is larger than that of PS at the corresponding shear rate, but for shear rates between 0.1 and 10 s$^{-1}$ the shape of the curves in the two figures are similar. However, instead of having identical $\eta^+$ over the range 0.0001-0.01 s$^{-1}$, the transient viscosity of the SC10 composites increases markedly as strain rate gets smaller than 0.01 s$^{-1}$. It takes longer for the shear viscosity of the composite to reach steady state than the pure polymer, if it ever does. Due to the lower torque limit of the torque transducer on the rheometer, tests at shear rates smaller than 0.0001 s$^{-1}$ cannot
produce reliable data and therefore are not shown. The corresponding normal stress differences $N_1$, shown in Figure 3.7b, generally experience larger overshoots than the $\eta^+$, and the overshoots occur at longer time. Normal stress differences at shear rates lower than 0.01s$^{-1}$ are too small to accurately measure.

### 3.3.4 Steady State Rheology

For CNF concentrations 2wt% and below and shear rates 0.01s$^{-1}$ or greater, we observed that the viscosity of the composite reaches a true steady state within 5 minutes. However for higher concentrations and lower shear rates the identification of steady shear viscosity presents some challenges, since the viscosity never reaches a steady state in times typical in polymer processing (see for instance Figure 3.7a, in which the viscosity of the SC 10wt% composite at shear rate 0.0001 s$^{-1}$is still evolving after 12 hours). For these cases, the value assigned in section V as the steady viscosity for the purpose of comparison to model predictions is the viscosity at strain in the range 2 to 4. Given this rule, the steady state viscosities of MB and SC composites are shown in Figure 3.8. Each data point was obtained from a start up of steady shear test with a fresh sample. Both MB and SC composites show increased viscosities and more shear thinning with higher CNF loadings, especially at low shear rates, with more pronounced increases in viscosity for SC than MB composites. Furthermore, the plateau of the viscosity at low shear rates gradually disappears with increasing CNF concentrations, especially for the SC10 composite. The slope of the viscosity curve for the SC10 composite on the log-log plot at low shear rates is -1, an indication of yield-stress behavior.

To further reveal the effects of CNF concentration and length on the steady state rheology of the melt composites, the relative viscosities $\eta_r$ (defined as of the ratio of the
viscosity of the composite to the viscosity of the pure polymer at the same strain rate) of the MB and SC composites are plotted against shear rate in Figure 3.9. Any deviation from the line $\eta_r = 1$ can be attributed to the CNFs in the composites. The relative viscosity $\eta_r$ for both types of composites decreases with increasing shear rate. Further, at any CNF concentration $\eta_r$ of the SC composite at low shear rates is much higher than that of the corresponding MB composite, an indication that the longer CNFs in the SC composites increase the viscosity of the composite much more than the short CNFs in the MB composites. This difference of relative viscosity between SC and MB composites increases with CNF concentration, and decreases as shear rates increases, until at shear rate of $10s^{-1}$ the relative viscosities of both types of composites are essentially the same.

Primary normal stress differences $N_1$ of the composites are displayed in Figure 3.10. In MB composites, the measured $N_1$ for all CNF concentrations is about the same as that of pure PS polymer. In contrast, $N_1$ measurements for SC composites show more dependence on CNF concentration, with higher CNF concentration leading to higher $N_1$. At a shear rate of $0.1s^{-1}$, the $N_1$ of SC10 is more than 10 times higher than that of pure PS polymer. However, the effects of CNFs on $N_1$ diminish at higher shear rates, with essentially no effect at $10s^{-1}$.

In subsection III.B we explain several features of the composites’ small amplitude oscillatory shear behavior by the conjecture that network structure is created in the CNFs at lower shear rates, with stronger structures in the long-fiber SC composites with high CNF concentration. This conjecture also explains several of the features of the steady shear behavior of the composites noted above: Such a nanostructure would increase flow resistance and hence the steady state viscosity $\eta$ and first normal stress difference $N_1$. 

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Since CNF length affects the strength of the nanostructure, the MB and SC composites exhibit different $\eta$ and $N_1$ at same shear rates. MB composites contain shorter CNFs than SC composites, so that the strength of the nanostructure is weaker and hence the enhancement of $\eta$ and $N_1$ in MB composites is smaller than that in SC composites. At low shear rates the nanostructure is strong enough to withstand the flow, resulting in the appearance of a yield stress for the composites with the highest CNF concentrations and CNF lengths, SC5 and SC10. High shear rate flow destroys some of the nanostructure, leading to a decrease of viscosity and a decrease of the effect of the CNFs on $N_1$.

The Peclet number ($Pe$) is the ratio of hydrodynamic force to the Brownian force. For fibers in a polymer melt the Peclet number in steady shear flow can be defined as

$$Pe = \eta_m \dot{\gamma} L^3/k_BT(\ln(L/D)-0.8),$$

where $\eta_m$ is the viscosity of the polymer melt, $\dot{\gamma}$ is the shear rate, $L$ is the fiber length, $D$ is the fiber diameter, $k_B$ is the Bolzmann constant, and $T$ is the temperature. From the steady shear viscosity measurements of this section for pure polymer (see Figure 3.8), and our measurements of CNF geometry summarized in Table 3.1, $Pe$ is calculated to be of order of $10^5$-$10^7$ for our systems. Therefore in the modeling to follow in section IV the Brownian forces can be neglected and the CNFs can be treated as non-Brownian particles.

### 3.3.5 Cox-Merz rule

The empirical Cox-Merz rule states that the complex viscosity ($\eta^*$) versus the dynamic frequency obtained from small amplitude oscillatory shear is numerically equal to the steady shear viscosity ($\eta$) versus the shear rate. Although there is no general explanation for such a relationship, it is widely successful in describing the observed behavior of isotropic polymeric solutions and polymer melts. As $\eta^*$ is more readily
measurable experimentally than $\eta$, this rule provides a convenient way to estimate the $\eta$ over a relatively wide range of shear rates. Figure 3.11 shows that the Cox-Merz rule holds for the MB2, MB5, and SC2 composites, but not the MB10, SC5, and SC10 composites. Steady state viscosities of the MB10 and SC5 composites are less than half an order of magnitude lower than the corresponding dynamic viscosity, while that of SC10 is more than an order of magnitude lower. As MB10, SC5, and SC10 show evidence of a yield stress, they are expected not to obey the Cox-Merz rule, just like other polymer composites with yield stress\textsuperscript{145,146}.

3.4 Nanoparticle/Polymer Melt Composite Constitutive Model

In this section we develop, benchmark, and validate models for the CNF/PS composite systems in their melt phase studied through experiments in sections 3.2 and 3.3. These models are motivated by the behavior we observed in the experiments, and have been found to accurately capture the relationships between the rheological properties, processing conditions, and fiber nanostructure measured in our experiments.

In a previous chapter we study composite systems of CNFs suspended in glycerol-water. Model systems of either elastic or rigid dumbbells in a Newtonian solvent with isotropic or anisotropic hydrodynamic drag, with or without hydrodynamic interaction are investigated; it is found that the most successful model (the elastic model with anisotropic hydrodynamic drag and negligible hydrodynamic interaction) successfully captures the rheological behavior we observed in our experiments on the CNF/ glycerol-water systems. The behavior of CNFs in a polymer melt we observed in the experiments described in section 3.2 and 3.3 of this chapter is fundamentally different from the behavior of CNFs in a glycerol-water solvent of the previous chapter, in that the polymer
melt matrix by itself, without nanoparticles, exhibits shear thinning, extensional, and viscoelastic properties not observed in the Newtonian glycerol-water solvent, and our experiments give strong evidence of significant interaction of the CNFs with the polymer matrix and/or other CNFs. The constitutive equations which we found to best capture the observed features of our CNF/PS melt composites are (in indicial notation):

\[
\tau_{ij}^\varepsilon = -p\delta_{ij} + 2\eta_s D_{ij} + \tau_{ij}^p + \tau_{ij}^{CNF},
\]  
(3.1)

\[
\tau_{ij}^p + \lambda \frac{D\tau_{ij}^p}{Dt} + \frac{\alpha}{\eta_p} \left( \tau_{ij}^p \tau_{ij}^p \right) = 2\eta_p D_{ij},
\]  
(3.2)

\[
\tau_{ij}^{CNF} = 2[\eta_s + \eta] \phi \left[ A D_{ij} a_{ij} + B (D_{ij} a_{ij} + a_D D_{ij}) + C D_{ij} + 2F a_D D_{ij} \right],
\]  
(3.3)

with

\[
\frac{da_{ij}}{dt} = (W_{ij} a_{ij} - a_{ij} W_{ij}) + \chi \left( D_{ij} a_{ij} - a_D D_{ij} - 2D_{ij} a_{ij} \right) + 4C_1 \Pi^{ij}_{12} \left( \delta_{ij} - ma_{ij} \right),
\]  
(3.4)

These coupled equations model the polymer melt matrix as viscoelastic and strain rate dependent, and model fiber-fiber and fiber-matrix interaction.

Equation (3.1), proposed by Azaiez$^{147}$, expresses the total stress \(\tau_{ij}^\varepsilon\) in the polymer/nanocomposite system as the sum of the stress contribution \(\tau_{ij}^p\) from polymer molecules with fiber inclusions, the stress contribution \(\tau_{ij}^{CNF}\) in the carbon nanofibers, the stress contribution \(2\eta_s D_{ij}\) from a Newtonian solvent (if present), and the pressure \(p\) maintaining incompressibility. In the Newtonian contribution, \(D_{ij}\) is the symmetric part of the Eulerian velocity gradient \(\frac{\partial v_j}{\partial x_i}\) and \(\eta_s\) the solvent viscosity.
Equation (3.2), the single-mode Giesekus model\textsuperscript{22}, predicts the strain-rate-dependent viscoelastic behavior of the polymer matrix. (In this chapter we investigate the ability of a single-mode model to describe the polymer contribution to the total stress in the composite. It is anticipated that multiple modes would result in more accurate prediction of the melt contribution, but with the cost of added complexity to the overall coupled model for the composite; for every additional mode to the melt model we must include new terms in the model for the fiber–fiber and fiber-matrix interactions.) In equation (3.2) the constants $\eta_p$, $\alpha$, $\lambda$ are the polymer viscosity, mobility factor, and relaxation time, respectively, of the melt phase of the polymer matrix, and the upper convected derivative of $\tau_{ij}^p$ is

$$\frac{D\tau_{ij}^p}{Dt} = \frac{d}{dt} \tau_{ij}^p - W_{ik}^l \tau_{lk}^p + \tau_{ik}^p W_{lk}^l - D_{ik}^l \tau_{lk}^p - \tau_{ik}^p D_{lk}^l$$ \hspace{1cm} (3.5)$$

where $W_{ij}$ is the skew part of the Eulerian velocity gradient. In our study we investigated the generalization of equation (3.2) presented in Azaiez\textsuperscript{147},

$$\lambda \frac{D\tau_{ij}^p}{Dt} + \sigma \tau_{ij}^p + \frac{\alpha \lambda}{\eta_p} \left( \tau_{ik}^p \tau_{lk}^p \right) + \frac{m(1-\sigma)}{2} \left( a_{ik}^l \tau_{lk}^p + a_{ik}^l \tau_{ik}^p \right) = 2\eta_p D_{ij}^p,$$ \hspace{1cm} (3.6)

which includes the effect of polymer-fiber interaction through the parameter $\sigma$; $m$ is the dimension of the space ($m=2$ for planar flows and $m=3$ for 3-dimensional flows). Through comparison with our experimental measurements of the composite systems we deduced that $\sigma$ is effectively 1 (see subsection 3.5.4 to follow), so that there is negligible polymer-fiber interaction and the modified Giesekus equation (3.6) reduces to the Giesekus equation (3.2).
In equation (3.3), derived by Tucker\textsuperscript{148}, \( \eta \) is the viscosity contribution from the polymer matrix; in simple shear in the 1-2 plane \( \eta = \frac{\tau_p}{\dot{\gamma}} \) with \( \dot{\gamma} \) the shear rate. \( D_r \) is the rotary diffusivity due to Brownian motion, and \( \phi \) is volume fraction of fibers. Parameters \( A, B, C, \) and \( F \) are in general functions of the particle aspect ratio \( h = L / D \), with \( L \) the particle length and \( D \) the particle diameter. In dilute regimes\textsuperscript{148}:

\[
A = \frac{h^2}{2[\ln(2h) - 1.5]}, \quad B = \frac{6\ln(2h) - 11}{h^2}, \quad C = 2, \quad F = \frac{3h^2}{\ln(2h) - 0.5},
\]

and in semi-dilute regimes\textsuperscript{10}:

\[
A = \frac{h^2}{3\ln(2h_j / D)}, \quad B = 0, \quad C = 0, \quad F = 0,
\]

with \( h_j \) a characteristic distance between a fiber and its nearest neighbors:

\[
\frac{2h_j}{D} = \frac{\pi}{\sqrt{\phi}} \quad \text{for aligned fibers},
\]

\[
\frac{2h_j}{D} = \frac{\pi}{2\phi h} \quad \text{for random fibers}.
\]

Since the melt composites we study in this chapter are in either the semi-dilute or concentrated regimes (see Table 3.1), we employ choices (3.8) of parameters \( A, B, C, \) and \( F \) derived in the semi-dilute regime, rather than (3.7) derived for the dilute regime (there have been no values of \( A, B, C, \) and \( F \) proposed in the literature for the concentrated regime). Note that the term multiplied by \( F \) in equation (3.3) embodies the effects of Brownian forces, so that the selection in (3.8) of \( F = 0 \) is consistent with our assessment in subsection 3.3.4 that the order of magnitude of the Peclet number in the flows we
investigate of our melt composites is such that the effects of the Brownian forces are negligible.

The properties of a nanoparticle/polymer composite, both during processing (e.g. viscosity and relaxation time) and in its end state (e.g. modulus and conductivities) are mesoscale properties, the result of combining the contributions of many nanoscale particles. A measure of nanostructure that combines the contributions of a collection of particles to dictate the mesoscale properties of the nanocomposite is the second order orientation tensor $a_{ij}$ that occurs in equation (3.3), defined as the dyadic product of fiber orientation $p$ with itself averaged over the orientation space containing a sufficient number of particles$^{24}$:

$$a_{ij} = \int p_i p_j \psi(p) dp,$$  \hspace{1cm} (3.11)

where $\psi(p)$ is the orientation distribution function, i.e. the probability that the fiber is oriented along the unit vector $p$. The evolution equation (3.4) for the mesoscale quantity $a_{ij}$ averaging the composite response over an ensemble of nanoparticles is obtained from the nanoscale equations governing the behavior of the individual particles as follows: The orientation distribution function $\psi(p)$ evolves according to the equation$^{24}$:

$$\frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial p_i} (p_i \psi),$$  \hspace{1cm} (3.12)

and the rate of change of orientation $p$ with time for a single nanoparticle is$^{24}$

$$\dot{p}_i = \frac{1}{2} (W_{ij} p_j) + \chi \left( D_{ij} p_j - D_{kl} p_i p_k p_l \right) - D_i \frac{1}{\psi} \frac{\partial \psi}{\partial p_i},$$  \hspace{1cm} (3.13)

where $\chi$ is a shape parameter related to the particle aspect ratio $h$ through

$$\chi = \frac{h^2 - 1}{h^2 + 1}.$$  \hspace{1cm} (3.14)
Following Advani\textsuperscript{24} as suggested by Folger and Tucker\textsuperscript{9} for concentrated suspensions of large fibers, in equation (3.13) we employ $D = 2C / \Pi_D^{1/2}$, where $\Pi_D$ is the second invariant of the symmetric part $D_{ij}$ of the velocity gradient and $C$ is the interparticle interaction parameter which measures the intensity of fiber interaction in the composite. Multiplying the kinetic equation (3.12) by $p_i p_j$, integrating over orientation space for a representative number of particles, and inserting equation (3.13) gives the evolution equation (3.4) of the second order orientation tensor $a_{ij}$.

Note that in addition to the second order orientation tensor $a_{ij}$, Equation (3.3) also involves the fourth order orientation tensor $a_{ijkl}$ defined as

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

(3.15)

For closure of the system (3.1)-(3.4) one must adopt an approximation that relates the fourth-order orientation tensor $a_{ijkl}$ in equations (3.3) and (3.4) to the second order orientation tensor $a_{ij}$. Popular closure approximations are:

1. The linear closure approximation,

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

(3.16)

works well when the fibers remain nearly random, but introduces an artificial instability into the equations for highly aligned suspensions\textsuperscript{149};

2. The quadratic closure approximation

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

(3.17)

performs well for highly aligned states, but introduces steady-state errors for more random states\textsuperscript{149};
3. The hybrid closure approximation,

\[ a_{ijkl} = (1 - f) \hat{a}_{ijkl} + f \tilde{a}_{ijkl} \text{ with } f = 1 - 27 \det(a_y), \]

mixes linear and quadratic forms according to scalar measure of orientation and performs well over the entire range of orientation\textsuperscript{149};

4. The orthotropic closure approximation\textsuperscript{150} is based on the assumptions that any approximate fourth-order tensor must be orthotropic, that its principal axes must match those of the second-order tensor, and that each principal fourth-order component is a function of just two principal values of the second-order tensor. For fiber–fiber interaction parameter \( C_1 \geq 0.01 \) and a wide variety of flows, the orthotropic closure approximation provides more accurate solutions than any previous closure approximation\textsuperscript{150}.

3.5 Application of the model to CNF/PS melt composites

3.5.1 Procedures to deduce material constants in the model from experimental measurements

To characterize our CNF/PS melt composites in the context of constitutive model (3.1)-(3.4), we deduce the parameters \( h, \lambda, \alpha, \eta_p, \eta_s, C_1 \) for each CNF/PS melt composite from the experimental morphological and flow measurements reported in section 3.3.

Recall from our measurements of the morphology of the nanofibers that the representative aspect ratio \( h \) for the MB composites is 40, and for the SC composites is 160 (see Table 3.1).
The constitutive parameters $\lambda$, $\alpha$, $\eta_p$, $\eta_s$ are constants and properties of the polymer melt alone. In the characterization of the MB composites, $\lambda$, $\alpha$, $\eta_p$, $\eta_s$ are deduced from steady and oscillatory shear measurements of the polystyrene melt MB0 that has been subjected to the melt blending process. In the characterization of the SC composites, $\lambda$, $\alpha$, $\eta_p$, $\eta_s$ are deduced from steady and oscillatory shear measurements of the polystyrene melt SC0 that has gone through the solvent casting process. As will be seen in section 3.5.2 and 3.5.3 to follow, these values are different for the two polystyrenes.

In detail, $\lambda$, $\alpha$, $\eta_p$, $\eta_s$ are deduced as follows: Since there is no solvent in the polymer melt, we take the solvent viscosity $\eta_s$ to be zero. Zero shear viscosity $\eta_0 = \eta_s + \eta_p$ is the limit in the steady shear flow $v = \dot{\gamma} x_s e_1$ of $\frac{\tau_0}{\dot{\gamma}}$ as $\dot{\gamma}$ becomes small; we identify $\eta_0$, and hence $\eta_p$, as the measured viscosity at shear rate $\dot{\gamma} = 0.001 \text{s}^{-1}$.

With viscosities $\eta_s$ and $\eta_p$ determined, we then obtain the relaxation time $\lambda$ from our small amplitude oscillatory shear experiments on MB0 and SC0. Equation (3.2) gives the functional dependence of the storage modulus $G'$ and loss modulus $G''$ on the material constants $\lambda$, $\alpha$, $\eta_p$, $\eta_s$ and frequency $\omega$ as

$$G''(\omega) = \left( \eta_s + \frac{\eta_0}{1 + (\lambda \omega)^2} \right) \omega, \quad G'(\omega) = \frac{\eta_p\lambda \omega^2}{1 + (\lambda \omega)^2}.$$  \hspace{1cm} (3.19)

(The mobility factor $\alpha$ does not appear in the linearized equations.) We obtain the relaxation time $\lambda$ of the pure PS melts by minimizing the error:
\[
\delta_i = \sum_{i=1}^{n} \left[ \log_{10} G''_{\text{exp}}(\omega_i) - \log_{10} \left( \eta_s + \frac{\eta_p}{1+(\lambda \omega_i)^2} \right)^{\omega_i} \right]^2 + \left[ \log_{10} G'_{\text{exp}}(\omega_i) - \log_{10} \left( \eta_p \lambda \omega_i^2 \frac{1}{1+(\lambda \omega_i)^2} \right)^{\omega_i} \right]^2, \tag{3.20}
\]

where \( G'_{\text{exp}}(\omega_i) \) and \( G''_{\text{exp}}(\omega_i) \) are the measured storage and loss moduli at frequency \( \omega_i \), and \( n \) is the number of frequencies where the moduli were measured; in our study for each of the MB and SC melts there are 24 experiments with frequency from \( \omega = 0.001 \) to \( 15 \text{s}^{-1} \) (refer to the points for MB0 and SC0 in Figure 3.3.) To minimize \( \delta_i \) we search over the physically reasonable domain \( 0 < \lambda < 10 \text{s} \), first using a coarse mesh, then restricting \( \lambda \) to a smaller domain with a refined mesh. Finally, we verify that the best fit is not near the edge of the domain.

We deduce the mobility factors \( \alpha \) from our steady shear measurements of the pure PS. For steady shear at shear rate \( \dot{\gamma} \), equation (3.2) implies that shear viscosity \( \eta(\dot{\gamma}) \) and first normal stress difference \( N_1(\dot{\gamma}) \) of the pure PS are of the forms

\[
\eta(\dot{\gamma}) = \eta_s + \eta_p \frac{(1-\psi)^2}{1+(1-2\alpha)\psi}, \quad N_1(\dot{\gamma}) = 2\lambda \eta_p \frac{\psi (1-\alpha \psi)}{\lambda^2 \alpha (1-\psi)}, \tag{3.21}
\]

with

\[
\psi = \frac{1 - \chi}{1 + (1 - 2\alpha) \chi}, \quad \chi = \sqrt{\frac{1 + 16\alpha (1 - \alpha) (\dot{\gamma} \lambda)^2}{8\alpha (1 - \alpha) (\dot{\gamma} \lambda)^2}} - 1.
\]

With \( \eta_s = 0 \), \( \eta_p \), and \( \lambda \) already deduced as described above, the mobility factors \( \alpha \) of the two pure polymer melts are obtained by minimizing the error
\[
\delta_2 = \sum_{i=1}^{n_1} \left[ \log_{10} \eta_{\exp} (\dot{\gamma}_i) - \log_{10} \left( \eta_p \frac{(1 - \psi)^2}{1 + (1 - 2\alpha)\psi} \right) \right]^2 \\
+ \sum_{i=1}^{n_2} \left[ \log_{10} N_{\exp} (\dot{\gamma}_i) - \log_{10} \left( 2\lambda \eta_p \frac{\psi (1 - \alpha\psi)}{\lambda^2 \alpha (1 - \psi)} \right) \right]^2 ,
\]

where $\eta_{\exp} (\dot{\gamma}_i)$ are the shear viscosities measured at $n_1=9$ shear rates from $\dot{\gamma} = 0.0001$ to $10\text{s}^{-1}$, and $N_{\exp} (\dot{\gamma}_i)$ are the first normal stress differences measured at $n_2=5$ shear rates in the smaller range $\dot{\gamma} = 0.1$ to $10\text{ s}^{-1}$ due to the lower torque limit of the torque transducer.

To minimize $\delta_2$, we search over the physically reasonable domain $0 < \alpha < 1$, first using a coarse mesh, then restricting to a smaller domain with a refined mesh, and finally verifying the best fit is not near the edge of the domain. This search method we have adopted to sequentially minimize the errors (3.20) and (3.22) is feasible since there are only two decoupled 1-parameter searches over well-defined domains.

The only parameter remaining to be determined in the models is the fiber-fiber interaction parameter $C_1$, which must be deduced from experiments on the composite systems, rather than their separate components.

With symmetric and skew parts $D$ and $W$ of the velocity gradient specified by the steady shear flow $\mathbf{v} = \dot{\mathbf{x}} = \dot{\gamma} \mathbf{x}_2 \mathbf{e}_1$ and inserted the orientation evolution equation (3.4), using closure approximation (3.17) and assuming homogeneous steady behavior ($\frac{d}{dt} a_y = 0$) produces the following system of equations for the components of the symmetric orientation tensor $a_y$:
In a study of the processing of CNF/PS melt composites we have used TEM images of sectioned samples to investigate the effect of shear processing on the development of nanofiber structure. One of our findings is that the end-state fiber orientation in a CNF/PS melt nanocomposite depends strongly on the strain rate the nanocomposite undergoes during processing. If interparticle interaction parameter \( C_I \) is considered to be independent of strain rate, the steady shear rate \( \dot{\gamma} \) cancels from all six equations (3.23), so that their solution is a second order orientation tensor \( a_{ij} \) that is a function only of the aspect ratio \( h \) and \( C_I \), independent of strain rate. This model prediction is unacceptable, given its inconsistency with the physically observed dependence of CNF orientation on strain rate. We conclude that in our model the interaction parameter \( C_I \) must be considered as a function of strain rate. Note that when \( C_I \) is a function of strain rate, strain rate does not cancel from equations (3.23), so that orientation tensor \( a_{ij} \) is a function of strain rate.

With aspect ratio \( h \) known from morphological measurements (40 and 160 for melt blended and solvent cast composites, respectively) and \( a_{ijkl} \) expressed in terms of \( a_{ij} \) through a closure approximation, we can solve equation (3.23) for \( a_{ij} \) as a function of
We then obtain $C_1$ pointwise at the discrete shear rates $\dot{\gamma}_i = 0.01, 0.03, 0.1, 0.3, 1, 3,$ and $10 \text{s}^{-1}$ where steady shear viscosities $\eta_{\text{exp}}(\dot{\gamma}_i)$ were measured by solving equations (3.1)-(3.4) separately at each of those shear rates, searching over $C_1$ to minimize the error

$$\delta_i = \sum_{i=1}^{N} \left[ \log_{10} \eta_{\text{exp}}(\dot{\gamma}_i) - \log_{10} \left( \eta_{\text{model}}(\dot{\gamma}_i) \right) \right]^2,$$  (3.24)

summed over the $N = 3$ viscosity measurements (2wt%, 5wt% and 10wt%) at that shear rate: With $a_{ij}$ known as a function of $C_1$, equations (3.1), (3.2), (3.3) are a closed set of coupled equations for $\tau_{ij}^p$, $\tau_{ij}^{\text{CNF}}$, and $\tau_{ij}^{c}$ as functions of $\dot{\gamma}$ and $C_1$. From its solution at each $\dot{\gamma}_i$ we compute the viscosity $\eta = \frac{\tau_{ij}^c(\dot{\gamma}_i)}{\dot{\gamma}}$ of the composite, compare with the measured value $\eta_{\text{exp}}(\dot{\gamma}_i)$, and adjust $C_1$ accordingly. We do not compute $C_1$ for shear rates lower than $0.01 \text{ s}^{-1}$ because these extremely low shear rates are below the typical processing range, and the sizeable increase of viscosity of SC10 and perhaps also SC5 for rates lower than $0.01 \text{ s}^{-1}$ shown in Figure 3.8 suggests that, for those composites at those low rates, there are relatively large interparticle interactions. Although the constitutive equations (3.1)-(3.4) contain an interparticle interaction parameter $C_1$, the structure of the equations are based on dilute or semi-dilute fiber suspensions$^9$, making the equations inappropriate where interparticle interactions are large. Note we only fit $C_1$ to the experimental measurements of steady shear viscosity $\eta_{\text{exp}}(\dot{\gamma}_i)$. The value of $C_1$ obtained by fitting to shear viscosity is then used to predict the first normal stress difference $N_1$.

As we will display in the next section, for both types of composites the values of $C_1$ at the seven discrete values of strain rate are found to lie on a curve that can be closely
approximated by the functional form $C_1 = p \dot{\gamma}^q$. Based on this observation we develop an alternative to the pointwise determination of $C_1$ which directly produces $C_1$ as a continuous function of strain rate. In this alternative procedure we propose $C_1$ is of the functional form $C_1 = p \dot{\gamma}^q$, and search through parameter space $(p, q)$ in the solutions of equations (3.1)-(3.4) to minimize error (3.24) summed over all the 21 experimental measurements of steady shear viscosity at all seven shear rates $\dot{\gamma} = 0.01$ to $10 \text{s}^{-1}$. (Again, we fit to only the measurements of steady shear viscosity and then predict the first normal stress difference $N_1$.)

3.5.2 Models for the Melt Blended composites

The measured zero shear rate viscosity for pure polymer subjected to the melt blending process is 9864 Pa s (see Figure 3.8), so that in the melt blended CNF/PS melt composite models for MB2, MB5, and MB10 we have $\eta_s = 0$ and $\eta_p = \eta_0 = 9864 \text{ Pa s}$. Minimizing error (3.20) in the domain $0 < \lambda < 10 \text{s}$ between model predictions (3.19) for $G'(\omega)$ and $G''(\omega)$ and the 24 measured moduli $G'_\text{exp}(\omega_i)$ and $G''_\text{exp}(\omega_i)$ at frequencies from $\omega = 0.001$ to $15 \text{s}^{-1}$ for the pure polymer melt MB0 produces $\lambda = 0.329 \text{s}$ and the fit shown in Figure 3.12a. Minimizing error (3.22) in MB0 over $0 < \alpha < 1$ for the 9 steady shear viscosities measurements from $\dot{\gamma} = 0.0001$ to $10 \text{s}^{-1}$ and the 5 first normal stress differences $N_1$ from $\dot{\gamma} = 0.1$ to $10 \text{s}^{-1}$ produces $\alpha = 0.392$ and the fits shown in Figure 3.12b.

With $C_1$ considered to be a function of strain rate, and aspect ratio assigned to be the MB value 40 we measured for MB composites, we search through solutions of equations (3.1)-(3.4) to minimize error (3.24) summed over the $N=3$ experimental
measurements of shear viscosities at each shear rate and obtain the pointwise values \( C_1 = 6.83 \times 10^{-2}, 6.83 \times 10^{-2}, 2.65 \times 10^{-2}, 9.70 \times 10^{-3}, 2.70 \times 10^{-3}, 1.90 \times 10^{-3} \) and \( 9.90 \times 10^{-3} \) corresponding to shear rates \( \dot{\gamma} = 0.01, 0.03, 0.1, 0.3, 1, 3, \) and \( 10 \text{s}^{-1} \), respectively. Table 3.3 exhibits these values of \( C_1 \) and the corresponding components of the second order orientation tensor \( a_{ij} \) computed from equations (3.23). Figure 3.13 compares the experimental measurements of the steady shear viscosity and first normal stress difference at shear rates \( \dot{\gamma} = 0.01, 0.03, 0.1, 0.3, 1, 3, \) and \( 10 \text{s}^{-1} \) to the pointwise model predictions at those rates. Recall that \( C_1 \) is fit only to the measured viscosities, not the measured first normal stress differences; the model prediction of \( N_1 \) displayed in Figure 13 is computed from the value of \( C_1 \) that optimizes agreement with viscosity.

In Figure 3.14 we plot the seven optimized pointwise values of \( C_1 \) versus shear rate, and observe they lie close to the power law fit \( C_1 = 0.0074 \dot{\gamma}^{-0.472} \). The power law form of \( C_1 \) for the melt blended composites as a function of strain rate deduced directly from all 21 experimental measurements of steady shear viscosity is \( C_1 = 0.0066 \dot{\gamma}^{-0.507} \). In addition to the pointwise values of \( C_1 (\dot{\gamma}) \), Figure 14 displays both of the power law expressions of \( C_1(\dot{\gamma}) \), the function \( C_1 = 0.0066 \dot{\gamma}^{-0.507} \) fit to the pointwise values of \( C_1 \) deduced from viscosity measurements, and the function fit directly to the viscosity measurements. Figure 3.15 shows the experimental measurements and model predictions of the viscosity and first normal stress difference of the steady shear experiments with the optimal form \( C_1 = 0.0066 \dot{\gamma}^{-0.507} \). Again, the function \( C_1 \) is fit to only the viscosity measurements, with \( N_1 \) the prediction produced by this function.
Comparing the model predictions and the experimental measurements shown in Figure 3.15, we conclude for the MB composite systems that the model with $\eta_s = 0$, $\eta_p = 9864$ Pa.s, $h = 40$, $\lambda = 0.329$ s, $\alpha = 0.392$, and $C_l = 0.0066s^{-0.507}\gamma^{-0.507}$ successfully capture shear thinning behavior at low shear rate and gives an accurate prediction of the composite viscosity magnitude. The model captures the correct trend of the first normal stress difference while it over-predicts the first normal stress difference magnitude for all CNF concentrations.

### 3.5.3 Models for the Solvent Cast composites

The measured zero shear rate viscosity for the pure polymer subjected to solvent casting is 11160 Pa.s, so that $\eta_p = \eta_0 = 11160$ Pa.s in the models for the solvent cast CNF/PS melt composites SC2, SC5, and SC10. Minimizing error (3.20) for the 24 oscillatory shear measurements of $G'_{\exp}(\omega_i)$ and $G''_{\exp}(\omega_i)$ ($\omega = 0.001$ to 15 s$^{-1}$) on the SC0 pure polymer melt produces $\lambda = 0.321$ s (Figure 3.16a), and minimizing error (3.22) for 9 steady shear viscosity measurements ($\dot{\gamma} = 0.0001$ to 10 s$^{-1}$) and 5 first normal stress difference $N_1$ measurements ($\dot{\gamma} = 0.1$ to 10 s$^{-1}$) produces $\alpha = 0.479$ (Figure 3.16b).

With $C_l$ considered to be a function of strain rate, and aspect ratio assigned to be the SC value 160, we minimize error (3.24) and obtain the pointwise values $C_l = 2.82 \times 10^{-3}$, $1.39 \times 10^{-3}$, $5.81 \times 10^{-4}$, $2.21 \times 10^{-4}$, $5.90 \times 10^{-5}$, $2.70 \times 10^{-5}$ and $9.80 \times 10^{-5}$ corresponding to shear rates $\dot{\gamma} = 0.01$, 0.03, 0.1, 0.3, 1, 3, and 10 s$^{-1}$, respectively. Table 3.4 exhibits these values of $C_l$ and the corresponding components of second order orientation tensor $a_{ij}$ computed from equations (3.23). Figure 3.14 plots the seven pointwise values of $C_l$ together with the power law fit to these pointwise values $C_l = 0.0001s^{-0.627}\gamma^{-0.627}$, and the
power law fit directly to the experimental viscosity measurements $C_1 = 0.0001s^{-0.729} \dot{\gamma}^{-0.729}$.

Figure 3.17 compares the pointwise model predictions of viscosity and first normal stress difference to the steady shear experiments. Figure 3.18 compares the continuous model predictions to the experiments.

Comparing the model predictions and the experimental measurements shown in Figure 3.18, we conclude for the SC composite system, the model with $\eta_s = 0$, $\eta_p = 11160 \text{ Pa.s}$, $h = 160$, $\lambda = 0.321 \text{ s}$, $\alpha = 0.479$, and $C_1 = 0.0001s^{-0.729} \dot{\gamma}^{-0.729}$ successfully captures shear thinning behavior and gives an accurate prediction of the composite viscosity magnitude. The model captures the correct trend of the first normal stress difference while it over-predict the stress magnitude for all mass concentrations.

We comment that the model captures the measured shear rate dependence of viscosity for all samples (including the higher load MB10, SC5, and SC10 composites) in the range of small shear rate down to $10^{-3} \text{ s}^{-1}$, but it cannot model the indications of pseudo-solid Bingham type measured in the SC10 composite as shear rate goes to zero (See Figure 3.8 b). When the shear rate approaches zero, our model predicts a finite viscosity.

### 3.5.4 Investigation of polymer-fiber interaction

In addition to modeling the polymer matrix with the Giesekus model, equation (3.2), we also investigated the modeling of the matrix with the generalization (3.6) of the Giesekus model proposed by Azaiez, which includes the effects of polymer-fiber interaction through a fiber/polymer matrix interaction parameter $\sigma$. This parameter $\sigma$, in general a function of mass concentration of the particles, characterizes the effect of
particle orientation on the hydrodynamic drag acting on the polymer molecules\textsuperscript{147}. In the special case $\sigma = 1$, the drag force on the polymer molecules is independent of the fiber orientation, and the usual Giesekus model (3.2) is obtained.

We assume the fiber/polymer matrix interaction parameter $\sigma$ is a function of CNF length (that is, whether the composite was prepared via melt blending or solvent casting) and CNF concentration, but independent of strain rate. Hence there is a different value of $\sigma$ for each of MB2, MB5, MB10, SC2, SC5, and SC10. To obtain $\sigma$ for MB composites, we set $C_1 = p(\dot{\gamma})^q$, $h = 40$, $m = 3$, and volume fraction $\phi = \frac{\rho_p \times \text{wt}\%}{\rho_f + (\rho_p - \rho_f) \times \text{wt}\%}$ = 1.12 for MB2, 2.84 for MB5, and 5.81 for MB10 ($\rho_p$, $\rho_f$ and wt\% are polymer density, CNF density and mass concentration of the MB composites, respectively) in equations (3.1), (3.6), (3.3) and (3.4), and search through parameter space ($p$, $q$, $\sigma_2$, $\sigma_5$, $\sigma_{10}$) for the minimum error (3.24) summed over the 21 measurements of the steady shear viscosity $\eta(\dot{\gamma})$ of MB2, MB5, MB10 at shear rates from $\dot{\gamma} = 0.01$ to 10 s\textsuperscript{-1}. The procedure to produce $\sigma$ for SC composites is the same, except $h = 160$.

Table 3.6 shows the fitting results of $C_1$ and $\sigma$ to the six composites using the modified Giesekus model. Figure 3.19 compares the model predictions (steady shear viscosity and first normal stress difference) of the Giesekus model to the modified Giesekus model for the two cases farthest from $\sigma = 1$, namely $\sigma_2 = 0.89$ for composite MB2, and $\sigma_2 = 0.78$ for composite SC2. From this study of the worst cases we observe that for MB and SC composites the model predictions of the modified Giesekus model and Giesekus model are almost same. Therefore we conclude that the interaction between
the nanofibers and the polymer are negligible in our experiments and the modified Giesekus equation (3.6) reduces to the Giesekus equation (3.2), which is capable of capturing the rheological behavior of our composite systems.

### 3.5.5 Investigation of closure approximation

In section 3.4, we introduced four different closure approximations: Linear closure approximation (equation (3.16)), Quadratic closure approximation (equation (3.17)), Hybrid closure approximation (equation (3.18)) and orthotropic closure approximation. In sections 3.5.2, 3.5.3, and 3.5.4, we model the rheological behavior of CNF/PS melt composites at steady state, where the fibers show good alignment, using quadratic closure approximation, which performs well for highly aligned states. In this section, we investigate the effects of linear and hybrid closure approximations on nanofiber/PS melt composite system.

Following the same procedures described in section 3.5.1 except that we inserted equation (3.16) and (3.18) to the evolution equation (3.4) and obtained different system of equations for the components of the symmetric orientation tensor $a_{ij}$ (equation 3.23) corresponding to linear and hybrid closure approximations, respectively.

Table 3.7 shows the pointwise values of shear-rate-dependent fiber-interaction parameter $C_i$ of MB composites based on different closure approximation at each discrete shear rate where viscosity was measured. Similarly, we propose that the $C_i$ is of power-law-dependent on strain rate. Table 3.8 shows the power law forms of the shear-rate-dependent interaction parameter $C_i = p\dot{\gamma}^q$ deduced directly from all experimental measurements of steady shear viscosity based on different closure approximation.
Figure 3.20 and Figure 3.21 show the continuous model predictions of the steady shear viscosity and first normal stress difference compared to the experimental measurements employing three different closure approximations for MB composites and SC composites, respectively. For MB composite, we conclude that all three closure approximations capture the shear thinning behavior and over-predict the first normal stress difference, while the linear and hybrid approximations fail to predict the high viscosities at low shear rate. For SC composites, the model predictions are close to the experimental measurements and there is no significant difference between the model predictions of three closure approximations. The error cumulating (equation (3.24)) demonstrate that the quadratic closure approximation has the minimum error. For both composite systems, the quadratic closure approximation gives the best results, which is consistent with the statement that quadratic closure approximation performs well for highly aligned states.

3.6 Conclusions

In this study we prepared PS/CNF composites through two different processes, which resulted in composites with different CNF lengths and dispersion: In composites prepared through melt blending using a microcompounder, the CNFs are uniformly dispersed in the PS matrix. However, the lengths of the CNFs are only about 1/4 of the lengths of the as-received CNFs. In the composites prepared using a solvent casting method, the lengths of the as-received CNFs are maintained, but the dispersion of CNFs in SC composites was not as uniform as in the MB composites.

Our small amplitude oscillatory shear rheological studies of these polymer/nanofiber composites in their melt phase showed that both the storage modulus
(\(G'\)) and loss modulus (\(G''\)) of both types of melt composites increase monotonically with the CNF concentration. Moreover, at low frequencies, plateau of \(G'\) occurs for SC composites at high CNF concentrations, showing solid-like behavior. The shifting factors derived from time-temperature superposition of the linear viscoelasticity measured at 140-220°C are almost identical for all composites. This indicates that the CNFs and the nanostructures formed by the CNFs in composites are non-Brownian. We observed in steady shear rheological studies that the steady state viscosities increase with CNF loading and the CNF/PS melt composites exhibit more shear thinning than the pure PS melt. SC composites possess higher relative viscosity than MB composites, a consequence of their longer fibers. At higher CNF concentrations, both MB and SC composites showed yield stress behavior.

The plateau of \(G'\) for SC composites at high CNF concentrations and the yield stress in both MB and SC composites are consistent with the existence of a network nanostructure. We conjecture that at high concentrations, the CNFs form continuous network of nanostructures whose longer relaxation times cause the \(G'\) to plateau at small frequencies. When subjected to flow at constant shear rates, the nanostructure is partially destroyed, with higher shear rates destroying the nanostructure to a larger degree, thus producing the observed shear thinning behavior. At very low shear rates the nanostructure remains intact, causing the yield stress at higher CNF concentrations.

We presented a nanostructurally based model for CNF/PS melt composites which applied to shear flows predicts steady state viscosities and normal stress differences of the melt composites as functions of shear rate, polymer matrix properties, fiber length, and mass concentration consistent with our experimental measurements. Except for two
coupling parameters, all material constants in the model for the composite systems are
deduced from morphological and shear flow measurements of the separate nanofiber and
polymer melt constituents of the composite. Through comparison with our experimental
measurements of the composite systems, we deduce that the polymer-fiber interaction
parameter $\sigma$ is effectively 1 (no polymer-fiber interaction) for all CNF/PS
nanocomposites studied. To allow for CNF orientation to depend on strain rate, as is
experimentally observed, in our model we consider the interfiber interaction parameter $C_i$
to be a function of strain rate, determined from steady flow measurements of the melt
composites.
### Table 3.1. Measured properties of the melt blended and solvent cast composites, and their nanofiber and polymer constituents.

<table>
<thead>
<tr>
<th></th>
<th>MB composites</th>
<th>SC composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF length ((L)), nm</td>
<td>1,000 - 20,000</td>
<td>4,000 - 60,000</td>
</tr>
<tr>
<td>CNF diameter ((D)), nm</td>
<td>100 - 200</td>
<td>100 - 200</td>
</tr>
<tr>
<td>CNF aspect ratio ((L/D))</td>
<td>10 - 100</td>
<td>20 - 500</td>
</tr>
<tr>
<td>CNF representative aspect ratio</td>
<td>40</td>
<td>160</td>
</tr>
<tr>
<td>CNF density, kg/l</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>PS melt density, kg/l</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>CNF mass fraction (wt%)</td>
<td>2  5  10  2  5  10</td>
<td></td>
</tr>
<tr>
<td>CNF volume fraction</td>
<td>1.12  2.84  5.81  1.12  2.84  5.81</td>
<td></td>
</tr>
<tr>
<td>CNF number density ((n)), m(^{-3})</td>
<td>4.5\times10(^{16})  1.1\times10(^{17})  2.3\times10(^{17})  1.1\times10(^{16})  2.8\times10(^{16})  5.8\times10(^{16})</td>
<td></td>
</tr>
<tr>
<td>regime</td>
<td>semi-dilute</td>
<td>concentrated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 3.2. Slopes of \(G'(\omega)\) and \(G''(\omega)\) at low frequencies.

<table>
<thead>
<tr>
<th>wt%</th>
<th>MB Composites</th>
<th>SC Composites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(d(\log G')/d(\log \omega))</td>
<td>(d(\log G'')/d(\log \omega))</td>
</tr>
<tr>
<td>10</td>
<td>1.14</td>
<td>0.85</td>
</tr>
<tr>
<td>5</td>
<td>1.53</td>
<td>0.97</td>
</tr>
<tr>
<td>2</td>
<td>1.68</td>
<td>0.97</td>
</tr>
<tr>
<td>0</td>
<td>1.93</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Table 3.3 Pointwise values of fiber-interaction parameter $C_I$ and corresponding second order orientation tensor components of MB composites at each discrete shear rate where viscosity was measured.

<table>
<thead>
<tr>
<th>shear rate (s$^{-1}$)</th>
<th>$C_I$</th>
<th>$a_{11}$</th>
<th>$a_{12}$</th>
<th>$a_{22}$</th>
<th>$a_{33}$</th>
<th>$a_{13} &amp; a_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>6.83x10$^{-2}$</td>
<td>0.6658</td>
<td>0.2037</td>
<td>0.1669</td>
<td>0.1672</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.03</td>
<td>6.83x10$^{-2}$</td>
<td>0.6658</td>
<td>0.2037</td>
<td>0.1669</td>
<td>0.1672</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.1</td>
<td>2.65x10$^{-2}$</td>
<td>0.8008</td>
<td>0.1862</td>
<td>0.0994</td>
<td>0.0998</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.3</td>
<td>9.70x10$^{-3}$</td>
<td>0.8917</td>
<td>0.1494</td>
<td>0.0539</td>
<td>0.0544</td>
<td>0.0000</td>
</tr>
<tr>
<td>1</td>
<td>2.70x10$^{-3}$</td>
<td>0.9521</td>
<td>0.1034</td>
<td>0.0237</td>
<td>0.0242</td>
<td>0.0000</td>
</tr>
<tr>
<td>3</td>
<td>1.90x10$^{-3}$</td>
<td>0.9619</td>
<td>0.0925</td>
<td>0.0187</td>
<td>0.0194</td>
<td>0.0000</td>
</tr>
<tr>
<td>10</td>
<td>9.90x10$^{-3}$</td>
<td>0.8903</td>
<td>0.1502</td>
<td>0.0547</td>
<td>0.0550</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Table 3.4 Pointwise values of $C_I$ and corresponding second order orientation tensor components of SC composites at each shear rate where viscosity was measured.

<table>
<thead>
<tr>
<th>shear rate (s$^{-1}$)</th>
<th>$C_I$</th>
<th>$a_{11}$</th>
<th>$a_{12}$</th>
<th>$a_{22}$</th>
<th>$a_{33}$</th>
<th>$a_{13} &amp; a_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>2.82x10$^{-3}$</td>
<td>0.9510</td>
<td>0.1064</td>
<td>0.0245</td>
<td>0.0246</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.03</td>
<td>1.39x10$^{-3}$</td>
<td>0.9692</td>
<td>0.0856</td>
<td>0.0154</td>
<td>0.0155</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.1</td>
<td>5.81x10$^{-4}$</td>
<td>0.9826</td>
<td>0.0649</td>
<td>0.0087</td>
<td>0.0087</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.3</td>
<td>2.21x10$^{-4}$</td>
<td>0.9908</td>
<td>0.0473</td>
<td>0.0046</td>
<td>0.0046</td>
<td>0.0000</td>
</tr>
<tr>
<td>1</td>
<td>5.90x10$^{-5}$</td>
<td>0.9962</td>
<td>0.0303</td>
<td>0.0019</td>
<td>0.0018</td>
<td>0.0000</td>
</tr>
<tr>
<td>3</td>
<td>2.70x10$^{-5}$</td>
<td>0.9977</td>
<td>0.0232</td>
<td>0.0011</td>
<td>0.0012</td>
<td>0.0000</td>
</tr>
<tr>
<td>10</td>
<td>9.80x10$^{-5}$</td>
<td>0.9946</td>
<td>0.0361</td>
<td>0.0027</td>
<td>0.0027</td>
<td>0.0000</td>
</tr>
</tbody>
</table>
Table 3.5. Material constants and functions of the melt blended and solvent cast composite models.

<table>
<thead>
<tr>
<th></th>
<th>Melt Blended (MB)</th>
<th>Solvent Cast (SC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>0.329 s</td>
<td>0.321 s</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.392</td>
<td>0.479</td>
</tr>
<tr>
<td>$\eta_p$</td>
<td>9864 Pa.s</td>
<td>11160 Pa.s</td>
</tr>
<tr>
<td>$\eta_s$</td>
<td>0 Pa.s</td>
<td>0 Pa.s</td>
</tr>
<tr>
<td>$h$</td>
<td>40</td>
<td>160</td>
</tr>
<tr>
<td>$C_i$</td>
<td>fit to pointwise values of $C_i$: $C_i = 0.0074 s^{-0.472} \dot{\gamma}^{-0.472}$</td>
<td>fit to pointwise values of $C_i$: $C_i = 0.0066 s^{-0.507} \dot{\gamma}^{-0.507}$</td>
</tr>
<tr>
<td></td>
<td>fit to $C_i = p(\dot{\gamma})^q$: $C_i = 0.0001 s^{-0.627} \dot{\gamma}^{-0.627}$</td>
<td>fit to $C_i = p(\dot{\gamma})^q$: $C_i = 0.0001 s^{-0.729} \dot{\gamma}^{-0.729}$</td>
</tr>
</tbody>
</table>

* measured from pure polymer that had undergone the melt blending process (MB0).
** from morphological study of MB composites
+ measured from pure polymer that had undergone the solvent casting process (SC0).
++ from morphological study of SC composites

Table 3.6 Material constants and functions of the modified Giesekus model incorporating fiber-matrix interactions.

<table>
<thead>
<tr>
<th></th>
<th>Melt Blended (MB)</th>
<th>Solvent Cast (SC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>0.329 s</td>
<td>0.321 s</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.392</td>
<td>0.479</td>
</tr>
<tr>
<td>$\eta_p$</td>
<td>9864 Pa.s</td>
<td>11160 Pa.s</td>
</tr>
<tr>
<td>$\eta_s$</td>
<td>0 Pa.s</td>
<td>0 Pa.s</td>
</tr>
<tr>
<td>$h$</td>
<td>40</td>
<td>160</td>
</tr>
<tr>
<td>$C_i$</td>
<td>$C_i = 0.0074 s^{-0.49} \dot{\gamma}^{-0.49}$</td>
<td>$C_i = 0.0001 s^{-0.71} \dot{\gamma}^{-0.71}$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>$\sigma_2 = 0.89$ (MB2)</td>
<td>$\sigma_2 = 0.78$ (SC2)</td>
</tr>
<tr>
<td></td>
<td>$\sigma_5 = 1.00$ (MB5)</td>
<td>$\sigma_5 = 0.83$ (SC5)</td>
</tr>
<tr>
<td></td>
<td>$\sigma_{10} = 1.00$ (MB10)</td>
<td>$\sigma_{10} = 1.00$ (SC10)</td>
</tr>
</tbody>
</table>

Table 3.6 Material constants and functions of the modified Giesekus model incorporating fiber-matrix interactions.
Table 3.7 Pointwise values of fiber-interaction parameter $C_I$ of MB composites based on different closure approximation at each discrete shear rate where viscosity was measured.

<table>
<thead>
<tr>
<th>Shear Rate (s⁻¹)</th>
<th>Quadratic</th>
<th>Hybrid</th>
<th>Linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>$6.83 \times 10^{-2}$</td>
<td>$2.81 \times 10^{-2}$</td>
<td>0.16</td>
</tr>
<tr>
<td>0.03</td>
<td>$6.83 \times 10^{-2}$</td>
<td>$2.81 \times 10^{-2}$</td>
<td>0.16</td>
</tr>
<tr>
<td>0.1</td>
<td>$2.65 \times 10^{-2}$</td>
<td>$2.81 \times 10^{-2}$</td>
<td>0.16</td>
</tr>
<tr>
<td>0.3</td>
<td>$9.70 \times 10^{-3}$</td>
<td>$2.81 \times 10^{-2}$</td>
<td>0.16</td>
</tr>
<tr>
<td>1</td>
<td>$2.70 \times 10^{-3}$</td>
<td>$3.50 \times 10^{-3}$</td>
<td>0.15</td>
</tr>
<tr>
<td>3</td>
<td>$1.90 \times 10^{-3}$</td>
<td>$2.38 \times 10^{-3}$</td>
<td>0.26</td>
</tr>
<tr>
<td>10</td>
<td>$9.90 \times 10^{-3}$</td>
<td>$2.81 \times 10^{-2}$</td>
<td>0.16</td>
</tr>
<tr>
<td>error</td>
<td>$3.957 \times 10^{-2}$</td>
<td>0.186</td>
<td>0.372</td>
</tr>
</tbody>
</table>

Table 3.8 Continuous forms of fiber-interaction parameter $C_I$ with $C_I$ power-law dependence on shear rate of MB composites using three different closure approximations.

<table>
<thead>
<tr>
<th>Closure Approximations</th>
<th>Melt Blended (MB): $C_I = p\gamma^q$</th>
<th>Solvent Cast (SC): $C_I = p\gamma^q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadratic</td>
<td>$0.0066s^{-0.507} \gamma^{-0.507}$</td>
<td>$0.0001s^{-0.729} \gamma^{-0.729}$</td>
</tr>
<tr>
<td>Hybrid</td>
<td>$0.0122s^{-0.206} \gamma^{-0.206}$</td>
<td>$0.0001s^{-0.786} \gamma^{-0.786}$</td>
</tr>
<tr>
<td>Linear</td>
<td>$0.1615s^0 \gamma^0$</td>
<td>$0.0276s^{-0.325} \gamma^{-0.325}$</td>
</tr>
</tbody>
</table>
Figure 3.1. Optical microscopy images of a 5wt% (a) melt blended (MB) composite and (b) solvent cast (SC) composite. Scale bar: 40 microns.

Figure 3.2. TEM micrographs of a 5 wt% (a) MB composite and (b) SC composite. Scale bar: 5 microns.
Figure 3.3. Master curve of elastic modulus ($G'$) for (a) MB and (b) SC composites with 0 to 10 wt% CNF concentrations: data measured from 140 to 220°C, shifted to 200°C.

Figure 3.4. Time temperature superposition shift factors of MB and SC composites.
Figure 3.5. Shift of crossover frequency of $G'$ (solid symbols) and $G''$ (open symbols) of (a) MB composites and (b) SC composites, at 200°C.

Figure 3.6. Transient shear viscosity $\eta^+$ of the pure PS at shear rates 0.0001-10 s$^{-1}$, and $T=200°C$. (Curves for 0.01 s$^{-1}$ and smaller fall on top of each other.)
Figure 3.7. Start up of steady shear at shear rates $0.0001 - 10 \text{ s}^{-1}$ for the SC 10 composite (a) transient shear viscosity, (b) primary normal stress difference. $T=200^\circ\text{C}$.

Figure 3.8. Steady shear viscosities of (a) MB composites and (b) SC composites, at $200^\circ\text{C}$.
Figure 3.9. Relative viscosity of MB and SC composites, at 200°C.

Figure 3.10. First normal stress difference $N_1$ in steady shear of (a) MB and (b) SC composites, at 200°C.
Figure 3.11. Complex viscosity vs. frequency and steady shear viscosity vs. shear rate of (a) MB and (b) SC composites, at 200°C.
Figure 3.12. (a) Fit of model with optimum value $\lambda = 0.329$ s to oscillatory shear measurements of melt-blended pure polymer melt MB0, (b) fit of model with optimum values $\lambda = 0.329$ s and $\alpha = 0.392$ to steady shear measurements of MB0.
Figure 3.13 Pointwise model predictions of (a) the viscosity and (b) first normal stress difference compared to the experimental steady shear measurements for melt blended composite systems. In this procedure the model selects parameter $C_I$ and predicts values of viscosity only at the discrete shear rates where viscosity is measured; these pointwise values for each CNF concentration are connected by lines for clarity.

Figure 3.14 Pointwise values of $C_I$ for the MB and SC composites, the power law functions fit to these pointwise values (MB: $C_I = 0.0074s^{-0.472}\gamma^{-0.472}$; SC: $C_I = 0.0001s^{-0.627}\gamma^{-0.627}$), and the power law functions fit directly to viscosity measurements (MB: $C_I = 0.0066s^{-0.507}\gamma^{-0.507}$; SC: $C_I = 0.0001s^{-0.729}\gamma^{-0.729}$).
Figure 3.15 Continuous model predictions for melt blended composite systems of (a) the viscosity and (b) first normal stress difference produced by $\eta_s = 0$, $\eta_f = 9864$ Nm/s², $h = 40$, $\lambda = 0.329$ s, $\alpha = 0.392$, and $C_1 = 0.0066s^{-0.507} \gamma^{0.507}$, compared to the experimental steady shear measurements.
Figure 3.16. (a) Fit of model with optimum value $\lambda = 0.321$ s to oscillatory shear measurements of solvent-cast pure polymer melt SC0, (b) fit of model with optimum values $\lambda = 0.321$ s and $\alpha = 0.479$ to steady shear measurements of SC0.
Figure 3.17 Pointwise model predictions of (a) the viscosity and (b) first normal stress difference compared to the experimental steady shear measurements for solvent cast composite systems. In this procedure the model selects parameter $C_I$ and predicts values of viscosity only at the discrete shear rates where viscosity is measured; these pointwise values for each CNF concentration are connected by lines for clarity.

Figure 3.18 Model predictions of (a) the viscosity and (b) first normal stress difference compared to the experimental steady shear measurements for melt blended composite systems based on $\eta_s = 0$, $\eta_p = 11160$ Nm/s$^2$, $h = 160$, $\lambda = 0.321$ s, $\alpha = 0.479$, and $C_I = 0.0001s^{-0.729} \gamma^{-0.729}$.
Figure 3.19 Comparisons of Giesekus model and modified Giesekus model predictions at 2wt% CNF for (a) MB composite and (b) SC composite.
Figure 3.20 Continuous model predictions for melt blended composite systems of the viscosity and first normal stress difference compared to the experimental steady shear measurements employing three different closure approximations: (a) Linear, (b) Quadratic, and (c) Hybrid closure approximation.
Figure 3.21. Continuous model predictions for solvent cast composite systems of the viscosity and first normal stress difference compared to the experimental steady shear measurements employing three different closure approximations: (a) Linear, (b) Quadratic, and (c) Hybrid closure approximation.
CHAPTER 4

TRANSIENT RHEOLOGY OF PS/CNF COMPOSITES AND CNF ORIENTATION INDUCED BY FLOW

4.1 Introduction

In the previous chapters, we discuss linear viscoelasticity and steady state shear rheology of the PS/CNF composites. However, the transient rheological behavior and the CNF orientation induced by flow are also of great importance since they significantly affect the final performance of the products. As a result, a better understanding of the transient shear rheology, fiber orientation characterization, and relationships of the CNFs and rheology of the CNF/PS melt composites is necessary.

In this chapter, we investigate the lack of knowledge on the transient shear rheology of the PS/CNF composites and the orientation of the CNFs induced by flow. Additionally, the effect of the CNF loadings and lengths will be examined.

4.2 Experimental Procedures

The materials investigated in this chapter are the same as were investigated in the previous chapter. In summary, two types of the polystyrene (PS)/carbon nanofiber (CNF) composites were prepared and used to study the effects of the CNF loadings
and lengths, namely melt blended (MB) composites and solvent cast (SC) composites with 2, 5, 10 wt% CNFs. The CNF lengths in SC composites are about 160 microns, and those in MB composites are about 40 microns.

The shear experiments were conducted on a strain controlled rheometer (ARES LS2 by TA Instruments) with 25 mm parallel plates. Two types of samples were made for shear rheology. One was made using an injection molding method with a center-gated mold. A micro-injection molding machine (DACA) was used. The barrel temperature was 200\(^{\circ}\)C and the mold temperature was 60\(^{\circ}\)C. The injection pressure was 50 psi. The other type of sample for shear rheology was made using a compression molding method. Although the CNFs in the pellets were oriented in the flow direction through the 1mm die, the orientation of the pellets in the compressed disks was random. The sample disks were stored in a vacuum oven at 70\(^{\circ}\)C prior to the measurement to prevent the absorption of moisture or air; if stored in open air, bubbles are generated during the re-melting in the rheometer. Unless otherwise mentioned, compression molded disks were used in all shear tests.

4.3 Experimental Results

4.3.1 Transient shear rheology

The stress response upon start up of steady shear was measured with the SC0 and SC10 composites at different shear rates to investigate the evaluation of the CNF orientation and structure. Figure 4.1 a,b display the results of the measured transient shear viscosity of these composites. The pure polymer exhibits typical behavior of a homogeneous linear polymer. At small shear rates, e.g. less than and equal to 0.01 s\(^{-1}\),
the SC0 shows linear viscoelasticity. The transient shear viscosity is independent of shear rate and the final steady state viscosities are identical. At higher shear rates, shear thinning and stress overshoot appear. The transient shear viscosities of the SC10 composite at relatively large shear rates, e.g. larger than 0.1s⁻¹, are very similar to those of the SC0 composite. However, at smaller shear rates, the transient viscosity as a function of time is quite different from that of pure polymer. Most significantly, the linear viscoelastic behavior is not observed. Instead of falling on top on each other, the transient shear viscosity at small shear rates, e.g. less than 0.01s⁻¹, increases markedly with decreasing shear rates. In other words, more shear-thinning behavior is observed.

The differences in the transient shear behavior between SC0 and SC10 can be seen more clearly when the reduced stress is plotted with strain, as seen in Figure 4.2. The reduced stress is defined as the ratio of transient stress to steady state stress \( \tau/\tau_\infty \). Shear rates between 0.1 and 10s⁻¹ were probed. The magnitude of the overshoot is a strong function of shear rate for both pure PS and SC10 composite. Figure 4.2a displays the reduced stress for pure PS. At shear rate of 0.1s⁻¹ and higher, measurable stress overshoot can be detected. Higher shear rates give rise to larger overshoot. In contrast with the reduced stress of SC10 composites (Figure 4.2a), three distinct features can be found. First, the height of the overshoot for SC10 composite is always larger than that of pure PS at the same shear rate. Second, the positions of the peek of the overshoot of the pure PS are almost identical for all shear rates, while they move towards smaller strain units for SC10 composites at higher shear rates. Thirdly, the
widths of the overshoot are about the same for pure PS for all shear rates, and they
decrease with higher shear rates for SC10 composites. The width of the overshoot is
defined as the distance between the two points where the reduced stress intersects
with the horizontal line where the reduced stress equals one.

All three features are due to the CNFs in the SC10 composite. More
pronounced overshoot in SC10 composite is due to the change of the CNF
nanostructure. The CNFs change their orientation during the flow. Before reaching
steady state, they introduce extra stress to the composite, leading to stress overshoot.
The shift of the peak position is the combination of the effects of the CNFs and
polymer in the SC10 composites. For comparison, the positions of the peaks are the
same, independent of the shear rate for the pure polymer. This is typical for most
homogeneous polymers and composites in which the fillers are non-Brownian.
However, although the CNFs in the SC10 composites are also non-Brownian, the
positions of the overshoot become dependent on the shear rates. This behavior is
mostly likely caused by the interactions of the CNFs. The shear flow tends to cause
the fibers to tumble, while the inter-particle interactions may prevent the CNFs from
tumbling. The flow competes with the interactions, such that the stress response is the
result of these two actions. In the un-sheared sample, the CNFs are randomly oriented.
When the sample is sheared, some CNFs are aligned to the flow direction induced by
shear flow. However, if the shear rate is small, the inter-particle interactions dominate.
This prevents the CNFs from being aligned to the flow direction, which means that
the CNFs are still close to random even when steady state is reached. If the shear rate
is large, the flow destroys the inter-particle interactions and aligns the CNFs to the flow direction better. The result of the competition between the flow and inter-particle interactions is that the peak of the overshoot occurs at a smaller strain unit for smaller shear rate flows than the larger ones. Moreover, if we observe Figure 4.2 carefully, we can see that the positions of the overshoot of SC0 and SC10 are about the same at 10 s\(^{-1}\) shear rates, and at smaller shear rates the overshoot occurs at a smaller strain for SC10 composites than for SC0 (pure polymer). This is also an indication that the strength of the inter-particle interactions of the CNFs is relatively large at smaller shear rates, and it can be neglected at higher shear rates. The width of the overshoot might also be the effect of the inter-particle interactions. As they are relatively stronger at smaller shear rates, the competition between the interactions and the flow lasts longer, and so the overshoot becomes wider. At higher shear rates, flow dominates so that the widths of the overshoot of SC10 and SC0 are almost the same.

The effects of inter-particle interactions of CNFs are also seen in the start up of steady shear experiments for all MB and SC composites as a function of CNF loading. Figure 4.3 shows the reduced stress of both MB and SC composites in the start up of steady shear at 1 s\(^{-1}\) shear rate. For MB composites (Figure 4.3a), the reduced stress is about the same with CNF loadings of 5 wt% and lower. At 10wt% CNF loading, the reduced stress is markedly higher. In contrast, The SC composites show much higher reduced stress than MB composites. At the same CNF loading, the SC composites (Figure 4.3b) show significantly higher overshoot than MB composites (Figure 4.3a). This is the effect of the length of the CNFs. As the CNFs in
the SC composites are much longer (aspect ratio of 160 in SC composites and 40 in MB composites), both the extra stress caused by pure length and the stress resulting from the more inter-particle interactions between CNFs are larger. Longer CNFs have more chances to contact each other and possibly entangle, therefore the inter-particle interactions of SC composites are larger than MB composites. That’s why larger stress overshoots are seen in the SC composites. In particular, the effects of the inter-particle interactions of CNFs can be seen in both MB composites and SC composites. The peeks of the overshoots shift to the left with higher CNF loadings, which can be contributed to higher interactions. If there were no inter-particle interactions, positions of the overshoots would be the same, as shown by other researchers\textsuperscript{15,87,92}. We can safely claim that this is the effect of increasing inter-particle interactions at higher CNF loadings since the overshoots shift to the left. Larger interactions prevent CNFs from tumbling, such that the peek of the overshoot occurs at smaller strain units. This is similar to the case when shear rate becomes smaller, and interactions becomes relatively larger, and the overshoots shift to the left, as seen in Figure 4.2b.

4.3.2 Orientation Characterization

As one can imagine, the rheology of the polymer/CNF composites is affected by the CNF orientation. In order to find out the relationship between the rheology and CNF orientation, we need to be able to measure both and then use models to couple them. In this study, we have developed a novel way to prepare the samples and measure the CNF orientation. The sample is deformed at elevated temperature and
then quenched using dry ice to solidify the sample, which fixes the CNF orientation. The sample is then cut in two perpendicular planes and TEM is used to examine the angle of the CNF with respect to the flow direction. The thickness of the TEM section is 800 nm. Challenges in this analysis include inference of 3-D orientation from 2-D micrographs, and the interplay between the nano-length-scales of particle geometry, width of a TEM section of the nanocomposite, and the transparency of the section.

Figure 4.4 are TEM micrographs showing the orientation induced during extensional flow in two perpendicular planes and histograms of the particle orientation and length distribution. These micrographs serve as benchmarks of the alignment of the CNFs in a plane parallel to the flow direction and a plane perpendicular to the flow direction in a nearly perfectly aligned sample. It is clear that the TEM micrograph of the plane parallel to the flow direction shows strong CNF alignment to the flow direction. The micrograph of the plane perpendicular to the flow direction shows a random orientation, as we expected. Another significant difference is that the lengths of the CNFs in the parallel plane are much longer than those in the perpendicular plane. This is understandable, since the CNFs are aligned in the parallel plane, so that the full length can be seen in the picture. While in the perpendicular plane, most of the CNFs were cut, so that we can only see the cross section of the CNFs. One of the most significant marks to identify a cross section view is the existence of a circular shape, as seen in Figure 4.4 b. This is the key to differentiate a short CNF from a cross section of a long CNF. The two 2-D pictures, such as those in Figure 4.4, can be viewed as projections of 3-D fibers on two orthogonal planes. We
have attempted to construct 3-D orientation distribution function from these two 2-D TEM micrographs, but we met insurmountable obstacles. The key missing information is that one fiber seen in one plane cannot be paired with its counterpart in another plane. In another word, we do not know which two projections come from the same fiber. Due to our imaging technique (TEM), there is no way to build this pair-wise relationship. The microtoming process used to prepare TEM sections destroys the sample. As a result, there is no way to reconstruct 3-D orientation from two 2-D projections and more work need to be done to overcome this difficulty.

4.4 Modeling

4.4.1 Modeling of transient rheology of simple shear flow

The nanoparticle/polymer melt composite constitutive model we employed in chapter 3 successfully predicted the shear rheology of melt blended composites and solvent cast composites at steady state. In this chapter, we employ this constitutive model to predict the transient rheological behavior of simple shear flow.

Recall that the constitutive models which we found to best capture the observed features of our CNF/PS melt composites are:

\begin{equation}
\tau_{ij}^p = -p\delta_{ij} + 2\eta_s D_{ij} + \tau_{ij}^p + \tau_{ij}^{\text{CNF}}, \tag{3.1}
\end{equation}

\begin{equation}
\tau_{ij}^p + \lambda \frac{D\tau_{ij}^p}{Dt} + \frac{\alpha\lambda}{\eta_p} \left( \tau_{ik}^p \tau_{kj}^p \right) = 2\eta_p D_{ij}, \tag{3.2}
\end{equation}

\begin{equation}
\tau_{ij}^{\text{CNF}} = 2[\eta_s + \eta] \phi \left[ AD_{ij}a_{ijkl} + B \left( D_{ik}a_{ij} + a_{ik}D_{ij} \right) + CD_{ij} + 2Fa_{ij}D_{ij} \right] \tag{3.3}
\end{equation}

with

\begin{equation}
\frac{da_{ij}}{dt} = (W_{ij}a_{ij} - a_{ij}W_{ij}) + \chi \left( D_{ik}a_{ij} - a_{ik}D_{ij} - 2D_{ik}a_{ijkl} \right) + 4C_1 \Pi_{1/2} \left( \delta_{ij} - ma_{ij} \right), \tag{3.4}
\end{equation}
Recall that equation (3.1) expresses the total stress $\tau^c_{ij}$ in the polymer/nanocomposite system\textsuperscript{147}. Equation (3.2) is Giesekus model\textsuperscript{22} which predicts the strain rate dependent viscoelastic behavior of the polymer matrix. In equation (3.2), the polymer viscosity $\eta_p$, mobility factor $\alpha$, and relaxation time $\lambda$ are properties of pure polymer matrix so that we adopted the same values obtained in chapter3. To solve the stress contribution from the polymer matrix during the transient state, we solved six coupled differential equations instead of six coupled non-linear equations at steady state. Equation (3.3) predicts the stress contribution from the nanofibers\textsuperscript{148}. The values of material constants $A$, $B$, $C$, and $F$ are different from what we used for steady state. Table 4.1. shows different expressions of material constant $A$, $B$, $C$, and $F$ depending on aspect ratio and particle concentration. In this chapter, we adopted the high order corrections for $A$ for semi-dilute composites proposed by Shaqfeh and Fredrickson\textsuperscript{152}:

$$
A = \begin{cases} 
\frac{16h^2}{3\ln\left(\frac{1}{\phi}\right) + \ln\left(\frac{1}{\phi}\right) + 1.4389} & \text{for aligned fibers} \\
\frac{16h^2}{3\ln\left(\frac{1}{\phi}\right)} \left[ 1 - \frac{\ln\left(\frac{1}{\phi}\right) + 0.6334}{\ln\left(\frac{1}{\phi}\right) \ln\left(\frac{1}{\phi}\right)} \right] & \text{for random fibers}
\end{cases}
$$

(4.1)

where $h$ is the aspect ratio and $\phi$ is the volume fraction. In our experiments, we measured the shear viscosities at seven shear rate $\dot{\gamma} = 0.01s^{-1}, 0.03s^{-1}, 0.1s^{-1}, 0.3s^{-1}, 1s^{-1}, 3s^{-1}, 10s^{-1}$. At shear rate $\dot{\gamma} = 0.01s^{-1}, 0.03s^{-1}$, we chose
\[
A = \frac{16h^2}{3\ln\left(\frac{1}{\phi}\right)}\left[1 - \frac{\ln\left(\frac{1}{\phi}\right)}{\ln\left(\frac{1}{\phi}\right) + \ln\left(\frac{1}{\phi}\right) + 0.6334}\right]
\]
for random fiber since the shear rate is quite slow and it takes long time to align the nanofibers so that most fibers are in different direction and the whole system shows random state. At the shear rate \(\dot{\gamma} = 0.1\,s^{-1}, 0.3\,s^{-1}, 1\,s^{-1}, 3\,s^{-1}, 10\,s^{-1}\), we chose the expression for aligned fiber
\[
A = \frac{16h^2}{3\ln\left(\frac{1}{\phi}\right) + \ln\left(\frac{1}{\phi}\right) + 1.4389}
\]
since the high shear rate tends to force the nanofibers to align in the same direction in a very short time so that most fibers would be aligned along the shear direction and the system shows good alignment at high shear rate. In semi-dilute regime, material constants \(B=C=F=0\) as in chapter 3.

Equation (3.4) is the evolution equation of the second order orientation tensor. Six differential equations need to be solved in order to obtain the changing of the second order orientation tensor \(a_{ij}\) during the transient state.

**4.4.2 Application of the model to CNF/PS melt blended composites**

To characterize the CNF/PS melt composites in the context of constitutive model (3.1)-(3.4), we deduce the particle aspect ratio \(h = 40\) from our measurements of the morphology of the nanofibers, and the constants \(\lambda = 0.329\,s, \alpha = 0.392, \eta_p = 9864\,Pa.s, \eta_s = 0\,Pa.s\), which are the constitutive properties of the polymer melt alone, from flow measurements in our steady shear and small amplitude oscillatory shear experiments of polystyrene that has gone through the melt blending process. The procedure details are reported in section 3.5.1.
With the constitutive parameters $\lambda$, $\alpha$, $\eta_p$, $\eta_s$ known, for a specified steady shear flow $\mathbf{v} = \dot{x} = \gamma x_2 \mathbf{e}_1$, we can solve six differential equation (3.2) to obtain the stress contribution from the pure polymer $\tau^{\rho}_{ij}$ and strain rate dependent polymer viscosity $\eta = \frac{\tau^{\rho}_{ij}}{\dot{\gamma}}$ in equation (3.3). Initial stress components must be specified to solve the differential equations. Since there is no shear stress at time $t=0s$, we assume that the initial stress components of $\tau^{\rho}_{ij}$ are zeros. Fourth order Runge-Kutta method is applied to solve the differential equation system.

Recall that in section 3.4, we mentioned that “the linear closure approximation works well when the fibers remain nearly random, but introduces an artificial instability into the equations for highly aligned suspensions; the quadratic closure approximation performs well for highly aligned states, but introduces steady-state errors for more random states; and the hybrid closure approximation mixes linear and quadratic forms according to scalar measure of orientation and performs well over the entire range of orientation”. In chapter 3, we adopted quadratic closure approximation to predict the shear viscosities and first normal stress difference at steady state, where the nanofibers are highly aligned. In this chapter, we study the shear rheology from transient state to steady state, where the nanofibers are orientated from random to aligned state, hybrid closure approximation is more appropriate since it is the combination of linear and quadratic forms and performs well over the entire range of orientation.
With symmetric and skew parts $D$ and $W$ of the velocity gradient specified by the steady shear flow $\mathbf{v} = \dot{x} x_2 e_1$ and inserted the orientation evolution Equation (3.4), using hybrid closure approximation (3.16) produces the following system of differential equations for the components of the symmetric tensor $a_{ij}$:

$$\frac{da_{11}(t)}{dt} = \dot{a}_{12}(t) + 2C_i \dot{\gamma} \left( 1 - 3a_{11}(t) \right)$$

$$+ \chi \dot{\gamma} \left( \frac{3}{7} \left( 27a_{11}(t)a_{22}(t)a_{33}(t) - 27a_{12}^2(t)a_{33}(t) + 27a_{12}(t)a_{33}(t)a_{11}(t) \right) a_{12}(t) \right)$$

$$+ \chi \dot{\gamma} \left( \frac{1}{35} + \frac{1}{7} a_{11}(t) + \frac{1}{7} a_{22}(t) \right),$$

$$\frac{da_{12}(t)}{dt} = \frac{1}{2} \dot{a}_{22}(t) - \frac{1}{2} \dot{a}_{11}(t) - 6C_i \dot{\gamma} a_{12}(t)$$

$$+ \chi \dot{\gamma} \left( \frac{1}{2} a_{22}(t) + \frac{1}{2} a_{11}(t) \right)$$

$$+ \chi \dot{\gamma} \left( \frac{1}{3} + \frac{1}{7} a_{11}(t) + \frac{1}{7} a_{22}(t) \right) + \chi \dot{\gamma} \left( a_{11}(t)a_{22}(t)a_{33}(t) + 27a_{12}^2(t)a_{33}(t)a_{12}(t) \right)$$

$$\frac{da_{22}(t)}{dt} = -\dot{a}_{12}(t) + 2C_i \dot{\gamma} \left( 1 - 3a_{22}(t) \right)$$

$$+ \chi \dot{\gamma} \left( \frac{1}{7} \left( 27a_{11}(t)a_{22}(t)a_{33}(t) - 27a_{12}^2(t)a_{33}(t) + 27a_{12}(t)a_{33}(t)a_{11}(t) \right) a_{12}(t) \right)$$

$$+ \chi \dot{\gamma} \left( \frac{1}{3} + \frac{1}{7} a_{11}(t) + \frac{1}{7} a_{22}(t) \right),$$

$$\frac{da_{33}(t)}{dt} = -2 \chi \dot{\gamma} \left( \frac{3}{7} \left( 27a_{11}(t)a_{22}(t)a_{33}(t) - 27a_{12}^2(t)a_{33}(t) + 27a_{12}(t)a_{33}(t)a_{11}(t) \right) a_{12}(t) \right)$$

$$-2 \chi \dot{\gamma} \left( \frac{1}{7} \left( 27a_{11}(t)a_{22}(t)a_{33}(t) - 27a_{12}^2(t)a_{33}(t) + 27a_{12}(t)a_{33}(t)a_{11}(t) \right) a_{12}(t) \right)$$

$$+ 2C_i \dot{\gamma} \left( 1 - 3a_{33}(t) \right).$$

Note, since we already know that for the simple shear flow, the second order orientation tensor components $a_{13}$ and $a_{23}$ are always zeros, we omit the expressions...
for $\frac{da_{11}}{dt}$ and $\frac{da_{23}}{dt}$ for simplification. If the quadratic closure approximation is employed, the system of four differential equations for the components of the symmetric tensor $a_{ij}$ would be much simpler:

\[
\begin{align*}
\frac{da_{11}}{dt} &= \dot{\gamma}a_{12}(t) + \chi\dot{\gamma}(a_{12}(t) - 2a_{12}(t)a_{11}(t)) + 2C_i\dot{\gamma}(1 - 3a_{11}(t)), \\
\frac{da_{12}}{dt} &= \frac{1}{2}\dot{\gamma}a_{22}(t) - \frac{1}{2}\dot{\gamma}a_{11}(t) + \chi\dot{\gamma}\left(\frac{1}{2}a_{22}(t) + \frac{1}{2}a_{11}(t) - 2a_{12}^2(t)\right) - 6C_i\dot{\gamma}a_{12}(t), \\
\frac{da_{13}}{dt} &= \frac{1}{2}\dot{\gamma}a_{23}(t) + \chi\dot{\gamma}\left(\frac{1}{2}a_{23}(t) - 2a_{12}(t)a_{13}(t)\right) - 6C_i\dot{\gamma}a_{13}(t), \\
\frac{da_{22}}{dt} &= -\dot{\gamma}a_{12}(t) + \chi\dot{\gamma}(a_{12}(t) - 2a_{12}(t)a_{22}(t)) + 2C_i\dot{\gamma}(1 - 3a_{22}(t)), \\
\frac{da_{23}}{dt} &= -\frac{1}{2}\dot{\gamma}a_{13}(t) + \chi\dot{\gamma}\left(\frac{1}{2}a_{13}(t) - 2a_{12}(t)a_{23}(t)\right) - 6C_i\dot{\gamma}a_{23}(t), \\
\frac{da_{33}}{dt} &= -2\chi\dot{\gamma}a_{12}(t)a_{33}(t) + 2C_i\dot{\gamma}(1 - 3a_{33}(t)).
\end{align*}
\]

(4.3)

To solve the above differential-equation systems, we need provide the initial values of orientation tensor component $a_{11}$, $a_{12}$, $a_{13}$, $a_{22}$, $a_{23}$, and $a_{33}$. Most of the papers work on random initial conditions\textsuperscript{24,149}, i.e. $a_{11}(0) = a_{22}(0) = a_{33}(0) = 1/3$ and $a_{12}(0) = a_{13}(0) = a_{23}(0) = 0$. In our experiments, the random initial conditions cannot be guaranteed according to the experimental observation. Since the initial conditions of the orientation tensor components, especially the non-zero off-diagonal element $a_{12}(0)$, have important effects on the transient rheology of the CNF/PS melt composites, we set $a_{12}(0)$ to be a fitting parameter. Since all the samples are produced by same procedure and processing conditions and there is no shear stress imposed on the samples at time $t=0$ at each shear rate, we assume that the initial value $a_{12}(0)$ is the
same constant for all mass concentrations and all shear rates. Therefore the initial values of the second order orientation tensor are

\[ a_i = \begin{bmatrix} 1/3 & a_{12}(0) & 0 \\ a_{12}(0) & 1/3 & 0 \\ 0 & 0 & 1/3 \end{bmatrix} \]

Recall that in chapter 3 we proposed that interfiber interaction parameter \( C_1 \) must be considered as a function of strain rate based on our study of measured effect of shear processing conditions on the development of nanofiber structure with TEM images of sectioned samples: the end-state fiber orientation in a polymer nanocomposite depends strongly on the strain rate the nanocomposite undergoes during processing. The final parameters remaining to be determined are the interparticle interaction parameter \( C_1 \) and the initial value of orientation tensor component \( a_{12} \). In summary, we have eight fitting parameters: seven strain-rate-dependent pointwise fitting parameters \( C_1 \) and one constant fitting parameter \( a_{12}(0) \).

With fixed representative aspect ratio \( h=40 \) for melt blended composites, we search over \( a_{12}(0) \) and seven \( C_i(\dot{\gamma}) \) at each shear rate \( \dot{\gamma} = 0.01, 0.03, 0.1, 0.3, 1, 3, 10\text{s}^{-1} \) by solving Equations (3.1)-(3.4) specialized to simple shear flow and minimizing error

\[ \delta_i = \sum_{i=1}^{N} \left[ \log_{10} \eta_{\text{exp}}(\dot{\gamma}_i) - \log_{10} (\eta_{\text{model}}(\dot{\gamma}_i)) \right]^2, \quad (3.24) \]

summed over the three viscosity measurements (2wt%, 5wt% and 10wt%) at that shear rate. Note the raw data obtained from the experimental measurements are not evenly spaced, neither in linear scale nor in logarithmic scale, which results in unbalanced error contribution from the transient state and steady state. In order to
balance the weight of the experimental measurements obtained during transient and steady states, we approached the raw data by smoothly connecting several pieces of high order polynomial curves, which maximally approximate the raw observations. On the smoothed curve, 40 (or less) logarithmically evenly spaced points are chosen from time $t = 0.1 \text{s}$ to $t = 1000 \text{s}$ and the error (3.24) are calculated and accumulated at these points. (Note in this chapter we concentrated on the model prediction of shear rheology at transient state, instead of model prediction at steady state in chapter 3. Therefore we selected evenly space measurements on a logarithmic scale, where most of the points are measured at transient state. Also the number of points N ranges from 26-40 depending on the amount of experimental measurements at each shear rate and mass concentration). Searching over $a_{12}(0)$ and $C_1$ by solving equations (3.1)-(3.4) and minimizing error (3.24) of MB composites produced the initial value $a_{12}(0)=0.0682$ and $C_1=0.4219, 0.4140, 0.4560, 0.4836, 0.6698, 0.5840$ and $0.4168$ corresponding to shear rate $\dot{\gamma} = 0.01, 0.03, 0.1, 0.3, 1, 3,$ and $10 \text{s}^{-1}$ using hybrid closure approximation.

Table 4.2 shows the point-wise values of $C_1$ at each shear rate and corresponding values of second orientation tensor components at initial state and steady state. Figure 4.5 shows the model predictions of shear viscosity of CNF/PS melt MB composites compared with the experimental measurements at each shear rate. Also the changing of fiber orientation tensor components $a_{11}(t), a_{12}(t), a_{13}(t), a_{22}(t), a_{23}(t), \text{and } a_{33}(t)$ with respect to time are plotted at different shear rate (Note that $a_{13}(t)$ and $a_{23}(t)$ are zeros in the simple shear flow). Figure 4.6 compare the shear
viscosities of the CNF/PS melt composites at different shear rates for each particular mass concentration

Comparing the model predictions and the experimental measurements shown in Figure 4.5 and Figure 4.6, we conclude the model successfully captures the rheological behavior of the MB composites during transient state and accurately predicts the composite viscosity magnitude. The shear viscosity increases with mass concentration increasing and decreases with shear rate increasing. Overall, the model predictions at low mass concentration are more accurate than the model predictions at high mass concentration (shown as Figure 4.6). In the range of shear rate from $10^{-1}$ s$^{-1}$ to $10$s$^{-1}$, the model prediction at low shear rate is closer to the experimental measurements than the model prediction at high shear rate, where the model tends to over-predict the shear viscosities. At transient state, the model over-predicts the shear viscosity, especially at low shear rate. At steady state, the model accurately predicts the shear viscosities at low shear rate while at high shear rate $\dot{\gamma} = 3$s$^{-1}$ and $\dot{\gamma} = 10$s$^{-1}$ the model over-predicts the shear viscosities, especially for samples with mass concentration $c=10\%$.

The plots of second orientation tensor components during transient state (Figure 4.5) demonstrate the shear rate dependence of fiber orientation. According to the orientation predictions shown in Figure 4.5 (a)-(g), the nanofibers reached steady state in $0.12$s at high shear rate $\dot{\gamma} = 10$s$^{-1}$, while it took $100$s for the nanofibers to get to steady at low shear rate $\dot{\gamma} = 0.01$s$^{-1}$. It indicates that the nanofibers in the CNF/PS melt composites are quickly aligned at high shear rate.
To study the shear rate dependence of the steady shear viscosities in the range of shear rate $\dot{\gamma} = 0.01 \text{s}^{-1}$ to $10 \text{s}^{-1}$, we applied the above fitting parameters $a_{12}(0)=0.0682$ and $C_{1}=0.4219, 0.4140, 0.4560, 0.4836, 0.6698, 0.5840$ and 0.4168 corresponding to shear rate $\dot{\gamma} = 0.01, 0.03, 0.1, 0.3, 1, 3,$ and $10 \text{s}^{-1}$ to equation (3.1)-(3.3) and plot the steady shear viscosity and first normal stress difference versus shear rate by hybrid closure approximation. Compared with the experimental measurements we obtained in chapter 3 (Figure 4.7), we comment that the model successfully captures shear thinning behavior of the MB composites and accurately predicts the viscosity magnitude. Also the model captures the correct trend of the first normal stress difference but over-predict the stress magnitude for all mass concentrations.

Recall that in chapter 3, Figure 3.13 shows the pointwise model predictions of steady shear viscosity and first normal stress difference with respect to shear rate for MB composite. We found that the model prediction shown in Figure 4.7 is not as accurate as the model prediction shown in Figure 3.13. Although the fitting parameters employed in Figure 3.13, which are obtained only by fitting to the experimental measurements at steady state, gave better approximations to the experimental measurements, we prefer the fitting parameters obtained in chapter 4, $a_{12}(0)=0.0682$ and $C_{1}=0.4219, 0.4140, 0.4560, 0.4836, 0.6698, 0.5840$ and 0.4168, since they not only works at steady state but also works well at transient state. When applied to predict the theological behavior at transient state, the fitting parameter
obtained in chapter 3 produced significant over-shoot of the transient shear viscosity which is not consistent with the experimental observations.

4.5 Conclusions

In this chapter, we studied the transient shear rheology of CNF/PS melt composites prepared through melt blending and solvent casting processes and the effects of the CNF loadings and lengths. We found inter-particle interactions in the composites play a large role in determining the rheological properties, especially at low shear rates. The peaks of the stress overshoot in the start up of steady shear tests shifts to smaller strain units for SC10 composites with increasing shear rate, and the widths of the overshoot become narrower. At the same CNF concentration, the height of stress overshoot is higher for SC composites, as the lengths of the CNFs in SC composites are much longer than those in MB composites. Longer CNFs also increases N1 in the SC composites.

CNF orientation has been experimentally quantified. 2-D TEM photographs have been taken for shear and extensional samples at different flow conditions. But the measurement of 3-D fiber orientation still cannot be accomplished. The 2-D TEM show that flow with higher shear rates induces better alignment of CNFs to the shear direction than low shear rate flows. Also, major change of the CNFs occurs at the peak of the stress overshoot.

We employed the nanostructurally based constitutive model in chapter 3 to predict the transient shear behavior of CNF/PS melt composites. We proposed that there were two fitting parameters. One is the initial value of second order orientation
tensor component $a_{12}(0)$, which is a constant for all shear rates and mass concentrations; the other fitting parameter is the strain-rate-dependent inter-particle interaction parameter $C_I$. Through comparison with experimental measurements of the composite systems, we conclude that the constitutive model could capture both the steady shear rheology and transient shear rheology.
<table>
<thead>
<tr>
<th>Shape factor</th>
<th>Nanoclay ((h&lt;1))</th>
<th>Nanofiber ((h&gt;1)) (steady)</th>
<th>Nanofiber ((h&gt;1)) (transient, semidilute)</th>
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<tr>
<td>A</td>
<td>(\frac{10}{3\pi h} + \frac{208}{9\pi^2} - 2)</td>
<td>(\frac{h^2}{2[\ln(2h) - 1.5]})</td>
<td>(\frac{h^2}{3\ln(2h_f / D)})*</td>
</tr>
<tr>
<td>B</td>
<td>(-\frac{8}{3\pi h} \pm \frac{128}{9\pi^2})</td>
<td>(\frac{6\ln(2h) - 11}{h^2})</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>(\frac{8}{3\pi h})</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>(-\frac{12}{\pi h})</td>
<td>(\frac{3h^2}{\ln(2h) - 0.5})</td>
<td>0</td>
</tr>
</tbody>
</table>

* \(h_f\) a characteristic distance between a fiber and its nearest neighbors:

\[
\frac{2h_f}{D} = \frac{\pi}{\sqrt{\phi}} \quad \text{for aligned fibers}
\]

\[
\frac{2h_f}{D} = \frac{\pi}{2\phi_h} \quad \text{for random fibers}
\]

**:

\[
Ai = \frac{16h^2}{3\left[\ln\left(\frac{1}{\phi}\right) + \ln\left(\frac{1}{\phi}\right) + 1.4389\right]} \quad \text{for aligned fibers}
\]

\[
Aa = \frac{16h^2}{3\ln\left(\frac{1}{\phi}\right)}\left[\frac{\ln\left(\frac{1}{\phi}\right)}{\ln\left(\frac{1}{\phi}\right)} + 0.6334\right] \quad \text{for random fibers}
\]

Table 4.1 Equations for material constants A, B, C, and F depending on aspect ratio and particle concentration
Initial conditions: $a_{12}(0)= 0.0682$, and $a_{11}(0)= a_{22}(0)= a_{33}(0)= 1/3$

<table>
<thead>
<tr>
<th>shear rate (s(^{-1}))</th>
<th>$C_I$</th>
<th>$a_{11}$ (steady)</th>
<th>$a_{12}$ (steady)</th>
<th>$a_{22}$ (steady)</th>
<th>$a_{33}$ (steady)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.4219</td>
<td>0.3657</td>
<td>0.07132</td>
<td>0.3095</td>
<td>0.3248</td>
</tr>
<tr>
<td>0.03</td>
<td>0.4140</td>
<td>0.3667</td>
<td>0.07221</td>
<td>0.3088</td>
<td>0.3245</td>
</tr>
<tr>
<td>0.1</td>
<td>0.4560</td>
<td>0.3614</td>
<td>0.06676</td>
<td>0.3127</td>
<td>0.3260</td>
</tr>
<tr>
<td>0.3</td>
<td>0.4836</td>
<td>0.3585</td>
<td>0.06355</td>
<td>0.3148</td>
<td>0.3268</td>
</tr>
<tr>
<td>1</td>
<td>0.6698</td>
<td>0.3469</td>
<td>0.04764</td>
<td>0.3232</td>
<td>0.3299</td>
</tr>
<tr>
<td>3</td>
<td>0.5840</td>
<td>0.3510</td>
<td>0.05393</td>
<td>0.3202</td>
<td>0.3288</td>
</tr>
<tr>
<td>10</td>
<td>0.4168</td>
<td>0.3663</td>
<td>0.07183</td>
<td>0.3091</td>
<td>0.3246</td>
</tr>
</tbody>
</table>

Table 4.2 Values of $C_I$ and corresponding second order orientation tensor components at initial condition and steady state of MB composites at different shear rate
Figure 4.1. Transient shear viscosity $\eta^+$ at shear rates $0.0001$-10$\text{s}^{-1}$ of (a) SC0 (Curves for $0.01$ $\text{s}^{-1}$ and below fall on top of each other.) and (b) SC10 composite. $T=200^\circ\text{C}$.

Figure 4.2. Start up of steady shear at different shear rates. (a) pure PS (SC0) and (b) SC10 composite. $T=200^\circ\text{C}$. 

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Figure 4.3. Start up of steady shear as a function of strain at shear rate of $1 \text{s}^{-1}$ of (a) MB composites and (b) SC composites. $T=200^\circ C$. 
Figure 4.4. CNF orientation induced by extensional flow. (a) plane parallel to the flow, (b) plane perpendicular to the flow, (c) histogram of orientation with respect to flow direction in the plane parallel to the flow, and (d) histogram of orientation with respect to cutting direction in the plane perpendicular to the flow direction.
Figure 4.5 Model predictions of the shear viscosity compared to the experimental measurements and model predictions of fiber orientation for melt blended composite systems based on the fitting results of Table 4.2 at shear rate (a) $\dot{\gamma} = 0.01\, \text{s}^{-1}$, (b) $\dot{\gamma} = 0.03\, \text{s}^{-1}$, (c) $\dot{\gamma} = 0.1\, \text{s}^{-1}$, (d) $\dot{\gamma} = 0.3\, \text{s}^{-1}$, (e) $\dot{\gamma} = 1\, \text{s}^{-1}$, (f) $\dot{\gamma} = 3\, \text{s}^{-1}$, and (g) $\dot{\gamma} = 10\, \text{s}^{-1}$.
Figure 4.6 Model predictions of the shear viscosity compared to the experimental measurements based on the fitting results of Table 4.2 at mass concentration (a) $c=2\%$, (b) $c=5\%$, and (c) $c=10\%$. 
Figure 4.7 Pointwise model prediction of (a) the viscosity and (b) first normal stress difference compared to the experimental steady shear measurements for melt blended composite systems based on the fitting parameter $C_I$ and $a_{12}(0)$ obtained by fitting to the experimental measurements from transient state to steady state of the simple shear flow. In this procedure the model selects parameter $C_I$ and predicts values of viscosity only at the discrete shear rates where viscosity is measured; these pointwise values for each CNF concentration are connected by lines for clarity.
5.1 Introduction

Recently, haptic devices have been in use to increase the effectiveness of human-machine interfaces. The world of haptics is a fast growing field of technology. The need for haptic devices in applications that range from increasing the entertainment value of videogames to increasing the effectiveness of medical surgeons has been demonstrated. Haptic devices create better human/machine interfaces through force feedback.\textsuperscript{153-155}

A telerobotic system consists of a pair of manipulators in which an operator handling one manipulator (the master) directly controls the second manipulator (the slave), which acts on an external object. Figure 1.3 shows a telerobotic surgical system, in particular for minimally invasive cardio-thoracoscopic (MICT) surgery.\textsuperscript{156-157} The surgeon, who sits at a workstation, handles one manipulator (the master) to directly control a robot, which is a remote manipulator (the slave) acting on an external object to conduct the surgery.\textsuperscript{34} Current MICT systems have only visual feedback, the performance
of telerobotic systems can be greatly improved if some form of kinesthetic (or force) feedback is employed. The systems are called “transparent” when the operator controlling the master has the feeling of direct interaction with the remote object without any distortions in forces or geometry caused by the slave. Transparency is greatly limited in state of the art systems because most systems have slave inertias that are in general considerably higher than their corresponding master inertias, leading to the feedback of large signals emanating from impacts between the slave and its external object. These abrupt signals must be significantly attenuated to prevent instability, but this attenuation produces nontransparent systems that have a characteristically “mushy” feel, requiring excessive amounts of operator training for safe operation.

The inertia of the slave system can be significantly reduced if the motorized system used for classical haptic feedback is replaced by a Magnetorheological (MR) fluid based system. By synergistically combining novel magnetorheological (MR) fluid devices with fully 3-D dimensional microstructural analysis and control system design, the capabilities of modern force feedback systems can be greatly improved to the point that they can be employed in MICT surgery: the slave would receive motion commands from the master and transmit force from the external object back to the master, thereby allowing the surgeon to “feel” the object.

Magnetorheological (MR) fluids, which consist of micron-sized ferrous particles suspended in a Newtonian fluid, are a special class of fluids whose relation between stress and deformation varies strongly with an applied magnetic field. In particular, MR fluids exhibit a yield stress (or threshold stress for initiating fluid flow) that is an increasing function of applied magnetic field. Since the yield stress of an MR fluid is
variable, a safe low-energy magnetic field can be precisely controlled by current-driven electromagnets to enable the MR fluid to achieve a large range fluid behavior. The simple designs possible with MR fluid devices, low power requirements for control, and fast response make MR fluids attractive in force feedback applications.

The MR fluids based haptic system works as follows: the master joystick which includes a rotary MR damper in parallel with a spring controls the movement of the slave end-effector. Force and displacement sensors in the slave sense the environment conditions along which the end effector moves. This information is then used to control the MR damper to provide appropriate force feedback to the user. For example if the slave encounters soft tissue (low force, small to no deceleration) a relatively small current signal will be sent to the MR damper which will give the user the slight resistance associated with soft tissue. Likewise if the slave encounters bone (high force, large deceleration) a large signal will be sent to the MR damper, which will give the user a larger resistance.

This chapter is devoted to the development of models for the haptic systems using MR fluids for telerobotic surgery. A microstructural, kinetic theory based model of MR fluids has been developed based on the successes in prior research developing microstructurally based models for composite systems of carbon nanoparticles in a Newtonian fluid. MR fluids are modeled as micron-sized ferrous particles in a Newtonian carrier fluid, subjected to magnetic forces. The only change from the previous modeling of CNFs in Newtonian solvent is that the magnetic field $\mathbf{H}$ results in a nonzero external force $f^{(e)}$ in equation (5.1). Therefore, the orientation equation and the constitutive equation will have a dependence on magnetic field $\mathbf{H}$. 

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5.2 The kinetic theory-based elastic dumbbell model of MR fluids

MR fluids consist of micron-sized ferrous particles suspended in a Newtonian fluid. These fluids belong to a special class of fluids whose yield stress (or threshold stress for initiating fluid flow) increases with an applied magnetic field. There are a number of simple models used to describe MR fluid operation such as the Bingham model\textsuperscript{158} and Herschel-Bulkley viscoplasticity model\textsuperscript{55}.

The Bingham plastic model relates the total shear stress $\tau$ in simple shear to the magnitude of the applied magnetic field $H$ based on the following equation

$$\tau = \tau_y(H) + \eta \dot{\gamma},$$

(1.10)

where the function $\tau_y(H)$ is the yield stress caused by the applied magnetic field, the constant $\eta$ is the effective bulk viscosity of the composite system, and $\dot{\gamma}$ is the shear rate. To accommodate the shearing thinning effect of MR fluids the Herschel-Bulkley model can be used, given by

$$\tau = \left[ \tau_y(H) + K \left| \dot{\gamma} \right|^m \right] \text{sgn}(\dot{\gamma}),$$

(1.11)

where $m, K$ are constants. When $m=1$ and $K=\eta$ this model reduces to Bingham model (1.10). Note that both models describe fluids which in shear exhibits a strict yield stress $\tau_y(H)$: there is no flow, i.e. $\dot{\gamma}$ identically zero, until $\tau$ exceeds $\tau_y(H)$.

While present MR fluid modeling techniques based on equations (1.10) or (1.11) work well for many devices, there are some advanced applications (e.g. tactile and force feedback systems) that require higher fidelity models. For these systems the Bingham plastic and Herschel-Buckley models are found to be lacking in two specific areas:
(i) These equations only model simple shear flow. Although the models are effective in modeling this specific 1-D phenomenon, they are incapable of modeling higher dimensional geometries, such as the force-feedback systems for telerobotic surgery, where the MR fluid based device is used to give tactile feeling to a doctor during surgery. The ball and socket joystick device shown in Figure 5.1 cannot be effectively modeled using the previously mentioned models because the flow and its corresponding magnetic field are spatially varying vector quantities. The model presented in this study is fully vectorial and relationships between the stress tensor and the applied magnetic field vector are exploited. The higher accuracy of the model in this regard gives better force representations of highly compliant objects.

(ii) The present state of the art models are purely phenomenological. A more accurate model can be developed when the constitutive relationships are derived directly from microstructural features (i.e. size and shape of the particles) and the properties of the MR fluid constituents (i.e. carrier fluid viscosity, anti settling agent viscosity, particle geometry).

The kinetic theory-based elastic dumbbell models for MR fluids developed in this study are three dimensional and applicable to any flow geometry. It reduces to forms similar to Bingham’s model in a simple shear flow, but with coefficients which arise from fundamental electromagnetic considerations and microstructural features such as geometrical, magnetic and mechanical characterization of the particles, quantities measured primitively from the carrier fluid, magnetic field and temperature.
5.2.1 Kinetic Equation of the Elastic Dumbbell Model

In the kinetic theory dumbbell model, the iron particles are described by two beads \((r_1, r_2)\) of mass \(m\) jointed by a connector \(q = r_2 - r_1\) (Figure 1.2). The mass center of the bead-spring pair is \(x = \frac{r_1 + r_2}{2}\). This connector \(q\) between two beads represents the orientation of the iron particle in the carrier fluid. The kinetic (or Smoluchowski) equation that describes the rate of change of the orientation vector \(q\) with time is

\[
\dot{q}_i = \left( L_g - \mu D_g \right) q_j + c_y \frac{2kT}{\psi} \frac{\partial}{\partial q_k} \left( \xi_{ij} \psi \right) + 2c_y f^{(\text{elastic})}_j + c_y \left( f^{(\text{mag})}_1 - f^{(\text{mag})}_2 \right), \tag{5.1}
\]

The left-hand side of equation (5.1) is the Lagrangian time derivative of particle orientation, and the terms on the right-hand side arise from four physical effects that contribute to this change of orientation.

The first term models the effect of carrier fluid to change particle orientation. \(L_g = \frac{\partial}{\partial x_j} v_i\) is the velocity gradient tensor, where \(v_i = v_i(x, t)\) is the velocity of the carrier fluid at location \(x\) and time \(t\), and \(D_g = \frac{1}{2} \left( L_g + L_i \right)\) is the symmetric part of the velocity gradient tensor. The scalar parameter \(\mu\) measures the magnitude of the nonaffine motion of the dumbbell.

The second term \(c_y \frac{2kT}{\psi} \frac{\partial}{\partial q_k} \left( \xi_{ij} \psi \right)\) is the effect of the Brownian motion caused by thermal fluctuation; \(k\) is the Boltzmann constant, \(T\) is absolute temperature, \(\psi(q, x, t)\) is the probability distribution function of the particle orientation, \(\xi_{ij}\) is the anisotropic tensor responsible for the anisotropic Brownian motion, and \(c_y\) is given by and
\[ c_{ij} = -\left( \delta_{im} - \xi_{mn} \Omega_{mn} \right) \xi_{nj}^{-1}, \quad (5.2) \]

with \( \xi_{ij} \) the friction tensor. The Oseen-Burgers tensor \( \Omega_{ij} \) accounting for the hydrodynamic interaction is

\[ \Omega_{ij} = \frac{1}{8 \eta_s |\mathbf{q}|} \left[ \delta_{ij} + \frac{1}{|\mathbf{q}|^2} q_i q_j \right], \quad (5.3) \]

with \( \eta_s \) the solvent viscosity.

The third term \( 2c_{ij} f_j^{\text{elastic}} \) is the effect of intraparticle forces, such as elasticity, on the particle orientation with \( f_j^{\text{elastic}} \) the force in the connector. The fourth term \( c_{ij} \left( f_1^{\text{mag}} - f_2^{\text{mag}} \right) \) is the effect of external forces (the magnetic field in this research); \( f_1^{\text{mag}} \) is the magnetic force on bead 1 and \( f_2^{\text{mag}} \) is the magnetic force on bead 2.

The second order orientation tensor provides concise interpretation of mesoscale orientation state (i.e. the orientation averaged over a suitably large region). The second order orientation tensor \( \langle \mathbf{q} \otimes \mathbf{q} \rangle \) of the particle is defined as the dyadic product of \( \mathbf{q} \) averaged over orientation space (the component form of \( \langle \mathbf{q} \otimes \mathbf{q} \rangle \) is \( \langle q_i q_j \rangle \)):

\[ \langle q_i q_j \rangle = \int q_i q_j \psi(\mathbf{q}, \mathbf{x}, t) dq_1 dq_2 dq_3. \quad (5.4) \]

The second order orientation tensor \( \langle \mathbf{q} \otimes \mathbf{q} \rangle \) is the measure of the orientation state which influences the stress in the material. To obtain the governing equation for \( \langle \mathbf{q} \otimes \mathbf{q} \rangle \), we multiply the evolution equation of the distribution function

\[ \frac{\partial}{\partial t} \psi = -\frac{\partial \langle \psi \mathbf{q} \rangle}{\partial \mathbf{q}} = -\frac{\partial \langle \mathbf{q} \psi \rangle}{\partial q_i}, \quad (5.5) \]
by \( q, q_j \) and integrate over the entire space \( \mathbb{R}^3 \):

\[
\int \frac{\partial \psi(q, x, t)}{\partial t} q, q_j dq, dq_j dq_j = -\int \frac{\partial}{\partial q_k} \left[ \dot{q}_k \psi \right] q, q_j dq, dq_j dq_j,
\]

\[
= -\int \frac{\partial}{\partial q_k} \left( \dot{q}_k \psi q_j \right) dq, dq_j dq_j + \int \left( \dot{q}_k \psi \right) \frac{\partial}{\partial q_k} \left( q, q_j \right) dq, dq_j dq_j,
\]

\[
= 0 + \int \psi \left( \dot{q}_k q_j + q_k \dot{q}_j \right) dq, dq_j dq_j,
\]

\[
= \left( \dot{q}_k q_j + q_k \dot{q}_j \right) = \frac{d}{dt} \left( q, q_j \right)
\]

where we have used the divergence theorem and \( \psi \to 0 \) as \( |q| \to \infty \). From equation (5.1) we then obtain:

\[
\left( \dot{q}_k q_j + q_k \dot{q}_j \right) = \frac{d}{dt} \left( q, q_j \right) = (L_{mn} - \mu D_{mn}) \left( q, q_j \right) + \left( q, q_m \right) \left( L_{jn} - \mu D_{nj} \right) + 2kT \left[ \left( \dot{q}_j \psi \right) \left( \dot{q}_j \psi \right) + q_j \left[ \left( \delta_{jmn} - \psi \Omega_{mn} \right) \psi^{-1} \right] \dot{q}_k \right] \left( 2 \psi \left( \text{elastic} \right) + \psi \left( \text{mag} \right) \right) q_j - \left[ \left( \delta_{kji} - \psi \Omega_{mki} \right) \psi^{-1} \left( 2 \psi \left( \text{elastic} \right) + \psi \left( \text{mag} \right) \right) \right] q_j
\]

The Gordon-Schowalter derivative is defined by

\[
\frac{D}{Dt} \left( q, q_j \right) = \frac{d}{dt} \left( q, q_j \right) - W \left( q, q_j \right) W_j - a \left[ D \left( q, q_j \right) + \left( q, q_k \right) D_j \right],
\]

with \( \frac{d}{dt} \left( q, q_j \right) (x, t) = \frac{\partial}{\partial t} \left( q, q_j \right) (x, t) + \frac{\partial}{\partial x_j} \left( q, q_j \right) \dot{x}_k \), \( W \) the skew part of the velocity gradient \( \frac{\partial v}{\partial x_j} \), and \( a = 1 - \mu \); \( a = 1, 0, -1 \) correspond to the upper convected, corotational, and lower convected derivative, respectively.

With definition (5.8), equation (5.7) can be written as:
\[
\frac{D}{Dt} \langle q_j q_i \rangle = 2kT \left\langle \frac{\partial}{\partial q_k} \left[ \left( \frac{\partial n_m - \zeta n_m \Omega_{nm} \zeta^{-1} \right] q_j + q_i \left[ \left( \frac{\partial n_m - \zeta n_m \Omega_{nm} \zeta^{-1} \right] \right] \zeta^{-1} \right] \right\rangle ,
\]

which is the evolution equation of the orientation tensor \( \langle q_j q_i \rangle \).

When anisotropic effect in the Brownian motion is neglected (i.e. \( \xi_{ij} = \delta_{ij} \)), the friction is isotropic (i.e. \( \zeta_{ij} = \zeta \delta_{ij} \)), and the hydrodynamics interaction is neglected (i.e. \( \Omega_{ij} = 0 \)), the evolution equation (5.9) of the orientation tensor simplifies to:

\[
\frac{D}{Dt} \langle q_j q_i \rangle = \frac{4kT}{\zeta} \delta_{ij} - \frac{2}{\zeta} \left\langle \left( q_i f_i^{\text{elastic}} + f_i^{\text{mag}} \right) q_j \right\rangle
\]

\[
- \frac{1}{\zeta} \left\langle \left( q_i f_i^{\text{mag}} - f_i^{\text{mag}} \right) + \left( f_i^{\text{mag}} - f_i^{\text{mag}} \right) q_j \right\rangle .
\]

The complete kinetic theory-based model for MR fluids consists of the evolution equation (5.9) for the orientation tensor \( \langle q_j q_i \rangle \), together with conservation of momentum, and a constitutive equation for Cauchy stress tensor \( \tau_{ij} \), yielding a closed system of equations for \( \langle q_j q_i \rangle \), \( \tau_{ij} \), and velocity of the carrier fluid and particles.

We assume the total stress tensor \( \tau_{ij} \) of the composite system is given by the sum of the constraint pressure \( p \) maintaining incompressibility, the viscous stress \( 2\eta_s D_{ij} \) due to the solvent, the mechanical stress \( \tau_{ij}^{\text{mech}} \) due to the particle, and, for the MR fluid, the stress \( \tau_{ij}^{\text{mag}} \) due to the magnetic field:

\[
\tau_{ij} = -p\delta_{ij} + 2\eta_s D_{ij} + \tau_{ij}^{\text{mech}} + \tau_{ij}^{\text{mag}} .
\]

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The mechanical stress $\tau_{ij}^{\text{mech}}$ consists of the contribution from the intraparticle force $f^{(\text{elastic})}$, and the bead motion:

$$\tau_{ij}^{\text{mech}} = \frac{n}{2} \left\langle q_i f_j^{(\text{elastic})} + f_i^{(\text{elastic})} q_j \right\rangle - nm \sum_{\nu=1}^{2} \left\langle (\dot{r}_\nu - \nu)(\dot{r}_\nu - \nu) \right\rangle + nkT \delta_{ij},$$  \hspace{1cm} (5.12)

where $n$ is the particle number density, $m$ is the unit mass for each particle, $\dot{r}_\nu$ denotes the velocity of the bead ($\nu=1,2$), and $\nu$ is the velocity of the solvent particle at $x$. With Maxwellian velocity distribution, mechanical stress due to the particle is simplified to:

$$\tau_{ij}^{\text{mech}} = \frac{n}{2} \left\langle q_i f_j^{(\text{elastic})} + f_i^{(\text{elastic})} q_j \right\rangle - nkT \delta_{ij}. \hspace{1cm} (5.13)$$

The magnetic stress $\tau_{ij}^{\text{mag}}$ is related to magnetic effects through

$$\tau_{ij}^{\text{mag}} = \frac{1}{2} \left\langle q_i (f_j^{(\text{mag})} - f_j^{(\text{mag})}) \right\rangle. \hspace{1cm} (5.14)$$

To effectively model the MR fluid, we must produce appropriate expressions for the intraparticle force $f^{(\text{elastic})}$, and the magnetic force $f^{(\text{mag})}$.

For example, for an elastic (Hookean) dumbbell the elastic potential of the linear spring is given by

$$U^{(\text{elastic})} = -\frac{1}{2} \beta q_i q_i = -\frac{1}{2} \beta q_j q_j,$$  \hspace{1cm} (5.15)

with $\beta$ the elastic spring constant, so that elastic force is

$$f_i^{(\text{elastic})} = -\frac{\partial}{\partial q_i} U^{(\text{elastic})} = \beta q_i. \hspace{1cm} (5.16)$$

For an elastic (Hookean) dumbbell with elastic spring constant $\beta$ the evolution equation (5.10) of the orientation tensor $\left\langle q_i q_j \right\rangle$ is simplifies to:
\[ \frac{D}{Dt}(q_i q_j) = \frac{4kT}{\zeta}\delta_{ij} - \frac{4\beta}{\zeta} \langle q_i q_j \rangle - \frac{1}{\zeta}\left\{ \langle q_i (f_{ij}^{(m))} - f_{2j}^{(m))} \rangle + \langle f_{ii}^{(m))} - f_{2i}^{(m))} \rangle q_j \rangle \right\} \]  
(5.17)

and the mechanical stress equation (5.13) is simplified to

\[ \tau_{ij}^{mech} = n\beta \langle q_i q_j \rangle - nkT\delta_{ij}. \]  
(5.18)

It only remains to specify the dependence of the magnetic force \( f_i^{(mag)} - f_i^{(mag)} \). We investigate the effect of \( f_i^{(mag)} - f_i^{(mag)} \) by comparing the model predictions of shear stress vs. shear rate and yield stress vs. magnetic field at steady state with the experimental measurements.

### 5.2.2 Model application to simple shear flow

#### 5.2.2.1 Experimental measurements

In simple shear flow, the velocity is assumed to be

\[ \mathbf{\dot{x}} = \mathbf{v} = \begin{bmatrix} \dot{\gamma} x_2 \\ 0 \\ 0 \end{bmatrix}, \]  
(5.19)

so that the velocity gradient tensor, and its symmetric and skew parts are

\[ \mathbf{L} = \dot{\gamma} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \mathbf{D} = \frac{1}{2} \left( \mathbf{L} + \mathbf{L}^T \right) = \frac{1}{2} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \mathbf{W} = \frac{1}{2} \left( \mathbf{L} - \mathbf{L}^T \right) = \frac{1}{2} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \]  
(5.20)

In our simple shear experiments the magnetic field is transverse to the flow:

\[ \mathbf{H} = \begin{bmatrix} 0 \\ H \\ 0 \end{bmatrix}. \]  
(5.21)

The following experimentally measured dependencies serve as checks on the constitutive assumptions made on the MR fluids. Figure 5.2a displays the steady state...
experimental measurements of shear stress vs. shear rate in magnetic fields of magnitudes 0, 10, 120 kAmp/m; Figure 5.2b displays the same measurements as shear stress vs. magnetic field, at three different shear rates. The measurements in Figure 5.2 were produced by experimental tests on a linear MR damper under an MTS machine. The input is current to the solenoid, which is controlled. The magnetic field strength $H$ is calculated analytically based on the material and geometry specifications of the damper and solenoid. Also we measure the magnetic field directly using a Gaussmeter. The applied force on the damper is measured by the MTS machine, and the shear stress is calculated based on the measured force and geometry of the damper and the area wetted by the MR fluid.

Figure 5.3a and Figure 5.3b, taken from LORD Corporation Product Bulletins, give measurements of shear stress vs. shear rate at two temperatures, in the absence of an applied magnetic field. Figure 5.4a and Figure 5.4b, from the same LORD Corporation Product Bulletins, are experimental measurements of yield stress vs. magnetic field at two different temperatures. (Note the vertical axes in Figure 5.3a and b are in Pa, whereas Figure 5.2 and Figure 5.4 are kPa.)

**5.2.2.2 Model prediction based on the magnetic force assumptions**

We assume the magnetic force

$$f_{li}^{(mag)} - f_{li}^{(mag)} = \frac{c\dot{\gamma}}{(1 + \chi')|H|} q_i,$$  \hspace{1cm} (5.22)

where $c$ is a constant. Substituting the external magnetic force to the evolution equation of the orientation tensor equation (5.17) produces:
\[
\frac{D}{Dt} \langle q_i q_j \rangle = \frac{4kT}{\zeta} \delta_{ij} - \left( \frac{4\beta}{\zeta} + \frac{2c\dot{\gamma}}{\zeta(1+\chi)|H|} \right) \langle q_i q_j \rangle.
\]  (5.23)

Substituting the external magnetic force equation (5.14), the stress contribution from the magnetic field is:

\[
\tau_{ij}^{\text{mag}} = \frac{1}{2} \frac{nc\dot{\gamma}}{(1+\chi)|H|} \langle q_i q_j \rangle.
\]  (5.24)

The total stress of the composite system is:

\[
\tau_{ij} = -pd_{ij} + 2\eta_s D_{ij} + n \left( \beta + \frac{1}{2} \frac{c\dot{\gamma}}{(1+\chi)|H|} \right) \langle q_i q_j \rangle - nkT \delta_{ij}.
\]  (5.25)

Setting \( \frac{\partial}{\partial t} \langle q_i q_j \rangle = 0 \), \( \frac{\partial}{\partial x_1} \langle q_i q_j \rangle = 0 \), and \( \frac{\partial}{\partial x_3} \langle q_i q_j \rangle = 0 \) for fully developed plane flow at steady state and solving equation (5.23) gives:

\[
\langle q_i q_2 \rangle = \frac{kT\zeta}{2\beta + \frac{c\dot{\gamma}}{(1+\chi)|H|}} \dot{\gamma}.
\]  (5.26)

Inserting the velocity \( \mathbf{\dot{x}} = \dot{\gamma}x_2 \mathbf{e}_1 \), magnetic field \( \mathbf{H} = He_2 \) and \( \langle q_i q_2 \rangle \) into equation (5.25) produces the shear stress:

\[
\tau_{12} = \eta_1 \dot{\gamma} + \frac{nkT\zeta\dot{\gamma}}{4 \left( \beta + \frac{c\dot{\gamma}}{2(1+\chi)|H|} \right)}.
\]  (5.27)

The plots of shear stress vs. shear rate, yield stress vs. magnetic field are shown in Figure 5.5a and Figure 5.5b, respectively. Figure 5.5a indicates that the dependences of shear stress on shear rate presented by equation (5.27) are consistent with the experimental observation shown in Figure 5.2a. Figure 5.5b indicates that the model prediction of yield
stress versus magnetic induction is in agreement with the observed behaviors shown in Figure 5.2b.

5.3 Conclusions

Haptic systems greatly increase the effectiveness of a human machine interface. However, these systems use passive devices in force feedback systems that are unable to recreate a reactive force that helps in disengaging an object. The relative, simplicity and quick dynamics of an MR damper makes it a viable option for a myriad of haptic applications. This chapter developed and validated microstructurally based, fundamental models for MR fluid devices, which relates flow, stress, and particle orientation. The dumbbell models in which two beads joined by an elastic connector were investigated and the iron particles are modeled as elastic dumbbells suspended in a carrier fluid. All coefficients in the constitutive models are specified not by a fit to macroscale experimental flow measurement but rather in terms of primitive measurements of particle microstructure, carrier fluid viscosity and density, and temperature. These new models for MR fluids are three dimensional and applicable to any flow geometry. The model developed in this study is fully vectorial and relationships between the stress tensor and the applied magnetic field vector are fully exploited.

These models ultimately will take the form of relations between the forces applied to the MR actuators and their subsequent motion, as functions of electric current. The relations between force, motion, and current will depend on the geometry of the device and a fundamental, microstructurally based characterization of the MR fluid.
Figure 5.1. Ball and Socket Tactile Device
Figure 5.2. Experimental measurements (*) at 23°C with an MTS machine, Intelligent Structures and Systems Laboratory, Ohio State University: (a) shear stress as a function of shear rate and magnetic field strength (------ model prediction), (b) the same experimental measurements as (a) but expressed as shear stress vs. magnetic field.
Figure 5.3. Measurements of shear stress vs. shear rate (a) at 40°C with no applied magnetic field, MRF-132AD Product Bulletin LORD Corporation; (b) at 25°C with no applied magnetic field, MRF-336AG Product Bulletin, LORD Corporation.
Figure 5.4. Measurements of yield stress vs. magnetic field strength (a) at 40°C with no applied magnetic field, MRF-132AD Product Bulletin LORD Corporation; (b) at 25°C with no applied magnetic field, MRF-336AG Product Bulletin, LORD Corporation.
Figure 5.5. Model prediction based on the proposed external magnetic force assumption: (a). model prediction of Shear stress as a function of shear rate, and (b). model prediction of yield stress versus magnetic field.
BIBLIOGRAPHY


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