RHEOLOGICAL CHARACTERIZATION AND MODELING OF MICRO- AND NANO-SCALE PARTICLE SUSPENSIONS

DISSERTATION

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By

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ABSTRACT

In recent years there has been increased interest in the broad areas of micro- and nano-technology due to the potential to create materials with unique properties which were previously unattainable. One area of special interest has been the use of nanoparticles such as nanoclays, nanofibers and carbon nanotubes and microscale carbonyl iron particles. Nanoclays and nanofibers have received attention due to their ability to be incorporated into polymer matrices and impart functionality such as electrical conductivity, increased tensile strength and modulus, and a reduction of gas and moisture permeability at much lower particle loadings when compared to traditional fillers such as carbon black and glass fibers. The addition of these nanoparticles also has a significant effect on the rheological properties of the composite. The rheological behavior of polystyrene/nanoclay composites under steady state shear flow and polystyrene/carbon nanofiber composites under transient shear and uniaxial extension is investigated. A constitutive model is developed that is capable of predicting the shear and extensional rheology of both types of composites and predicts orientation changes to the nanoparticles due to flow. The model is validated through comparison to the experimental rheological measurements of both composite types and experimental measurements of carbon nanofiber orientation in the polystyrene/carbon nanofiber composites under uniaxial extension.
The addition of magnetizable carbonyl iron particles to a non-magnetizable carrier fluid has been done to create a smart fluid, known as a magnetorheological fluid, whose rheological properties can be modified through the application of a magnetic field. This added functionality is being utilized in applications such as shock absorbers, dampers, brakes, and clutches. The use of these fluids in engineering applications requires rheological models capable of capturing their complex flow behavior under various flow conditions. The rheological behavior of four magnetorheological fluids were characterized under steady state shear and small amplitude oscillatory shear flow in order to quantify the effects of carrier fluid viscosity and particle size. A constitutive model is developed to predict the shear flow response of the MR fluids which accounts for hydrodynamic forces and the magnetic effects on the carbonyl iron particles. The model is validated through comparison with the experimentally measured data.

Carbon nanotubes have tremendous potential to be used in a wide range of applications because their tensile strength, electrical conductivity and thermal conductivity are among the greatest of all known materials. The performance properties currently achieved in macroscopic assemblies of CNTs are significantly less than those of individual nanotubes and are highly dependant upon processing conditions. There is a need to understand the principals controlling the behavior of carbon nanotube assemblies in order to realize the full potential of these materials and create marketable products.
Several different properties of CNTs and CNT structures were measured in an attempt to identify the significant differences which result in the observed behaviors.
Dedicated to my wife, Allyson
I would like to thank my advisor, Dr. Kurt Koelling, for all of the support and guidance that has allowed me to reach this point. I would also like to thank my co-advisor, Dr. Stephen Bechtel, for all of the useful discussions and insight concerning experiments and constructive comments concerning written documents.

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CHAPTER 1

INTRODUCTION

A significant amount of research in the past twenty years has been focused on the properties and uses of nanoparticles. Nanoparticles are particles with at least one dimension in the nanoscale such as nanoclays, carbon nanofibers (CNFs), and carbon nanotubes. These particles have generated so much interest because of their unique properties and their ability to be dispersed in materials, such as polymers, and impart properties such as electrical conductivity or improved tensile strength to those materials.

Nanoclays have been known about since as early as 1950 when the National Lead Company reported the use of nanoclays in polymer composites. However, research in this area didn’t attract much attention until the early 1990’s when a Toyota research group reported substantial improvements to the thermal and mechanical properties of Nylon-6 with the addition of a very small amount of montmorillonite clay. The area of nanoclay composites was advanced further in 1993 when Vaia et al. [1] demonstrated that polystyrene/nanoclay composites could be made without the use of organic solvents through means of direct melt mixing. Since this time much has been discovered about nanoclay’s potential to provide materials with improved strength, reduced weight, lowered costs, enhanced barrier properties to air and moisture, and increased flame
retardance [2]. One of the reasons nanoclays make excellent reinforcing agents is because of its large surface area per unit weight (750 m²/g) which allows for more interaction with the polymer compared to traditional fillers such as carbon black or glass fibers.

In 1991, around the same time as the breakthroughs with nanoclay composite technology, the single walled carbon nanotube (SWNT) was discovered [3] providing another area of interest for nanocomposite research. Research has shown that the addition of these particles to a polymer matrix also leads to materials with improved properties. Although the use of SWNTs provides many benefits to material properties, their cost remains prohibitively high for use on a large scale. CNFs, which, like SWNTs, are a rod-like particle composed of carbon although with a slightly different structure, may be used in place of SWNTs and provide similar property enhancements such as increased thermal and electrical conductivities and increased mechanical strength but at a fraction of the cost, nearly 1/500, making CNFs a more reasonable choice for the mass production of composite goods.

Both nanoclays and CNFs are similar in that their unique physical properties and small size lead to composites with greatly improved properties at very small loading levels. They are already in use in a variety of areas such as automobile parts, food packaging, and wire and cable coating. Both particles also have very large aspect ratios and therefore, when incorporated into polymer matrices, the rheological and mechanical properties of the resultant composite are strongly dependent upon the morphology of the nanoparticles which changes during processing due to the forces generated by shear and/or extensional flows. Optimization of a composite material’s performance properties
therefore requires an understanding of the effects of nanoparticle size, shape and orientation on the flow behavior of the composite and how flow affects the nanostructure within the composite.

Micron-sized particles have also found use in smart materials, which are materials that possess the ability to significantly change their material properties when subjected to an external stimulus. An example of such a fluid is a magnetorheological (MR) fluid. MR fluids were first discovered by Rabinow in 1948 [4] and consist of micron-sized magnetically polarizable particles suspended in a carrier fluid. These fluids are able to rapidly and reversibly undergo significant changes in their rheological properties upon application of an external magnetic field. The ability to control the flow behavior of these fluids has led to their use in such applications as shock absorbers [5], dampers [6], brakes [7], and clutches [8].

There has been a great deal of work in recent years characterizing the rheological behavior of magnetorheological fluids as well as attempts to model the observed behaviors. Commonly used models are the Bingham model and Herschel-Bulkley model, Equations 1.1 and 1.2, respectively.

\[
\tau = \left[ \tau_y(H) + \eta |\dot{\gamma}| \right] \text{sgn} \left( \dot{\gamma} \right) \quad (1.1)
\]

\[
\tau = \left[ \tau_y(H) + K |\dot{\gamma}|^{1/m} \right] \text{sgn} \left( \dot{\gamma} \right) \quad (1.2)
\]

In these equations \( \tau \) is the total shear stress, \( \tau_y(H) \) is the yield stress, \( \eta \) is the effective bulk viscosity of the composite system, and \( K \) and \( m \) are constants. The Bingham model is used to describe a fluid with Newtonian viscosity and a yield stress, which is a threshold stress level that must be overcome before the fluid will flow. The Herschel-
Bulkley model is similar to the Bingham model in that it contains a yield stress term however shear stress has been raised to the power, $1/m$, which accounts for any shear thinning behavior. While these models can be fit reasonably well to the experimentally observed rheological behaviors of dilute and semi-dilute fluids, they do not do well describing concentrated suspensions which are commonly used in practical applications. Further, these models do not provide any insight on the balance between forces (i.e. hydrodynamic, magnetic forces) that result in the observed behavior. The use of these smart materials in engineering applications requires models that can predict the properties of the fluids under changing magnetic field strengths and shear rates.

This thesis is organized as follows:

Chapter 2 is a review of the use of nanoclays and carbon nanofibers in polymer composites and the characterization of their rheological properties. Carbon nanotubes are also introduced and discussed as well as many of the common methods used to characterize them. Finally, a brief review of magnetorheological fluids is discussed.

Chapter 3 presents experimental measurements of the shear rheology of polystyrene/nanoclay composites at different nanoclay concentrations and a constitutive model is introduced that can predict the steady state shear rheology of the composites. A discussion of the model parameters is given as well as a procedure for the optimization of the model.

Chapter 4 discusses the transient shear rheology of polystyrene/carbon nanofiber composites. The polystyrene used is the same as that used in Chapter 3, however the reinforcement particle has a rod-like shape compared to the disk-like shape of the
nanoclays. The constitutive model from Chapter 3 is again used, however, the equations must be solved as non-linear differential equations because time derivatives eliminated during steady-state must be included. The model is also made more complicated through the use of multiple modes to describe the rheology of pure polystyrene.

Chapter 5 presents a novel method for measuring the three-dimensional orientation distribution of carbon nanofibers in a polymer composite. The orientation tensor (which is used to define nanofiber orientation) and the theory behind the measurement technique are discussed. A computer simulation is used to validate the technique and to optimize measurement conditions. Finally, experimental measurements of the orientation distribution of carbon nanofibers in a real polystyrene/carbon nanofiber sample subjected to uniaxial extensional flow are performed at different times during the flow.

Chapter 6 presents experimental measurements of the transient extensional viscosity of polystyrene/carbon nanofiber composites. The nanofiber orientation measurement technique from Chapter 5 is applied to in this chapter to provide three-dimensional orientation tensors for the composites at different points in time during extensional flow. The constitutive model from Chapters 3 and 4 is modified to apply to extensional flows and a procedure for determining the model parameters is included. For the first time, model predictions of nanofiber orientation are compared to experimental measurements.

Chapter 7 presents experimental measurements of the linear viscoelastic and steady state shear rheology of MR fluids composed of different carrier fluid viscosities
and magnetic particle size distributions. A model is derived from first principles that accounts for forces such as hydrodynamic drag, particle-particle interaction and magnetic attraction and is capable of predicting the steady state shear rheology of MR fluids. Predictions of the model are compared to experimental results.

Chapter 8 presents experimental measurements of the performance properties of thin films composed of single-walled carbon nanotubes. Properties such as the tensile strength, tensile modulus and creep flow were measured in order to determine their dependence on the properties of the individual nanotubes, the structure of the nanotubes in bundles and the structure of those bundles which were measured using techniques such as Raman spectroscopy and scanning electron microscopy.
CHAPTER 2

LITERATURE REVIEW

2.1 Polymer/Nanoclay Composites

In the early 1990’s a research group at Toyota created a polymer composite composed of nylon and clay [9-11]. While composites (a material composed of two or more distinct substances combined to produce structural or functional properties not present in any individual component) have been around for thousands of years, this particular composite was unique because the reinforcing agent, the clay, had at least one dimension in the nanometer scale. It was believed that if the dimensions of the reinforcement could be reduced the amount of enhancement could be increased. It was found that the addition of clay to nylon 6 resulted in a composite with improved strength and modulus compared to pure nylon 6 [11]. In the years following this groundbreaking work much research has been conducted in order to gain more knowledge of the nanoclay’s structure, methods to disperse the clay in a matrix, and the mechanical and rheological properties of nanoclay composites.

One of the most commonly studied nanoclays is montmorillonite (MMT) which is classified as a 2:1 mica type layered silicate [12] with dimensions of approximately 1 nm thick and 100-150 nm in length [2]. A 2:1 mica type layered silicate is a clay composed
of two sheets of tetrahedrally bound silicon atoms and one octahedrally bound sheet primarily composed of Al$^{3+}$ with the occasional substitution of an Mg$^{2+}$ cation. The substitution of Mg$^{2+}$ cations results in a net negative charge of the clay layer which is balanced by the adsorption of cations to the surface of the clay. The presence of these interlayer cations renders the MMT hydrophilic making them miscible with water or hydrophilic polymers such as poly(ethylene oxide) or poly(vinyl alcohol). In order to make the naturally hydrophilic clay hydrophobic, and thus miscible with hydrophobic polymers, a cation exchange reaction is usually performed. In this reaction the interlayer cations are replaced with cationic surfactants which have a positively charged head group which balances the charge in the clay and a hydrophobic tail which makes the clay compatible with hydrophobic substances. The structure of a montmorillonite clay layer is shown in Figure 2.1.

Nanoclays typically occur as stacks of these clay layers. In order to make use of their small size for property enhancements the stacks need to be broken down into individual layers. In general there are three things that will happen when mixing nanoclays with polymers. If the clay and the polymer are immiscible, the clay will remain as stacks and not interact with the polymer. If the clay and the polymer are compatible the polymer can penetrate the space between the clay layers resulting in a structure of alternating polymer and clay layers [13]. This type of composite is known as intercalated. There is also an exfoliated composite which occurs when the clay is separated into individual layers within a polymer matrix.
Two techniques are commonly used to determine which type of composite is formed: x-ray diffraction (XRD) and transmission electron microscopy (TEM). Using XRD, plots are made of intensity vs. 2θ. The presence of closely spaced clay layers in the intercalated composites results in peaks on the plots. From the magnitude and positioning of the peaks it is possible to determine the distance between clay layers. In the case of exfoliated composites, there is no layering of the clay as all platelets have been delaminated from one another, which results in the absence of peaks on the XRD plots. TEM micrographs allow one to visually determine the distance between clay layers or if the layers have been delaminated.

The improvement of polymer mechanical properties with the addition of nanoclays was first shown by Kojima et al. [11]. Several mechanical property tests were performed on nylon 6/MMT composites at different temperatures and different MMT concentrations. At 23°C the tensile strength of nylon 6 was found to be 68.6 MPa. With the addition of 4.7 wt% MMT the tensile strength increased to 97.2 MPa. The same increase in tensile strength with nanoclay addition was observed at 120°C with the tensile strength of nylon 6 being 26.6 MPa and nylon 6/4.7 wt% MMT composite being 32.3 MPa. A study was also performed on the dependence of tensile modulus with nanoclay concentration which revealed an increase in tensile modulus with increasing clay content.

Park and Jana [14] investigated the mechanical properties of polymethylmethacrylate (PMMA) melt-blended with different concentrations of Closite 30B nanoclay. They found the tensile modulus of PMMA was increased from 925 MPa to 1225 MPa with the addition of 3.8 wt% nanoclay; a 32% increase. However, the
tensile strength and strain at break, and impact and tensile toughness were found to decrease with increasing nanoclay content. The tensile strength and strain of PMMA, for example, were found to decrease by 50 and 30%, respectively with the addition of 3.8 wt% nanoclay. Wide angle x-ray diffraction (WAXD) was performed on the composites and it was determined the clay had an intercalated structure. Composites with an exfoliated clay structure were made using epoxy as a dispersing agent in the PMMA. The addition of clay resulted in an increase in tensile modulus, strength and strain at break, and in impact and tensile toughness over the virgin polymer. However, tensile strength and toughness decreased when nanoclay content increased from 7.7 to 15.5 wt%, although the values were still greater than pure PMMA. Further study revealed that PMMA-epoxy composites had decreased values of all measured properties therefore the increased property values seen in the PMMA-epoxy-nanoclay composites can be attributed to the presence of exfoliated nanoclay.

Many other research groups have also studied the effects of nanoclays on the mechanical properties of a variety of polymer composites such as polypropylene [15], polyethylene [16], polyimide [17], ethylene propylene diene methylene (EPDM) [18] and poly(ethylene terephthalate) (PET) [19].

The addition of nanoclay to polymers not only affects mechanical properties but rheological properties as well. In order to effectively process composites containing nanoclays it is necessary to understand the effects of the clay on the flow properties of the composite. Typically, composites are studied under extensional flow and dynamic oscillatory, transient, and steady state shear flows. One of the earliest studies on the
effects of nanoclay on the rheology of polymer composites was performed by Krishnamoorti et al. [20]. In this work composites were formed by combining clay and one of the following polymers: poly(dimethyldiphenyl siloxane), poly(dimethylsiloxane) or nylon-6/clay. The behavior of these composites was studied under steady state shear and small amplitude oscillatory shear. Steady state shear experiments performed on the poly(dimethyldiphenyl siloxane) and poly(dimethylsiloxane) composites revealed that viscosity increased with increasing nanoclay content, the Newtonian plateau present in pure polymer at low shear rates was no longer present with the addition of nanoclay, and the viscosities of the pure polymer and the composites began to converge at high shear rates (~100 s$^{-1}$). Dynamic oscillatory shear experiments performed on nylon-6/clay composites revealed an increase in the storage (G’) and loss (G”) modulus with increasing nanoclay content. They also observed nonterminal behavior (a decrease in the slope of G’ at low frequencies) once nanoclay was added to the polymer. The slope of G’ decreased in the low frequency region with increasing nanoclay concentration. Krishnamoorti and Giannelis [21] performed another set experiments in order to further study the behavior of nylon-6/clay composites under small amplitude oscillatory shear. This work validated all previous observations and led to the conclusion that nonterminal rheological behavior was present only if there was strong interaction between the polymer and the nanoclay. They also found the slope of G’ and G” in the low frequency region stopped decreasing with nanoclay additions above 5 wt%.

The role of polymer molecular weight on the rheological properties of nylon 6/nanoclay composites was studied by Fornes et al. [22]. The nyons used in the
experiments had number average molecular weights of 16,400; 22,000 and 29,300. TEM analysis revealed that as the molecular weight of the polymer increased the average number of clay platelets seen in a stack decreased meaning the clay was more delaminated. The complex viscosity was measured using small amplitude oscillatory shear and showed that none of the composites had a Newtonian plateau at low frequencies, however, as molecular weight increased the amount of shear thinning also increased. A measure of G’ also showed decreasing slope at low frequencies with increasing molecular weight. The conclusions drawn from this work are that the increase in polymer molecular weight led to higher stresses on mixing with the nanoclay which led to an increase in the amount of nanoclay exfoliation which explains the observed shear thinning and nonterminal behavior under oscillatory shear flow.

The linear viscoelastic behavior of polypropylene/nanoclay composites was studied by Solomon et al. [23]. As with previous studies, G’ and G” were found to increase with increasing nanoclay content. Nonterminal behavior was also observed for composites containing concentrations of nanoclay greater than 2 wt%. Terminal behavior was observed for composites containing 1.3 wt% nanoclay. One unique experiment performed in this work was the evaluation of different surfactants on the storage modulus of 4.8 wt% composites. The experiments revealed that choice of surfactant played a large role in the properties of the composite. Some composites displayed terminal behavior while others displayed nonterminal behavior. The cause of this difference was most likely due to the increased interlayer spacing of the clay particles in the composites that
displayed nonterminal behavior. It is also likely that these composites were exfoliated to a higher degree since the interlayer spacing was increased.

Okamoto et al. [24] studied the extensional rheology and nanoclay structure development in polypropylene/nanoclay composites. In typical homopolymers the relationship between extensional viscosity and shear viscosity follows the Trouton rule, which is the extensional viscosity is equal to three times the zero shear viscosity. Okamoto et al. observed a deviation of the composite’s behavior from this rule. The extensional viscosity was found to be significantly greater than three times the zero shear viscosity. The observed difference was theorized to be due to the difference in the nanostructure developed during shear and extensional flows.

2.2 Polymer/CNF Composites

Carbon nanotubes (CNTs) were first discovered in 1991 by Iijima [25] and since this time there has been a vast amount of research conducted characterizing the unique thermal, electrical and mechanical properties they possess and developing means to take advantage of those properties. One area that has received a great deal of attention is the use of CNTs in polymer composites because of the potential to add functionality, such as high electrical conductivity and increased strength, to low cost polymers at very low loading levels. Although promising results have been shown, their relatively high cost, ~$500/g, has inhibited their widespread use.

An alternative to high priced CNTs are carbon nanofibers (CNFs) which cost approximately $500/kg, 0.1% of the cost of CNTs. CNFs are composed of stacks of
Graphene sheets which form fibers with typical diameters of 70-200 nm and lengths of 50-100 μm. These fibers are larger than CNTs but are smaller than conventional carbon fibers which have diameters of 5-10 μm. While CNFs do not possess the superior mechanical strength and thermal and electrical conductivities of CNTs (few materials do), they do outperform traditional fillers such as carbon black and short glass fibers. CNFs have been successfully incorporated into polymer matrices leading to improvements in the mechanical strength and electrical conductivity of the resulting composite.

A wide variety of polymers have been used by researchers studying the performance properties of CNF/polymer composites including polyacrylonitrile [26], epoxy [27] polyethylene [28], polypropylene [29] polycarbonate [30] polystyrene [31] acrylonitrile-butadiene-styrene (ABS) [32], nylon [33], poly(phenylene sulfide) [34], phenylethynyl terminated polyimide [35], poly(methyl methacrylate) [36], poly(ethylene terephthalate) (PET) [37], and poly(p-phenylene benzobisthiazole) (PBZT) [38]. Guo et al. [26] studied the tensile and electrical properties of polyacrylonitrile/CNF composite films with CNF loadings of 5, 10, 20, 40, 60, 80 and 90 wt%. It was found that the tensile strength of the composites with CNF concentrations of 40 wt% or less were greater than the tensile strength of the polymer, which was measured as 53 MPa. A CNF loading of 5 wt% had the greatest tensile strength, 80 MPa, and increased CNF loading resulted in decreased tensile strength. Electrical conductivity was found to increase with increasing CNF concentration. Composites containing 90 wt% CNF were found to have a conductivity of $1.67 \times 10^3$ S/m.
Kumar et al. [39] produced polypropylene and polypropylene/CNF composite fibers with diameters of 55 μm. The tensile strength was found to increase from 490 MPa to 570 MPa with the addition of 5 wt% CNF while the tensile modulus increased from 4.6 GPa to 7.1 GPa. Both the addition of the nanofibers and their alignment with the major axis of the fiber were thought to affect the magnitude of improvement.

Choi et al. [27] studied the mechanical and electrical properties of CNF/epoxy composites as well as the effects of treating the nanofibers with ozone. The ozone treatment was done in order to increase the amount of oxygen attached to the surface of the nanofibers which increased the miscibility of the fibers and epoxy which resulted in an improvement in the dispersion of the nanofibers. The study found that the tensile strength of the composites was increased, relative to the epoxy, with the addition of 5 wt% CNF however the tensile strength was lower at CNF concentrations of 10 and 20 wt%. The composites made with ozone treated CNFs always had a greater tensile strength than the composites made with untreated CNFs. Measurements of electrical resistivity revealed a decrease in resistivity with increasing CNF loading with the ozone treated CNF composites having lower electrical resistances than the untreated CNF composites. This study indicates that CNF concentration, dispersion and affinity for the polymer matrix are important factors in the properties of the composite.

While CNTs and CNFs can add functionality to polymer matrices, their presence also has major implications on a composite’s rheology. While there have been several studies conducted to understand the relationship between the properties of rod-like nanoparticles (CNTs and CNFs) and the flow properties of the composite that contain
them, there are very few studies that focus on the rheology of polymer/CNF composites. Lozano et al. [40] studied the small amplitude oscillatory shear response of polypropylene/CNF composites at various CNF loadings. It was found that $G'$ and $G''$ increased and the crossover point of $G'$ and $G''$ occurred at lower frequencies with increasing CNF content. The complex viscosity was also observed to increase with increasing CNF content with all composites showing shear thinning behavior. It was also seen that as frequency increased the viscosity values for all composites began converging to similar values.

Lozano et al. [28] also studied the rheological properties of polyethylene/CNF composites by conducting experiments similar to those used to study the polypropylene/CNF composites. Once again the rheological behavior showed a strong dependence upon CNF concentration and frequency. It was also shown that temperature had an effect on flow properties with increasing temperatures leading to lower viscosities.

The rheological properties of CNT/polymer composites have been investigated with particular attention being paid to the influence of nanotube dispersion, concentration, aspect ratio and alignment. Most researchers have focused on measuring the linear viscoelastic response of these composites. The behavior is similar to that seen for both polymer/CNF and polymer/nanoclay systems. A study by Mitchell et al. [41] compared the linear viscoelastic properties of polystyrene mixed with different concentrations of pristine single-walled carbon nanotubes (SWNTs) or functionalized SWNTs. The functionalized SWNTs were found to be more dispersed than the pristine SWNTs and as a result the linear viscoelastic properties were much different. The
functionalized SWNT composites had much greater values of \( G' \) at low frequencies than the pristine SWNT composites at the same SWNT concentration and the functionalized SWNT composites showed non-terminal behavior which was not evident for the pristine SWNT composites.

Fan and Advani [42] studied the effects of nanotube dispersion, aspect ratio and orientation on \( G' \), \( G'' \), and complex and steady shear viscosities of multi-walled carbon nanotube (MWNT)/epoxy suspensions. High aspect ratio MWNTs were created by ultrasonicallyating a suspension of the nanotubes while lower aspect ratio MWNTs were created by acid treating the nanotubes followed by ultrasonication. The acid treatment attacked defect sites in the MWNT thereby shortening their lengths. A comparison of \( G' \) and \( G'' \) for 0.5 wt\% MWNT/epoxy suspensions made with either high or low aspect ratio MWNTs showed that the high aspect ratio suspensions had values of \( G' \) and \( G'' \) that were approximately one order of magnitude larger than the low aspect ratio suspensions. Like in the previously discussed research [28,40,41], Fan and Advani also found that \( G' \), the complex viscosity and the steady shear viscosity increased with increasing MWNT concentration. The effect of MWNT orientation was studied by measuring \( G' \) and \( G'' \) of a 1 wt\% MWNT/epoxy suspension before and after a shear rate of 20 s\(^{-1}\) was applied for 10 min. The results showed that \( G' \) and \( G'' \) were greater for the pre-shear suspensions than the post-shear suspensions. The applied shear had the effect of aligning the MWNTs, therefore the experiment shows that as MWNTs are aligned with the direction of shear within a suspension there will be a decrease in the observed modulus.
These studies show the importance of nanoparticle network structure to the flow behavior of composites. Concentration, aspect ratio, orientation, and dispersion all affect how the particles interact with themselves and the surrounding matrix which in turn affects the way the composite or suspension flows. Attempts to model the flow of composites should include terms that account for these affects in order to be successful.

2.3 Magnetorheological Fluids

Magnetorheological (MR) fluids, which are non-colloidal suspensions of magnetically polarizable particles, were first discovered in 1948 by Jacob Rabinow [4] who was investigating their use in a clutch. In recent years there has been an increased interest in characterizing the rheological properties of these fluids and using them in applications such as shock absorbers [5], dampers [6], brakes [7], and clutches [8].

It has been found that the properties of these fluids are greatly dependent upon the properties of the carrier fluid and magnetic particles. The most common magnetic particle used in MR fluids is carbonyl iron which is a spherical particle formed from the thermal decomposition of iron pentacarbonyl [43]. The typical size range for these particles is 0.1-10 μm which makes them large enough to be non-colloidal and to disaggregate when a magnetic field has been removed [44]. One of the drawbacks of the use of carbonyl iron is that it is very expensive, causing the price of MR fluids to be high thus limiting their commercial applications. Because of this there have been several proposed lower-cost particle alternatives including a water-atomized iron [45], iron-nickel and iron-cobalt alloys [46] and magnetic stainless steel [47], though their use is not widespread.
There are several commonly used carrier fluids that are used although typically they are oils such as silicone oil or mineral oil. The use of alcohols and ethers has been proposed [48] however there have not been detailed studies of the properties of MR fluids in which they are used as the suspension medium. Ultimately, the choice of carrier fluid is determined by the application and the target properties of the fluid. High temperature stability and viscosity are two common parameters used to judge the suitability of a carrier fluid.

A significant issue with MR fluids is that the high density of carbonyl iron (~7 g/cm$^3$) relative to the density of the carrier fluid (~1 g/cm$^3$) results in a high rate of settling of the carbonyl iron particles. Several means have been attempted to prevent or slow the sedimentation rate including the use of surfactants [49], thixotropic agents such as guar gum [50], silica gel [51] and carboxylic acids [52]. Nanotubes have also been added [53] to MR fluids in an attempt to reduce the rate of carbonyl iron settling. While the addition of these agents can reduce the settling rate of the carbonyl iron particles there is also the potential to change the rheological behavior of the suspension and to reduce the response of the fluid to a magnetic field.

Experimental measurements of the rheological behavior of MR fluids have revealed several common features. In general, these fluids exhibit a yield stress that increases with increasing magnetic field strength, viscosity increases with increasing magnetic field strength, and the storage and loss modulus increase with increasing magnetic field strength with the storage modulus being greater than the loss modulus in the presence of a magnetic field indicating a solid-like response. Ginder et al. [54] studied
the yield stress of magnetorheological fluids at different magnetic field strengths. They found that at low magnetic field strengths, well below the magnetic saturation of the magnetic particle, the increase in yield stress was proportional to the magnetic field strength squared, $H^2$. At higher magnetic field strengths, with the magnetic particles nearing their magnetic saturation point, the yield stress became less dependent on the magnetic field and was proportional to $H^{1.5}$. Chin et al. [55] measured the dependence of yield strength on magnetic field strength of fluids with varying particle concentrations and also found yield stress to be proportional to $H^{1.5}$, however the magnitude of the yield stress increased with increasing magnetic particle concentration.

Chin et al. [55] also studied the steady state shear and small amplitude oscillatory shear response of MR fluids at different magnetic field strengths and particle loadings. Under steady shear in the absence of a magnetic field, shear stress was found to increase with increasing shear rate and particle concentration. When a magnetic field was applied the stress response was found to increase with increasing magnetic field strength and became nearly independent of shear rate. There continued to be an increase in stress with increasing shear rate as was seen in the absence of a magnetic field, however, the magnitude of the change was much smaller.

This group [55] is one of very few that has attempted to report the small amplitude oscillatory shear response of MR fluids. They found that the linear viscoelastic response of their fluids was restricted to strain amplitudes less than 0.03%. Like the steady state shear response, the storage and loss modulus of the MR fluids were found to
increase with increasing magnetic field strength and the storage modulus was greater than the loss modulus indicating a solid-like response of the fluid.

The same rheological properties of MR fluids measured by Chin et al., although they were not the first to do so, have been measured numerous times by a variety of researchers on a number of MR fluids and the same general trends are observed: increasing particle concentration, magnetic field strength, and shear rate increase the stress response of the MR fluid. The differences are typically in what type of magnetic particle was used, experimental temperature, particle concentration, particle size, type of carrier fluid, the use of stabilizers. For example, Dang et al. [56] suspended carbonyl iron particles in silicone oil using varying amounts of oleic acid as a surfactant. Yield stress measurements were performed over a range of magnetic field strengths and were found to increase with increasing carbonyl iron content and oleic acid concentration. Genç and Phulé [57] measured the yield stress of MR fluids made with two different sizes of carbonyl iron particles and found that the fluids made with the larger particles (7-9 μm) had higher yield stresses at the same magnetic field strengths than the fluids made with the smaller particles (~2 μm). They concluded that the difference was primarily due to differences in the magnetic saturation of the particles.

There are several models that have been proposed to predict the rheological behavior of MR fluids. The simplest model is the Bingham model, Equation (2.1), which predicts Newtonian behavior above a threshold yield stress:

$$\tau = \tau_y + \eta \dot{\gamma}, \tau > \tau_y$$

(2.1)
where \( \tau \) is the stress in the fluid, \( \tau_y \) is the yield stress, \( \eta \) is the viscosity and \( \dot{\gamma} \) is the shear rate. This model fails for concentrated MR fluids because of the introduction of particle-particle interactions which creates non-Newtonian shear thinning behavior. To account for this the Herschel-Bulkley model, Equation (2.2) has been proposed which is similar to the Bingham model, however, an extra term is introduced that accounts for any shear thinning or thickening behavior:

\[
\tau = \tau_y + \frac{1}{K} \dot{\gamma}^m, \quad \tau > \tau_y
\]  

(2.2)

where \( \tau \) is the stress in the fluid, \( \tau_y \) is the yield stress, \( \dot{\gamma} \) is the shear rate and \( K \) and \( m \) are constants.

A desire to understand the mechanisms governing the flow of these fluids has led to the development of more complicated models. Brigadnov and Dorfmann [58] developed a set of constitutive equations to describe the rheological behavior of MR fluids and predicted their flow behavior between two parallel plates, however the validity of the model was not verified with experimental results. Jolly et al. [59] proposed a model based on the dipolar interaction of particles and accounted for the magnetic saturation of the particles and demonstrated the accurateness of the model through comparison with experimental measurements of the yield stress as a function of magnetic field strength. Ciocanel et al. [60] developed a kinetic theory based particle pair model capable of predicting the transient shear stress of an MR fluid at different magnetic field strengths and shear rates. Many other models have been proposed for MR fluids with the goal of being able to predict the behavior of these fluids in complex flows under a variety
of conditions that would be present in real engineering applications. Computationally complex models, such as those developed using finite element modeling, are impractical for this purpose therefore there is a need to develop simple constitutive equations that can predict the complex flow behaviors seen for MR fluids.

2.4 Carbon Nanotubes

2.4.1 Structure and Properties

Carbon nanotubes are a form of pure carbon that can best be described as a sheet of graphite, the structure of which is shown in Figure 2.2, that has been rolled into a tube. The structure of a nanotube rolled from this graphite sheet can be described by it’s chirality which is defined by a chiral vector, $C_h$, and a chiral angle ($\theta$) [61]. The chiral vector is defined by Equation (2.3):

$$\bar{C}_h = n\bar{a}_1 + m\bar{a}_2$$  \hspace{1cm} (2.3)

where $\bar{a}_1$ and $\bar{a}_2$ are unit vectors and $n$ and $m$ are integers that are the number of steps along the zig-zag carbon bonds. These vectors are shown on the graphite structure in Figure 2.2. Two extremes of nanotube structure are achieved with chiral angles of 0° and 30°, known as the zig-zag and armchair structures, respectively. These structures are shown in Figure 2.3. The chirality of the nanotubes has significant effects on their mechanical and electrical properties. For example, nanotubes may behave as metallic or semiconducting depending on their chirality. If the value of $(n+m)/3 = \text{integer}$, the nanotubes will be metallic, otherwise they will be semiconducting [62].
Carbon nanotubes are commonly produced by one of three methods: arc discharge, laser ablation, or chemical vapor decomposition (CVD). In the arc discharge method [63] there are two electrodes composed of graphite. The graphite anode will have a hollow core that is filled with a metal catalyst and graphite powder. An electric current is applied and a constant potential is kept between the two electrodes and carbon nanotubes are formed. In the laser ablation method [64] a cylindrical material composed of carbon and a metallic catalyst is placed is a stream of flowing argon (Ar) gas. The cylinder of material is hit with laser pulses and CNTs are formed. The stream of Ar gas removes the CNTs from the surface of the cylinder exposing a fresh surface to the laser. In the typical CVD process [65] a metal catalyst is supported in a quartz tube which is placed in a furnace. The system is heated to 600-1000°C and a gas stream containing Ar and a hydrocarbon gas is passed over the catalyst forming carbon nanotubes on the catalyst surface. There are many variations to each of these methods, for example: the use of different metal catalysts, laser intensities, gas stream compositions, etc. New variations are constantly being investigated to optimize the yield, quality, and composition of the nanotubes while reducing the costs of the process.

The great deal of interest generated by carbon nanotubes is due to their unique mechanical, electrical and thermal properties. There have been many attempts to experimentally and theoretically measure the mechanical properties of carbon nanotubes and it has been found that they are among the strongest materials on earth. Wong et al. [66] directly measured the elastic modulus of multi-walled carbon nanotubes produced by the arc discharge method using atomic force microscopy. They found an average
Young’s modulus of 1.28 TPa which was independent of nanotube diameter. By comparison, steel has a Young’s modulus of 200 GPa. While the properties of individual carbon nanotubes are impressive, it is very rare to have isolated nanotubes in real systems. Due to strong van der Waal’s forces nanotubes are usually found in bundles which contain many nanotubes. Yu et al. [67] directly measured the tensile strength and modulus of single-walled carbon nanotube bundles having diameters in the range of 20 to 40 nm. They found the average tensile strength to range from 13 to 52 GPa with a mean of 30 GPa and the average tensile modulus to range from 320 to 1470 GPa with a mean of 1002 GPa. These values are less than those measured by Wong et al. indicating that the mechanical strength of nanotube bundles are less than those of individual nanotubes.

In addition to tremendous mechanical strength, carbon nanotubes have been shown to have very high electrical conductivity and an electric current carrying capacity 1000 times greater than copper [68]. Additionally, single-walled carbon nanotubes have been found to behave in a metallic or semiconducting manner depending on their structure [69]. The electrical conductivity of carbon nanotubes has also been found to be highly sensitive to exposure to different chemical species. For example, single-walled nanotubes exposed to NO\textsubscript{2} have shown up to a three orders of magnitude increase in conductivity while when exposed to NH\textsubscript{3} the conductivity can decrease by up to two orders of magnitude [70]. This behavior has led to interest in using nanotubes as chemical sensors.
2.4.2 Characterization

One of the most useful methods of characterizing the structure of carbon nanotubes is Raman spectroscopy. Raman spectroscopy is a characterization technique that is typically used to identify the structures of molecules or crystals [71,72], however this technique can also be used to determine the electrical and structural properties of carbon nanotubes. This technique is made possible by a phenomenon known as Raman scattering. When a substance is bombarded with photons, those photons are usually elastically scattered (i.e. the scattered photons possess same energy as incident photons) [73,74]. However, a small number of photons, on the order of 1 in $10^7$ [73,75], undergo inelastic scattering. This shift in energy after inelastic scattering is known as the Raman shift and is unique for different structures [74].

When photons reach a molecule they will interact with the cloud of electrons that surround the molecule, usually the electrons that constitute the bonds between atoms. This interaction causes the electron cloud to go to an energetically higher virtual state [73,74,76,77]. This virtual state is one where the energy in the system has increased but not enough to make an electron change orbitals [73]. During normal elastic scattering (Rayleigh scattering) the photon interacts with the electron cloud, the molecule goes to the excited virtual state and then decays to a vibrational state that is energetically equal to the initial state. Raman scattering occurs when the system decays to an energetic state that is not equal to the initial state. In the case of Raman scattering there are two possibilities called Stokes scattering and anti-Stokes scattering. A system that decays to an energy level higher than the initial one is referred to as Stokes scatter while a system
that decays to an energy level lower than the initial state is referred to as anti-Stokes scatter. Stokes scatter results in scattered photons having higher wavelengths than the incident photon \([71,73-76]\). See Figure 2.4 for a representation of these energy changes.

Modern spectrometers use a laser as a monochromatic light source which passes through a notch filter in order to concentrate the frequency range of the laser light then the light moves on to a microscope to focus the beam on the sample \([74]\). The reflected light is passed through another filter in order to filter out the Rayleigh scattered light. The beam is then directed to a monochrometer which disperses the radiation into its individual wavelengths and directs these onto a charge-coupled device detector (CCD) which detects photons that have been scattered to different frequencies \([71,74,76]\). The difference between the wavelength of the Raman scattered light and the wavelength of the incident photons is called the Raman shift \([72,73]\). Results from Raman spectroscopy are reported by plotting the intensity (or number of photons) versus the Raman shift frequency \([71]\).

The use of lasers is advantageous for several reasons. Laser light is mostly monochromatic and produces light in a very narrow frequency range thus there are more photons available to interact with molecules after filtering than if a light source was used that produced a broad range of light frequencies like, for example, white light. Lasers also produce a large quantity of photons \([74]\). Producing more photons and filtering less out is beneficial in Raman spectroscopy because Raman scattering does not occur that frequently (1 in \(10^7\) photons) and more photons making it to the target means more photons that will be Raman scattered.
The frequencies of the light used are typically somewhere in the near infrared, visible, or near ultraviolet region [76]. The choice of wavelength is important because the photons need to have enough energy to get the target molecule into the virtual excited state but not too much to promote an electron to the next highest orbital. If there is too little or too much energy the technique will not work.

A unique feature in the Raman spectrum of carbon nanotubes is the low frequency radial breathing mode (RBM). This feature occurs in the frequency range 100-500 cm\(^{-1}\) and is the result of a bond stretching out of plane phonon mode which occurs when all carbon atoms move in the radial direction. This motion is reminiscent of the motion that occurs during respiration, hence the name radial breathing mode. It has been found that the frequency of the RBM is inversely proportional to the diameter of the nanotubes using the following relationship:

\[
\omega_{\text{RBM}} = C / d_i (nm)
\]  

where \(\omega_{\text{RBM}}\) is the frequency of the RBM peak in cm\(^{-1}\), \(d_i\) is the average nanotube diameter in nanometers and \(C\) is a constant for which several values have been proposed including: 157 cm\(^{-1}\), 165 cm\(^{-1}\), 175 cm\(^{-1}\), 195 cm\(^{-1}\) [78], 223.75 cm\(^{-1}\), 248 cm\(^{-1}\) [79,80]. Thus measurement of the RBM of a carbon nanotube sample enables the determination of the average diameter of a carbon nanotube sample. It has also been observed that the RBM of isolated NTs is lower than bundled NTs due to NT-NT interactions present in the bundles. It has been predicted that there could be as much as a 10-20 cm\(^{-1}\) increase in \(\omega_{\text{RBM}}\) depending on the size of the bundle [79].
In addition to the RBM, carbon nanotubes have characteristic Raman peaks known as the D and G bands with the G band being broken down further into a G$^+$ and G$^-$ band. The D band is so named because it results from the presence of defects in the nanotube structure [81] such as carbon atom vacancies, substitutional impurities, finite grain or particle effects, or any other symmetry-breaking phenomena [82]. The location of this band depends on the frequency of the laser used because different frequencies produce different excitation energies. Table 2.1 illustrates the dependence of the D band peak location on laser frequency [81]. The breadth of the D-band peak can also give clues as to whether there are defects in the nanotube structure or if there is amorphous carbon present. The width of the D-band for defects in the nanotube structure is usually on the order of 10-20 cm$^{-1}$ while the width of the D-band for amorphous carbon is typically around 100 cm$^{-1}$ [81].
Table 2.1 Approximate D-band values for different laser excitation energies.

<table>
<thead>
<tr>
<th>Laser line (nm/eV)</th>
<th>785 / 1.58</th>
<th>633 / 1.96</th>
<th>514 / 2.41</th>
<th>488 / 2.54</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-band (cm⁻¹)</td>
<td>~1290</td>
<td>~1330</td>
<td>~1345</td>
<td>~1360</td>
</tr>
</tbody>
</table>
Figure 2.1 The structure of a montmorillonite clay layer.
Figure 2.2 Schematic diagram showing the atomic structure of graphite along with the vectors $\vec{a}_1$ and $\vec{a}_2$ as well as the chiral vector ($C_h$) and chiral angle ($\theta$).
Figure 2.3 Representation of the atomic structure of (a) armchair and (b) zig-zag nanotubes.
Figure 2.4 Representation of energy changes during Rayleigh, Stokes, and anti-Stokes scattering.
CHAPTER 3

STEADY STATE SHEAR RHEOLOGY OF POLYSTYRENE/NANOCLAY COMPOSITES

3.1 Introduction

There has been much interest and research in layered silicate-based polymer nanocomposites (PNCs) in recent years because of the potential to create materials with enhanced mechanical, thermal, electrical, and barrier properties while using much lower particle loadings than traditional fillers [20,66,83-91]. Layered silicates, also known as nanoclays, are effective reinforcement agents because of their large surface area per volume and high aspect ratios. The anisotropic nature of these nanoparticles makes the rheological and mechanical properties of the PNC greatly dependent upon the orientation of the dispersed particles within the polymer matrix. Much of the research on PNCs has been to identify the parameters important in understanding the processing properties (e.g. the rheology of the melt) and performance properties (e.g. moduli and electrical conductivity) of the solid composite. Important parameters reported in the literature include the viscoelastic properties of the polymer matrix, particle aspect ratio, particle volume fraction, polymer-particle interactions, particle-particle interactions [92], and particle orientation [93].
There have been fewer modeling studies of PNC systems than experimental studies. Kim et al. [94,95] fit the nonlinear viscous, inelastic Cross-Williamson model and Carreau model to the steady state shear viscosity data of PS/nanoclay composites at different particle loadings. Aubry et al. [96] used a second-order Einstein-type equation and a modified Krieger’s empirical equation to predict the changes in Newtonian relative viscosity as a function of nanoclay volume fraction. These viscous models can be adjusted to closely fit the measured steady shear rheology but are unable to capture measured elastic response.

Molecular dynamics simulations incorporating the parameters identified by earlier researchers to be important (e.g. particle shape and the interactions of the particles with themselves and the surrounding polymer matrix) have also been used to predict rheological and mechanical behavior. Pryamitsyn and Ganesan [97] used coarse-grained computer simulations to determine the steady state shear rheology of different types of PNCs. Kairn et al. [98] determined the effects of shear rate on viscosity for polymers containing spherical nanoparticles. Zhu and Narh [99] attempted to predict the tensile modulus of polymer/nanoclay composites using finite elements. While these models work well to predict the property of interest, they are not amenable to parameter studies due to large run times.

In previous work [100] a constitutive model that accurately predicts the steady state shear rheology of a polymer filled with rod-like nanoparticles was proposed and validated against the measured steady state shear rheology of a PS/CNF composite. The model offers several advantages: For the first time it includes terms that explicitly
account for the effects of the viscoelastic properties of the polymer matrix, particle aspect ratio, particle volume fraction, polymer-particle interactions, hydrodynamic particle-particle interactions (as proposed by Folgar and Tucker [101]), and particle orientation. This gives the model the ability to predict the effects of using material components with different properties (e.g. a different polymer matrix or a different nanoparticle). Most models consist of a scalar relation between viscosity and shear rate; our model is developed in its 3D tensorial form making it possible to predict the behavior of the PNC under flows other than steady state shear, such as dynamic and transient shear or extensional flow. Also, because the model consists of algebraic equations the time required to solve the system with the average computer is on the order of seconds.

We will show that this model, previously validated in nanorod-based composites [100], also accurately predicts the behavior of nanoplatelet-based composites, validated against the measured steady state shear rheology of PS/nanoclay composites. Hence, the nanoparticle/polymer melt model spans the entire range of nanoparticle aspect ratios, from very small (nanoplatelets) to very large (nanorods). This addresses the ability of the constitutive model to predict how steady state shear viscosity is affected when the polymer matrix is unchanged and the reinforcing nanoparticle shape changes from rod-like with aspect ratios much greater than 1 (CNFs) to plate-like with aspect ratios much less than 1 (nanoclays). We demonstrate that our constitutive model accurately predicts the steady state shear rheology of composites for all of the nanoparticle shapes we investigated. This is accomplished through the use of parameters referred to as shape factors which can be changed to match the shape of the particle being used, in this case
rod-like or disk-like. In addition, we solve for the model parameters that account for the viscoelastic properties of the polymer matrix, the polymer-nanoparticle interaction, and the hydrodynamic particle-particle interactions. We find that the polymer-nanoparticle interaction parameter does not significantly impact the viscosity predictions.

3.2 Materials and Sample Preparation

The polymer used was PS of the brand name Fina (CX5197) and was produced by Atofina with a density of 1,000 g/m$^3$, a weight average molecular weight of 200,000, and a polydispersity index of 2.4. The nanoclay used was Closite 20A made by Southern Clay Products, Inc. The clay is a natural montmorillonite that is modified by Southern Clay Products with dimethyl, dihydrogenatedtallow, quaternary ammonium (2M2HT) at a concentration of 95 meq/100g clay. The clay was used as received without further chemical treatments.

The composite material was created by melt blending PS and nanoclay for four minutes in a DACA Instruments twin-screw microcompounder at 200°C at a screw rotation rate of 250 rpm. Nanoclay concentrations of 2, 5, and 10wt% were used. This set of melt blending parameters provided even dispersion of the nanoclay within the polymer matrix. We processed pure PS in the microcompounder under the same conditions because the mixing process caused enough degradation of the polymer to show a difference in the steady shear viscosity of processed and unprocessed polystyrene. Wide angle x-ray diffraction revealed that the spacing between the clay layers increased from 2.3 nm to 3.4 nm indicating an intercalated structure.
The pellets formed from the melt blending procedure were compression molded into 25 mm diameter disks of 0.5-1 mm thickness using a hot press at 200°C. The pellets were placed into molds and allowed to melt for 15 minutes followed by a cycle of quickly compressing and decompressing the samples four consecutive times in order to eliminate air bubbles. Pressure was then reapplied and held for 10 minutes and after that time the heat to the press was turned off and the samples were allowed to cool to below 100°C, the glass transition temperature. Once cool, the pressure was released and the samples were removed from the mold. The disks were placed in a vacuum oven at 70°C for at least 24 hrs and remained there until the time they were tested in order to prevent them from absorbing moisture or air from the atmosphere.

3.3 Experimental Results

We experimentally measured the rheological behavior of PS/nanoclay composites at several nanoclay concentrations during transient, steady state and dynamic oscillatory shear flows in order to determine how the presence of nanoparticles affected the rheology of the polymer. All shear flow rheological tests were performed on a strain-controlled TA Instruments rheometer (ARES LS2) with a torque transducer (0.02 g.cm to 2000 g.cm) and a normal force transducer (2 g to 2000 g). All measurements were made using a set of 25 mm diameter parallel plates with a gap distance ranging from 0.5 to 1 mm.

Two types of rheological tests were performed: dynamic oscillatory shear and transient shear. Although stated earlier the steady shear flow behavior of the composite was studied, this information was obtained from the transient shear tests because those
tests eventually reached a steady state condition. That is, at long times the viscosity of the material at a constant shear rate no longer changed with time.

The dynamic oscillatory tests performed were strain amplitude sweeps and frequency sweeps. These tests were performed to provide information about the linear viscoelastic responses of the pure PS and three nanocomposite (2, 5, and 10wt% nanoclay) samples. The linear viscoelastic range of the materials was determined by performing strain amplitude sweeps where the samples were strained in the range 0.01% to 10% at a frequency of 100 rad/s at both 140°C and 220°C. These temperatures were chosen because they were the bounds of the temperature range being investigated. It was assumed that if a strain was found that was in the linear viscoelastic range at the low and high temperature extremes then that same strain would be in the linear viscoelastic range for all temperatures tested in between. Also, the frequency used for the strain amplitude sweep tests was chosen to be 100 rad/s because this was the highest frequency being tested and if a material shows linear viscoelastic behavior at a given frequency then it will have linear viscoelastic behavior at all lesser frequency values. The linear regime was determined to be the location where the storage and loss modulus, \( G' \) and \( G'' \), respectively, remained constant. That is, their response was independent of the applied strain. For these materials it was determined that a strain of 1% was in the linear regime.

Frequency sweeps were performed on the PS/nanoclay samples using a strain of 1% and varying frequency from \( 0.1 \; \text{s}^{-1} \) to \( 100 \; \text{s}^{-1} \). Values for \( G' \) and \( G'' \) were recorded over the temperature range 140-220°C in 10°C intervals and master curves, shown in Figures 3.1 a and b, respectively, were generated using the principal of time temperature
superposition. The master curves show that the addition of small amounts of nanoparticles has pronounced effects on the rheology of the composite. \(G'\) and \(G''\) increase monotonically with increasing nanoclay content and it is also apparent that the slopes of \(G'\) and \(G''\) at low frequencies are influenced by the addition of nanoclay. For reference, typical homopolymers in a fully relaxed state have a \(G'\) slope of 2 in the low frequency region. It can also be seen that the crossover frequency, where \(G'\) and \(G''\) intersect, decreases with increasing nanoclay content.

A review of the literature for polymer/nanoclay composites reveals several common characteristic responses of these composites to dynamic small amplitude oscillatory shear that are consistent with the results we have seen. First, \(G'\) and \(G''\) increase at all frequencies with increasing nanoclay content [21,23,95,102-104]. Second, the slope of \(G'\) and \(G''\) decrease in the low frequency region with increasing nanoclay content [21,23,103,104]. This phenomenon is known as nonterminal behavior [21]. While the trends are consistent, the magnitudes or values of these parameters vary based on the matrix polymer, the type of nanoclay used, the degree of nanoclay exfoliation or intercalation, and types of surface treatment used. There have also been several theories proposed to explain the occurrence of such phenomena.

Lee and Han [102] studied the rheology of poly (ethylene-ran-vinyl acetate), poly (ethylene-ran-vinyl alcohol, and poly (ethylene-ran-vinyl acetate-ran-vinyl alcohol) mixed with Closite 30B or Closite 15A nanoclays. They observed an increase in \(G'\) and \(G''\) with the addition of the nanoclay, however, only some of the composites had a decrease in the slope of \(G'\) at low frequencies. Since the structures of the polymers were
different they interacted differently with the clays which also had different surface treatments. It was proposed that the presence of a reduced slope of $G'$ at low frequencies was due to attractive interactions between the polymer and nanoclay due to hydrogen bonding. Without the presence of the hydrogen bond interactions the polymer was unrestricted and behaved the same as pure polymer with no nanoclay added. Zhang et al. [105] studied nylon-11/nanoclay composites and also observed that differences in the compatibility of the polymer and the nanoclay would lead to differences in behavior at low frequency. Highly compatible composites had more hydrogen bonding and a decrease in the slope of $G'$ at low frequencies compared to pure polymer. Composites with no hydrogen bonding did not see a change in the slope of $G'$ at low frequencies compared to pure polymer. Krishnamoorti and Giannelis [21] studied poly ($\varepsilon$-caprolactone) and nylon-6 nanoclay composites. They observed nonterminal behavior and believed it could be caused by many ends of the polymer chains being bound to the nanoclay surface thereby increasing the relaxation time of the polymer.

Kim et al. [95] studied PS/nanoclay composites and claimed that the changes in the magnitudes of $G'$ and $G''$ was due to the formation of a supermolecular structure. Solomon et al. [23], studying polypropylene and nanoclay, witnessed the same behavior and also suggested that the explanation could be the presence of a percolated, network microstructure. Hoffman et al. [103], using polystyrene/nanoclay composites, attributed the non-terminal behavior they observed to network formation by the nanoclay platelets.

The principle of time temperature superposition (TTS) has also been brought up in the discussion of the linear viscoelastic properties of the PS/nanoclay system we are
studying. TTS is used by collecting small amplitude oscillatory shear data at different temperatures and then shifting that data to a single temperature in order to create a master curve. Shifting is accomplished by multiplying the frequencies of data collected at one temperature by a shift factor, $a_T$. If all of the shifted data falls onto one curve then TTS is valid. Using this principle, information about a material’s linear viscoelastic response at different temperatures over a frequency range larger than typically measured can be predicted. TTS has been shown to be valid for homopolymers, however the literature is not conclusive on its applicability to polymer nanocomposites.

Hoffman et al. [103] and Meincke et al. [104] found TTS to be valid for PS/nanoclay composites. Solomon et al. [23] studied polypropylene/nanoclay composites and determined that TTS was valid. Some researchers have found that the validity of TTS to be dependant upon the properties of the material or the range of frequencies being tested. For instance, Zhong et al. [12] showed that TTS was valid for in situ polymerized PS/nanoclay composites but did not hold for solution blended PS/nanoclay composites. Yang and Hu [106] studying poly (butyl methacrylate)/nanoclay composites found that TTS did not hold at low frequencies. Also, Hsieh et al. [107] studied polycarbonate/nanoclay composites and found TTS to hold at high frequencies but fail at low frequencies. An evaluation of the data we present in Figure 3.1 shows that TTS is valid for pure PS as expected. TTS also seems to be valid for the PS/nanoclay composites as well, however, some separation of the curves is evident at frequencies less than 0.01 s$^{-1}$. Therefore, like Yang and Hsieh, we conclude that TTS is valid at high frequencies but fails at frequencies less than 0.01 s$^{-1}$. 

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The transient shear viscosities of the pure polymer and composite samples were measured at 200°C over the shear rate range 0.01-10 s\(^{-1}\). Shear rates lower than 0.01 s\(^{-1}\) were not used because the torque response from the rheometer was not strong enough to provide accurate data and shear rates above 10 s\(^{-1}\) were not used because the high normal forces caused by shear resulted in inaccurate readings due to edge effects. Since the transient response of all samples eventually reached a steady state, as can be seen from the transient viscosity data in Figure 3.2, the viscosity at that steady state could be used to make steady shear viscosity curves. Edge effects prevented the presence of a true steady state in the 10wt% nanoclay/PS composites at shear rates greater than 1s\(^{-1}\) as can be seen in Figure 3.2b. For this data the viscosity values at a strain value of 70 were used because this is the strain that all other shear rates reached a steady state. The amount of time it took to reach steady state was a function of the polymer matrix, the shear rate being applied, the amount of nanoclay present, and the temperature. The composites used the same polymer matrix and were tested at the same temperature therefore the time to reach steady state varied for each shear rate and for composites of differing nanoclay content. In several cases it took longer than 1,000 s to reach steady state and there was evidence that long-term exposure to these elevated temperatures caused some polymer degradation. Samples were tested only once and at only one particular shear rate in order to minimize errors caused by degradation. This method of creating the steady shear viscosity plots was more tedious than the usual method, where one sample is tested over the entire shear rate range, but more accurate because the steady state, which took varied times to reach, was clearly identifiable.
The steady shear data showed, as expected, that pure PS has Newtonian behavior at low shear rates and shear thinning behavior at high shear rates [108,109], however, the nanoclay composites do not exhibit this behavior (Figure 3.3). The nanoclay composites are shear thinning over the entire range of shear rates tested while at high shear rates their viscosities are similar to that of pure PS with the composite viscosities increasing monotonically with increasing nanoclay content. This agrees well with results seen for various polymer/nanoclay composites [23,93-95]. The deviation from Newtonian behavior at low shear rates has been attributed to the formation of a network structure caused by particle-particle interactions [93]. At high shear rates the structure is destroyed and the shearing forces orient the nanoclay along the direction of flow, minimizing the effects of their presence and resulting in the viscosities of the PNCs to be similar to those of unfilled PS [93].

PS/CNF composites tested in a previous work [100] also show similar behavior. The solvent cast composites showed shear thinning behavior over all shear rates at the concentrations of CNFs tested: 2, 5, and 10 wt%. However, the melt blended composites were not shear thinning over all shear rates. The composites containing 2 and 5 wt% CNFs exhibited a Newtonian like response at low shear rates while the 10 wt% composites were shear thinning over the entire shear rate range. Both melt blended and solvent cast composites show an increase in viscosity with increasing CNF content and viscosities that are nearly equal at high shear rates. The melt blended and solvent cast composites are named so because of the procedure used to incorporate the nanofibers into the polymer matrix. The major difference is the length of the nanofibers that result in the
composite; the solvent cast composites have fibers that are approximately four times longer than those in the melt blended composites because the melt blending procedure causes more damage to the fibers. A complete discussion of the rheological response of these composites and the melt blending and solvent casting procedures can be found in Wang et al. [100].

3.4 Modeling

After characterizing the rheological properties of the PS/nanoclay composites we fit a constitutive model to the experimental measurements that was capable of predicting the steady state shear rheology of the composite. The composite model incorporated the rheological properties of the polymer matrix, the aspect ratio and characteristic length scale of the nanoparticles, the orientation of the nanoparticles, hydrodynamic particle-particle interactions, the interaction between the nanoparticles and the polymer, and flow conditions of melt processing. Since particle orientation plays an important role in the rheological properties of the composite the model also provided predictions on how particle orientation evolved under different flow conditions.

We focused on predicting the steady state shear viscosity of the PS/nanoclay composites because the steady state viscosity was the least complicated aspect of the rheology to model. The following series of coupled constitutive equations have been developed to describe the rheology of a polymer melt composite and were the basis for our model [100].

\[
\tau^c_y = -p\dot{\gamma} + 2\eta_s D_y + \tau^p_y + \tau^{CNF}_y
\]  

(3.1)
\[
\lambda \frac{D \tau_y^p}{Dt} + \sigma \tau_y^p + \frac{\alpha \lambda}{\eta_p} (\tau_y^p \tau_h^p) + \frac{3(1-\sigma)}{2} (a_{ik} \tau_{kj}^p + \tau_{ik}^p a_{kj}) = 2\eta_p D_g \tag{3.2}
\]

\[
\tau_y^{NC} = 2\eta_p \left[ AD_{kl} a_{gkl} + B \left( D_{ik} a_{kj} + a_{ik} D_{kj} \right) + CD_{g} + 2Fa_g D_r \right] \tag{3.3}
\]

\[
\frac{d a_{ij}}{d t} = \left( W_{ik} a_{kj} - a_{ik} W_{kj} \right) + \chi \left( D_{ik} a_{kj} + a_{ik} D_{kj} - 2D_{kl} a_{ijkl} \right) + 4C_i \Pi_{D}^{1/2} \left( \delta_{ij} - 3a_{ij} \right) \tag{3.4}
\]

These four equations describe a different aspect of the composite’s behavior.

Equation (3.1), proposed by Azaiez [110], expresses the total stress, \( \tau_y^c \), of the polymer/nanocomposite system as the sum of the stress contribution from polymer molecules with fiber inclusions, \( \tau_y^p \), the stress contribution from the carbon nanofibers, \( \tau_y^{CNF} \), the stress contribution from a Newtonian solvent (if present), \( 2\eta_s D_{ij} \), and the pressure maintaining incompressibility, \( P \). In the Newtonian solvent contribution, \( D_{ij} \) is the symmetric part of the Eulerian velocity gradient, \( \frac{\partial v_i}{\partial x_j} \), and \( \eta_s \) is the solvent viscosity.

For shear flows:

\[
D_{ij} = \begin{bmatrix}
0 & \dot{\gamma} / 2 & 0 \\
\dot{\gamma} / 2 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix} \tag{3.5}
\]

where \( \dot{\gamma} \) is the shear rate. Also, in the PS/nanoclay system being investigated there is no solvent present therefore \( \eta_s = 0 \) and Equation (3.1) simplifies to:

\[
\tau_y^c = -P \delta_{ij} + \tau_y^p + \tau_y^{NC} \tag{3.6}
\]
Equation (3.2), the single-mode Giesekus model [111], predicts the strain rate-dependent viscoelastic behavior of the polymer matrix. In Equation (3.2) the upper convected derivative of $\tau_{ij}^p$ is

$$\frac{D\tau_{ij}^p}{Dt} = \frac{d}{dt} \tau_{ij}^p - W_{ik} \tau_{kj}^p + \tau_{ik}^p W_{kj} - D_{ik} \tau_{kj}^p - \tau_{ik}^p D_{kj}$$ (3.7)

where $W_{ij}$ is the skew part of the Eulerian velocity gradient given by:

$$W_{ij} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ -\frac{\dot{\gamma}}{2} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$ (3.8)

for shear flows. The constants $\eta_p$, $\alpha$, $\lambda$ are the polymer viscosity, mobility factor, and relaxation time, respectively, for the polymer matrix in the melt phase. The values used for these constants are determined from rheological experiments performed on the pure polymer matrix and will be discussed later. Also in Equation (3.2) is the term $\sigma$, which is the polymer particle interaction parameter which is an immeasurable quantity and must therefore be treated as a fitting parameter. The determination of this value will also be discussed later.

In Equation (3.3), derived by Tucker [112], $\eta$ is the viscosity contribution from the polymer matrix; for simple shear in the 1-2 plane, $\eta = \frac{\tau_{12}^p}{\dot{\gamma}}$. $D_r$ is the rotary diffusivity due to Brownian motion, and $\phi$ is volume fraction of the nanoparticles. The values $A$, $B$, $C$, and $F$ are material constants that are function of the particle aspect ratio, $h = L/D$, 

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with $L$ the particle length and $D$ the particle diameter. Several values for these constants have been proposed for different concentration regimes (dilute or semi-dilute), states of nanoparticle orientation (isotropic or aligned), flow conditions (transient or steady state), and particle shape (platelets or rods). A summary of some of these definitions is given in Table 3.1.

Equation (3.4) is the evolution equation of the second order orientation tensor, $a_{ij}$, which is a measure of nanostructure that combines the contributions of a collection of particles that dictate the mesoscale properties of the nanocomposite. $\chi$ is a shape parameter related to the particle aspect ratio, $h$, through

$$\chi = \frac{h^2 - 1}{h^2 + 1}$$  \hfill (3.9)

In Equation (3.4), following Advani and Tucker [113] as suggested by Folgar and Tucker [101] for concentrated suspensions of large fibers, we employ $D_r = 2C_I \Pi_D^{1/2}$, where $\Pi_D$ is the second invariant of the symmetric part of the velocity gradient $D_{ij}$, and $C_I$ is the hydrodynamic particle-particle interaction parameter which measures the intensity of a nanofiber’s interaction with the fibers surrounding it. $C_I$ is another parameter that cannot be directly measured and is therefore treated as a fitting parameter and the determination of its value will be discussed later. For shear flows, $\Pi_D^{1/2} = \frac{\dot{\gamma}}{2}$, therefore $D_r = C_I \dot{\gamma}$. 
Note that Equations (3.3) and (3.4) involve the fourth order orientation tensor, $a_{ijkl}$. We adopt the following three closure approximation methods to relate the fourth order orientation tensor to the second order orientation tensor, $a_{ij}$:

1. The linear closure approximation,

\[ \hat{a}_{ijkl} = -\frac{1}{35}(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \frac{1}{7}(a_{ij}\delta_{kl} + a_{ik}\delta_{jl} + a_{il}\delta_{jk} + a_{jk}\delta_{il} + a_{jl}\delta_{ik}) \]  

(3.10)

works well when the particles are close to being oriented randomly, but introduces an artificial instability for highly aligned suspensions [114].

2. The quadratic closure approximation

\[ \hat{a}_{ijkl} = a_{ij}a_{kl} \]  

(3.11)

performs well for highly aligned states, but introduces steady-state errors for more random states [114].

3. The hybrid closure approximation,

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

(3.12)

mixes the linear and quadratic forms according to scalar measure of orientation and performs well over the entire range of orientation [114].

Since we are interested in solving these equations for the case of steady shear flow some simplifications can be made. The derivatives with time present in Equations (3.2) and (3.4) can be eliminated therefore Equation (3.2) can be written as:

\[ \sigma \tau_{ij}^p + \frac{\alpha\lambda}{\eta_p}(\tau_{ik}^p \tau_{lj}^p) + \frac{3(1-\sigma)}{2}(a_{ik} \tau_{lj}^p + \tau_{ij}^p a_{kl}) = 2\eta_p D_{ij} \]  

(3.13)
and Equation (3.4) can be written as:

$$0 = \left( W_{ik} a_{kj} - a_{ik} W_{kj} \right) + \chi \left( D_{ik} a_{kj} + a_{ik} D_{kj} - 2 D_{ik} a_{ijkl} \right) + 4 C_1 \Pi_{ij}^{1/2} \left( \delta_{ij} - 3 \alpha_{ij} \right) \quad (3.14)$$

When solving Equation (3.4) there are six components of the orientation tensor, $a_{11}, a_{22}, a_{33}, a_{12}=a_{21}, a_{13}=a_{31},$ and $a_{23}=a_{32},$ however, only four components are non-zero ($a_{13}=a_{23}=0$) therefore only four equations need to be solved. As mentioned earlier, within Equation (3.4) is the fourth order orientation tensor, $a_{ijkl}.$ Using different closure approximations to solve for $a_{ijkl}$ resulted in a different set of equations that had to be solved. Since we evaluated three different closure approximations we had three separate sets of four equations that had to be solved for Equation (3.4). Making the appropriate substitutions we have the following equations for each closure approximation.

Linear closure approximation solution to Equation (3.4):

$$\frac{da_{11}(t)}{dt} = 0 = j a_{12}(t) + 2 C_1 \dot{\gamma} \left( 1 - 3 a_{11}(t) \right) + \frac{1}{7} \chi \dot{\gamma} a_{12}(t) \quad (3.15)$$

$$\frac{da_{12}(t)}{dt} = 0 = \frac{\dot{\gamma} \left[ a_{22}(t) - a_{11}(t) \right]}{2} - 2 C_1 \dot{\gamma} a_{12}(t) + \chi \frac{\dot{\gamma} \left[ a_{22}(t) + a_{11}(t) \right]}{2} - 2 \chi \dot{\gamma} \left( \frac{1}{35} + \frac{a_{22}(t) + a_{11}(t)}{7} \right) \quad (3.16)$$

$$\frac{da_{22}(t)}{dt} = 0 = - j a_{12}(t) + 2 C_1 \dot{\gamma} \left( 1 - 3 a_{22}(t) \right) + \frac{1}{7} \chi \dot{\gamma} a_{12}(t) \quad (3.17)$$

$$\frac{da_{33}(t)}{dt} = 0 = 2 C_1 \dot{\gamma} \left( 1 - 3 a_{33}(t) \right) - \frac{2}{7} \chi \dot{\gamma} a_{12}(t) \quad (3.18)$$

Quadratic closure approximation solution to Equation (3.4):

$$\frac{da_{11}(t)}{dt} = 0 = j a_{12}(t) + 2 C_1 \dot{\gamma} \left( 1 - 3 a_{11}(t) \right) + \chi \dot{\gamma} a_{12}(t) - 2 \chi \dot{\gamma} a_{11}(t) a_{12}(t) \quad (3.19)$$
\[
\frac{da_{12}(t)}{dt} = 0 = \frac{\dot{\gamma}}{2} [a_{22}(t) - a_{11}(t)] - 6C_i \dot{a}_{12}(t) + \chi \frac{a_{22}(t) + a_{11}(t)}{2} - 2 \chi \dot{a}_{12}^2(t) \quad (3.20)
\]

\[
\frac{da_{22}(t)}{dt} = 0 = -\dot{a}_{12}(t) + 2C_i \dot{\gamma}(1 - 3a_{22}(t)) + \chi \dot{a}_{12}(t) - 2 \chi \dot{a}_{22}(t)a_{12}(t) \quad (3.21)
\]

\[
\frac{da_{33}(t)}{dt} = 0 = 2C_i \dot{\gamma}(1 - 3a_{33}(t)) - 2 \chi \dot{a}_{33}(t)a_{12}(t) \quad (3.22)
\]

Hybrid closure approximation solution to Equation (3.4):

\[
\frac{da_{11}(t)}{dt} = 0 = \dot{a}_{12}(t) + 2C_i \dot{\gamma}(1 - 3a_{11}(t))
\]

\[
+ \chi \frac{\dot{a}_{12}(t) + 2a_{22}(t)}{2} - \frac{3}{7} \left[ 27a_{11}(t)a_{22}(t)a_{33}(t) - 27a_{12}^3(t)a_{33}(t) \right] a_{12}(t)
\]

\[
+ \left[ 1 - 27a_{11}(t)a_{22}(t)a_{33}(t) + 27a_{12}^2(t)a_{33}(t) \right] a_{12}(t)a_{12}(t) \quad (3.23)
\]

\[
\frac{da_{12}(t)}{dt} = 0 = \frac{\dot{\gamma}}{2} [a_{22}(t) - a_{11}(t)] - 6C_i \dot{a}_{12}(t)
\]

\[
+ \chi \frac{[27a_{11}(t)a_{22}(t)a_{33}(t) - 27a_{12}^3(t)a_{33}(t)]}{2}
\]

\[
+ \left[ -\frac{1}{35} + \frac{a_{11}(t) + a_{22}(t)}{2} \right]
\]

\[
+ \left[ 1 - 27a_{11}(t)a_{22}(t)a_{33}(t) + 27a_{12}^2(t)a_{33}(t) \right] a_{12}^2(t) \quad (3.24)
\]

\[
\frac{da_{22}(t)}{dt} = 0 = -\dot{a}_{12}(t) + 2C_i \dot{\gamma}(1 - 3a_{22}(t))
\]

\[
+ \chi \frac{\dot{a}_{12}(t)}{2} - \frac{3}{7} \left[ 27a_{11}(t)a_{22}(t)a_{33}(t) - 27a_{12}^3(t)a_{33}(t) \right] a_{12}(t)
\]

\[
+ \left[ 1 - 27a_{11}(t)a_{22}(t)a_{33}(t) + 27a_{12}^2(t)a_{33}(t) \right] a_{22}(t)a_{12}(t) \quad (3.25)
\]
\[
\frac{da_{33}(t)}{dt} = 2C_1\dot{\gamma}\left(1-3a_{33}(t)\right)
- 2\chi\dot{\gamma}\left(\frac{1}{7}\left[27a_{11}(t)a_{22}(t)a_{33}(t) - 27a_{12}^2(t)a_{33}(t)\right]a_{12}(t)
\right)
\]

\[
-\frac{1}{7}\left[1 - 27a_{11}(t)a_{22}(t)a_{33}(t) + 27a_{12}^2(t)a_{33}(t)\right]a_{33}(t)a_{12}(t)
\]

\begin{equation}
(3.26)
\end{equation}

In order to apply the model we need to determine which parameters in the model are material constants that can be determined from experimental measurements and which cannot be directly measured and are treated as fitting parameters. We first identified which parameters were constants and made the appropriate measurements to determine their value. Equation (3.2) contains the constants \(\lambda\), \(\alpha\), and \(\eta_p\). These represent material constants that depend solely on the properties of the polymer and were solved for by conducting small amplitude oscillatory shear and steady shear flow experiments on the pure polymer. First, the value of \(\eta_p\), the zero shear viscosity of pure PS, was equal to the limit of \(\frac{\tau_{12}}{\dot{\gamma}}\) as the shear rate, \(\dot{\gamma}\), became small. Pure PS behaves as a Newtonian fluid at low shear rates and the zero shear viscosity is equal to the viscosity at any shear rate where the polymer is in this Newtonian regime, therefore the viscosity at the shear rate 0.01 \(s^{-1}\) was used (see Figure 3.3). It was found that \(\eta_p = 6,230 \text{ Pa-s}\) for this batch of PS that had been processed in the microcompounder.

The constants \(\lambda\) and \(\alpha\) were determined from small amplitude oscillatory shear experiments. The storage and loss modulus of the polymer could be written as functions of \(\eta_p\), frequency \((\omega)\), and the relaxation time of the polymer \((\dot{\lambda})\) as shown in Equations (3.27) and (3.28).
\[ G'(\omega) = \frac{\eta_p \lambda \omega^2}{1 + (\lambda \omega)^2} \] (3.27)

\[ G''(\omega) = \left( \frac{\eta_p}{1 + (\lambda \omega)^2} \right) \omega \] (3.28)

The only unknown in Equations (3.27) and (3.28) was \( \lambda \), which was determined by fitting the two equations to the experimental data collected from small amplitude oscillatory experiments performed on samples of pure PS, shown in Figure 3.4, and minimizing the error according to Equation (3.29).

\[
error = \sum_{i=1}^{N} \left[ \log_{10} G'_{\text{exp}}(\omega_i) - \log_{10} G'(\omega_i) \right]^2 + \left[ \log_{10} G''_{\text{exp}}(\omega_i) - \log_{10} G''(\omega_i) \right]^2 \] (3.29)

\( G'_{\text{exp}}(\omega_i) \) and \( G''_{\text{exp}}(\omega_i) \) are the experimentally determined values of the storage and loss modulus, \( G'(\omega_i) \) and \( G''(\omega_i) \) are the predicted values according to Equations (3.27) and (3.28), and \( N \) is the total number of experimental points. The range of \( \omega \) over which the equations were fit was restricted to 0.01-10 s\(^{-1}\) at 200\(^{\circ}\)C because this was the shear rate range and temperature that the steady state viscosity experiments were performed at whose data the constitutive equations modeled making this fitting range the most relevant. Accurate modeling of polymer behavior over a wide range of frequencies typically requires the use of several relaxation times due to a distribution of polymer molecular weights, however, the proposed constitutive equation uses one relaxation time to simplify the model and because the range of frequencies tested was narrow enough to allow it. The values of \( \lambda \) were restricted to the physically reasonable range 0 < \( \lambda \) < 10s and was found to be 0.18. The single value for \( \lambda \) was found to give a reasonably good fit
of the Giesekus model (Equation (3.2)) to the pure polymer data in the frequency range being investigated, however, if a larger frequency range or flows other than simple steady shear were modeled, more than one relaxation time would be necessary.

The last unknown determined from the properties of pure PS, after determining \( \eta_p \) and \( \lambda \), was the mobility factor, \( \alpha \). This constant was used in Equations (3.30)-(3.32), which describe the shear viscosity, \( \eta(\dot{\gamma}) \), of pure PS at steady shear rates, \( \dot{\gamma} \).

\[
\eta(\dot{\gamma}) = \eta_p \frac{(1 - \psi)^2}{1 + (1 - 2\alpha)\psi} \tag{3.30}
\]

\[
\psi = \frac{(1 - \chi)}{1 + (1 - 2\alpha)\chi} \tag{3.31}
\]

\[
\chi = \sqrt{\frac{1 + 16\alpha(1 - \alpha)(\dot{\gamma}\lambda)^2}{8\alpha(1 - \alpha)(\dot{\gamma}\lambda)^2}} \tag{3.32}
\]

The constant \( \alpha \) was found by fitting these equations to the experimental steady shear viscosity data collected over the shear rate range 0.01-10 s\(^{-1}\), shown in Figure 3.5, and minimizing the error of Equation (3.33)

\[
error = \sum_{i=1}^{N}[\log_{10} \eta_{exp}(\dot{\gamma}_i) - \log_{10} \eta(\dot{\gamma}_i)]^2 \tag{3.33}
\]

where \( \eta_{exp}(\dot{\gamma}_i) \) was the measured viscosity from experiments and \( \eta(\dot{\gamma}_i) \) was the predicted viscosity calculated from Equation (3.30) and \( N \) was the total number of experimental points. The value of \( \alpha \) was restricted to the physically reasonable domain \( 0 < \alpha < 1 \) and was found to be 0.59.
The other parameters appearing in the constitutive equations that were directly measured are $\phi$, the volume fraction of the nanoclays which appears in Equation (3.3), and $h$, the nanoclay aspect ratio, which appears in Equations (3.3) and (3.4). The nanoclay volume fraction was controlled when the composites were made. A rough estimate of the particle aspect ratio was gathered from TEM images but there were large variations due to the nature of the nanoclay. As mentioned previously, nanoclays exist as stacks of platelets in their as-received state. Mixing and interactions with the polymer cause these stacks to delaminate into smaller stacks or individual platelets. It has been observed that the nanoclay particles can agglomerate, forming one large particle and unless complete exfoliation and dispersion occurs there will be a distribution of stack sizes and therefore aspect ratios. Thus, the aspect ratio used in the model was an average of many aspect ratios since a single aspect ratio does not exist. We determined from the model fit and from TEM micrographs that the aspect ratio was 0.01.

The remaining unknowns in the constitutive model are $\sigma, C_i$; and the shape factors $A, B, C$ and $F$. Phan-Thien and Graham [115] proposed equations to calculate the shape factors for disk-like particles (the same shape as nanoclays) for use in a similar constitutive model in order to describe the rheology of homogeneous suspensions containing macrosized fibers. These equations that were used to determine the shape factors for the nanoclay are shown in Table 3.1.

The 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 [110]. In the special case $\sigma = 1$, the drag force on the polymer
molecules is independent of the particle orientation, and the usual Giesekus model (3.34) is obtained.

\[ \tau_{ij}^p + \lambda \frac{D\tau_{ij}^p}{Dt} + \frac{\alpha \lambda}{\eta_p} \left( \tau_{ik}^p \tau_{kj}^p \right) = 2\eta_p D_{ij} \]  
(3.34)

The term \( C_I \), also known as the Folgar-Tucker constant [101] was used to describe hydrodynamic particle-particle interactions and was used in the calculation of the stress contribution from the nanoparticles, Equation (3.3), and the evolution of the second order orientation tensor \( a_{ij} \), Equation (3.4).

We assumed the polymer/particle matrix interaction parameter \( \sigma \) to be independent of nanoclay mass concentration and strain rate, hence we determined a single value for \( \sigma \). This was done because results from the PS/CNF system showed a weak dependence of \( \sigma \) upon particle mass concentration [100]. Like \( \sigma \), \( C_I \) was assumed to be independent of nanoparticle mass concentration, but it was assumed to be a function of shear rate therefore seven values of \( C_I \) were solved for. To obtain \( \sigma \) and \( C_I \) for the composites we applied the quadratic closure approximation and solved Equations (3.1)-(3.4) while searching through parameter space (\( C_I, \sigma \)) for the minimum error, Equation (3.33), summed over the 21 measurements of the steady shear viscosity, \( \eta(\dot{\gamma}) \), of the 2, 5, and 10wt\% composites at shear rates ranging from \( \dot{\gamma} = 0.01 \) to \( 10s^{-1} \). We began searching for \( C_I \) over the range \( 10^{-7} \) to \( 10^{-2} \) although it was expanded slightly to give a better model prediction because \( C_I \) was a fitting parameter and had no physical significance limiting its bounds. The term \( \sigma \) was restricted to the range 0-1, with 1 indicating no polymer-fiber interaction.
Our results indicated that the best fit was achieved when $\sigma = 1$ which was also observed for PS/CNF composites. This value for $\sigma$ indicates that the interaction between the polymer and the nanoparticles does not significantly contribute to the shear stress developed during flow of the composite. A plot of the best-fit values for $C_I$ at the seven different shear rates is shown in Figure 3.6. It can be seen that the values show a power law dependence upon shear rate. A line following the power law form was fit point-wise to the data in order to create an expression for $C_I$ as a function of shear rate so that intermediate values of viscosity could be predicted. Knowing that $C_I$ could be approximated with a power law form, the expression $C_I = p(\dot{\gamma})^q$ was substituted in the model replacing the point-wise determination of $C_I$ and Equations (3.1)-(3.4) were solved by searching over the new parameter space ($p$, $q$, and $\sigma$). These two lines are also shown in Figure 3.6. It is apparent that whether fitting point-wise or by power law expression, approximately the same solution is achieved. Table 3.2 summarizes the material constants determined from the model and Figure 3.7 shows the model predictions of steady state viscosity for point-wise and power law forms of $C_I$.

3.5 Closure Approximation Evaluation

Using the constitutive model presented in Section 3.4 we investigate the effects of choice of closure approximation on the model predictions for PS/nanoclay composite systems. Initial modeling of the steady state rheology of PS/nanoclay composites presented in Section 3.4 was first performed using the quadratic closure approximation to solve for the fourth order orientation tensor ($a_{ijkl}$) because the nanoclay particles were
expected to be highly aligned at steady state; recall from Section 3.4.1 that the quadratic closure approximation performs well for highly aligned states, but introduces steady-state errors for more random states [114]. In order to evaluate different closure approximations the hybrid and linear closure approximations were substituted for the quadratic closure approximation and the model equations were solved procedure described in Section 3.4.2. Note that Equations (3.3) and (3.4) will be derived differently depending on what closure approximation is chosen. The final form of Equation (3.4) using the linear and quadratic closure approximations are given in Equation (3.15) to (3.22) in Section 3.4.1. Equation (3.3) is affected by the closure approximation choice by the presence of the fourth order orientation tensor $a_{ijkl}$. The appropriate definition of the fourth order tensor was substituted into Equation (3.3) when solving the constitutive model.

The constitutive model predictions of viscosity were optimized for each closure model by treating $C_I$ as a fitting parameter as was done when using the quadratic closure approximation. Since the constitutive model presented in Section 3.4 was already fit to the PS/nanoclay composites using the quadratic closure approximation, all of the model parameters except for the $C_I$ values for the new closure approximations were known. A summary of the known model parameters is given in Table 3.2. The optimized power law forms of the predicted values of $C_I$ for the PS/nanoclay composite based on the quadratic, hybrid, and linear closure approximations are given in Table 3.3.

The model predictions of steady shear viscosity and first normal stress difference (N1) using the three different closure approximations are shown in Figure 3.8. A comparison of the model predictions with experimental results for the PS/nanoclay
The quadratic closure approximation predictions of viscosity for this composite with plate-like nanoparticles are near the experimental values over the entire shear rate range tested. This is in contrast to the linear closure approximation results which predicts Newtonian behavior at low shear rates and over predicts the stress of high weight percent composites at high shear rates. The hybrid closure approximation, like the linear closure approximation, incorrectly predicts Newtonian behavior at low shear rates, and does not predict high shear rate viscosities as accurately as the quadratic closure approximation.

Based on the comparison of our model predictions with our corresponding experimental measurements we conclude that the quadratic closure approximation produces more accurate predictions of the steady state shear rheology than either the linear or hybrid closure approximations.

3.6 Conclusions

Samples of PS/nanoclay composites were prepared by melt blending and were rheologically characterized. Both linear oscillatory shear and nonlinear transient shear experiments were performed. Steady-state shear viscosity data was generated from the transient shear experiments. A constitutive model containing terms accounting for the rheological properties of the polymer matrix, the aspect ratio and characteristic length scale of the nanoparticles, the orientation of the nanoparticles, hydrodynamic particle–particle interactions, the interaction between the nanoparticles and the polymer, and flow conditions of melt processing was used to predict the rheological behavior of the
PS/nanoclay system. The model showed that the polymer–particle interaction for the composite was not significant in predicting the rheology of the system as the parameter representing this interaction, $\sigma$, was equal to a value of 1.

Quadratic, hybrid, and linear closure approximations have been proposed as a means of solving the orientation evolution equation which is a key component of the constitutive model. Model predictions of steady shear viscosity and first normal stress difference using each closure approximation were compared to experimentally measured values in order to determine which produced the most accurate results. The quadratic closure approximation was shown to give solutions with the least error.
Table 3.1 Equations used to calculate the shape factors for plate-like nanoclays and rod-like nanofibers. $R$ is defined as the aspect ratio.

<table>
<thead>
<tr>
<th>Shape Factor</th>
<th>Nanoclay [115]</th>
<th>Nanofiber</th>
<th>Nanofiber</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dilute $^{[112]}$</td>
<td>Semidilute $^{[116]}$</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>$\frac{10}{3\pi R} + \frac{208}{9\pi^2} - 2$</td>
<td>$\frac{R^2}{2[\ln(2R) - 1.5]}$</td>
<td>$A = \frac{R^2}{3\ln(2h_f/D)}$ *</td>
</tr>
<tr>
<td>B</td>
<td>$-\frac{8}{3\pi R} + 1 - \frac{128}{9\pi^2}$</td>
<td>$\frac{6\ln(2R) - 11}{R^2}$</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>$\frac{8}{3\pi R}$</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>$-\frac{12}{\pi R}$</td>
<td>$\frac{3R^2}{\ln(2R) - 0.5}$</td>
<td>0</td>
</tr>
</tbody>
</table>

* $h_f$ is a characteristic distance between a fiber and its nearest neighbors defined by:

$$\frac{2h_f}{D} = \sqrt{\frac{\pi}{\phi}}$$

for aligned fibers, and

$$\frac{2h_f}{D} = \frac{\pi}{2\phi R}$$

for random fibers.
Table 3.2 Material constants and functions of the melt blended nanoclay composite system.

<table>
<thead>
<tr>
<th></th>
<th>Melt Blended (MB) Nanoclay composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>0.18 s</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.59</td>
</tr>
<tr>
<td>$\eta_p$</td>
<td>6,230 Pa s</td>
</tr>
<tr>
<td>$\eta_s$</td>
<td>0 Pa s</td>
</tr>
<tr>
<td>$R$</td>
<td>0.01</td>
</tr>
<tr>
<td>$C_i$</td>
<td>fit to point-wise values of $C_1$: $C_i = 6.0 \times 10^{-6} \gamma^{-2.07}$</td>
</tr>
<tr>
<td></td>
<td>fit to power law, $C_i = p (\gamma)^\gamma$: $C_i = 7.1 \times 10^{-6} \gamma^{-2.08}$</td>
</tr>
</tbody>
</table>
Table 3.3 Power law forms of the particle-particle interaction parameter $C_I$ with respect to the strain rate based on three different closure approximations for PS/nanoclay composites.

<table>
<thead>
<tr>
<th>Closure Approximation</th>
<th>PS/Nanoclay: $C_I = p\dot{\gamma}^q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadratic</td>
<td>$7.1 \times 10^{-6} s^{-2.08} \dot{\gamma}^{-2.08}$</td>
</tr>
<tr>
<td>Hybrid</td>
<td>$8.5 \times 10^{-5} s^{-0.27} \dot{\gamma}^{-0.27}$</td>
</tr>
<tr>
<td>Linear</td>
<td>$1.5 \times 10^{-3} s^{-1.08} \dot{\gamma}^{-1.08}$</td>
</tr>
</tbody>
</table>
Figure 3.1  PS/nanoclay (a) storage modulus ($G'$) and (b) loss modulus ($G''$) master curves shifted to 200°C.
Figure 3.2 Transient shear viscosity of (a) pure PS and (b) PS/10wt% nanoclay measured at 200°C. Viscosity curves for shear rates less than or equal to 0.3 s$^{-1}$ were identical for pure PS.
Figure 3.3  Steady shear viscosity of PS/nanoclay composites measured at 200°C.
Figure 3.4  Model predictions (solid lines) of experimental dynamic oscillatory shear data (dots) collected at 200°C on samples of processed PS with 0wt% nanoclay used to calculate λ.
Figure 3.5  Model predictions (solid lines) of experimental steady shear data (dots) used to calculate $\alpha$. 
Figure 3.6 Model predictions of $C_I$ (dots) and best-fit lines determined by point-wise and power law fits.
Figure 3.7 Model predictions of PS/nanoclay shear viscosity at steady state with (a) point-wise and (b) power-law determination of $C_I$. 
Figure 3.8 Model predictions of (a,c,e) steady shear viscosity and (b,d,f) first normal stress difference of PS/nanoclay melt blended composites using (a,b) quadratic, (c,d) hybrid, and (e,f) linear closure approximations.
Figure 3.8 continued

(c)

(d) continued
Figure 3.8 continued

(e) 

(f)
CHAPTER 4

POLYSTYRENE/CARBON NANOFIBER TRANSIENT SHEAR RHEOLOGY AND MODELING

4.1 Introduction

In this chapter we measure transient shear rheology of PS/CNF composites and produce a constitutive model for this transient behavior. Since the discovery of carbon nanotubes by Iijima [25] a tremendous amount of research has been conducted on polymer composites reinforced by single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and vapor grown carbon nanofibers (CNFs) because of the potential to create materials with enhanced mechanical [117,118], thermal [119-122], and electrical [123] properties while using much lower particle loadings than microscale fillers such as carbon black, carbon fibers, and glass fibers [124,125]. The unique properties of these nanocomposites have been exploited for use in a wide range of applications such as electromagnetic interference shielding [122], foams [126], transparent conductive coatings [127], and electromechanical actuators [127].

The mechanical, thermal, and electrical performance properties of the nanocomposite are greatly dependent upon the orientation and the dispersion of the particles within the polymer matrix [128-133], thus it is desirable to be able to predict
how particle orientation evolves during processing flow. Accurate models provide the predictive capability necessary to design manufacturing processes that optimize the desired performance properties.

We prepare nanocomposites consisting of CNFs added to a polystyrene (PS) polymer matrix and study the transient shear rheology of the resulting composite in the melt phase. CNFs were studied because their composites have the potential to be used in applications such as electromagnetic interference shielding, electrostatic spraying, or where electrostatic discharge is desired [134] and, at ~$100/kg, they are a lower cost alternative than nanotubes which cost ~$500/g. There are several investigations of the enhancements of the mechanical, thermal, and electrical properties of polymers with the addition of CNFs however we found very few studies of the effects of CNFs on the rheological properties of the composite in the melt phase [28,40,100] and therefore seek to improve understanding in this area.

In Wang et al. [100] a constitutive model for PS/CNF composites was validated by showing agreement of the model predictions of steady state shear viscosity against experimental measurements. In this chapter we show that the time dependent form of the same model accurately predicts the measured transient shear viscosity and predicts as a function of time the evolution of the average orientation of the nanoparticles in three dimensions at various shear rates. We identify fitting parameters (particle-particle interaction and nanoparticle shape factors) and study their effects on the model in order to optimize the fit to experimental results.
4.2 Experimental Procedure

4.2.1 Materials

The polymer used in this study was PS of the brand name Fina (CX5197) and was produced by Atofina with a density of 1,000 g/m$^3$, a weight average molecular weight of 200,000, and a polydispersity index of 2.4. The CNFs 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. The nanofibers are pyrolytically stripped after production to remove polyaromatic hydrocarbons from the surface of the fibers. 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 (SEM) to have diameters of 100 to 200 nm and lengths of 1 to 50 µm. A SEM image of the as-received fibers is shown in Figure 4.1. The same polymer and nanofibers were used in a previous study of steady state shear rheology [100].

4.2.2 Sample Preparation

Two methods were used to disperse the CNF agglomerates in the PS matrix: melt blending and solvent casting. The composites made by melt blending are referred to hereafter as melt-blended (MB) composites and those made by solvent casting as solvent-cast (SC) composites. Two different dispersion methods were used in order to create samples with different fiber length distributions.
The CNF agglomerates in the MB samples were dispersed by feeding PS and CNFs to a DACA Instruments twin-screw microcompounder at 200°C with a screw rotation rate of 250 rpm and mixing for four minutes. MB composites contained nanofibers in concentrations of 2, 5, and 10 wt%. The sample exits the microcompounder in the form of a rod that was later cut into pellets. We subjected PS without nanofibers to the same melt blending procedure to take into account any possible degradation that occurs. Figure 4.2a is a transmission electron microscopy (TEM) image showing the dispersion of CNFs in the melt blended composite.

In the solvent casting process, CNF agglomerates were dispersed by sonication into PS dissolved in an organic solvent. The organic solvent was necessary to create a solution with a low enough viscosity that the nanofiber agglomerates could be effectively dispersed with sonication. PS pellets were dissolved in tetrohydrofuran (THF) followed by addition of the CNFs. The resulting 90% THF suspension was then sonicated for 0.5 h using a Sonic Dismembrator (Fisher Scientific) at 20 kHz and a power level of 760 W/l. After sonication, the suspensions were heated to evaporate as much solvent as possible. The residual material, still containing about 5 wt% THF, was 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 was heated to 200°C and compressed through a 1-mm diameter die, and the resulting rod was cut into pellets with approximate lengths of 2 mm. This pelletization avoids the trapped air that would be present in the compression molding of the powder to make disks, described below, resulting in the growth of bubbles in the sample. Composites containing 0, 2, 5, and 10 wt% CNF were prepared using the
solvent casting method. Figure 4.2b is a TEM image showing the dispersion of CNFs in the solvent cast composite.

The pellets formed from the melt blending and solvent casting procedures were compression molded into 25 mm diameter disks of 0.5-1 mm thickness using a hot press at 200°C. The pellets were placed into molds and allowed to melt for 15 minutes followed by a cycle of quickly compressing and decompressing the samples four consecutive times in order to eliminate air bubbles. Pressure was then reapplied and held for 10 minutes and after that time the heat to the press was turned off and the samples were allowed to cool to below 100°C, the glass transition temperature of the polystyrene. Once cool, the pressure was released and the samples were removed from the mold. The disks were placed in a vacuum oven at 70°C for at least 24 hrs and remained there until the time they were tested in order to prevent them from absorbing moisture or air from the atmosphere.

For this study we prepared eight samples, labeled MB0, MB2, MB5, MB10, SC0, SC2, SC5, and SC10. In this labeling MB and SC denote the sample as melt-blended or solvent-cast, respectively, and the number denotes the mass concentration of CNFs.

The aspect ratios of the CNFs in the melt blended and solvent cast composites were measured through optical microscopy. Approximately 1 g of the MB or SC material was dissolved in THF and spread on a glass slide, leaving behind the CNFs. An image of the nanofibers was captured using a camera attached to an optical microscope and the lengths and diameters of thousands of nanofibers were measured by drawing digital lines, in AutoCAD, parallel or perpendicular to the major fiber axis in order to measure length.
or diameter, respectively, then the data was compiled using an AutoLISP program. Optical microscopy images of the MB and SC nanofibers are shown in Figures 4.3a and 4.3b, respectively. The experimentally measured average diameter of the CNFs was 100 nm for both MB and SC composites and the number average fiber lengths were 3.3 and 4.5 μm for MB and SC composites, respectively. Thus the CNF aspect ratio for MB composites is 33 and for SC composites, 45.

Fiber suspensions are classified into one of three concentration regimes: dilute, semidilute or concentrated. In the dilute regime fibers can rotate freely without contacting other fibers, in the semidilute regime the hydrodynamic interactions between fibers become significant and there is some inter-particle contact, and in the concentrated regime there are frequent contacts between fibers [135]. Tucker and Advani [136] defined these regimes in terms of particle volume fraction, \( \phi \), and aspect ratio, \( r \), as \( \phi < 1/r^2 \) for dilute suspensions, \( 1/r^2 < \phi < 1/r \) for semidilute suspensions, and \( \phi > 1/r \) for concentrated suspensions. Using the experimentally measured aspect ratios and the volume fraction of each sample we determine that the MB2, MB5 and SC2 composites are in the semidilute regime while the MB10, SC5, and SC10 composites are in the concentrated regime. Table 4.1 summarizes the properties of the melt blended and solvent cast composites.

4.2.3 Rheological and Morphological Characterization

All shear flow rheological tests were performed on a strain-controlled TA Instruments rheometer (ARES LS2) with a torque transducer (0.02 g.cm to 2000 g.cm)
and a normal force transducer (2 g to 2000 g). All measurements were made using a set of 25 mm diameter parallel plates with a gap distance ranging from 0.5 to 1 mm. The temperature for each experiment was held constant at 200°C.

4.3 Experimental Results

4.3.1 Transient Shear Rheology

The stress response upon startup of constant shear was measured for the eight composite systems. Figures 4.4a and 4.4b display the measured transient shear viscosities versus time of the SC0 and SC10 composites, respectively, at shear rates from 0.0001 to 10 s\(^{-1}\). The pure polymer (SC0) exhibits behavior typical of a homogeneous linear polymer, Newtonian behavior at small strain rates and shear thinning at higher shear rates (in Figure 4.4a the plots for shear rates 0.01, 0.001, and 0.0001 s\(^{-1}\) overlap). With the addition of CNFs (see Figure 4.4b) the viscosities at shear rates larger than 0.1 s\(^{-1}\) are largely unaltered, but for shear rates less than 0.1 s\(^{-1}\) the viscosities are greatly increased and display a highly shear thinning behavior. It should also be noted that for all samples measured the viscosities from multiple shear rates superimpose at times less than 0.1 s.

Other differences in the transient shear behavior of polymers with and without CNFs can be seen when the data from Figure 4.4 is plotted as the reduced stress versus strain, as seen in Figure 4.5. The reduced stress, \(\tau_{\text{red}}\), is defined as the ratio of transient shear stress to the steady state shear stress, \(\tau_{\text{red}} = \tau^\prime / \tau_\infty\), therefore at long times (or high strains) the reduced stress approaches a value of one. It should be noted that because the data in Figure 4.5 is plotted as a function of strain the superposition of the data at short
times as seen in Figure 4.4 is no longer apparent. This is simply because at short times the stress response is a function of time and not strain.

For both the SC0 and the SC10 samples, Figures 4.5a and 4.5b, respectively, the magnitude of the overshoot increases with increasing shear rate. Three distinct differences between the SC0 and SC10 samples are observed when comparing their reduced stresses. First, at identical shear rates, the overshoot magnitude in the SC10 sample is always larger than in the SC0 sample. Second, the strain value corresponding to the overshoot peak is independent of shear rate for the SC0 sample while the strain value corresponding to the overshoot peak decreases with increasing shear rate for the SC10 sample. Third, the overshoot widths are approximately the same at all shear rates in the SC0 sample while the overshoot widths decrease with increasing shear rate in the SC10 sample.

These differences between the SC0 and SC10 samples are due to the presence of CNFs. The more pronounced overshoot in the SC10 sample is caused by additional shear stress from the tumbling of the CNFs during flow. The position shift of the overshoot peaks with changing shear rate in the SC10 samples is likely due to particle-particle interactions within the polymer matrix. The positions of the peaks in the SC0 samples are independent of the shear rate which is typical for most homogeneous polymers and for composites in which the fillers are non-Brownian [23,137]. The Peclet number, a dimensionless quantity that is the ratio of hydrodynamic forces to Brownian forces, can be calculated for each composite type (MB or SC) in order to determine if the particles are Brownian. A Peclet number much greater than 1 is an indication that Brownian forces
are not significant. As in Sepher et al. [138], the Peclet number is defined as

\[ Pe = \frac{\eta_m \dot{\gamma} \pi L^3}{3k_B T \ln r} \]

where \( \eta_m \) is the matrix viscosity, \( \dot{\gamma} \) is the shear rate, \( L \) is the length of the fibers, \( k_B \) is the Boltzmann’s constant, \( T \) is the absolute temperature and \( r \) is the CNF aspect ratio. At the lowest shear rate tested, 0.01 s\(^{-1}\), the Pe number is equal to 1.6\( \times 10^5 \) and 3.8\( \times 10^5 \) for MB and SC composites, respectively, both much greater than 1 indicating the particles are non-Brownian.

The CNFs in the SC10 samples are non-Brownian yet the positions of the overshoots are a function of the shear rate. The Pe number for the SC composites increases with increasing shear rate from a value of 3.8\( \times 10^5 \) at a shear rate of 0.01 s\(^{-1}\) to a value of 1.1\( \times 10^6 \) at a shear rate of 10 s\(^{-1}\). This indicates that as shear rate increases the hydrodynamic forces on the CNFs become more significant. Applying a homogeneous shear flow to the composite causes the CNFs to align in the direction of flow, however, at low shear rates the reduced hydrodynamic forces may not highly align the CNFs in the flow direction leaving them in more randomly oriented state. If the shear rate is large, the hydrodynamic forces are much greater possibly making it easier for the CNFs to align in the flow direction. The result of the competition between flow and inter-particle interactions is that the overshoot peak occurs at smaller strains for smaller shear rates. Moreover, if we observe Figure 4.5 carefully, we can see that the positions of the overshoots in the SC0 and SC10 samples are about the same at a shear rate of 10 s\(^{-1}\) where the Pe number is at its greatest. As shear rate decreases, and as Brownian forces
become more significant, the overshoot in the SC10 sample occurs at a smaller strain than for the SC0 sample.

The differences between the SC0 and SC10 sample overshoot widths could also be the result of particle-particle interactions. Since the inter-particle interactions are 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 the flow quickly dominates therefore the widths of the overshoots of the SC0 and SC10 samples are almost identical.

The effect of CNF length can also be seen in the startup of constant shear experiments by comparing the MB and SC composites at various CNF loadings. Figure 4.6 shows the reduced stress of both MB and SC composites at different CNF concentrations during the startup of a constant shear rate of 1 s⁻¹. The reduced stresses of the MB composites (Figure 4.6a) containing CNF loadings less than and equal to 5wt% are nearly identical, however, the reduced stress is significantly different at a CNF loading of 10wt%. The SC composites (Figure 4.6b) show significantly higher stress overshoots than the MB composites (Figure 4.6a) when comparing samples with the same CNF loadings. The difference is the CNFs in the SC composites are longer than those in the MB composites (aspect ratio of 45 in SC composites and 33 in MB composites). The extra length creates more inter-particle interactions resulting in higher stresses in the SC composites during shear flow than in the MB composites.
4.3.2 Effects of Process Developed Orientation

The evolution of the CNF structure during flow was studied with flow reversal experiments. In these experiments samples were sheared at a shear rate of 1 s⁻¹ for 40 s in a counterclockwise (CCW) direction, shearing was then stopped and the sample was allowed to rest for 0, 120, 1200, or 2400 s. Shearing was restarted at the same shear rate but in a clockwise (CW) direction and the stress response was recorded with time. Figure 4.7 shows the reduced stress response of SC0 and SC10 samples during CCW and CW flows for different amounts of rest time (tᵣₑₛᵗ). As seen in Figure 4.7a, the stress overshoot of the SC0 samples during CW flow with 0 s of rest time was smaller than the overshoot of the sample during CCW flow. When the SC0 sample was allowed to rest for 120 s or longer the stress overshoot in the CW flow was exactly the same as in the initial CCW flow. The stress overshoot in the SC10 sample (Figure 4.7b) during CW flow was more dependent upon the length of rest time than in the SC0 sample. When the rest time was 0 s, the stress gradually increased to a steady state and showed no overshoot. At 1200 s rest time a pronounced overshoot appeared and at 2400 s rest time the overshoot was even greater, however, the magnitude of the overshoot was still less than that observed in the initial CCW flow.

Similar experiments were performed by Sepehr et al. on polybutene/glass fiber and Boger fluid/glass fiber suspensions [138] and polypropylene/glass fiber composites [139]. For all systems it was observed that upon reversal of flow, with tᵣₑₛᵗ = 0 s, shear stress increased slowly approaching a steady value then produced an overshoot at strains between 10 and 40. As the amount of time between the initial flow and reverse flow was
increased the location of the reverse overshoot peak shifted to shorter strain values, and at very long times ($t_{\text{rest}} = 1000 \text{ s}$) the stress growth behavior of the reverse flow was nearly identical to that of the initial flow. This was attributed to the complete recovery of the polymeric chains and the subsequent loss of fiber orientation.

A slightly different flow reversal experiment was performed to further study the development of nanofiber structure during transient shear. In this test samples were first sheared at a shear rate of $1 \text{ s}^{-1}$ for $40 \text{ s}$ (enough time to reach steady state) in a CCW direction, then shearing was stopped and the samples were allowed to rest for $120 \text{ s}$. After resting, shearing was resumed either in the same or reverse directions, CCW or CW, respectively. The results for the SC0 and SC10 samples are shown in Figure 4.8. The reduced shear stresses in the SC0 sample for all three flows (initial shearing in the CCW followed by shear in the CCW or CW directions) were identical (Figure 4.8a) meaning a rest time of $120 \text{ s}$ was long enough to allow the polymer chains to relax to the original pre-shear condition. As will be shown in Section 4.2, the longest relaxation time of the polymer is $2.636 \text{ s}$ therefore $120 \text{ s}$ of rest time is more than enough time for the polymer chains to relax.

It can be seen in Figure 4.8b that when the SC10 samples were sheared in the CCW direction following a $120 \text{ s}$ rest period the stress overshoot was smaller than the initial CCW shear overshoot, however, as shown previously, if the post initial shear flow was in the CW direction, there was no overshoot. If the relaxation time of the polymer chains is unchanged by the presence of CNFs and the orientation of the CNFs does not significantly change during the rest time we would expect to see the results result from
the CCW flow ($t_{\text{rest}} = 120$ s). The polymer chains would relax to their original pre-shear condition and when shearing is resumed in the CCW direction there would be a stress overshoot that is less than the overshoot in the first CCW flow because the CNFs are aligned in the shear direction. If the polymer chains were fully relaxed we would expect to see an overshoot in the CW flow for the same reasons as one would be seen in the CCW flow, however, this is not the case implying the relaxation time of the polymer chains has increased.

Another possibility is that the orientation of the CNFs changes during the rest time, however, the rotary diffusion coefficient $D_r$, defined as $D_r = \frac{3k_B T \ln r}{\eta_m \pi L^3}$ [138], where all symbols have the same definition as in the $Pe$ number, was calculated to be $6.19 \times 10^{-8}$ s$^{-1}$ and $2.66 \times 10^{-8}$ s$^{-1}$ for the melt blended and solvent cast samples, respectively. These values of $D_r$ combined with the time scale of the experiments (~1000 s or less) indicate that the nanofibers do not reorient during the rest time due to Brownian motion. Any orientation changes of the fibers that occur during the experiments are caused by hydrodynamic drag. The relaxation of the polymer molecules during the rest time could be creating enough hydrodynamic drag to reorient the nanofibers, however, experimental measurements of CNF orientation during flow reversal experiments would be necessary to determine if that is occurring. At the present there is no method available to measure the three dimensional structure of nanofibers in a polymer composite.
4.4 Modeling

4.4.1 Modeling Transient Simple Shear Flow

The constitutive model we found best captures the rheological behavior of CNF/PS composites in steady shear and startup of steady shear flow of our CNF/PS melt composites is [136]:

\[
\tau_{ij}^c = -p\delta_{ij} + 2\eta_s D_{ij} + \tau_{ij}^p + \tau_{ij}^{CNF}
\]  

\(4.1\)

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

\(4.2\)

\[
\tau_{ij}^{CNF} = 2[\eta_s + \eta] \phi \left[ AD_{il}a_{kj,l} + B \left( D_{ik}a_{kj} + a_{ik}D_{kj} \right) + CD_{lj} + 2Fa_{ij}D_{lj} \right]
\]

\(4.3\)

\[
\frac{da_{ij}}{dt} = (W_{ik}a_{kj} - a_{ik}W_{kj}) + \chi \left( D_{ik}a_{kj} + a_{ik}D_{kj} - D_{ik}a_{kj,l} \right) + 4C_i \Pi_D^{1/2} \left( \delta_{ij} - ma_{ij} \right)
\]

\(4.4\)

Equation (4.1), proposed by Azaiez [110], expresses the total stress, \(\tau_{ij}^c\), of the polymer/nanocomposite system as the sum of the stress contribution from polymer molecules with fiber inclusions, \(\tau_{ij}^p\), the stress contribution from the carbon nanofibers, \(\tau_{ij}^{CNF}\), the stress contribution from a Newtonian solvent (if present), \(2\eta_s D_{ij}\), and the pressure maintaining incompressibility, \(p\). In the Newtonian solvent contribution, \(D_{ij}\) is the symmetric part of the Eulerian velocity gradient, \(\frac{\partial v_i}{\partial x_j}\), and \(\eta_s\) is the solvent viscosity.

Equation (4.2), the multi-mode Giesekus model [111], predicts the strain rate-dependent viscoelastic behavior of the polymer matrix. The total polymer stress is a summation of the stress of each mode:
\[ \tau_{ij}^p = \sum_{m=1}^{N} \tau_{ij,m} \]  

(4.5)  

where \( N \) is the number of modes. In Equation (4.2) the upper convected derivative of \( \tau_{ij}^p \) is

\[ \frac{D\tau_{ij}^p}{Dt} = \frac{d}{dt} \tau_{ij}^p - W_{ik}\tau_{kj}^p + \tau_{ik}^p W_{kj} - D_{ik}\tau_{kj}^p - \tau_{ik}^p D_{kj} \]  

(4.6)  

where \( W_{ij} \) is the skew part of the Eulerian velocity gradient. The constants \( \eta_p, \alpha \) and \( \lambda \) are the polymer viscosity, mobility factor, and relaxation time, respectively, for the polymer matrix in the melt phase. The constant \( \sigma \) is a measure of the polymer-particle interaction and is a value less than or equal to 1. Since the stress tensor is symmetric, \( \tau_{ij} \) contains six components (\( \tau_{11}, \tau_{22}, \tau_{33}, \tau_{12} = \tau_{21}, \tau_{13} = \tau_{31}, \tau_{23} = \tau_{32} \)), however, in shear flow, only four of the components are non-zero (\( \tau_{11}, \tau_{22}, \tau_{33}, \tau_{12} \)). The solution to Equation (4.2) for a transient shear flow is found by simultaneously solving the four coupled non-linear differential equations of the non-zero stress tensor components.

In Equation (4.3), derived by Tucker [112], \( \eta \) is the viscosity contribution from the polymer matrix; for simple shear in the 1-2 plane, \( \eta = \frac{\tau_{12}^p}{\dot{\gamma}} \), and \( \dot{\gamma} \) is the shear rate. \( D_r \) is the rotary diffusivity due to Brownian motion, and \( \phi \) is volume fraction of the nanofibers. The values \( A, B, C, \) and \( F \) are shape factors that are functions of nanofiber volume fraction and nanofiber aspect ratio, \( r = L / D \), with \( L \) the particle length and \( D \) the particle diameter. Several definitions for these shape factors have been proposed [112,116,140] for different concentration regimes (dilute or semidilute) and states of
nanoparticle orientation (isotropic or aligned). A summary of some of these proposed constants is given in Table 4.2. A discussion of the appropriate choice of shape parameter will be given later in the chapter.

Equation (4.4) is the evolution equation of the second order orientation tensor, \( a_{ij} \), which is a measure of nanostructure that combines the contributions of a collection of particles that dictate the mesoscale properties of the nanocomposite. In order to clarify the concept of an orientation tensor we will first describe the orientation of one fiber in space, shown in Figure 4.9, with the unit vector \( \mathbf{p} \). The orientation vector \( \mathbf{p} \) of a single fiber in three dimensional space can be expressed using two Eulerian angles, \( \theta \) and \( \phi \), as the components along the reference axes as follows:

\[
\mathbf{p} = (p_1, p_2, p_3) = (\cos \theta, \sin \phi \sin \theta, \cos \phi \sin \theta)
\]  

(4.7)

In real systems, such as our composite samples which contain large numbers of fibers with a variety of fiber orientations, it is necessary to be able to describe the average fiber orientation. This is done with the use of the probability distribution function \( \psi(p) \) which describes the probability of finding a fiber between angles \( \theta_i \) and \( (\theta_i + d\theta) \), and \( \phi_i \) and \( (\phi_i + d\phi) \) [113]. Using these definitions of \( \mathbf{p} \) and \( \psi(p) \) we can define second order and fourth order orientation tensors as the dyadic product of fiber orientation, \( \mathbf{p} \), with itself averaged over the orientation space containing a sufficient number of particles as follows [113]:

\[
a_{ij} = \int p_i p_j \psi(p) dp
\]  

(4.8)

\[
a_{ijkl} = \int p_i p_j p_k p_l \psi(p) dp
\]  

(4.9)
To close the system of Equations (4.1)-(4.4) one must adopt an approximation that relates the fourth-order orientation tensor $a_{ijkl}$ in Equations (4.3) and (4.4) to the second order orientation tensor $a_{ij}$. Popular closure approximations are:

1. The linear closure approximation,

$$
\hat{a}_{ijkl} = -\frac{1}{35} \left( \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \right) + \frac{1}{7} \left( a_{ij} \delta_{kl} + a_{ik} \delta_{jl} + a_{il} \delta_{jk} + a_{kl} \delta_{ij} + a_{jl} \delta_{ik} + a_{jk} \delta_{il} + a_{kl} \delta_{ij} \right) \quad (4.10)
$$

which works well when the fibers remain nearly random, but introduces an artificial instability into the equations for highly aligned suspensions [114].

2. The quadratic closure approximation

$$
\tilde{a}_{ijkl} = a_{ij}a_{kl} \quad (4.11)
$$

which performs well for highly aligned states, but introduces steady-state errors for more random states [114].

3. The hybrid closure approximation,

$$
a_{ijkl} = (1 - f) \hat{a}_{ijkl} + f \tilde{a}_{ijkl} \text{, with } f = 1 - 27 \det(a_{ij}) \quad (4.12)
$$

which mixes linear and quadratic forms according to scalar measure of orientation and performs well over the entire range of orientation [114].

Choosing a closure approximation allows one to solve Equations (4.1)-(4.4) where Equation (4.4) solves for the six components of the orientation tensor $(a_{11}, a_{22}, a_{33}, a_{12} = a_{21}, a_{13} = a_{31}, a_{23} = a_{32})$ which describe the orientation evolution of the nanofibers, and Equations (4.1)-(4.3) which solve for the transient rheological response of the composite system during simple shear flow.
In Equation (4.4), following Advani and Tucker [113] as suggested by Folgar and Tucker [141] for concentrated suspensions of large fibers, we employ \( D_r = 2C_I \Pi_D^{1/2} \)

where \( \Pi_D^{1/2} \) is the square root of the second invariant of the symmetric part of the velocity gradient \( D_y \), which for shear flow is equal to \( \dot{\gamma}/2 \), and \( C_I \) is the hydrodynamic particle-particle interaction parameter which measures the intensity of a nanofiber’s interaction with the fibers surrounding it. Also present is \( \chi \), a parameter related to the particle aspect ratio, \( r \), through

\[
\chi = \frac{r^2 - 1}{r^2 + 1}
\]

(4.13)

4.4.2 The Effects of Parameter Values on Model Predictions

In order to get a better understanding of how each of the parameters in the constitutive model affect the predictions of transient and steady state shear viscosity, the values for the parameters \( \eta_p, \alpha, \lambda, C_I, r \) and \( \sigma \) were varied and the model predictions were compared. Because the constitutive model defines the stress of a polymer nanocomposite as the summation of the stress contribution of the polymer and the stress contributed by the presence of nanofibers, the evaluation of these parameters was simplified by first considering those components which affected the stress contribution of the polymer only (\( \eta_p, \alpha \) and \( \lambda \)) without the addition of stress from the nanoparticles, then evaluating the remaining constants (\( C_I \) and \( r \)) which affect the predictions of the stress contribution due to the presence of the nanofibers. Note that \( \sigma \) is the polymer-particle interaction coefficient and when \( \sigma \neq 1 \) the predictions of polymer viscosity are coupled
to the orientation of the nanofibers, therefore this parameter was evaluated using the entire constitutive model. Until \( \sigma \) is evaluated it will be assumed that \( \sigma = 1 \) for simplicity.

First, the steady state shear viscosity of a polymer with \( \eta_p = 3,000; \ 10,000 \) or \( 30,000 \) with \( \alpha = 0.5 \) and \( \lambda = 1 \) was calculated using Equation (4.2) and the results are plotted in Figure 4.10. As this figure shows, as the value of \( \eta_p \) increases the value of steady shear viscosity also increases however the shape of the viscosity curve is the same. At low shear rates the steady state viscosity is equal to the value of \( \eta_p \).

Next, \( \eta_p \) and \( \alpha \) were held constant at a value of 10,000 and 0.5, respectively, and \( \lambda \) values of 0.1, 1 and 10 were used to predict the steady state viscosity. These results, shown in Figure 4.11, show that as \( \lambda \), the polymer relaxation time, increases, the shear rate at which shear thinning occurs decreases. The rate at which shear thinning occurs is the same for all values of \( \lambda \) and the value of the low shear Newtonian plateau also remains unchanged.

The effects of \( \alpha \) on steady shear viscosity were determined by solving Equation (4.2) with \( \eta_p = 10,000; \ \lambda = 1 \) and \( \alpha = 0.25, 0.5 \) or 0.75. These results are shown in Figure 4.12 and show that as \( \alpha \) increases the rate of shear thinning also increases. The low shear Newtonian plateau remains unchanged as does the shear rate at which shear thinning begins to occur.

The effects of \( C_1, r \) and \( \sigma \) were evaluated under transient shear flow conditions for a composite containing 2 wt\% CNF at a shear rate of 0.01 \( s^{-1} \). For the purpose of evaluating these constants the hybrid closure approximation was used as well as the
shape factor definitions \( A = \frac{r^2}{3\ln\left(\sqrt{\pi/\phi}\right)} \), \( B = C = F = 0 \). First, the transient shear viscosity was solved using \( \eta_p = 10,000; \lambda = 1; \alpha = 0.5; r = 50 \) and \( C_I = 0.9, 0.1 \) or 0.01. The results, shown in Figure 4.13a, demonstrate that as the value of \( C_I \) decreases the predicted transient shear viscosity also decreases. Figure 4.13b shows the corresponding values of the orientation tensor component \( a_{11} \) (the direction of the applied shear flow) as a function of time for each of the \( C_I \) values used. As this figure demonstrates, \( C_I \) significantly impacts the orientation of the carbon nanofibers predicted for a given shear flow with lower values of \( C_I \) predicting higher alignment of the carbon nanofibers in the direction of the applied flow.

Next, transient shear viscosity was solved using \( \eta_p = 10,000; \lambda = 1; \alpha = 0.5; C_I = 0.1 \) and \( r = 10, 50 \) or 100. As seen in Figure 4.14, as the value of \( r \) increases the predicted values of transient viscosity also increase. The increase that is observed is a simple vertical shift.

Finally, the effects of the parameter \( \sigma \) were determined by solving for the transient shear viscosity using the parameters \( \eta_p = 10,000; \lambda = 1; \alpha = 0.5; C_I = 0.1; r = 50 \) and \( \sigma = 1, 0.75, 0.5 \) or 0.25. The results are shown in Figure 4.15 and show that \( \sigma \) does not significantly affect the predictions of transient viscosity. There is a very slight increase in viscosity predicted that occurs around a time of 100 s, however this is not seen experimentally. Because of this, all model calculations presented in the remainder of this chapter will be performed with \( \sigma = 1 \).
4.4.3 Application of the Model to CNF/PS Melt Blended Composites

To finish the system of Equations (4.1)-(4.4) we must determine values for the parameters present in those equations. For the purpose of clarity and brevity we determine parameter values only for the MB composite experimental results. The procedure would be the same for the SC composites, however, since our purpose is to show the effectiveness of the model in fitting to transient shear data, one data set is sufficient.

In order to optimize the model we first determined what variables were present and how each one affected the model’s behavior. The main objective is to accurately predict the transient shear rheology of PS/CNF composites for the range of nanofiber concentrations tested including accurate prediction of the location and magnitude of the stress overshoot that occurs at low strains as well as accurately predicting steady state viscosities at high strains.

In the model there are three types of parameters: constants associated with the properties of the polymer or nanofibers that can be physically measured, variables which cannot be determined from physical measurements and are treated as fitting parameters, and parameters that have several definitions and must be evaluated to determine the best choice. We first identified the parameters that were measurable quantities of the polymer and nanofiber properties. The constants \( \eta_p, \lambda \) and \( \alpha \) found in Equation (4.2) are the polymer viscosity coefficient, relaxation time, and mobility factor, respectively, for the polymer matrix in the melt phase. The values for \( \eta_p, \lambda \) and \( \alpha \) were found by fitting the
following multi-mode equations to the experimental measurements of the steady state shear viscosity over the shear rate range 0.01-10 s⁻¹:

\[ \eta(\dot{\gamma}) = \sum_{m=1}^{N} \eta_{p,m} \frac{(1 - \psi_m)^2}{1 + (1 - 2\alpha_m)\psi_m} \]  

(4.14)

\[ \psi_m = \frac{1 - \chi_m}{1 + (1 - 2\alpha_m)\chi_m} \]  

(4.15)

\[ \chi_m = \sqrt{\frac{1 + 16\alpha_m (1 - \alpha_m)(\dot{\gamma} \lambda_m)^2}{8\alpha_m (1 - \alpha_m)(\dot{\gamma} \lambda_m)^2}} - 1 \]  

(4.16)

and minimizing the error according to Equation (4.17):

\[ \text{error} = \sum_{i=1}^{M} \left[ \log_{10} \eta_{\text{exp}}(\dot{\gamma}_i) - \log_{10} \eta(\dot{\gamma}_i) \right]^2 \]  

(4.17)

where \( \eta_{\text{exp}}(\dot{\gamma}_i) \) is the experimentally determined value of the steady state viscosity, \( \eta(\dot{\gamma}_i) \) is the predicted value of viscosity according to Equation (4.14), N is the total number of modes and M is the total number of experimental points. Equations (4.14)-(4.17) were solved with one, two, three and four–mode models to determine which provided the most accurate predictions of the experimentally measured steady state shear data. A four-mode model was found to give the least error according to Equation (4.17).

Experimentally measured values of the steady state shear viscosity are compared to one-mode and four-mode model predictions in Figure 4.16. The experimentally determined values of \( \eta_p, \lambda \) and \( \alpha \) for the four-mode model are summarized in Table 4.3.

The other constants in the constitutive equations determined from properties of the nanofibers were \( \phi \), the volume fraction of the nanofibers, and \( r \), the nanofiber aspect
ratio, which both appear in Equation (4.3). Both quantities are known as the nanofiber volume fraction is fixed and the aspect ratio, as mentioned in Section 4.2.2, was experimentally measured using optical microscopy and found to be 33 for MB composites and 45 for SC composites.

Having identified the constants, Equations (4.1)-(4.4) were evaluated to determine how to achieve the best model predictions of the experimentally measured rheology. Equation (4.1) defines the stress in the composite as the summation of the stress due to the polymer [Equation (4.2)], added to the stress due to the nanofibers [Equation (4.3)]. As shown previously, all parameters in Equation (4.2) have been determined and a four-mode model was found to provide the best fit. The fourth order Runge-Kutta method was applied to solve Equation (4.2) for the stress contribution from the pure polymer, \( \tau^p_{ij} \). The corresponding strain rate dependent polymer viscosity, \( \eta \), was solved using the following relationship: \( \eta = \frac{\tau^p_{12}}{\dot{\gamma}} \). The components of the stress tensor were defined as \( \tau_{ij} = 0 \) at time \( t = 0 \) s since there was no shear stress applied to the sample before startup of flow. Figure 4.17 is a comparison of the four-mode model transient viscosity predictions with the experimentally measured values of pure PS at shear rates ranging from 0.01-10 s\(^{-1}\).

Equations (4.3) and (4.4) contained the shape parameters A, B, C, and F which have several definitions; and the fourth order orientation tensor \( a_{ijkl} \) which can be calculated by one of several different closure approximations. In order to determine the appropriate definition of the shape factors and closure approximation we evaluated each
combination in order to decide which gave the most accurate viscosity predictions. An analysis of these definitions will be presented later in the chapter.

Equation (4.4) is used to predict nanofiber orientation changes during flow by calculating the orientation tensor $a_{ij}$. There are two variables in this equation that can affect the orientation predictions. One is shear rate, in the form of $D$ and $W$, which is a known quantity and therefore cannot be changed. The other variable is $C_I$, which can be used as a fitting parameter and impacts the model’s prediction of CNF orientation which in turn determines the amount of shear stress predicted by the model during flow. An important point to note is that Equation (4.4) is independent of Equations (4.1)-(4.3) therefore nanofiber orientation predictions are based only on the type of flow (in this case shear flow), the shear rate, the closure approximation, and $C_I$. An analysis of the effects of $C_I$ will be presented later in the chapter.

The orientation evolution Equation (4.4) was solved by substituting for the symmetric and skew parts ($D$ and $W$, respectively) of the velocity gradient specified by the steady shear flow $\nu = \dot{x} = \dot{x}_x e_1$, and by inserting the definition of the chosen closure approximation. This produced a unique set of differential equations for the symmetric tensor $a_{ij}$ as shown in Appendix C. It should be noted that the second order orientation tensor components $a_{13}$ and $a_{23}$ are always zero for simple shear flow and thus $\frac{da_{13}}{dt}$ and $\frac{da_{23}}{dt}$ are also equal to zero. When solving this system of equations the assumption was...
made that the initial state of the fiber orientation was random, i.e. \( a_{11} = a_{22} = a_{33} = 1/3 \) and \( a_{12} = 0 \).

As stated previously, the unknown model variables which can be used to optimize the model’s transient viscosity predictions are \( C_I \), shape factor and the closure approximation. The best fit values of \( C_I \) giving the least error between the predicted transient shear viscosities and the experimentally measured values were found for each shape factor and closure approximation combination. The predictions were compared and the shape factor/\( C_I \)/closure approximation combination providing the best fit was chosen. Only the three shape factor definitions, given in Table 4.2, for semidilute nanofiber concentrations were evaluated. In these definitions \( A \) is the only non-zero constant and are given as follows:

\[
A_2 = \frac{r^2}{3 \ln \left( \sqrt{\pi/\phi} \right)}
\]  
(4.18)

\[
A_3 = \frac{16r^2}{3 \ln \left( \frac{1}{\phi} \right)} \left[ 1 - \frac{\ln \ln \left( \frac{1}{\phi} \right)}{\ln \left( \frac{1}{\phi} \right)} + 0.6344 \right]
\]  
(4.19)

\[
A_4 = \frac{16r^2}{3 \left[ \ln \left( \frac{1}{\phi} \right) + \ln \ln \left( \frac{1}{\phi} \right) + 1.4389 \right]}
\]  
(4.20)

The definition \( A = A_1 = \frac{r^2}{2 \left[ \ln(2r) - 1.5 \right]} \), \( B = \frac{6 \ln (2r) - 11}{r^2} \), \( C = 2 \),

\[
F = \frac{3r^2}{\ln(2r) - 0.5}
\]
was not used because it is intended for dilute suspensions and, as seen
in Table 4.1, the composite samples used in this study are in the semidilute and concentrated regimes.

Having three shape factor and three closure approximation definitions meant there were nine possible shape factor/closure approximation combinations to be evaluated. For each of these combinations there was an ideal value or expression for \( C_I \) as a function of shear rate that needed to be determined which created an enormous number of possible solutions. The best fit solution could be achieved by creating a program that automated the procedure and every shape factor/closure approximation/\( C_I \) value combination could be evaluated by comparing the model predicted viscosity values with the experimental measurements. A lack of time prevented the creation of such a program.

An alternative method was developed to find the best fit solution by reducing the number of potential optimum parameter values. The basic assumptions used in this method are that the choice of shape factor, closure approximation and \( C_I \) are independent of CNF concentration. It is also assumed that \( C_I \) could be a function of shear rate. The first step taken was to calculate the stress caused by the presence of the CNFs. Since the model predicts the stress in the composite to be composed of the stress due to the polymer, Equation (4.2), and the stress due to the presence of the nanofibers, Equation (4.3), the stress caused by the presence of the nanofibers \( (\tau_{ij}^{\text{CNF}}) \) for the MB2, MB5 and MB10 composites was calculated by subtracting the model predictions of the transient shear viscosity of MB0 from the experimentally measured values of the transient shear viscosity of the MB2, MB5 and MB 10 composites. The model predictions of the MB0 shear viscosity were used because it was desired to determine what values predicted by
Equation 4.3 would result in the exact prediction of the experimentally measured values of shear viscosity.

Evaluation of Equation (4.3) showed that if $\tau_{ij}^{CNF}$ was known and a shape factor definition was chosen, the value of $a_{ijkl}$ at each shear rate needed to exactly predict the experimentally measured viscosity of each composite sample could be solved for. To simplify things further it was assumed that $a_{ijkl}$ was independent of mass concentration thus the value of $a_{ijkl}$ at different mass concentrations would be averaged to find a single ideal value and $a_{ijkl}$ would be evaluated only at steady state. Therefore, for each shape factor the dependence of $a_{ijkl}$ on shear rate was known and was graphed and a best-fit equation was found to describe the relationship. These graphs and equations are shown in Figure 4.18. The best fit equations for $a_{ijkl}$ as a function of shear rate for the different shape factors are:

$$A_2: \quad a_{ijkl} = -0.0076 \ln(\dot{\gamma}) + 0.0385 \quad (4.21)$$

$$A_3: \quad a_{ijkl} = 0.0103 \exp(-0.1146\dot{\gamma}) \quad (4.22)$$

$$A_4: \quad a_{ijkl} = -0.0013 \ln(\dot{\gamma}) + 0.0064 \quad (4.23)$$

The value of $a_{ijkl}$ calculated from the orientation tensor $a_{ij}$ depends on the choice of closure approximation and the value of $a_{ij}$ depends on the choice of closure approximation and $C_l$. Using the steady state solutions of the orientation evolution equation (Equation 4.4) and the definitions of the closure approximations (Equations 4.10-4.12) the values of $a_{ijkl}$ were calculated for a range of values of $C_l$ and a plot was
made of $a_{ijkl}$ as a function of $C_I$ for each closure approximation. A function was found to describe the dependence of $a_{ijkl}$ on $C_I$. These plots and functions are shown in Figure 4.19.

An evaluation of Figure 4.19 reveals that the use of the quadratic closure approximation is not the best choice because most $a_{ijkl}$ values are predicted by more than one $C_I$ value therefore there is no unique solution for $C_I$. The best fit equations for $a_{ijkl}$ as a function of $C_I$ for the hybrid and linear closure approximations are:

Hybrid:

$$a_{ijkl} = 0.1876 C_I^{0.5006}$$  \hspace{1cm} (4.24)

Linear:

$$a_{ijkl} = -0.0099 C_I + 0.0748$$  \hspace{1cm} (4.25)

By setting Equations (4.24) and (4.25) equal to Equations (4.21)-(4.23), six best fit expressions for $C_I$ as a function of shear rate can be found:

Hybrid, A2:

$$C_I = \left[ \frac{-0.0076 \ln(\dot{\gamma}) + 0.0385}{0.1876} \right]^{1/0.5006}$$  \hspace{1cm} (4.26)

Hybrid, A3:

$$C_I = \left[ \frac{0.0103 \exp(-0.1146 \dot{\gamma})}{0.1876} \right]^{1/0.5006}$$  \hspace{1cm} (4.27)

Hybrid, A4:

$$C_I = \left[ \frac{-0.0013 \ln(\dot{\gamma}) + 0.0064}{0.1876} \right]^{1/0.5006}$$  \hspace{1cm} (4.28)

Linear, A2:

$$C_I = \frac{0.0076 \ln(\dot{\gamma}) + 0.0363}{0.0099}$$  \hspace{1cm} (4.29)

Linear, A3:

$$C_I = \frac{0.0103 \exp(-0.1146 \dot{\gamma}) - 0.0748}{-0.0099}$$  \hspace{1cm} (4.30)

Linear, A4:

$$C_I = \frac{0.0013 \ln(\dot{\gamma}) + 0.0684}{0.0099}$$  \hspace{1cm} (4.31)
These six possible best fit solutions can be evaluated by using them to solve the constitutive model and comparing the viscosity predictions. The transient shear viscosity predictions of these possible solutions at a shear rate of 0.01 s\(^{-1}\) are shown in Figure 4.20. As the figure shows, the best fit solution can be achieved using the Hybrid/A\(_2\) or Linear/A\(_2\) combination; the other four combinations over-predict the shear viscosity. While the viscosity predictions of the Hybrid/A\(_2\) and Linear/A\(_2\) combinations are nearly identical, the predictions of CNF orientation are very different. Figure 4.21, which is a plot of the predicted value of the orientation tensor component \(a_{11}\) (the direction of shear) as a function of strain at a shear rate of 10 s\(^{-1}\), shows that using the hybrid closure approximation the value of \(a_{11}\) approaches a steady state value of \(~0.87\) while when using the linear closure approximation a steady state value of \(a_{11}\) of \(~0.33\) is predicted. This demonstrates that the hybrid closure approximation predicts the alignment of the CNFs in the direction of flow while the linear closure model predicts the CNFs will remain randomly oriented. The experimentally observed trend that the difference between the viscosities of the composites and the pure polymer decreases as shear rate increases indicates that alignment of the CNFs in the direction of shear, which reduces the hydrodynamic drag on the particles and thus the viscosity of the composite, is likely occurring. Thus the best fit of the constitutive model to the experimental measurements is achieved when the hybrid closure approximation, shape factor A\(_2\) and

\[ C_I = \left[ \frac{-0.0076 \ln(\dot{\gamma}) + 0.0385}{0.1876} \right]^{1/0.5006} \] are used.
Equations (4.1)-(4.4) were solved using these best fit parameters and those presented in Table 4.3 in order to predict the transient shear viscosity of the melt blended composite samples at shear rates ranging from 0.01-10 s$^{-1}$. Figure 4.22 shows model predictions of the transient viscosities of MB0, MB2, MB5 and MB10 composites compared to the experimentally measured values. From this comparison we can conclude that the model successfully captures the transient shear rheological behavior and viscosity magnitude of the composites for the CNF concentrations and shear rates used in this study. Like the experimental measurements, the shear viscosity is predicted to increase with increasing mass concentration and decrease with increasing shear rate.

4.5 Conclusions

In this chapter, we experimentally measured the transient shear rheology of melt blended and solvent cast CNF/PS composites and observed the effects of CNF loading and length. We found that inter-particle interactions play a large role in determining the rheological properties of the composites, especially at low shear rates. The evidence for the importance of the inter-particle interaction was seen during tests performed on SC10 composites which measured the viscosity during the startup of steady shear. We observed an increase in the strain at which the stress overshoot peak occurred with increasing shear rate. As shear rate increased the widths of the overshoot also became narrower. Both effects were due to inter-particle interactions. The effect of CNF length was seen when MB and SC composites with the same CNF concentrations were sheared and the SC composites had a larger stress overshoots than the MB composites. The only difference
was the SC samples had longer carbon nanofibers than the MB composites, demonstrating that longer nanofibers create more shear stress.

We employed the microstructurally based constitutive model to predict the transient shear behavior of CNF/PS melt composites. We proposed that there is one fitting parameter: the Folgar-Tucker inter-particle interaction parameter $C_I$ and evaluated its effects on the model predictions. We also evaluated several definitions of the material constants $A$, $B$, $C$, and $F$ and the closure approximation in order to determine which was most appropriate. We found that $C_I$ could be expressed as a function of shear rate but was independent of CNF concentration. Overall, the model was able to capture the magnitudes and locations of the stress overshoots and steady state viscosity plateaus over a range of CNF concentrations and shear rates.
Table 4.1 Properties of the melt blended and solvent cast composites.

<table>
<thead>
<tr>
<th></th>
<th>Melt Blended (MB) Composites</th>
<th>Solvent Cast (SC) Composites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MB2</td>
<td>MB5</td>
</tr>
<tr>
<td>CNF average length (L), μm</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>CNF average diameter (D), μm</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>CNF aspect ratio, r</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>CNF density, kg/l</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td>PS density, kg/l</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>1/r²</td>
<td>0.00092</td>
<td></td>
</tr>
<tr>
<td>1/r</td>
<td>0.030</td>
<td></td>
</tr>
<tr>
<td>Fiber mass fraction</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Fiber volume fraction, ϕ</td>
<td>0.012</td>
<td>0.029</td>
</tr>
<tr>
<td>Regime</td>
<td>Semidilute</td>
<td>Semidilute</td>
</tr>
</tbody>
</table>
Table 4.2 Expressions of material constants A, B, C and F as functions of aspect ratio and particle concentration.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>A_1</td>
<td>A_2</td>
<td>A_3</td>
<td>A_4</td>
</tr>
<tr>
<td>B</td>
<td>( \frac{6 \ln(2r) - 11}{r^2} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>( \frac{3r^2}{\ln(2r) - 0.5} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\[
A_1 = \frac{r^2}{2\ln(2r) - 1.5} \\
A_2 = \frac{r^2}{3\ln(\sqrt{\pi/\phi})} \\
A_3 = \frac{16r^2}{3\ln\left(\frac{1}{\phi}\right)}\left[1 - \frac{\ln\ln\left(\frac{1}{\phi}\right)}{\ln\left(\frac{1}{\phi}\right) + 0.6344}\right] \\
A_4 = \frac{16r^2}{3\left[\ln\left(\frac{1}{\phi}\right) + \ln\left(\frac{1}{\phi}\right) + 1.4389\right]} 
\]
Table 4.3 Optimized values of $\eta_p$, $\lambda$ and $\alpha$ for the four-mode Giesekus model.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\eta_p$</th>
<th>$\lambda$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>306</td>
<td>2.00</td>
<td>0.001</td>
</tr>
<tr>
<td>2</td>
<td>3524</td>
<td>2.64</td>
<td>0.374</td>
</tr>
<tr>
<td>3</td>
<td>3481</td>
<td>0.47</td>
<td>0.313</td>
</tr>
<tr>
<td>4</td>
<td>2474</td>
<td>0.08</td>
<td>0.994</td>
</tr>
</tbody>
</table>
Figure 4.1 Scanning electron microscopy image of as-received carbon nanofibers.
Figure 4.2 Transmission electron microscopy image showing the dispersion of carbon nanofibers in (a) melt blended and (b) solvent cast composites.
Figure 4.3 Optical microscopy images of carbon nanofibers from (a) melt blended and (b) solvent cast composites used to determine the fiber aspect ratio.
Figure 4.4 Transient shear viscosities vs. time at several constant shear rates for (a) SC0 and (b) SC10 composites. Corresponding shear rates are shown in the legend.
Figure 4.5 Reduced stress at the startup of constant shear for several shear rates for (a) SC0 and (b) SC10 samples. Corresponding shear rates are shown in the legend.
Figure 4.6 Reduced stress as a function of strain at startup of constant shear at a shear rate of $1 \text{s}^{-1}$ for (a) MB and (b) SC composites at nanofiber concentrations of 0, 2, 5, and 10 wt%.
Figure 4.7 Reduced stress as a function of time for (a) SC0 and (b) SC10 samples at a shear rate of 1 s⁻¹. Samples were initially sheared in a counterclockwise direction then in a clockwise direction following various amounts of rest time.
Figure 4.8  Effect of pre-shear on the transient shear stress of (a) SC0 and (b) SC10 samples at a shear rate of 1 s$^{-1}$. Samples were initially sheared in a counterclockwise direction then in either a clockwise or counterclockwise direction following various amounts of rest time.
Figure 4.9 The orientation of a single fiber in three dimensions described by vector $\mathbf{p}$. 
Figure 4.10 Model predictions of steady state shear viscosity of a polymer with $\alpha = 0.5$; $\lambda = 1$; and $\eta_p = 3,000; 10,000$ or $30,000$. 
Figure 4.11 Model predictions of steady state shear viscosity of a polymer with $\eta_p = 10,000$; $\alpha = 0.5$; and $\lambda = 0.1$, 1 or 10.
Figure 4.12 Model predictions of steady state shear viscosity of a polymer with $\eta_p = 10,000$; $\lambda = 1$ and $\alpha = 0.25, 0.5$ or $0.75$. 
Figure 4.13 Model predictions of (a) transient shear viscosity and (b) the orientation tensor component $a_{11}$ of a composite containing 2 wt% CNF using the hybrid closure approximation; $A = \frac{r^2}{3\ln(\sqrt{\pi/\phi})} ; \; B = C = F = 0 ; \; \sigma = 1 ; \; \eta_p = 10,000 ; \; \lambda = 1 ; \; \alpha = 0.5 ; \; r = 50$ and $C_l = 0.9 , 0.1 \text{ or } 0.01$. 
Figure 4.14 Model predictions of transient shear viscosity of a composite containing 2 wt% CNF using the hybrid closure approximation; \( A = \frac{r^2}{3 \ln(\sqrt{\pi/\phi})} \), \( B = C = F = 0; \sigma = 1; \eta_p = 10,000; \lambda = 1; \alpha = 0.5; C_I = 0.1 \) and \( r = 10, 50 \) or 100.
Figure 4.15 Model predictions of transient shear viscosity of a composite containing 2 wt% CNF using the hybrid closure approximation: $A = \frac{r^2}{3\ln(\sqrt{\pi/\phi})}$, $B = C = F = 0$; $\eta_p = 10,000$; $\lambda = 1$; $\alpha = 0.5$; $C_i = 0.1$; $r = 50$ and $\sigma = 1, 0.75, 0.5 \text{ or } 0.25$. 

\begin{align*}
&\sigma = 1, \\
&\sigma = 0.75, \\
&\sigma = 0.5, \\
&\sigma = 0.25.
\end{align*}
Figure 4.16 Experimentally measured values of the steady state shear viscosity of MB0 compared to (a) one-mode and (b) four-mode model predictions.
Figure 4.17 Comparison of the four-mode model transient viscosity predictions with the experimentally measured values of MB0 at shear rates ranging from 0.01-10 s\(^{-1}\). Corresponding shear rates are shown in the legend.
Figure 4.18 The average value of $a_{ijkl}$ (points) needed in the constitutive model to exactly predict the steady state shear viscosity of the MB2, MB5 and MB10 composites when using the shape factor definitions (a) A₂, (b) A₃ and (c) A₄. An equation to describe the dependence of $a_{ijkl}$ on shear rate was found for each shape factor and the equation predictions are shown as lines in the graphs.
Figure 4.18 continued

\[ a_{\text{obj}} = -0.0013 \ln(\gamma) + 0.0064 \]

Shear Rate (s\(^{-1}\))

(c)
Figure 4.19 The value of $a_{ijkl}$ (points) predicted by the (a) hybrid, (b) quadratic and (c) linear closure approximations for different values of $C_I$. An equation to describe the dependence of $a_{ijkl}$ on $C_I$ was found for the hybrid and linear closure approximations and the equation predictions are shown as lines in the graphs.
Figure 4.19 continued

\[ a_{ul} = -0.0009 C_f + 0.0748 \]
Figure 4.20 A comparison of model predictions to experimental measurements of transient shear viscosity at a shear rate of 0.01 s\(^{-1}\) using the (a) hybrid and (b) linear closure approximations and shape factors A\(_2\), A\(_3\) and A\(_4\).
Figure 4.21 A comparison of the predictions of the orientation tensor component $a_{11}$ at various values of strain using the quadratic and linear closure approximations and the shape factor $A_2$. 
Figure 4.22 Model predictions of transient shear viscosity compared to experimental measurements for (a) MB2, (b) MB5 and (c) MB10 composites over the shear rate range 0.01-10 s⁻¹.
Figure 4.22 continued

(c)
CHAPTER 5

MEASUREMENT OF CARBON NANOFIBER ORIENTATION

5.1 Introduction

As seen in Chapters 3 and 4, the rheological response of polymer/nanoparticle composites depends a great deal on the orientation of the nanoparticles in three dimensional space. In addition, composite performance properties such as electrical conductivity, thermal conductivity and tensile strength are also affected by nanoparticle orientation. The constitutive model presented in Chapters 3 and 4 predicts the evolution of the average nanoparticle orientation during flow of the composite in the melt state. If the dependence of composite properties on nanoparticle orientation and nanoparticle orientation on flow strength and type are both known then it would be possible to design processes that create composites with the desired properties. In this chapter a novel method for experimentally measuring the three dimensional orientation of carbon nanofibers is presented which can be used to validate the predictions of the constitutive model. In the past several researchers have presented descriptions of the two dimensional orientation of carbon nanofibers however this is the first time, to the authors knowledge, that a method to measure the orientation of carbon nanofibers in three dimensions has been presented.
The form and function of the orientation tensor will be described as well as the theory behind its experimental measurement. It will also be shown how ‘virtual composite samples’ with a known fiber orientation distribution were created in AutoCAD and the orientation measurement technique was applied to both validate and optimize the method. Finally, the method will be applied to real samples and the orientation tensor will be calculated for samples that have undergone a controlled extensional deformation. The results will be compared with what is predicted from the constitutive model.

5.2 The Orientation Tensor

As mentioned in the preceding chapters, a useful means of describing the average orientation of a large ensemble of anisotropic particles is the orientation tensor. In order to better understand the three-dimensional orientation tensor we will begin by examining the orientation of a single fiber in three dimensions. Figure 5.1 shows a single fiber oriented in space described by the unit vector \( \mathbf{p}(\theta, \phi) \). The orientation vector \( \mathbf{p} \) of a single fiber in three-dimensional space can be expressed using two Eulerian angles, \( \theta \) and \( \phi \), as the components along the reference axes as follows:

\[
\mathbf{p} = (p_1, p_2, p_3) = (\cos \theta \sin \phi \sin \theta, \cos \phi \sin \theta )
\]  

(5.1)

If a large group of fibers is being considered, each fiber’s orientation can be described by angles \( \theta \) and \( \phi \) set to the same arbitrary frame of reference. The average orientation of all of these fibers is then described by a continuous probability distribution function (PDF), \( \psi(\theta, \phi) \), where the probability \( P \) that a fiber is oriented in the region bounded by the angles \( \theta_i \) and \( \theta_i + d\theta \) and \( \phi_i \) and \( \phi_i + d\phi \) is:
\[ P(\theta_i \leq \theta \leq \theta_i + d\theta, \phi_i \leq \phi \leq \phi_i + d\phi) = \psi(\theta, \phi) \sin \theta d\theta d\phi \]  \hspace{1cm} (5.2)

with every fiber described by some angle pair \((\theta, \phi) \in S^2\), where \(S^2\) is the surface of a unit sphere. The integral of the distribution function over \(S^2\) must equal one:

\[ \int \int_{\theta=0}^{2\pi} \int \int_{\phi=0}^{2\pi} \psi(\theta, \phi) \sin \theta d\theta d\phi = 1 \]  \hspace{1cm} (5.3)

Using these definitions of \(\psi\) and \(\psi(p)\) we can define second order and fourth order orientation tensors as the dyadic product of fiber orientation, \(p\), with itself averaged over the orientation space containing a sufficient number of particles as follows \cite{113}:

\[ a_{ij} = \int p_i p_j \psi(p) dp \]  \hspace{1cm} (5.4)

\[ a_{ijkl} = \int p_i p_j p_k p_l \psi(p) dp \]  \hspace{1cm} (5.5)

Combining Equation (5.1) with Equation (5.4) the second order orientation tensor can be described in terms of angles \(\theta\) and \(\phi\) by:

\[ a_{ij} = \begin{pmatrix}
\cos^2 \theta & \sin \theta \cos \theta \sin \phi & \sin \theta \cos \theta \cos \phi \\
\sin \theta \cos \theta \sin \phi & \sin^2 \phi \sin^2 \theta & \sin \theta \sin \phi \cos \phi \\
\sin \theta \cos \theta \cos \phi & \sin \theta \sin \phi \cos \phi & \cos^2 \phi \sin^2 \theta 
\end{pmatrix} \]  \hspace{1cm} (5.6)

As Equation (5.6) demonstrates, if \(\theta\) and \(\phi\) are known for a given fiber then its orientation in three dimensions can be described using the second degree orientation tensor, \(a_{ij}\). For a nanocomposite system it is necessary to have an orientation tensor that describes the average orientation of all fibers. This can be done by averaging the Eulerian angles of a sufficiently large number of nanofibers and calculating the orientation tensor.
from the average angles. In the case of real nanocomposite systems the orientation of hundreds of nanofibers are typically measured.

5.3 Experimental Theory and Technique

As shown in the previous section, a second degree orientation tensor capable of describing the three-dimensional orientation state of the nanofibers contained in a polymer composite can be calculated by measuring and averaging two angles, \( \theta \) and \( \phi \), for a sufficiently large number of fibers. The three-dimensional orientation of CNFs in a composite system can be experimentally measured through the analysis of the orientation and length of CNFs seen in a two dimensional TEM image. To understand this concept, first imagine a thin slice of a composite material is taken in the x-y plane as illustrated in Figure 5.2. Viewing this slice along the z-axis with a TEM allows the Euler angle \( \phi \) of every fiber visible to be directly measured by defining \( \phi \) as the angle a fiber makes with the x-axis.

Because TEM images are two-dimensional, the determination of the out-of-plane angle \( \theta \) is not as straightforward as was the determination of \( \phi \). In order to calculate \( \theta \), it is necessary to slice the composite thin enough so that all, or nearly all, of the fibers within the slice are cut on the two opposing faces of the slice. If every fiber is cut on both ends the angle \( \theta \) can be calculated by measuring the projected length of the fiber seen on the TEM micrograph using the following equation:

\[
\theta = \tan^{-1}\left( \frac{l}{h} \right) \tag{5.7}
\]
where \( l \) is the measured projected length of the fiber and \( h \) is the thickness of the slice. As the projected length of the fiber increases the out-of-plane angle \( \theta \) also increases. Figure 5.3 illustrates this method of determining \( \theta \).

One potential difficulty with slicing the composite perpendicular to the direction of flow is that as the fibers become aligned in the direction of flow the projected length decreases until all that remains to be seen is the cross section of the fiber. Since it was anticipated that flow of the composite would result in alignment of the fibers with the direction of flow we attempted to limit the number of fiber cross-sections seen by slicing samples at an angle, \( \alpha \), greater than 0° from the y-axis as illustrated in Figure 5.4. Taking slices at an angle, \( \alpha \neq 0^\circ \), an orientation tensor is calculated describing fiber position in the coordinate system labeled \( x_n-y_n-z_n \) in Figure 5.4. In order to calculate the orientation tensor for the \( x-y-z \) coordinate system the angles \( \theta \) and \( \phi \) must be adjusted to the correct reference plane using the following equations [142]:

\[
\theta = \cos^{-1} \left( \sin \alpha \sin \theta_n \sin \phi_n + \cos \alpha \cos \theta_n \right) \tag{5.8}
\]

\[
\phi = \tan^{-1} \left( \frac{\cos \alpha \sin \theta_n \sin \phi_n - \sin \alpha \cos \phi_n}{\sin \theta_n \cos \phi_n} \right) \tag{5.9}
\]

where \( \theta_n \) and \( \phi_n \) are angles measured from the TEM images in the \( x_n-y_n-z_n \) reference frame and \( \theta \) and \( \phi \) are angles in the \( x-y-z \) reference frame. The diagonal components of the 3D orientation tensor, \( a_{11} \), \( a_{22} \) and \( a_{33} \) for each fiber were calculated from:

\[
a_{11} = \cos^2 \theta \tag{5.10}
\]

\[
a_{22} = \sin^2 \phi \sin^2 \theta \tag{5.11}
\]
where the subscripts 11, 22 and 33 refer to orientation in the z, y and x directions, respectively, as identified in Figure 5.2.

One source of error with this method is that because it is impossible to distinguish between the fiber ends exiting the top and bottom surfaces of the slice, a fiber oriented at angle $\phi$ will look exactly the same as one that is oriented at $\phi + 180^\circ$. When the slicing angle $\alpha = 0^\circ$, this is not an issue because, substituting into Equations 5.8 and 5.9, $\theta = \theta_n$ and $\phi = \phi_n$, and when calculating the diagonal orientation tensor components using Equations (5.10)-(5.12) we find $\cos^2(\phi) = \cos^2(\phi + 180^\circ)$ and $\sin^2(\phi) = \sin^2(\phi + 180^\circ)$. However, since we will be taking slices at an angle other than $\alpha = 0^\circ$, the orientation of the fibers in the $x_n$-$y_n$-$z_n$ slicing plane of Figure 5.4 are not the same as those in the $x$-$y$-$z$ coordinate system. To illustrate this mathematically, first assume we slice a sample at an angle $\alpha = 70^\circ$ and within that slice we see a fiber that has a calculated out-of-plane angle $\theta_n = 10^\circ$ and the in-plane angle is either $\phi_n = 90^\circ$ or $\phi_n = 270^\circ$. If we assume that $\phi_n = 90^\circ$ then using Equation (5.8) we find that $\theta = 60^\circ$ and using Equation (5.9) $\phi = 90^\circ$. If we assume that $\phi_n = 270^\circ$ then using Equation (5.8) we find that $\theta = 80^\circ$ and using Equation (5.9) $\phi = 90^\circ$. This difference in orientation is illustrated in Figure 5.5 Calculating the orientation tensor components $a_{11}$, $a_{22}$ and $a_{33}$ using Equations (5.10)-(5.12) we find that when $\phi_n = 90^\circ$: $a_{11} = 0.25$, $a_{22} = 0.75$ and $a_{33} = 0$, and when $\phi_n = 270^\circ$: $a_{11} = 0.03$. \[ a_{33} = \cos^2 \phi \sin^2 \theta \] (5.12)
$a_{22} = 0.75$ and $a_{33} = 0$. This illustrates that even if two fibers appear identical on the TEM micrograph they may have two very different orientations. The decision as to which fiber end is the top and which is the bottom plays a significant role in what the final orientation tensor calculated will be.

5.4 Computer Generated Sample Analysis

There are two key variables in this method of measuring the three-dimensional orientation tensor: the slice thickness and the angle of cut. The slice must be thick enough so that there is a distribution of fiber lengths; if the slice is too small all fibers will appear as very small and it will be hard to distinguish the fiber angle and length, both of which are necessary for accurate orientation calculations. If the slice is too thick, the fibers will not be cut on two ends invalidating the calculations of $\theta$ from Equation (5.7). The angle of cut must be chosen so that there are few nanofiber cross sections within the TEM image, therefore angles of cut greater than $0^\circ$ are desirable, especially in instances where fibers are highly aligned in the direction perpendicular to the plane of the cut. Angles of cut close to $90^\circ$ are also not desirable because if the nanofibers become highly aligned in the direction of flow the slice will be taken in a plane parallel to the flow direction and it will be less likely that the fibers will be cut on two ends and the calculation of angle $\theta$ will be flawed.

Determination of the ideal slice thickness and cut angle using real composite samples would be time consuming since the composite sample would need to be fabricated, the samples would have to be cut at a number of different thicknesses and
angles, and TEM images of the samples would have to be analyzed. Even if time was not a factor the true orientation of the fibers would be unknown and therefore it would not be possible to determine which preparation conditions produce the most accurate results. In order to solve this problem, several virtual nanofiber distributions were created in a specified volume using AutoCAD to simulate a nanofiber reinforced composite where the number of fibers and their 3D orientation are known precisely. These virtual samples, an example of which is shown in Figure 5.6, were then “sliced” into several sections with thicknesses ranging from 200 to 500 nm. The samples were also cut at four different angles to estimate the effects on measurement accuracy. Measurements of $\theta$ and $\phi$ could be performed using the previously described method and compared with the known orientation of the sample and the optimum slicing parameters could be determined. This virtual sample could also be used to determine if the inability to differentiate between a fiber oriented at $\phi$ or $\phi + 180^\circ$ would impair the accuracy of the technique.

An example of one of the virtual slices can be seen in Figure 5.7. Once the virtual slices were prepared, the virtual nanofibers were digitized in AutoCAD by drawing straight lines that joined the two ends of each nanofiber projection. The image was placed in a template so that the baseline for the measurement of angle $\phi$ was aligned with the reference frame of the simulated image. An AutoLISP code was used to collect all the digitized data which consisted of the length (used to calculate $\theta_n$) and in-plane angle $\phi_n$ of each nanofiber in the composite slice. Using this data the out-of-plane inclination angle $\theta$ was calculated using Equation (5.8) and the in-plane angle $\phi$ was calculated using
Equation (5.9). The orientation tensor $a_{ij}$ represented in Equation (5.6) was then calculated using the values of $\theta$ and $\phi$.

5.4.1 TEM Slice Thickness Analysis

As mentioned previously, the effects of slice thickness on the accuracy of the orientation tensor calculations was investigated by slicing the virtual samples into thicknesses of 200, 300 and 500 nm. Slices greater than 500 nm were not considered because as the slice becomes larger it is more difficult to view with a TEM because the TEM operates by passing electrons through the sample. As the slice increases in thickness the number of electrons able to pass from the electron source through the sample and onto a detector decreases, thus the contrast between the polymer matrix and nanofibers also decreases making it difficult to identify nanofibers. The lower limit was set to be the diameter of the nanofibers.

The diagonal tensor component values ($a_{11}$, $a_{22}$, $a_{33}$), calculated from the image analysis data, were compared with the predetermined values in order to evaluate accuracy. Figure 5.8 compares the experimentally measured values of the diagonal tensor components (solid lines) with the predetermined values of the diagonal tensor components (dashed lines) as a function of slice thickness. It is evident from the figure that 200 nm thick slices provide the best match to the actual values of the orientation tensor.
5.4.2 Angle of Cut Analysis

The optimum angle of cut was determined by making 200 nm thick slices (found to be the ideal slice thickness) at $\alpha$ angles of $20^\circ$, $50^\circ$, $60^\circ$ and $70^\circ$ as shown in Figure 5.4. The $20^\circ$ and $70^\circ$ angles of cut are the limits the microtome knife can be tilted to provide a proper cut of real samples. Figure 5.9 compares the experimentally measured values of the diagonal tensor components (solid lines) with the predetermined values of the diagonal tensor components (dashed lines) as a function of cut angle. As the figure demonstrates, the calculated values become more accurate as the angle of cut increases with a $70^\circ$ angle of cut providing the most accurate results. From both the slice thickness and angle of cut analyses it appears that the results are not significantly affected by the inability to determine if a fiber is oriented at an angle of $\phi$ or $\phi + 180^\circ$.

5.5 Real Composite Orientation Analysis

The orientation tensor measurement method presented in the previous sections is applied to actual carbon nanofiber composite samples prepared in the lab. Composite samples were subjected to uniaxial extension at a constant extension rate of 0.1 s$^{-1}$ and orientation tensors were measured at total strains of 0, 0.1, 1 and 3. This experiment was performed to demonstrate the ability of the measurement theory to be applied to a real system and to compare the experimentally measured values of orientation to the orientation predicted by the Folgar-Tucker equation which was presented in Chapters 3 and 4 as Equations 3.4 and 4.4, respectively.
5.5.1 Materials

Polystyrene (PS) supplied by Chevron Phillips Chemical Company LP (MC3600) was used as received in this study. The PS has a specific gravity of 1.03, melt flow rate of 13.0 g/10min (200°C/5kg, method: ASTM D1238). The carbon nanofibers used in this study are Pyrograf III (type PR-24-PS) made by Applied Sciences.

5.5.2 Composite Sample Preparation

A DACA microcompounder, at a temperature of 200°C and a screw rotation rate of 250 rpm, was used to disperse the carbon nanofibers in the polystyrene matrix at a ratio of 2 wt% CNF. Each batch was mixed for four minutes before being extruded from the microcompounder. The composite material emerged from the micro-compounder in the melt phase in the form of strands ~1 mm in diameter which were cooled and cut into 1 mm long pellets that were compression molded into rectangular bars, 52 mm long, 7 mm wide and 1.55 mm thick for use as elongational flow test specimens. A mold containing the composite pellets was placed in a 200°C press for 15 minutes to allow the pellets to melt. After 15 minutes, pressure was quickly applied and released four times in order to release air bubbles trapped within the molten composite. The pressure was reapplied and held for ten minutes to lock in the shape of the samples, after which the heat supplied to the press was turned off. The temperature of the sample was allowed to fall below 100°C, the glass transition temperature of the polymer. Once the sample cooled the pressure was released and the samples were removed from the mold. They
were placed in a vacuum oven at 70°C for at least 24 hours to ensure that they did not absorb any moisture from the surrounding air.

The samples were cut with a diamond knife in an instrument called an ultramicrotome at a 70° angle of cut to a thickness of 200 nm, both quantities determined from the virtual sample analysis to give the most accurate results. The slices were placed on a copper grid and viewed with a TEM using a FEI Technai G2 Spirit. The TEM was operated at 120 kV with a resolution of 0.2 nanometers.

5.5.3 Sample Deformation in Extensional Flow

The test specimens were subjected to uniaxial extension using a RME rheometer from Rheometrics Scientific. The samples were allowed to melt at 170°C for 15 minutes after which they were stretched to a total strain of 0.1, 1.0 or 3.0 at a constant extension rate of 0.1 s⁻¹. One of the samples was kept undeformed to provide information on the initial orientation of the test bars. Each sample was cut with an ultramicrotome at an angle of 70° relative to the stretching direction and to a thickness of 200 nm. The nanofibers in the TEM micrographs were digitized in AutoCAD and the fiber length and in-plane angle distributions were used to calculate an orientation tensor at each strain following the orientation measurement procedure described in this Chapter. An example of a TEM micrograph and the digitized version are shown in Figures 5.10a and 5.10b, respectively.

The experimentally measured values of the orientation tensor component $a_{11}$ are given in Table 5.1 and a plot of those values are shown in Figure 5.11. This component
was chosen to be analyzed since it describes the orientation of the nanofibers in the
direction of flow. As described previously, as the fibers become more aligned in the
direction of flow the value of $a_{11}$ approaches 1. Upon examination of Figure 5.11 there
are several statements that can be made about the orientation evolution of the nanofibers.
First, the initial orientation of the nanofibers is not completely random as the value of $a_{11}$
is 0.586 at a strain of 0; recall that if the orientation was random completely random
$a_{11} = a_{22} = a_{33} = 0.33$. One possible explanation for this is that when the samples are
compression molded from the composite pellets those pellets may have their own micro-
scale orientation. The process of extruding the pellets from the microcompounder may
create enough flow to align the fibers in the direction of flow. Therefore, while the
overall orientation in the sample may be random, the area analyzed in the TEM image is
very small (~20 μm × 20 μm) and may only describe the orientation of the fibers in one
of the pellets thus resulting in the measurement of a non-random orientation. It is
believed that the flow process tends to create a more uniform orientation of the
nanofibers and therefore these zones of dissimilar orientation will not be seen as the
amount of strain applied increases.

Another conclusion that can be drawn from the analysis of Figure 5.11 is that as
strain increases the alignment of the fibers in the direction of flow also increases, i.e. the
value of $a_{11}$ approaches a value of 1. The value of $a_{11}$ does not change greatly from a
strain of 1 to a strain of 3 indicating that the changing fiber orientation has reached a
steady state. Due to the fact that the samples become very narrow during extensional flow
we were unable to collect any samples beyond a strain of 3 for the purpose of orientation
analysis therefore we could not determine that this was in fact the true steady state or if
the nanofiber alignment could be further improved.

5.5.4 Folgar-Tucker Equation Predictions

The constitutive model presented in Chapters 3 and 4 contained the equation

$$\frac{d a_{ij}}{dt} = \left( W_{i} a_{ij} - a_{i} W_{j} \right) + \chi \left( D_{i} a_{ij} + a_{i} D_{j} - 2D_{ij} a_{i} \right) + 2D_{r} \left( \delta_{ij} - ma_{ij} \right)$$  \hspace{1cm} (5.13)

which describes the evolution of the orientation tensor, $a_{ij}$, during flow. As mentioned
earlier $W_{ij}$ and $D_{ij}$ are the skew and symmetric parts of the Eulerian velocity gradient,
respectively. For extensional flows:

$$W_{ij} = 0$$  \hspace{1cm} (5.14)

$$D_{ij} = \begin{bmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon}/2 & 0 \\ 0 & 0 & -\dot{\varepsilon}/2 \end{bmatrix}$$  \hspace{1cm} (5.15)

where $\dot{\varepsilon}$ is the extension rate. As suggested by Folgar and Tucker [101] $D_{r}$ is the rotary
diffusivity due to Brownian motion defined as $D_{r} = 2C_{f} \Pi_{D}^{1/2}$ where $\Pi_{D}$ is the second
invariant of the symmetric part of the velocity gradient, $D_{ij}$. For uniaxial extensional
flow $\Pi_{D} = -\frac{3\dot{\varepsilon}^2}{4}$, therefore $D_{r} = C_{f}\dot{\varepsilon}\sqrt{3}$. $C_{f}$ is the hydrodynamic particle-particle
interaction parameter which measures the intensity of a nanofiber’s interaction with the
fibers surrounding it and $\chi$ is a shape parameter related to the particle aspect ratio, $r$,
through:
\[ \chi = \frac{r^2 - 1}{r^2 + 1} \]  

(5.16)

It should also be noted that the fourth order orientation tensor \( a_{ijkl} \) is present and must be solved for using a closure approximation. In this case we choose the hybrid closure approximation which is given by:

\[ a_{ijkl} = (1 - f) \hat{a}_{ijkl} + f \tilde{a}_{ijkl} \]  

(5.17)

where

\[ f = 1 - 27 \det(a_{ij}) \]  

(5.18)

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

(5.19)

\[ \tilde{a}_{ijkl} = a_{ij} a_{kl} \]  

(5.20)

In uniaxial extensional flow there are only three non-zero components of the orientation tensor, \( a_{11}, a_{22}, a_{33} \), therefore a solution to the Folgar-Tucker equation can only be solved by solving for the non-zero orientation tensor components simultaneously.

Substituting into Equation (5.13) the definitions of \( W_{ij}, D_{ij}, D_r, \chi \) and \( a_{ijkl} \) we find

\[ \frac{da_{11}}{dt} = 2\sqrt{3} C_1 \dot{\varepsilon} \left( 1 - 3a_{11} \right) + 2 \chi \dot{\varepsilon} a_{11} - 2 \chi \dot{\varepsilon} \left[ \frac{27a_{11}a_{22}a_{33}}{35} + \frac{-2a_{11} - a_{22} - a_{33}}{14} \right] + \left( 1 - 27a_{11}a_{22}a_{33} \right) \left( a_{11}^2 - \frac{a_{11}a_{22} + a_{11}a_{33}}{2} \right) \]  

(5.21)
\[
\frac{da_{22}}{dt} = 2\sqrt{3}C_I \dot{\varepsilon} (1 - 3a_{22}) - \chi \dot{\varepsilon} a_{22} - 2\chi \dot{\varepsilon} \\
\begin{bmatrix}
27a_{11}a_{22}a_{33} \left( \frac{1}{35} + \frac{2a_{11} - 5a_{22} - a_{33}}{14} \right) \\
+ (1 - 27a_{11}a_{22}a_{33}) \left( a_{11}a_{22} - \frac{a_{22}^2 + a_{33}a_{33}}{2} \right)
\end{bmatrix} (5.22)
\]

\[
\frac{da_{33}}{dt} = 2\sqrt{3}C_I \dot{\varepsilon} (1 - 3a_{33}) - \chi \dot{\varepsilon} a_{33} - 2\chi \dot{\varepsilon} \\
\begin{bmatrix}
27a_{11}a_{22}a_{33} \left( \frac{1}{35} + \frac{2a_{11} - a_{22} - 5a_{33}}{14} \right) \\
+ (1 - 27a_{11}a_{22}a_{33}) \left( a_{11}a_{33} - \frac{a_{22}a_{33} + a_{33}^2}{2} \right)
\end{bmatrix} (5.23)
\]

The only unknown in Equations (5.21)-(5.23) is \( C_I \), which cannot be directly measured however it can be determined using the experimental measurements of the orientation tensor. If we assume that the orientation of the nanofibers has reached steady state at a strain of three this allows us to substitute \( \frac{da_{ij}}{dt} = 0 \) into the left hand side of Equations (5.21)-(5.23). Using the experimental measurements of the orientation tensor we find at a strain of 3, \( a_{11} = 0.940 \). Assuming: \( a_{22} = a_{33} = \frac{1 - 0.940}{2} = 0.030 \), the aspect ratio of the nanofibers (measured by optical microscopy in Chapter 4) is 33, \( \chi = \frac{33^2 - 1}{33^2 + 1} = 0.998 \), and \( \dot{\varepsilon} = 0.1 \text{s}^{-1} \), all variables in Equations (5.21)-(5.23) are defined except for \( C_I \). Making the substitutions and solving gives \( C_I = 0.029 \). The Folgar-Tucker equation can now be solved to provide predictions of the evolution of nanofiber orientation during uniaxial extensional flow by solving the set of Equations (5.21)-(5.23) using the initial conditions \( a_{11} = 0.586 \) and \( a_{22} = a_{33} = 0.207 \) (found from experimental measurements).
The predicted orientation is plotted with the measured orientation in Figure 5.12. As can be seen in this figure the predicted orientation provides good agreement with the experimental results. Like the experimental measurements the Folgar-Tucker equation predicts the orientation of the fibers to increase in the direction of flow with increasing strain and reaches a steady state around a strain value of 2. From these results we conclude that the proposed measurement technique provides reasonable estimates of the orientation state of the nanofibers and the experimental measurements are validated by predictions from the Folgar-Tucker equation.

5.6 Conclusions

In this chapter, the potential of a practical method for estimating the 3D orientation of carbon nanofibers in a polymer composite has been assessed through application to both virtual created samples and real samples. This technique is capable of reconstructing the 3D nanostructure of CNF/polymer composites from a single TEM image of a microtomed section of the nanocomposite. Parameters for the sectioning of the composite (slice angle and thickness) were optimized through a study on slices of a virtually created nanocomposite. The optimized slicing technique was then applied to a real compression molded nanocomposite to monitor changes in nanofiber orientation that occur during uniaxial extensional flow. The orientation tensors calculated from these experiments show the orientation of the CNFs became highly aligned in the direction of uniaxial extension. Our experimental observations were found to be in accordance with the nanofiber orientation tensor predictions from the Folgar-Tucker equation.
Table 5.1 Experimentally measured values of the orientation tensor component $a_{11}$ at different amounts of strain for the fibers contained in a composite sample undergoing uniaxial extension at a rate of 0.1 s$^{-1}$.

<table>
<thead>
<tr>
<th>Strain (Strain Rate = 0.1 s$^{-1}$)</th>
<th>$a_{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.586</td>
</tr>
<tr>
<td>0.1</td>
<td>0.580</td>
</tr>
<tr>
<td>1</td>
<td>0.929</td>
</tr>
<tr>
<td>3</td>
<td>0.940</td>
</tr>
</tbody>
</table>
Figure 5.1  The orientation of a single fiber in three dimensions described by vector p.
Figure 5.2  Method to determine the in-plane angle $\phi$ of a fiber by taking a thin slice of a sample and viewing with a TEM.
Figure 5.3 Side view of a TEM slice illustrating the determination of the out-of-plane angle, $\theta$, through measurement of the projected fiber length, $l$, and slice thickness, $h$. 

$l =$ projected fiber length

$h =$ slice thickness
Figure 5.4  Slicing of a sample at an angle $\alpha$, which is greater than $0^\circ$ showing the reference frame of the cut ($x_n$-$y_n$-$z_n$) and the reference frame for which deformation occurred ($x$-$y$-$z$).
Figure 5.5 Fibers with two different orientations in the x-y-z reference frame may appear to have the same orientation in the x_\text{n}-y_\text{n}-z_\text{n} reference frame due to the fact that fiber ends are indistinguishable.
Figure 5.6  AutoCAD generated virtual sample showing a three-dimensional distribution of nanofibers.
Figure 5.7 A simulated sample after cutting into slices. Red lines are drawn over the simulated fibers in order to measure the projection lengths and angles.
Figure 5.8 Experimental measurements (solid lines) of the diagonal components of the three-dimensional orientation tensor of a virtual sample with a known fiber orientation (dashed lines) taken at different slice thicknesses for the purpose of determining which slice thickness provides the most accurate measurements of the orientation components.
Figure 5.9  Experimental measurements (solid lines) of the diagonal components of the three-dimensional orientation tensor of a virtual sample with a known fiber orientation (dashed lines) taken at different angles of cut ($\alpha$) for the purpose of determining which cut angle provides the most accurate measurements of the orientation components.
Figure 5.10 TEM image of a real composite sample that (a) is unmodified and (b) contains digitized nanofibers.
Figure 5.11 Experimentally measured values of the orientation tensor component $a_{i1}$ at several values of strain for a CNF/PS composite undergoing uniaxial extension at a constant extension rate of $0.1 \text{ s}^{-1}$. 
Figure 5.12 Fogar-Tucker equation predictions of the orientation component $a_{11}$ as a function of strain (solid line) for a composite undergoing uniaxial extension at a constant extension rate of $0.1 \text{ s}^{-1}$ compared with experimentally measured values of $a_{11}$. The aspect ratio of the fibers is assumed to be 33 and $C_f = 0.029$. 
6.1 Introduction

In this Chapter we seek to improve the understanding of how nanoparticle concentration and orientation affect the uniaxial extensional flow behavior of polymer/nanoparticle composites and how the nanostructure of the particles evolves during flow. The extensional viscosities of polystyrene (PS)/carbon nanofiber (CNF) composites containing CNF concentrations of 0, 2, 5 and 10 wt% were measured over a range of extension rates. Three dimensional orientation tensors describing the state of CNF orientation at various points during extensional flow were also constructed using the measurement technique presented in Chapter 5. The constitutive model presented in Chapters 3 and 4 will be adapted to predict viscosities of the composites and the orientation evolution of the CNFs as a function of strain and strain rate for extensional flows. The process of model parameter determination will be discussed and the predictions of the optimized model will be compared with experimental results.
6.2 Experimental Procedure

6.2.1 Materials

Polystyrene (PS) supplied by Chevron Phillips Chemical Company LP (MC3600) was used as received in this study. The PS has a specific gravity of 1.03, melt flow rate of 13.0 g/10min (200°C/5kg, method: ASTM D1238). 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. Furthermore, its molecular structure is simple, with no crystalline structure present in the solid phase, which allows the nanostructure of the CNFs developed during flow in its molten phase to be preserved when cooled to its solid phase. The CNFs used in this study were Pyrograf® III (type PR-24-PS) manufactured by Applied Sciences, Inc. and were used as-received in this study. The nanofibers we obtained were in powder form consisting largely of fiber agglomerates, most of which were less than 1 mm in diameter.

6.2.2 Sample Preparation

Carbon nanofibers were dispersed in the polymer matrix by feeding PS and CNFs to a DACA Instruments twin-screw microcompounder at 200°C with a screw rotation rate of 250 rpm and were mixed for four minutes. Composites were made which contained a nanofiber concentration of 2, 5, or 10wt%. The composite samples were extruded from a 2mm die in the microcompounder and, after cooling, were cut into ~2-3 mm long pellets. PS without nanofibers underwent the same melt blending procedure in order to take into account any possible degradation (oxidation, chain breaking) that
occurs. The processing conditions used resulted in good dispersion of the nanofibers and limited the effects of polymer degradation.

The pellets formed from the melt blending procedure were compression molded using a hot press at 200°C into either 25 mm diameter disks of 0.5-1 mm thickness to be used in shear flow tests or rectangular bars 52 mm long, 7 mm wide and 1.55 mm thick for use as uniaxial extensional flow test specimens. The pellets were placed into molds and allowed to melt for 15 minutes followed by a cycle of quickly compressing and decompressing the samples four consecutive times in order to eliminate air bubbles. Pressure was then reapplied and held for 10 minutes and after that time the heat to the press was turned off and the samples were allowed to cool to below 100°C, the glass transition temperature of the polystyrene. Once cool, the pressure was released and the samples were removed from the mold. The specimens were placed in a vacuum oven at 70°C for at least 24 hrs and remained there until the time they were tested in order to prevent them from absorbing moisture or air from the atmosphere.

6.2.3 Rheological and Morphological Characterization

Shear rheology of the melt composites was measured using a strain-controlled rheometer from TA Instruments (ARES LS2) with both torque transducer (0.02 to 2,000 g cm) and normal force transducer (2 to 2,000 g). Parallel plates of 25-mm diameter were used for all shear measurements. The gap distance was kept in the range 0.9–1.2 mm for all tests. The molded disks were allowed to rest at the measurement temperature (160°C unless otherwise stated) for 15 min so the polymer could reach thermal equilibrium with
the surroundings and in order to relax any residual stress introduced by the compression molding process. Extensional rheology of the melt composites was measured using a RME rheometer from Rheometrics Scientific. The molded rectangular bars, like the disks, were allowed to rest at the measurement temperature (160°C unless otherwise stated) for 15 min so the polymer could reach thermal equilibrium with the surroundings and in order to relax any residual stress introduced by the compression molding process.

A transmission electron microscope (FEI Technai G2 Spirit) was used at 100 kV to observe the nanometer-scale CNF dispersion and structure in the composites. An optical microscope (Zeiss Axioskop) was used to observe the state of CNF length and diameter distributions at a magnification of 400x.

6.3 Experimental Results

6.3.1 CNF Morphology

One of the factors that can influence the rheological behavior of a composite is the aspect ratio of the filler particles, therefore it was important to directly measure this quantity. As-received CNFs are very long and have a very high aspect ratio, however the high shear forces used in the melt blending process which disperse the fibers in the polymer matrix also shorten the fibers. To determine the average aspect ratio of the post-melt-blended samples each type of sample (CNF concentration of 2, 5 or 10 wt%) was dissolved in THF and a small amount of each solution was placed on a glass slide and viewed under an optical microscope. An image of the nanofibers, shown in Figure 6.1, was captured using a camera attached to an optical microscope and the lengths and
diameters of thousands of nanofibers were measured by drawing digital lines, in AutoCAD, parallel or perpendicular to the major fiber axis in order to measure length or diameter, respectively, then the data was compiled using an AutoLISP program. By averaging the length and diameter of \( \sim 800 \) - 1000 CNFs the number average aspect ratio was calculated to be 33.

6.3.2 Transient Extensional Viscosity

The stress response of PS and PS/CNF composites undergoing uniaxial extension was measured at extension rates ranging from \( 0.01 \) - 1 \( \text{s}^{-1} \). The results of these experiments are shown in Figure 6.2. It is clear from the results that strain hardening occurs at Hencky strains greater than 3 for both pure polymer and the composites. The addition of nanoparticles does not appear to affect the time at which strain hardening occurs. The results also show that the extensional viscosity increases monotonically with increasing CNF concentration. This is consistent with the behavior seen in Chapters 3 and 4 where the steady state and transient shear viscosities of the nanocomposites increased with increasing nanoparticle concentration.

6.3.3 Shear Rheology

The rheological properties of the polymer matrix and the composites were also measured under dynamic oscillatory and transient shear flows. A complete discussion of the effects of CNFs on the transient shear rheology of polystyrene/CNF composites is presented in Chapter 4 therefore we will not present a thorough discussion here. In this
Chapter a different PS matrix was used than in Chapter 4 therefore it was necessary to re-measure some shear rheological properties for the purposes of modeling (which will be discussed in subsequent sections) and for comparison with the uniaxial extension behavior. Dynamic oscillatory shear and steady state shear data for the polymer matrix without CNFs was needed for modeling and transient shear data for all samples was needed for comparison with the extensional flow data. The effects of CNF addition remained the same however the magnitudes of the various quantities measured were different from those previously measured due to the differences in the properties of the polymer matrix.

6.4 Modeling

6.4.1 Constitutive Model Description

The following is a description of a constitutive model that is capable of predicting the experimentally measured rheological behavior of polystyrene/carbon nanofiber composites in extensional flow presented in the previous sections and the methods used to define the model’s parameters. As was demonstrated in Chapters 3 and 4, this model accurately predicts the rheological behavior of polystyrene/nanoclay and polystyrene/carbon nanofiber composites during steady state shear and startup of steady shear. The success of the model in predicting the shear flow behavior of polymer nanocomposites motivated the application to transient extensional flows. To review, the constitutive model is composed of the following four equations, which were presented in Chapters 3 and 4:
\[ \tau_{ij}^p = -p\delta_{ij} + 2\eta_s D_{ij} + \tau_{ij}^{\text{pD}} + \tau_{ij}^{\text{CNF}} \]  
(6.1)

\[ \sigma\tau_{ij,m}^p + \frac{D\tau_{ij,m}^p}{Dt} + \frac{\alpha_m\lambda_m}{\eta_{p,m}}(\tau_{ik,m}^p \tau_{kj,m}^p) + \frac{3(1-\sigma)}{2}(a_{ik}\tau_{kj,m}^p + \tau_{ik,m}^p a_{kj}) = 2\eta_{p,m} D_{ij} \]  
(6.2)

\[ \tau_{ij}^{\text{CNF}} = 2[\eta_s + \eta]\phi\left[AD_{kl}a_{ijkl} + B(D_{ik}a_{kj} + a_{ik} D_{kj}) + CD_{ij} + 2Fa_{ij} D_{ij}\right] \]  
(6.3)

\[ \frac{da_{ij}}{dt} = (W_{ik} a_{kj} - a_{ik} W_{kj}) + \chi\left(D_{ik} a_{kj} + a_{ik} D_{kj} - 2D_{kl} a_{ijkl}\right) + 4C_i\Pi_i^{1/2}(\delta_{ij} - 3a_{ij}) \]  
(6.4)

These equations are used to find the total stress in the composite during flow (Equation 6.1), the flow induced stress in the polymer (Equation 6.2), the flow induced stress caused by the presence of nanoparticles (Equation 6.3) and the evolution of nanoparticle orientation during flow (Equation 6.4). In Equation (6.1), proposed by Azaiez [110], the total stress (\( \tau_{ij}^p \)) of the polymer/nanocomposite system is defined as the sum of the stress contribution from polymer molecules (\( \tau_{ij}^{pD} \)), the stress contribution from the carbon nanofibers (\( \tau_{ij}^{\text{CNF}} \)), the stress contribution from a Newtonian solvent (\( 2\eta_s D_{ij} \), if present) and the pressure maintaining incompressibility (p). In the PS/CNF composite system being studied there is no solvent present therefore \( 2\eta_s D_{ij} = 0 \). Extensional viscosity is defined as:

\[ \eta_{E}^+ = \frac{\tau_{11} - \tau_{22}}{\dot{\epsilon}} \]  
(6.5)

Substituting Equation (6.1) into Equation (6.5) results in an expression for the extensional viscosity of the polymer composite as shown in Equation (6.6):

\[ \eta_{E}^+ = \frac{\tau_{11}^c - \tau_{22}^c}{\dot{\epsilon}} = \left(\frac{\tau_{11}^p + \tau_{11}^{\text{CNF}}}{\dot{\epsilon}}\right) - \left(\frac{\tau_{22}^p + \tau_{22}^{\text{CNF}}}{\dot{\epsilon}}\right) \]  
(6.6)
Equation (6.2) is the multi-mode Giesekus model [111] which predicts the strain rate-dependent viscoelastic behavior of the polymer matrix. The total polymer stress is a summation of the stress of each mode:

\[
\tau_{ij}^p = \sum_{m=1}^{N} \tau_{ij,m}^p
\]  

(6.7)

where \(N\) is the number of modes. In Equation (6.2) the upper convected derivative of \(\tau_{ij}^p\) is

\[
\frac{D\tau_{ij}^p}{Dt} = \frac{d}{dt} \tau_{ij}^p - W_{ik} \tau_{kj}^p + \tau_{ik}^p W_{kj} - D_{ik} \tau_{kj}^p - \tau_{ik}^p D_{kj}
\]  

(6.8)

where \(W_{ij}\) and \(D_{ij}\) are the skew and symmetric parts of the Eulerian velocity gradient, respectively. In extensional flows:

\[
W_{ij} = 0
\]  

(6.9)

\[
D_{ij} = \begin{bmatrix}
\dot{\varepsilon} & 0 & 0 \\
0 & -\dot{\varepsilon}/2 & 0 \\
0 & 0 & -\dot{\varepsilon}/2
\end{bmatrix}
\]  

(6.10)

where \(\dot{\varepsilon}\) is the extension rate. In extensional flow there are three non-zero components of the stress tensor (\(\tau_{11}\), \(\tau_{22}\) and \(\tau_{33}\)) therefore the solution for Equation (6.2) requires solving the three components of the stress tensor as three coupled differential equations (which are presented in Appendix C). The constants \(\eta_p\), \(\lambda\), and \(\alpha\) are the polymer viscosity coefficient, relaxation time, and mobility factor, respectively, for the polymer matrix in the melt phase. The constant \(\sigma\) is a measure of the polymer-particle interaction and is a value less than or equal to 1. For simplification the model has been solved using
\( \sigma = 1 \), however the effects of \( \sigma \) on the predictions of the model will be discussed later in the chapter. Typically the values for \( \eta_p \) and \( \lambda \) are found by fitting the equations:

\[
G'(\omega) = \sum_{m=1}^{N} \frac{\eta_{p,m} \lambda_m \omega^2}{1 + (\lambda_m \omega)^2} \tag{6.11}
\]

\[
G''(\omega) = \sum_{m=1}^{N} \frac{\eta_{p,m} \omega}{1 + (\lambda_m \omega)^2} \tag{6.12}
\]

to the experimentally measured small amplitude oscillatory shear response of the pure polymer and minimizing the error according to Equation (6.13):

\[
error = \sum_{i=1}^{N} \left\{ \log_{10} G'_{\text{exp}} (\omega_i) - \log_{10} G'(\omega_i) \right\}^2 + \left[ \log_{10} G''_{\text{exp}} (\omega_i) - \log_{10} G''(\omega_i) \right\}^2 \tag{6.13}
\]

where \( G'_{\text{exp}} (\omega_i) \) and \( G''_{\text{exp}} (\omega_i) \) are the experimentally determined values of the storage and loss modulus, \( G'(\omega_i) \) and \( G''(\omega_i) \) are the predicted values according to Equations (6.11) and (6.12), and \( N \) is the total number of experimental points. Figure 6.3 shows the experimentally measured values of storage and loss modulus vs. frequency compared to predictions from Equations (6.11) and (6.12) using best fit values of \( \eta_p \) and \( \lambda \) for single-mode (Figure 6.3a) and five-mode models (Figure 6.3b).

The remaining unknown in Equation (6.2), \( \alpha \), was determined by fitting the following equations to the experimental measurements of the steady state shear viscosity of the pure polymer as a function of shear rate:

\[
\eta(\dot{\gamma}) = \sum_{m=1}^{N} \eta_{p,m} \frac{(1 - \psi_m)^2}{1 + (1 - 2 \alpha_m \psi_m \nu_m)} \tag{6.14}
\]
\[ \psi_m = \frac{1 - \chi_m}{1 + (1 - 2\alpha_m)\chi_m} \]  \hspace{1cm} (6.15) 

\[ \chi_m = \sqrt{\frac{1 + 16\alpha_m(1 - \alpha_m)(\dot{\gamma} \dot{\lambda}_m)^2 + 2}{8\alpha_m(1 - \alpha_m)(\dot{\gamma} \dot{\lambda}_m)^2} - 1} \]  \hspace{1cm} (6.16) 

and minimizing the error according to Equation (6.17):

\[ error = \sum_{i=1}^{N} \left[ \log_{10} \eta_{\text{exp}}(\dot{\gamma}_i) - \log_{10} \eta(\dot{\gamma}_i) \right]^2 \]  \hspace{1cm} (6.17) 

where \( \eta_{\text{exp}}(\dot{\gamma}_i) \) is the experimentally determined value of the steady state viscosity, \( \eta(\dot{\gamma}_i) \) is the predicted value of viscosity according to Equations (6.14)-(6.16), and \( N \) is the total number of experimental points. Figure 6.4 shows the experimentally measured values of steady shear viscosity vs. shear rate compared to predictions from Equations (6.14)-(6.16) using best fit values of \( \alpha \) for single-mode (Figure 6.4a) and five-mode models (Figure 6.4b).

Table 6.1 summarizes the parameters determined for both the one-mode and five-mode Giesekus models. Figures 6.3 and 6.4 clearly demonstrate that a five-mode model provides a more accurate prediction of the experimentally measured small amplitude oscillatory and steady state shear rheology of the polymer melt than the one-mode model. Having determined all model parameters used in Equation (6.2) from shear flow measurements and having shown the superior predictions of the five-mode model, the extensional viscosity predictions of pure polystyrene using the five-mode Giesekus model can be compared with the experimental measurements. The results are shown in Figure 6.5. As can be seen, the model agrees well with the experimental measurements at strains.
less than one however it does not predict the strain hardening that is observed at $\gamma < 1$. Strain hardening is an important feature of the extensional viscosity and should be predicted by the model. To correct this, values for $\eta_p$, $\lambda$ and $\alpha$ were determined by fitting to the small amplitude oscillatory shear, steady state shear, and transient extensional viscosities simultaneously and minimizing the error. The intent of this global parameter fitting method was to find parameters that could provide accurate predictions of both the shear and extensional flow rheology simultaneously. The new parameters for a five-mode model fit are shown in Table 6.2.

The predictions of small amplitude oscillatory shear, steady state shear and transient extensional viscosity using the newly determined five-mode model parameters are shown in Figure 6.6. Figure 6.6c clearly demonstrates that the use of the new parameters in the model results in the prediction of strain hardening. The accuracy of the model predictions of extensional viscosity have been improved however the predictions of the storage and loss modulus and the steady state shear viscosity have decreased in accuracy when compared with the predictions made using the parameters fit to only the small amplitude oscillatory shear and steady state shear flow data. We can conclude that using five modes in the Giesekus model is more accurate than using one mode, parameters optimized for small amplitude oscillatory shear and steady shear data alone do not predict strain hardening in extensional flow, and improved predictions of extensional viscosity results in decreased accuracy in the predictions of storage and loss modulus and steady shear viscosity.
Having fully defined the behavior of the polymer we can now evaluate the contribution of the nanoparticles to the flow induced nanocomposite stress. In Equation (6.3), derived by Tucker [112], $\eta$ is the extensional viscosity of the polymer matrix (calculated from Equation (6.2)), $\phi$ is the volume fraction of the nanofibers, and $D_r$ is the rotary diffusivity due to Brownian motion defined as $D_r = 2C_I \Pi_D^{1/2}$ where $\Pi_D$ is the second invariant of the symmetric part of the velocity gradient $D_v$ and is equal to $\frac{3\varepsilon^2}{4}$ for extensional flows and $C_I$ is the hydrodynamic particle-particle interaction parameter which measures the intensity of a nanofiber’s interaction with the fibers surrounding it. The determination of $C_I$ will be discussed later in the paper. The coefficients $A$, $B$, $C$, and $F$ are shape factors that are functions of the particle aspect ratio, $h = L/D$, with $L$ the particle length and $D$ the particle diameter. As presented earlier in the paper, the aspect ratio of the CNFs in the melt blended composites was found to be 33 as determined by optical microscopy. Definitions for the shape factors have been proposed [112,116,140] for different concentration regimes (dilute or semi-dilute), states of nanoparticle orientation (isotropic or aligned), and flow conditions (transient or steady state). A summary of some of these proposed constants is given in Table 6.3. The proper selection of the shape parameters will be given later in the paper.

Equation (6.4) is the evolution equation of the second order orientation tensor, $a_y$, which is a measure of nanostructure that combines the contributions of a collection of particles that dictate the mesoscale properties of the nanocomposite. In order to clarify the concept of an orientation tensor we will first describe the orientation of one fiber in
space, shown in Figure 6.7, with the unit vector $\mathbf{p}$. The orientation vector $\mathbf{p}$ of a single fiber in three dimensional space can be expressed using two Eulerian angles, $\theta$ and $\phi$, as the components along the reference axes as follows:

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

(6.18)

In real systems, such as our composite samples which contain large numbers of fibers with a variety of fiber orientations, it is necessary to be able to describe the average fiber orientation. This is done with the use of the probability distribution function $\psi(p)$ which describes the probability of finding a fiber between angles $\theta_i$ and $(\theta_i + d\theta)$, and $\phi_i$ and $(\phi_i + d\phi)$[113]. Using these definitions of $\mathbf{p}$ and $\psi(p)$ we can define second order and fourth order orientation tensors as the dyadic product of fiber orientation, $\mathbf{p}$, with itself averaged over the orientation space containing a sufficient number of particles as follows [113]:

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

(6.19)

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

(6.20)

If we examine Equation (6.4) we see that we need to define four parameters: $D_{ij}$, $\chi$, $a_{ijkl}$ and $C_i$. $D_{ij}$, as stated previously, is related to the extension rate and therefore is defined when the extension rate being modeled is defined. $\chi$ is a shape parameter related to the particle aspect ratio, $r$, through:

$$\chi = \frac{r^2 - 1}{r^2 + 1}$$

(6.21)
The fourth order orientation tensor, $a_{ijkl}$, can be found through the use of a closure approximation which relates the fourth order tensor to the second order orientation tensor $a_{ij}$. Popular closure approximations are:

1. The linear closure approximation,

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

which works well when the fibers remain nearly random, but introduces an artificial instability into the equations for highly aligned suspensions [114].

2. The quadratic closure approximation

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

which performs well for highly aligned states, but introduces steady-state errors for more random states [114].

3. The hybrid closure approximation,

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

which mixes linear and quadratic forms according to scalar measure of orientation and performs well over the entire range of orientation [114]. The final parameter in Equation (6.4) is $C_I$, the hydrodynamic particle-particle interaction parameter, which plays a significant role in the degree of CNF orientation predicted. Determination of the proper closure approximation and value(s) of $C_I$ must be done through comparison of model predictions of nanoparticle orientation with experimental measurements of CNF orientation at various times and at various extension rates.
6.4.2 Measurement of CNF Orientation

Experimental measurements of the three-dimensional orientation tensor describing the state of orientation of the carbon nanofibers in our composite using were made using the procedure developed in Chapter 5. As mentioned previously, the orientation of a fiber in space can be described by two angles in polar coordinates, \( \theta \) and \( \phi \). In order to construct a 3D orientation tensor for the composite system the orientation angles \( \theta \) and \( \phi \) are needed for every fiber. Since measuring these two angles for every fiber in the composite is impossible, the angles of fibers in a small representative area are measured instead. Looking at Figure 6.7 we consider the z-axis to be the direction of the applied elongational flow and therefore \( \theta \) and \( \phi \) will be referred to as the out-of-plane and in-plane angles, respectively. If a sample is sliced in the x-y plane and this slice is viewed under TEM, it can be seen that the in-plane angle \( \phi \) for each fiber can easily be measured as the angle the fiber makes with the x-axis as shown in Figure 6.8.

Determination of \( \theta \) is slightly more complicated. The first step is to slice the sample with a microtome thin enough so that all fibers within the slice are cut on two ends at the opposing faces of the slice. If every fiber is cut on both ends the angle \( \theta \) can be calculated by measuring the projected length of the fiber seen on the TEM micrograph. Combining the measured fiber length with the known slice thickness, the out-of-plane angle \( \theta \) can be calculated from:

\[
\theta = \tan^{-1}\left(\frac{l}{h}\right)
\]  

(6.25)
where \( l \) is the measured projected length of the fiber and \( h \) is the thickness of the slice. As the projected length of the fiber increases the out-of-plane angle \( \theta \) also increases. Figure 6.9 illustrates this method of determining \( \theta \).

One potential difficulty with slicing the composite perpendicular to the direction of flow is that as the fibers become aligned in the direction of flow the projected length decreases until all that remains to be seen is the cross section of the fiber. Since it was anticipated that stretching flows would result in highly aligned fibers we avoided the situation of having TEM images showing only fiber cross sections by slicing samples at an angle, \( \alpha \), greater than 0° as illustrated in Figure 6.10. If slices are taken at some angle \( \alpha \neq 0° \), the orientation tensor calculated for the composite will be for the coordinate system labeled \( x_n-y_n-z_n \) in Figure 6.10. In order to calculate the orientation tensor for the \( x-y-z \) coordinate system the angles \( \theta \) and \( \phi \) must be adjusted to the correct reference plane using the following equations [142]:

\[
\theta = \cos^{-1} \left( \sin \alpha \sin \theta_n \sin \phi_n + \cos \alpha \cos \theta_n \right) \quad (6.26)
\]

\[
\phi = \tan^{-1} \left( \frac{\cos \alpha \sin \theta_n \sin \phi_n - \sin \alpha \cos \phi_n}{\sin \theta_n \cos \phi_n} \right) \quad (6.27)
\]

where \( \theta_n \) and \( \phi_n \) are angles measured from the TEM images in the \( x_n-y_n-z_n \) reference frame and \( \theta \) and \( \phi \) are angles in the \( x-y-z \) reference frame. The diagonal components of the 3D orientation tensor, \( a_{11}, a_{22} \) and \( a_{33} \) for each fiber were calculated from:

\[
a_{11} = \cos^2 \theta \quad (6.28)
\]

\[
a_{22} = \left( \sin \phi \sin \theta \right)^2 \quad (6.29)
\]
\[ a_{33} = \left( \cos \phi \sin \theta \right)^2 \]  

(6.30)

where the subscripts 11, 22 and 33 refer to orientation in the z, y and x directions, respectively.

In Chapter 5 this method was validated and the optimum slice thickness and slice angle were determined to be 200 nm and \( \alpha = 70^\circ \), respectively. Orientation tensors for 2 wt\% CNF/PS samples at extension rates of 0.01, 0.1 and 1 s\(^{-1}\) and strains of 0.1, 1, 2 and 3 were constructed from TEM micrographs using this technique. Images of the nanofibers in the TEM micrographs were digitized using AutoCAD by connecting both ends of a fiber with a straight line. An example of a raw TEM image and one with AutoCAD lines overlaying the fibers is shown in Figure 6.11. An AutoLISP code collected the length and orientation (\( \phi_n \) measured with respect to reference axis \( x_n \)) information for each digitized fiber which was then collected in Excel where the data was used to calculate angles \( \theta_n, \theta \) and \( \phi \) using Equations (6.25)-(6.27), and the orientation tensor components \( a_{11}, a_{22} \) and \( a_{33} \) using Equations (6.28)-(6.30). The average orientation tensor was found by averaging the corresponding tensor component values for all fibers measured. Figure 6.12 is a plot of the \( a_{11} \) component values found for each extension rate and strain investigated and Table 6.4 is a list of these values.

From this figure there are several points that can be made. First, the initial carbon nanofiber orientation measured was not completely random as expected which would have been indicated by diagonal components of the orientation tensor being equal to 1/3. Second, as the amount of strain applied increases the orientation of the fibers increases in the direction of the applied strain and there is a rapid increase in fiber orientation from a
strain of 0 to a strain of 1. From a strain of 1 to a strain of 3 there is only a slight increase in fiber orientation. Finally, the orientation evolution of the nanofibers is independent of extension rate over the extension rates presented here.

Concerning the first observation, there could be several reasons the measured orientation of the nanofibers was not completely random. Since the extensional flow test samples were created from pellets made in a microcompounder, the process of creating the pellets most likely induced some alignment of the nanofibers within the pellets. Because of the size of the pellets relative to the size of the molds it was difficult to totally randomize the orientation of the pellets in three dimensions therefore the test samples did not contain completely randomized nanofibers. It is also possible that the fibers within the sample were totally random however only a small area of the total sample was viewed with the TEM micrograph and the orientation of the nanofibers within that small area were not totally random.

This method of measuring nanofiber orientation was also applied to samples undergoing transient shear flow. Samples containing 2 wt% CNFs were subjected to shear rates of 0.01, 0.3 and 10 $s^{-1}$ and orientation tensor measurements were taken at strains of 0, 3 and 70. The experimentally measured values of the $a_{11}$ component (the direction of shear flow) are shown in Figure 6.13. These results are much different from those seen for extensional flow. First, as the amount of strain increases the amount of orientation in the direction of shear increases, as was seen in extensional flow, however the amount of orientation is not as great as in extensional flow. Second, nanofiber orientation in shear flow appears to be a function of shear rate. The results presented here
indicate that as shear rate decreases the amount of nanofiber orientation increases. These results are preliminary and will need to be confirmed in the future with additional measurements at different shear rates and different values of strain.

6.4.3 Application of the Model

The information contained in Table 6.4 was then used in conjunction with Equation (6.4) to calculate a value for \( C_I \). As mentioned previously, the value chosen for \( C_I \) significantly affects the predicted orientation tensor values. In order to calculate \( C_I \) it was first assumed that nanofiber orientation reached a steady state value at a strain of 3 and the value of the \( a_{11} \) component at steady state was equal to the average experimentally measured \( a_{11} \) component over all strain rates: 0.936. By substituting the steady state values of \( a_{11} = 0.936 \) and \( a_{22} = a_{33} = (1 - a_{11})/2 = 0.032 \) into Equation (6.4), choosing a closure approximation to calculate \( a_{ijkl} \), and setting the left-hand side of Equation (6.4) equal to zero (steady state), \( C_I \) becomes the only unknown and can easily be solved for. \( C_I \) was found to be 0.031, 0.029 and 0.105 for the hybrid, quadratic and linear closure approximations, respectively. Equation (6.4) allows us to predict nanofiber orientation changes during flow as a function of time. Figure 6.14 plots the predicted values of the \( a_{11} \) orientation tensor component as a function of strain compared to the experimentally measured values using the hybrid closure approximation. Two curves are shown on the graph which represent two different initial conditions: an initial value of \( a_{11} \) equal to the experimentally observed value of 0.586 and an initial value of \( a_{11} \) equal to the theoretical value of 0.333 which represents a random fiber orientation.
It can be seen from the figure that after a strain of 2 is reached both curves are nearly identical and reach the same steady state. At a strain of 1 the curve representing an initial $a_{11}$ value of 0.586 is very close to the experimentally measured values corresponding to an extension rate of 1 and 0.1 s$^{-1}$ while the curve representing an initial $a_{11}$ value of 0.333 is very close to the experimentally measured values corresponding to an extension rate of 0.01. The two points measured at a strain of 0.1 lie in-between the predicted values for the two different initial conditions. Figure 6.15 shows a comparison of the extensional viscosities predicted by the model using the shape factor $A_2$ (Table 6.3) and the hybrid closure approximation when the initial values of $a_{11}$ is either 0.586 or 0.333 for a 2wt% CNF composite undergoing uniaxial extension at a rate of 0.01 s$^{-1}$. The figure shows that the predicted viscosities are nearly identical however the predicted values are slightly higher when the initial $a_{11}$ value is 0.586. Since there is only a slight difference in the predicted viscosity values we will assume in all future calculations that the initial fiber orientation is random, thus the $a_{11}$ value is 0.333.

Having determined the appropriate values of $C_I$ for each closure approximation, the full constitutive model can be solved by choosing a closure approximation and set of shape factors. Each combination of closure approximation and shape factor (a total of twelve) was used in the model to determine which provided the most accurate predictions of extensional viscosity. It was found that the use of the shape factor $A_2$ and the hybrid closure approximation gave the least error. Plots of the model predictions compared to the experimental results are shown in Figure 6.16. From this figure it can be seen that the model qualitatively captures the rheological behavior of the composites; strain hardening
is predicted and occurs at approximately the same time as is observed experimentally. The predicted viscosities, however, are greater than the measured values and the degree of over-prediction increases with increasing CNF concentration. Experimentally, it was seen that an increase in CNF concentration led only to slight increases in the extensional viscosities of the composites.

This overprediction can be corrected in the model by changing the aspect ratio of the fibers. Since the overall stress in the composite is defined in the model as the sum of the stress contribution from the polymer (Equation 6.2) and the stress contribution from the presence of the nanofibers (Equation 6.3), and Figure 6.6c demonstrates that the stress contribution from the polymer is accurately predicted, we can conclude that the overprediction of the extensional viscosity is caused by an overprediction of the stress caused by the presence of the nanofibers. Thus, Equation (6.3) will be reevaluated to determine which parameters could be modified to improve the model predictions. Within Equation (6.3) are parameters accounting for the viscosity of the polymer ($\eta$), the volume fraction of the nanofiber ($\phi$), the extension rate ($D_{ij}$), the fourth order orientation tensor ($a_{ijkl}$), and the shape factor ($A$). The first three parameters mentioned: $\eta$, $\phi$, and $D_{ij}$, are fixed and cannot be changed. The fourth order orientation tensor is affected by the choice of closure approximation and the value of the orientation tensor $a_{ij}$ which is predicted by Equation (6.4). The predictions of extensional viscosity when the value for $a_{11}$ at steady state is close to totally random ($C_I = 0.999$) or nearly perfectly aligned in the direction of extension ($C_I = 0.0001$) are compared in Figure 6.17 for a 2wt% CNF composite at an extension rate of 0.01 s$^{-1}$ using the hybrid closure approximation. This figure shows that
there is little difference between the viscosities predicted at these two extremes of nanofiber orientation therefore changes to this parameter will not provide enough improvement to the model predictions.

The only remaining parameter is the shape factor $A$. Four definitions of $A$ were already evaluated and the best definition was chosen: $A = \frac{h^2}{3\ln\left(\sqrt{\pi} / \Phi\right)}$. Within this parameter the value of $h$, the aspect ratio, could be adjusted to provide better prediction of the viscosity. In order to determine the value of $h$ that provides the ideal fit of the model predictions to the experimental results requires several steps. First, the model predictions of the pure polymer extensional viscosities at all extension rates are subtracted from the experimentally measured values of extensional viscosity for the MB2, MB5 and MB10 composites. This determines what value for $\tau_{ij}^{CNF}$ is needed to be predicted by Equation (6.3) to have accurate model predictions. These values for $\tau_{ij}^{CNF}$ at strains between 0.1-1 were compared to those previously predicted by the model in order to determine how much the model predictions needed to be reduced. Strain values of 0.1-1 were chosen because the viscosity curves in these regions are nearly constant. By averaging the difference between the model predicted and ideal values of $\tau_{ij}^{CNF}$ for all composites, we determined that $\tau_{ij}^{CNF}$ needed to be reduced by a factor of 6.58. Therefore the new value of aspect ratio, $h_2$, can be found using the equation:

$$h_2^2 = \frac{h^2}{6.58} \quad (6.31)$$
Substituting in \( h = 33 \) and solving we find that \( h_2 = 12.86 \). This new aspect ratio can be called an ‘effective’ aspect ratio since it is not the same as the experimentally measured aspect ratio of 33. It is possible that the experimentally measured extensional viscosity of the composites is not as large as predicted by the model because there is some clumping of the nanofibers which would decrease the effective aspect ratio of the nanofibers thus this adjusted aspect ratio reflects that. Model predictions of the extensional viscosities of the MB2, MB5 and MB10 composites using the effective aspect ratio compared with the experimentally measured values are shown in Figure 6.18. As this figure shows, the use of the effective aspect ratio greatly improves the accuracy of the model predictions of extensional viscosity.

6.4.4 The Effects of Parameter Values on Model Predictions

In order to get a better understanding of how each of the parameters in the constitutive model affect the predictions of transient and steady state shear viscosity, the values for the parameters \( \eta_p, \alpha, \lambda, C_I, r \) and \( \sigma \) were varied and the model predictions were compared. Because the constitutive model defines the stress of a polymer nanocomposite as the summation of the stress contribution of the polymer and the stress contributed by the presence of nanofibers, the evaluation of these parameters was simplified by first considering those components which affected the stress contribution of the polymer only (\( \eta_p, \alpha \) and \( \lambda \)) without the addition of stress from the nanoparticles, then evaluating the remaining constants (\( C_I \) and \( r \)) which affect the predictions of the stress contribution due to the presence of the nanofibers. Note that \( \sigma \) is the polymer-particle
interaction coefficient and when $\sigma \neq 1$ the predictions of polymer viscosity are coupled to the orientation of the nanofibers, therefore this parameter was evaluated using the entire constitutive model. Until $\sigma$ is evaluated it will be assumed that $\sigma = 1$ for simplicity. For all parameters evaluated the transient extensional viscosity will be predicted using an extension rate of $1 \text{ s}^{-1}$.

First, the transient extensional viscosity of a polymer with $\eta_p=3,000; 10,000$ or $30,000$ with $\alpha = 0.5$ and $\lambda = 1$ was calculated using Equation (6.2) and the results are plotted in Figure 6.19. As this figure shows, as the value of $\eta_p$ increases the value of transient extensional viscosity also increases however the shape of the viscosity curve is the same.

Next, $\eta_p$ and $\alpha$ were held constant at a value of $10,000$ and $0.5$, respectively, and $\lambda$ values of $0.1, 1$ and $10$ were used to predict the transient extensional viscosity. These results, shown in Figure 6.20, show that as $\lambda$, the polymer relaxation time, increases, the length of time it takes to reach a plateau value also increases. This results in predictions of lower extensional viscosities at short times for polymers with longer relaxation times. At long times, polymers with longer relaxation times are predicted to have a higher viscosity.

The effects of $\alpha$ on steady shear viscosity were determined by solving Equation (6.2) with $\eta_p = 10,000; \lambda = 1$ and $\alpha = 0.01, 0.1, 0.5$ or $0.9$. These results are shown in Figure 6.21 and show that as $\alpha$ increases the extensional viscosity predicted at long times
decreases. The parameter $\alpha$ affects the amount of strain hardening predicted with lower values predicting more strain hardening.

The effects of $C_I$, $r$ and $\sigma$ were evaluated under transient extensional flow conditions for a composite containing 2 wt% CNF at a shear rate of 1 s\(^{-1}\). For the purpose of evaluating these constants the hybrid closure approximation was used as well as the shape factor definitions

\[ A = \frac{r^2}{3\ln\left(\sqrt{\pi/\phi}\right)}, \quad B = C = F = 0. \]

First, the transient shear viscosity was solved using $\eta_p = 10,000$; $\lambda = 1$; $\alpha = 0.5$; $r = 50$ and $C_I = 0.9$, 0.1 or 0.01. The results, shown in Figure 6.22a, demonstrate that as the value of $C_I$ decreases the predicted extensional viscosity increases. Figure 6.22b shows the corresponding values of the orientation tensor component $a_{11}$ (the direction of the applied extensional flow) as a function of time for each of the $C_I$ values used. As this figure demonstrates, $C_I$ significantly impacts the orientation of the carbon nanofibers predicted for a given shear flow with lower values of $C_I$ predicting higher alignment of the carbon nanofibers in the direction of the applied flow.

Next, transient extensional viscosity was calculated using $\eta_p = 10,000$; $\lambda = 1$; $\alpha = 0.5$; $C_I = 0.1$ and $r = 10, 50$ or 100. As seen in Figure 6.23, as the value of $r$ increases the predicted values of extensional viscosity also increase. The increase that is observed is a simple vertical shift.

Finally, the effects of the parameter $\sigma$ were determined by solving for the transient extensional viscosity using the parameters $\eta_p = 10,000$; $\lambda = 1$; $\alpha = 0.5$; $C_I = 0.1$; $r = 50$ and $\sigma = 1$, 0.5 or 0.25. The results are shown in Figure 6.24 and show that as $\sigma$
decreases the predicted transient extensional viscosity also decreases. The amount of the
decrease appears to be a nonlinear relationship as there is a significant decrease in
extensional viscosity predicted when going from $\sigma = 1$ to $\sigma = 0.5$ and a very slight
decrease when going from $\sigma = 0.5$ to $\sigma = 0.25$.

6.5 Conclusions

In this paper we measured the uniaxial extensional flow behavior of molten
polystyrene and polystyrene/carbon nanofiber composites containing nanofiber
concentrations of 2, 5 or 10 wt%. Both the pristine polymer and the composite showed
strain hardening behavior at strains greater than 3 for all strain rates tested. It was also
found that an increase in CNF concentration led to an increase in extensional viscosity.

A constitutive model, previously shown to accurately predict the shear rheological
behavior of PS/CNF composites, was used to predict the rheological behavior of the
composites under extensional flow. It was found that a multi-mode Giesekus model could
predict the viscoelastic behavior of polystyrene in both shear and extensional flows using
the same material constants for both types of flow. It was found that model parameters
optimized to give the best fit of just the shear rheological data are more accurate when
predicting only the transient shear flow behavior compared to the globally fit model
parameters. A unique set of material constants for each type of flow would provide the
best fit, however the globally fit values provide a reasonable fit to both types of flow.

Experimental measurements of CNF orientation at various points in time during
flow were taken and used to construct three-dimensional orientation tensors. These
orientation tensors provided information on how the nanostructure within the composite evolved during flow. This experimental data was used in conjunction with the model to determine the value of the hydrodynamic fiber-fiber interaction parameter $C_I$. The value of $C_I$ is the most important parameter in predicting CNF orientation and the determination of its value through comparison with experimental measurements improves the predictive capabilities of the model. This technique of experimentally measuring nanofiber orientation could be applied to other types of flow, such as shear flow, in order to gain a better understanding of the effects of flow on nanostructure development. This knowledge could be used when applying the constitutive model presented here to that flow in order to improve predictions of orientation evolution.

Several closure approximations and shape factors were evaluated to find which provided the most accurate model predictions. It was found that the hybrid closure approximation and the shape factors: $A = \frac{h^2}{3\ln\left(\frac{\pi}{\phi}\right)}$, $B = C = F = 0$ gave the most accurate solutions. The constitutive model captures the qualitative features of the experimentally observed rheological behavior of the composites but overpredicts viscosity with increasing CNF concentration. The overprediction of viscosity can be eliminated through the use of an ‘effective’ aspect ratio.
Table 6.1 One-mode and five-mode Giesekus model parameters optimized by fitting to small amplitude oscillatory shear and steady shear data.

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<th>Five-Modes</th>
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<td>2</td>
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<td>30.5</td>
</tr>
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<tr>
<td>5</td>
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Table 6.2  Five-mode Giesekus model parameters optimized by fitting to small amplitude oscillatory shear, steady shear, and extensional viscosity data.

<table>
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<th>$\lambda$</th>
<th>$\alpha$</th>
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<td>1</td>
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<td>356</td>
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<td>98.9</td>
<td>0.999</td>
</tr>
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<td>5</td>
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Table 6.3  Expressions of material constants A, B, C, and F as functions of aspect ratio and particle concentration.

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<td>$A_3$</td>
<td>$A_4$</td>
</tr>
<tr>
<td>B</td>
<td>$\frac{6\ln(2r)-11}{r^2}$</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>$\frac{3r^2}{\ln(2r)-0.5}$</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>

\[
A_1 = \frac{r^2}{2[\ln(2r)-1.5]}
\]

\[
A_2 = \frac{r^2}{3\ln(\pi/\phi)}
\]

\[
A_3 = \frac{16r^2}{3\ln\left(\frac{1}{\phi}\right)} \left[ \frac{\ln \left\{ \frac{1}{\phi} \right\}}{\ln \left\{ \frac{1}{\phi} \right\}} + 0.6344 \right]
\]

\[
A_4 = \frac{16r^2}{3\left[ \ln \left\{ \frac{1}{\phi} \right\} + \ln \left\{ \frac{1}{\phi} \right\} + 1.4389 \right]}
\]
Table 6.4  Orientation tensor component $a_{11}$ at various strains and strain rates.

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<th>1</th>
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<td>0.586</td>
<td>0.586</td>
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<tr>
<td>0.1</td>
<td>0.527</td>
<td>0.580</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.84</td>
<td>0.929</td>
<td>0.881</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.899</td>
<td>0.831</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.928</td>
<td>0.940</td>
<td>0.940</td>
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Figure 6.1  Optical microscopy images of carbon nanofibers from used to determine the fiber aspect ratio.
Figure 6.2 Experimentally measured uniaxial extensional viscosities of PS/CNF composites containing (a) 0 (pure PS), (b) 2, (c) 5 and (d) 10 wt% CNF at shear rates ranging from 0.01-1 s$^{-1}$. The shear rates are identified in the legend.
Figure 6.2 continued

(c)  

(d)
Figure 6.3  Experimental measurements of storage and loss modulus (points) compared to predictions from Equations (6.10) and (6.11) using a (a) one-mode and (b) five-mode model.
Figure 6.4  Experimental measurements of steady shear viscosity (points) compared to predictions from Equations (6.13)-(6.15) using a one-mode and five-mode model.
Figure 6.5  Experimental measurements of extensional viscosity (points) at different extension rates compared to predictions made with a five-mode Giesekus model (lines).
Figure 6.6  Experimental measurements (points) compared to model predictions of (a) storage and loss modulus, (b) steady state shear viscosity and (c) extensional viscosity using values of $\eta_p$, $\lambda$, and $\alpha$ optimized by fitting to all three data sets simultaneously.
Figure 6.6 continued
Figure 6.7  The orientation of a single fiber in three dimensions described by vector p.
Figure 6.8  Method to determine the in-plane angle $\phi$ of a fiber by taking a thin slice of a sample and viewing with a TEM.
Figure 6.9 Determination of the out-of-plane angle, $\theta$, through measurement of the projected fiber length and slice thickness.
Figure 6.10 Slicing of a sample at an angle $\alpha$, which is less than $90^\circ$. 
Figure 6.11 TEM micrographs of (a) CNFs in a 2wt% sample and (b) the same image with the nanofibers digitized in AutoCAD.
Figure 6.12 Experimentally measured values of the orientation tensor component $a_{11}$ for a 2 wt% composite subjected to uniaxial extension at extension rates of 0.01, 0.1 and 1 s$^{-1}$ measured at strains of 0, 0.1, 1, 2 and 3.
Figure 6.13  Experimentally measured values of the orientation tensor component $a_{11}$ for a 2 wt% composite subjected to transient shear at shear rates of 0.01, 0.3 and 10 s$^{-1}$ measured at strains of 0, 0.1, 1, 2 and 3.
Figure 6.14 Plot of the values of $a_{11}$ predicted from Equation (6.4) as a function of strain using initial values of $a_{11}$ of 0.586 (dashed line) and 0.333 (solid line) compared to experimentally measure values.
Figure 6.15 Comparison of the extensional viscosity predicted for a 2 wt% CNF/PS sample at an extension rate of 0.01 s\(^{-1}\) where the initial \(a_{11}\) component of the fiber orientation tensor is 0.586 (dashed line) or 0.333 (solid line).
Figure 6.16 Extensional viscosity model predictions (lines) compared to experimental measurements (dots) for PS/CNF composites containing (a) 2, (b) 5 and (c) 10 wt% CNF at extension rates ranging from 0.01 to 1 s\(^{-1}\).
Figure 6.16 continued

(c)
Figure 6.17 Model predictions of extensional viscosity when the value for $a_{11}$ at steady state is close to totally random ($C_I = 0.999$) or nearly perfectly aligned in the direction of extension ($C_I = 0.0001$) for a 2wt% CNF composite at an extension rate of 0.01 s$^{-1}$ using the hybrid closure approximation.
Figure 6.18 Extensional viscosity model predictions (lines) compared to experimental measurements (dots) for PS/CNF composites containing (a) 2, (b) 5 and (c) 10 wt% CNF at extension rates ranging from 0.01 to 1 s\(^{-1}\) using an 'effective' nanofiber aspect ratio of 12.86.
Figure 6.18 continued
Figure 6.19 Model predictions of transient extensional viscosity of a polymer with $\alpha = 0.5; \; \lambda = 1; \; \text{and} \; \eta_p = 3,000; 10,000 \; \text{or} \; 30,000.$
Figure 6.20 Model predictions of transient extensional viscosity of a polymer with $\eta_p = 10,000$; $\alpha = 0.5$ and $\lambda = 0.1$, 1 or 10.
Figure 6.21 Model predictions of transient extensional viscosity of a polymer with $\eta_p = 10,000$; $\lambda = 1$ and $\alpha = 0.01, 0.1, 0.5$ or 0.9.
Figure 6.22 Model predictions of (a) transient extensional viscosity and (b) the orientation tensor component $a_{11}$ of a composite containing 2 wt% CNF using the hybrid closure approximation, $A = \frac{r^2}{3\ln\left(\sqrt{\pi} / \phi\right)}$, $B = C = F = 0$, $\sigma = 1$; $\eta_p = 10,000$; $\lambda = 1$; $\alpha = 0.5$; $r = 50$ and $C_i = 0.9$, 0.1 or 0.01.
Figure 6.23 Model predictions of transient extensional viscosity of a composite containing 2 wt% CNF using the hybrid closure approximation,

\[ A = \frac{r^2}{3\ln\left(\sqrt{\pi/\phi}\right)}, \quad B = C = F = 0; \quad \sigma = 1; \quad \eta_p = 10,000; \quad \lambda = 1; \quad \alpha = 0.5; \quad C_I = 0.1 \]

and \( r = 10, 50 \) or 100.
Figure 6.24 Model predictions of transient extensional viscosity of a composite containing 2 wt% CNF using the hybrid closure approximation,

\[ A = \frac{r^2}{3\ln\left(\sqrt{\pi/\phi}\right)}, \quad B = C = F = 0; \quad \eta_\rho = 10,000; \quad \lambda = 1; \quad \alpha = 0.5; \quad C_I = 0.1; \quad r = 50 \]

and \( \sigma = 1, 0.5 \) or 0.25.
CHAPTER 7

RHEOLOGY AND MODELING OF MAGNETORHEOLOGICAL FLUIDS

7.1 Introduction

Smart materials have the potential to be used in a wide array of applications because they possess the ability to significantly change their material properties when subjected to an external stimulus. A magnetorheological (MR) fluid is a unique type of smart material that consists of micron-sized magnetizable particles suspended in a nonmagnetic carrier fluid, typically a mineral or silicone oil. These fluids exhibit the ability to rapidly undergo significant, and reversible, changes in their rheological properties upon application of an external magnetic field. One example is that MR fluids exhibit a controllable yield stress-like behavior in shear, whereby the application of a magnetic field transverse to the direction of flow creates a resistance to flow which increases monotonically with increasing magnetic field strength. It is this field-dependent yield stress, combined with their rapid response to changes in magnetic field, that make MR fluids an attractive technology for many applications. Applications of MR fluids range from automotive to biomedical devices.
MR fluid properties in both the steady-shear and post-yield regimes under an applied magnetic field have been studied extensively [143]. However, it is important to characterize the material behavior across a broad range of conditions since dynamic control of MR devices require both the pre-yield and post-yield regimes. Furthermore, only a few research groups have reported studies of the dynamic viscoelastic behavior of MR fluids. Weiss et al. [144] compared MR and ER fluid viscoelastic properties. Their results showed that the yield strain of both fluids was less than 1%, while the storage modulus $G'$ of their MR fluid was on the order of $2.5 \times 10^6$ Pa with an applied field of 2 kOe. Their study was limited in the frequency range of 2.5-6.8 Hz. Chin et al. [55] studied the rheological behavior of MR suspensions in a parallel-plate oscillatory shear rheometer under varying particle volume fraction, strain amplitude, frequency, and magnetic field strength. They reported that as the magnetic field strength, $H$, was increased, the dynamic yield stress increased as $H^{3/2}$, likely due to magnetic saturation of the suspended particles. In addition, they found that both the storage modulus, $G'$, and loss modulus, $G''$, decreased as strain increased and the shear modulus, $G$, exhibited a slight increase with increasing frequency.

The rheological investigations of the MR fluids show that the viscosity of a MR fluid even in the absence of a magnetic field is non-Newtonian due to the presence of the suspended particles, with shear-thinning behavior evident at higher shear rates. As the magnetic field strength increases, this shear resistance to flow increases quasi-linearly. Models utilizing a variable yield stress concept are commonly used for MR fluids. A model particularly useful at low magnetic-field strength is the Bingham plastic model.
The Bingham model relates the total shear stress $\tau$ in simple shear to the shear rate $\dot{\gamma}$ and magnitude $H$ of a transverse applied magnetic field according to the equation

$$\tau = \left(\tau_y(H) + \eta|\dot{\gamma}|\right)\text{sgn}(\dot{\gamma})$$  \hspace{1cm} (7.1)$$

where $\tau_y(H)$ is a yield stress, assumed to be a function of the magnitude of the magnetic field, and the constant $\eta$ is the effective bulk viscosity of the composite system. Felt et al. [145] have shown that the Bingham model cannot replicate the shear thinning behavior of monodisperse MR fluids. The Herschel-Bulkley model generalizes the Bingham model to accommodate the shearing thinning observed in MR fluids [146,147]

$$\tau = \left(\tau_y(H) + K|\dot{\gamma}|^m\right)\text{sgn}(\dot{\gamma})$$  \hspace{1cm} (7.2)$$

where $m$ and $K$ are constants. We note that these models describe fluids which exhibit a strict yield stress $\tau_y(H)$ in shear with no-flow (i.e. $\dot{\gamma} = 0$) until $\tau$ exceeds $\tau_y(H)$. Dynamic and static shear-yield stresses have been reported [148]. The static shear-yield stress being the minimum shear stress required to induce flow while the dynamic shear-yield stress is the extrapolated ‘shear stress at zero shear rates’. Bossis et al. [149] explained that the static yield stress is due to the particle-fluid interaction while the dynamic yield stress is associated with the rupture of the particle aggregates in the presence of a magnetic field. Microstructural chain models have been proposed to predict the yield stress by several authors based on magnetic dipole interactions between adjacent particles within a particle chain [150,151]. These interparticle interactions are then averaged over the entire sample to yield a model of the bulk magnetorheological effect similar to interparticle interactions within ER fluids [152,153]. The point-dipole model
by Ginder [59,154,155] accurately predict proportional relationship of yield stress to \( \mu \) under weak magnetic fields, \( \phi \) is the volume fraction of particles, \( H \) is the permeability of the vacuum and \( \phi \mu H^2 \) is the applied magnetic field. However, linear point-dipole models are unable to treat the nonlinearity due to magnetic saturation at stronger magnetic fields, requiring multi-zone models for yield stress. Furthermore, point-dipole models are reported to overestimate yield stress magnitude in comparison to experimental data [156].

In this paper we study the rheological properties of four types of MR fluids under various shear rates and magnetic field strengths using a commercial parallel-plate rheometer. By varying carrier fluid viscosities and particle sizes we are able to quantify the effects of these factors on the viscosities and yield strengths of the MR fluids. We employ a particle-level model to predict the shear flow response of the MR fluids. The hydrodynamic forces are approximated by Stokes drag and the magnetic effects on the carbonyl iron particles are expressed in terms of the magnetic susceptibility and orientation of the particle pair with respect to the magnetic field direction. The present model examines the magneto-rheological properties of magnetically permeable spherical particle pairs. In particular, a magnetic field is applied perpendicular to the shearing direction of the MR fluid and the shear stress of the chains caused by interparticle magnetic force is modeled. It is assumed that if these particle pairs are considered within a viscoelastic material, then the viscoelastic properties in the composite are the sum of the viscoelastic properties of the composite with no field applied and the elastic/plastic
properties induced by interparticle magnetic force. This theory is then compared to the experimentally measured data.

7.2 Experimental Procedure

7.2.1 Materials

Polydimethylsiloxane (silicone oil) was used as a carrier fluid in these experiments and was obtained from two sources. A low viscosity oil ($\eta = 10$ cSt, $\rho = 0.935$ g/cm$^3$) was obtained from Clearco and a higher viscosity silicone oil ($\eta = 350$ cSt, $\rho = 0.971$ g/cm$^3$) was obtained from Dow Corning.

Carbonyl iron (Fe(CO)$_5$) powder was used as the MR fluid particle and was obtained from Kennametal. Two grades of powder were obtained; FE023 which has an apparent density of 2.0-3.0 g/cm$^3$ and average particle size of 2.0-5.0 μm, and FE042 which has an apparent density of 2.2-3.2 g/cm$^3$ and average particle size of 4.0-7.0 μm. The morphology of the particles was characterized by scanning electron microscopy (SEM) using a XL-30 ESEM. Figure 7.1 shows an SEM image of the FE042 carbonyl iron particles. The particles are mostly spherical with some aggregation creating irregular shapes.

7.2.2 Fluid Preparation

Four different MR fluids were prepared from these materials. The low viscosity oil ($\eta = 10$ cSt) was mixed with FE023 particles or the FE042 particles. These fluids are referred to as MR10S and MR10L, respectively; MR refers to the fluid being a
magnetorheological fluid, the number, in this case 10, referring to the viscosity of the carrier fluid in units of cSt, and the last letter referring to the carbonyl iron particle size as the smaller (S) grade FE023 or the larger (L) grade FE042. Similarly, the high viscosity oil (\(\eta = 350\) cSt) was mixed with the same particles and labeled as MR350S and MR350L. Table 7.1 summarizes the names and properties of these fluids. All fluids contained 75 wt% carbonyl iron.

7.2.3 Rheological Characterization

The small amplitude oscillatory shear and steady state shear responses of each of the MR fluids were characterized at 25°C with an Anton Paar Physica MCR 500 rheometer. A MRD 180/1T measurement cell was connected to the rheometer and was used to produce a magnetic field perpendicular to the direction of shear. Shear flow was applied to the fluid by a pair of 20mm parallel plates with a separation of 0.5 mm. The response of the fluid to steady state shear and dynamic oscillatory shear flows at various magnetic field strengths was measured. The strength of the magnetic field was controlled by varying the amount of current passing through coils of wire contained within the measurement cell.

While the amount of current applied was a known quantity, the strength of the magnetic field was unknown because field strength is a function of the relative permeability of the fluid (which is different for each of the four fluids tested) and no sensor is present in the rheometer to provide direct measurements. Equations provided by
the rheometer manufacturer relate the applied current ($I$) to the magnetic flux density ($B$) and the magnetic field strength ($H$) as shown in Equations (7.3) and (7.4).

$$B = \frac{7.539 \times 10^{-4} \times K \times I}{(0.0035 - d (\mu_r - 1)/\mu_r)}$$  \hspace{1cm} (7.3)

$$H = \frac{B}{\mu_0 \mu_r}$$  \hspace{1cm} (7.4)

$B$ = Flux density in [T]

$H$ = Magnetic field strength in [A/m]

$K$ = Calibration factor (set to 1 for these experiments)

$I$ = Current in [A]

$d$ = Measuring gap in [m]

$\mu_r$ = Relative permeability of the fluid

$\mu_0$ = Permeability of a vacuum = $1.256 \times 10^{-6}$ $\frac{V \cdot s}{A \cdot m}$

As can be seen in Equation (7.3), the magnetic flux density can be calculated given the applied current, which is known, and the relative permeability of the MR fluid, which is unknown. For each MR fluid, two pieces of information are needed to determine their relative permeability: the dependence of field strength ($H$) on flux density ($B$) and an equation that expresses field strength as a function of flux density and applied current. The dependence of field strength on flux density for each fluid was found by conducting experiment where each MR fluid was placed in a small chamber and the magnetic flux density was varied while the magnetic field strength was measured. The relationship between flux density and field strength for each fluid was then plotted, as shown in
Figure 7.2, and a polynomial equation was fit to the data. The polynomial fit to the data shown in Figure 7.1 is the following:

\[ H = 31B^5 - 158B^4 + 321B^3 - 330B^2 + 180B \]  \hspace{1cm} (7.5)

An expression for field strength as a function of flux density and applied current can be found using Equations (7.3) and (7.4). Rearranging Equation (7.4) allows \( \mu_r \) to be expressed as:

\[ \mu_r = \frac{B}{\mu_0 H} \]  \hspace{1cm} (7.6)

which can be substituted into Equation (7.3), eliminating \( \mu_r \) as shown in Equation (7.7).

\[ B = \frac{7.539 \times 10^{-4} \times K \times I}{0.0035 - d \left( \frac{B}{\mu_0 H} \right) - 1} \]  \hspace{1cm} (7.7)

Rearranging Equation (7.7) and substituting for \( d \), \( K \) and \( \mu_0 \) gives an expression for field strength in terms of flux density \( (B) \) and applied current:

\[ H (kA/m) = -4777.1 \times B(T) + 1200.048 \times I(A) \]  \hspace{1cm} (7.8)

The magnetic field strength at a given current for each fluid is found by setting each fluid’s polynomial expression of field strength as a function of flux density equal to Equation (7.8), with the appropriate value of current substituted into Equation (7.8). As an example we will solve for the magnetic field strength when the fluid MR10L is in the rheometer and a current of 0.05A is applied. First we will set Equation (7.5) equal to Equation (7.8) and set the current in Equation (7.8) equal to 0.05.
\[31B^4 - 158B^3 + 321B^2 - 330B + 180B = -4777.1B + 60.0024 \]  \hspace{1cm} (7.9)

Solving this polynomial expression we find \( B = 0.012 \) T. Substituting this value into Equation (7.5) or (7.8) gives \( H = 2.14 \) kA/m. This process is repeated for all fluids over the applied current range 0.05-1.00 A. Table 7.2 lists the results of the applied current and the corresponding magnetic field strength for each fluid.

7.3 Experimental Results

7.3.1 Steady State Shear

The steady state shear behavior of the four MR fluid samples was measured over a range of shear rates and magnetic field strengths. Prior to this it was necessary to determine the response time of an MR fluid to an applied magnetic field. The reason for this was it was unknown whether the structure of the carbonyl iron particles would develop instantaneously upon application of a magnetic field or if the structure would take time to develop. Obtainment of accurate measurements required that tests were performed on a fluid in equilibrium with it’s surroundings. The structure response time was tested by placing an MR fluid between the parallel plates and applying a magnetic field by setting the current to 1 A. The actual magnetic field applied varied between fluids as can be seen in Table 7.2. The MR fluid was exposed to the magnetic field for 1, 2, or 4 minutes then a steady shear rate sweep from 0.1 to 500 s\(^{-1}\) was performed with a measuring time of 30 s per shear rate. There was no significant difference found between the different data sets therefore it was determined that the structure of the carbonyl iron particles developed quickly in response to an imposed magnetic field. All future
experiments were performed after exposing the MR fluid to the applied magnetic field for one minute.

Another set of experiments was performed to determine the length of time it took for the fluid’s viscosity to reach steady state under constant shear. The viscosity of the MR fluids was measured at shear rates ranging from 0.1 to 500 s\(^{-1}\) with a measurement time of either 30 s or 60 s per shear rate. The measurements were made over the magnetic field strength range of 0 to ~40 kA/m (the applied current was varied from 0-1 A). It was found that the viscosity values measured at 30 s/point were nearly identical to the viscosity values measured at 60 s/point therefore 30 s of shearing at each shear rate was determined to be sufficient time to reach steady state.

Having determined the an appropriate length of time for the MR fluid to reach structural equilibrium with the applied magnetic field and the length of time needed for the viscosity to reach steady state we could measure the steady state shear behavior of the MR fluids under various magnetic field strengths and shear rates. The response of the fluids was measured at shear rates ranging from 0.1 to 500 s\(^{-1}\) and varying the magnetic field strength from 0 to ~40 kA/m by adjusting the applied current from 0-1 A. The steady state shear viscosity of each fluid is shown in Figure 7.3. From this figure it is apparent that in the absence of an applied magnetic field all of the MR fluids are shear thinning and plateau at a shear rate of ~100 s\(^{-1}\). The plateau viscosities of the MR350L and MR350S fluids are greater than the MR10L and MR10S fluids which is expected because the viscosity of the carrier fluid used in the MR350L and MR350S fluids is greater than the viscosity of the carrier fluid used in the MR10L and MR10S fluids. This
non-Newtonian behavior of the fluids in the absence of a magnetic field is consistent with that of other concentrated suspensions and is a result of microstructures formed by the suspended particles which are deformed during shear flow [157]. The presence of a magnetic field and its strength changes the microstructure within the fluid as well as how it deforms under flow. As a result the viscosity of all of the MR fluids monotonically increases with increasing magnetic field strength and continue to show shear thinning behavior. This behavior has been seen by others working with MR fluids [158,159].

It should be noted that the viscosities of the MR10L and MR10S fluids are nearly identical, and the viscosities of the MR350L and MR350S fluids are nearly identical indicating viscosity is not significantly affected by particle size at least in the size range of particles we investigate. The use of magnetic particles with greater differences in size may result in significant differences in the rheological behavior.

A plot of the steady state shear stress response as a function of shear rate (shown in Figure 7.4) of all MR fluids shows stress increases with increasing magnetic field strength. While the steady shear viscosities of each fluid were similar the stress response reveals significant differences. The two MR fluids containing the 10 cSt silicone oil carrier fluid, MR10L and MR10S, show a shear stress that is nearly independent of shear rate for all applied magnetic field strengths. This type of behavior was also seen by Chin et al. [55] who studied the steady state shear stress response of carbonyl iron suspensions in a 0.10 Pa.s silicon oil using particle volume fractions of 0.2 and 0.4.

In contrast, the steady shear stresses of the two MR fluids containing the 350 cSt silicone oil carrier fluid, MR350L and MR350S, increase rapidly with increasing shear
rate at shear rates less than 50 s\(^{-1}\) and begin to plateau at shear rates greater than 50 s\(^{-1}\). This behavior was also observed by See [160] who was using MR fluids composed of carbonyl iron particles at a volume fraction of 0.8 suspended in paraffinic spindle oil with a kinematic viscosity of \(6.5 \times 10^{-6} \text{ m}^2/\text{s}\) which is equal to 6.5 cSt. The exact density of the spindle oil was not specified, however, if it is assumed to be 0.8 g/cm\(^3\), which is a common value for spindle oils, the viscosity would be 0.0052 Pa.s.

The silicon oil viscosity used by Chin et al. was in-between the two carrier fluid viscosities used in this study and the particle volume fraction of the Chin et al. fluids was smaller: 0.2 and 0.4, compared to 0.5 in this study. The carrier fluid used by See had the lowest viscosity of all the fluids investigated and the highest carbonyl iron particle volume fraction at 0.8. This data seems to suggest that the transition from a fluid that has a nearly constant stress response under all steady shear rates to one with stress that rapidly increases at low shear rates and plateaus at high shear rates does not solely depend upon the viscosity of the carrier fluid or the concentration of the magnetic particles but is a function of both properties.

7.3.2 Yield Stress

One of the non-Newtonian behaviors displayed by the MR fluids is the presence of a yield stress which is a threshold stress level that must be reached before certain fluids will flow. If a stress is applied that is below the yield stress value the fluid will behave like a solid and there will be no flow. Common fluids that exhibit this behavior are mayonnaise, ketchup and concentrated particle suspensions. The yield stress for each of
the MR fluids can be determined by extrapolating the shear stress vs. shear rate curves (Figure 7.4) to a shear rate value of zero.

Figure 7.5 plots the yield stress of the MR350S fluid as a function of magnetic field strength. As seen in the figure the yield stress increases exponentially with increasing magnetic field strength. This behavior is seen for all of the fluids investigated. The non-linear growth of yield stress with increasing magnetic field strength was also seen by Chin et al. [55].

7.3.3 Linear Viscoelastic Response

The linear viscoelastic response of the magnetorheological fluids was studied by first determining the linear viscoelastic range of the fluids by performing strain sweeps over a range of different magnetic field strengths. The linear viscoelastic regime was identified as the range of strains where G’ and G” remained constant. The linear regime was different for each fluid and for each magnetic field therefore the strain used in the dynamic frequency sweep experiments varied. A representative sample of the strain sweep results can be seen in Figure 7.6. This data is for strain sweeps performed on the fluid MR350S at magnetic field strengths of 0 kA/m and 33.47 kA/m. As Figure 7.7 shows, the response of the fluid to oscillatory shear is inconsistent. The value for G’ can vary several orders of magnitude and the variability in G” is even greater. There are several reasons why this may be occurring. First, the greater variability in G” could be caused by the value of G’ being several orders of magnitude larger than G”. When the values of G’ and G” are calculated based on fitting to a stress response curve the value of
G’ will dominate and G” will contribute very little. By plotting the data on a log scale the small variations in G” are exaggerated; if the data was plotted on a linear scale these variations would not appear as great. Second, there is a very small strain being applied to the fluid which means the torque response will also be very small which means that slight changes in the torque due to vibrations, fluid inhomogeneity, etc. will be greatly amplified resulting in scattered data points.

Looking at Figure 7.7, which shows a plot of G’ vs. frequency for the MR350S fluid at several different magnetic field strengths, we can draw some conclusions about the behavior of these fluids in dynamic oscillatory shear. First, G’ is essentially constant when a magnetic field is applied. When there is no magnetic field the value of G’ increases with increasing frequency. Second, G’ increases with increasing magnetic field. This data indicates that when a magnetic field is applied, the MR fluids behave like elastic solids at all frequencies when low levels of strain are applied. This is consistent with the steady shear viscosity observations where the MR fluids exhibited a yield stress that increases with increasing magnetic field strength.

7.4 Modeling the MR Fluid Behavior

A model capable of predicting the flow behavior of magnetorheological fluids subjected to an external magnetic field has been developed by adapting the kinetic theory of polymers, particularly the elastic dumbbell model [161]. The proposed model is intended develop an elementary and broad understanding of the relationship between the macromolecular motions of the magnetic particles and the observed rheological
phenomena. The rheological properties of MR fluids can be predicted in various flow conditions using constitutive equations developed from the proposed model using kinetic theory derivations. A probability distribution function describes the configuration of the MR fluid at the microscale. The Fokker-Planck equation provides a definition of the evolution of this probability distribution function which can be used to evaluate the ensemble average. A constitutive relation is also proposed that accounts for the various mechanics by which forces are transmitted through the fluid. MR fluids are described by a microstructural model of the motion of particle pairs in a Newtonian carrier fluid. This model accounts for viscous drag on the spherical particles as well as external magnetic field forces that arise from the attraction of interacting particle pairs to other interacting particle pairs. Brownian forces and attractive forces between the particles are also considered.

The particle pair model is developed considering two spherical magnetizable particle connected by a center-to-center position vector \( q = r_2 - r_1 \) as shown in Figure 7.8. The connecting vector, \( q \), describes the overall orientation and the internal configuration of the two particles. In writing the equations of motion for each particle immersed in a solvent, it was considered that the particle diameter is small enough that the inertial force of the particles could be neglected. Hence, the equations of motion for the particle pair is:

\[
F^b_v + F^b_v + F^c_v + F^{mag}_v = 0
\]  

(7.10)
where the forces $F_v^h$, $F_v^b$, $F_v^c$, and $F_v^{mag}$ are the hydrodynamic force, Brownian force, inter-particle pair force and external magnetic force, respectively, and $v = 1, 2$. Bird [161] describes the hydrodynamic force and Brownian force as:

$$F_v^h = -\zeta (\dot{r}_v - v_v)$$  \hspace{1cm} (7.11)$$

$$F_v^b = -kT \frac{\partial}{\partial r_v} \psi$$  \hspace{1cm} (7.12)$$

The interparticle connector force resulting from the magnetic attraction between the particle pair is postulated as

$$F_v^c = \beta |\mathbf{H}| q_v$$  \hspace{1cm} (7.13)$$

where, $\beta$ is the magnetic moment constant resulting from the magnetic attraction between the particle pairs, $k$ is the Boltzmann constant, $T$ is temperature, $\zeta$ is the Stokes constant, $\psi$ is the probability distribution function.

According to Equation (7.11) the hydrodynamic force is proportional to the difference between the particle velocity, $\dot{r}_v$, and the velocity of the carrier fluid near the particle, $v_v$. The velocity of the carrier fluid near the particle is the imposed homogeneous flow field near the particle and is expressed as $v_v = v_0 + \nabla v \cdot r_v$.

Substituting $v = 1, 2$ into Equation (7.10) and subtracting gives the equation:

$$\left( F_1^h - F_2^h \right) + \left( F_1^b - F_2^b \right) + \left( F_1^c - F_2^c \right) + \left( F_1^{mag} - F_2^{mag} \right) = 0$$  \hspace{1cm} (7.14)$$

Using Equation (7.14) and following Bird [161] leads to an expression for the rate of change of the particle pair connector vector $\mathbf{q}$:
\[
\dot{\psi} = \nabla \cdot \mathbf{q} - \frac{2kT}{\zeta} \frac{\partial}{\partial \mathbf{q}} (\ln \psi) - \frac{2}{\zeta} \mathbf{F}^c + \frac{2}{\zeta} (\mathbf{F}_{2}^{\text{mag}} - \mathbf{F}_{1}^{\text{mag}}) \tag{7.15}
\]

The Fokker-Planck equation of continuity for \(\psi(\mathbf{q},t)\) is given as:

\[
\frac{\partial \psi}{\partial t} = -\left(\frac{\partial \psi}{\partial \mathbf{q}} \cdot \dot{\mathbf{q}} \right) \tag{7.16}
\]

Substituting Equation (7.15) in (7.16) leads to an expression for the diffusion equation:

\[
\frac{\partial \psi}{\partial t} = -\left(\frac{\partial \psi}{\partial \mathbf{q}} \left\{ \nabla \cdot \mathbf{q} \psi - \frac{2kT}{\zeta} \frac{\partial}{\partial \mathbf{q}} \psi - \frac{2}{\zeta} \mathbf{F}^c \psi + \frac{2}{\zeta} (\mathbf{F}_{2}^{\text{mag}} - \mathbf{F}_{1}^{\text{mag}}) \psi \right\} \right) \tag{7.17}
\]

Multiplying Equation (7.17) by \(\mathbf{q} \mathbf{q} \) and integrating over all the configuration space gives an equation for the rate of change of tensor \(\langle \mathbf{q} \mathbf{q} \rangle\):

\[
\frac{d}{dt} \langle \mathbf{q} \mathbf{q} \rangle - \nabla \cdot \langle \mathbf{q} \mathbf{q} \rangle - \langle \mathbf{q} \mathbf{q} \rangle \cdot \nabla \psi^T = \frac{4kT}{\zeta} \delta - \frac{4}{\zeta} \langle \mathbf{q} \mathbf{F}^c \rangle + \frac{1}{\zeta} \left( \langle \mathbf{F}_{2}^{\text{mag}} - \mathbf{F}_{1}^{\text{mag}} \rangle \mathbf{q} + \mathbf{q} \langle \mathbf{F}_{2}^{\text{mag}} - \mathbf{F}_{1}^{\text{mag}} \rangle \right) \tag{7.18}
\]

Where \(\delta\) is the unit tensor and the ensemble average \(\langle \cdot \rangle\) is defined by

\[
\langle \cdot \rangle = \int \psi (\mathbf{q},t) dq_1 dq_2 dq_3 \tag{7.19}
\]

Equation (7.18) can be written in compact form as:

\[
\frac{D}{Dt} \langle \mathbf{q} \mathbf{q} \rangle = \frac{4kT}{\zeta} \delta - \frac{4}{\zeta} \langle \mathbf{q} \mathbf{F}^c \rangle + \frac{1}{\zeta} \left( \langle \mathbf{F}_{2}^{\text{mag}} - \mathbf{F}_{1}^{\text{mag}} \rangle \mathbf{q} + \mathbf{q} \langle \mathbf{F}_{2}^{\text{mag}} - \mathbf{F}_{1}^{\text{mag}} \rangle \right) \tag{7.20}
\]

For convenience of hand computations we now revert to the indicial notation. We assume the attraction between the particle pair is defined by \(\mathbf{F}^c_\psi = \beta |\mathbf{H}| \mathbf{q}\) and introducing the external magnetic force to be

\[
\mathbf{F}_{1}^{\text{mag}} - \mathbf{F}_{2}^{\text{mag}} = \frac{c \gamma}{(1 + \gamma)(\mathbf{H} + c_1)} \mathbf{q} \tag{7.21}
\]

Substitution of Equation (7.21) into Equation (7.20) leads to:
\[
\frac{D}{Dt} \langle q_i q_j \rangle = \frac{4kT}{\zeta} \delta_{ij} - \frac{4\beta |H|}{\zeta} \langle q_i q_j \rangle - \frac{2c\dot{\gamma}}{(1+\chi)(H+c_1)} \langle q_i q_j \rangle
\]  
(7.22)

where \( \dot{\gamma} \) is the rate of strain tensor.

For simple shear, \( \mathbf{v} = \begin{bmatrix} \dot{\gamma} x_2 \\ 0 \\ 0 \end{bmatrix}, \mathbf{H} = \begin{bmatrix} 0 \\ H \\ 0 \end{bmatrix} \) where \( \dot{\gamma} \) is the shear rate.

At steady state, \( \frac{\partial}{\partial t} \langle q_i q_j \rangle = 0 \), \( \frac{\partial}{\partial x_i} \langle q_i q_j \rangle = 0 \), \( \frac{\partial}{\partial x_2} \langle q_i q_j \rangle = 0 \), \( \frac{\partial}{\partial x_3} \langle q_i q_j \rangle = 0 \) and by setting \( i = j = 1 \) on the left-hand side of Equation (7.22)

\[
\frac{D}{Dt} \langle q_1 q_1 \rangle = -\dot{\gamma} \langle q_2 q_1 \rangle - \dot{\gamma} \langle q_1 q_2 \rangle
\]  
(7.23)

Since \( \langle q_1 q_2 \rangle = \langle q_2 q_1 \rangle \), then

\[
\frac{D}{Dt} \langle q_1 q_1 \rangle = -2\dot{\gamma} \langle q_1 q_2 \rangle
\]  
(7.24)

Similarly, substituting \( i = 1, j = 2 \) on the left-hand side of Equation (7.22)

\[
\frac{D}{Dt} \langle q_1 q_2 \rangle = \dot{\gamma} \langle q_2 q_2 \rangle
\]  
(7.25)

Similarly, substituting \( i = 2, j = 1 \) on the left-hand side of Equation (7.22)

\[
\frac{D}{Dt} \langle q_2 q_1 \rangle = -\dot{\gamma} \langle q_2 q_2 \rangle
\]  
(7.26)

Similarly, substituting \( i = 2, j = 2 \) on the left-hand side of Equation (7.22)

\[
\frac{D}{Dt} \langle q_2 q_2 \rangle = 0
\]  
(7.27)

After simplifying the right hand side of Equation (7.22) we get
\[
\frac{D}{Dt} \langle q_1 q_2 \rangle = \frac{4}{\zeta} \left( \beta |H| + \frac{c' \gamma}{2(1 + \chi)(H + c_1)} \right) \langle q_1 q_2 \rangle
\]  
(7.28)

Replacing the left side of this equation with Equation (7.25)

\[
\dot{\gamma} \langle q_2 q_2 \rangle = \frac{4}{\zeta} \left( \beta |H| + \frac{c' \gamma}{2(1 + \chi)(H + c_1)} \right) \langle q_1 q_2 \rangle
\]  
(7.29)

To find the value of \( \langle q_2 q_2 \rangle \) we use Equation (7.22) with \( i = 2 \) and \( j = 2 \)

\[
\frac{D}{Dt} \langle q_2 q_2 \rangle = \frac{4kT}{\zeta} - \frac{4}{\zeta} \left( \beta |H| + \frac{c' \gamma}{2(1 + \chi)(H + c_1)} \right) \langle q_2 q_2 \rangle
\]  
(7.30)

Using Equation (7.27) in the above equation and rearranging we find:

\[
\langle q_2 q_2 \rangle = kT \left( \beta |H| + \frac{c' \gamma}{2(1 + \chi)(H + c_1)} \right)^{-1}
\]  
(7.31)

Combining Equations (7.31) and (7.29) results in:

\[
\langle q_1 q_2 \rangle = \frac{\dot{\gamma} k T \zeta}{4} \left( \beta |H| + \frac{c' \gamma}{2(1 + \chi)(H + c_1)} \right)^{-2}
\]  
(7.32)

The total stress tensor in the suspension is presumed to be a sum of the contributions from the carrier fluid with the particles \( \tau^c \) and the contribution of the particles due to the applied magnetic forces, \( \tau^p \). The extra energy dissipation due the presence of the spherical particles will be reflected by a proportional increase in viscosity. Stress contribution from the carrier fluid is given by:

\[
\tau_{ij}^c = -p^c \delta_{ij} + 2\eta_i D_{ij} \left( 1 + 2.5\phi + \alpha \phi^2 \right)
\]  
(7.33)

Here, \( \phi \) is the volume fraction of the suspended particles and \( \alpha \) is a fitting parameter. An earlier version of this relation was presented by Einstein in his classic
paper of 1906. Since Einstein’s equation was derived for very dilute suspensions, the power series expression of this equation is utilized to incorporate the hydrodynamic interactions between neighboring particles for the concentrated MR suspensions.

Elementary physical derivations provided by Kramers [16] are slightly modified to express the stress contributions of the suspended magnetic particles in presence of magnetic fields $\tau^p$. The forces resulting in these terms arise from both magnetic interactions between the particles as well as the hydrodynamic effects due to the presence of a magnetic field. The total stress tensor can be obtained by combining the $\tau'$ and $\tau^p$ contributions, which is given by the constitutive relation [162]

$$\tau_{ij} = -(p + nkT)\delta_{ij} + 2\eta_s D_{ij} \left(1 + \frac{5}{2} \phi + \alpha \phi^2 \right) + n\langle q, F_j^c \rangle + \frac{n}{2}\langle q, (F_{1j}^{mag} - F_{2j}^{mag}) \rangle \quad (7.34)$$

Here, $\eta_s$ is the carrier fluid viscosity, and $n$ is the number of particles per unit volume. The Maxwellian average of the momentum flux due to the motion of the particles across an arbitrary plane is represented by the term $nkT\delta_{ij}$. This is a direct consequence of ‘equilibrium in momentum space’ under isotropic considerations. Substituting Equation (7.21) and (7.32) into (7.34) for $i=1$ and $j=2$ we have

$$\eta = \frac{\tau_{12}}{\dot{\gamma}} = \eta_s \left(1 + \frac{5}{2} \phi + \alpha \phi^2 \right) + \frac{nkT\dot{\gamma}}{4\beta|H| + \frac{2c\dot{\gamma}}{2(1 + \chi)(H + c_1)}} \quad (7.35)$$

This is the expression for viscosity in the MR fluid due to applied shear and magnetic field. Using the parameters this model is fitted to MR fluids rheological data. This final expression provides an analytical solution for the steady state viscosity of
a magnetorheological fluid at various shear rates as a function of the carrier fluid viscosity, the volume fraction of the magnetic particles and the strength of an applied magnetic field.

Several of the parameters in this model are known or can be directly measured, including: the carrier fluid viscosity, $\eta_s$; the volume fraction of the magnetic particles, $\phi$; the temperature, $T$; and $k$ the Boltzmann constant. The magnetic field strength, $H$, and shear rate, $\dot{\gamma}$, are both independent variables and can be set to any desired value. The number of carbonyl iron particles in 1 m$^3$ of oil is given by $n$ and an approximate value for each fluid can be calculated using the dimensions of the particles and the volume fraction in the fluid. The bulk magnetic susceptibility of the fluid, $\chi$, can be directly measured for each fluid. The remaining variables in Equation (7.35): $\alpha$, $\beta$, $\zeta$, $c$ and $c_1$, cannot be directly measured and are therefore treated as fitting parameters.

7.5 Modeling Results

The model developed in Section 7.4 was used to predict the steady state shear rheological behavior of the MR fluids presented in Section 7.3.1. The important features of the experimentally measured rheology that the model should capture include shear thinning, a Newtonian plateau at high shear rates when no magnetic field is applied, increasing viscosity with increasing magnetic field strength, and higher viscosities of the MR10 fluids compared to the MR350 fluids for the same magnetic field strength. Many other models developed to describe MR fluid rheology predict Newtonian behavior in the absence of a magnetic field however this was not the behavior observed for the fluids.
tested in this work. The proposed model is therefore an improvement in that it predicts non-Newtonian behavior when no magnetic field is applied.

As stated in Section 7.4, the majority of the model parameters are defined or can be directly measured, including $\eta$, $\phi$, $T$, $k$, $n$ and $\chi$. Values for these constants can be found in Table 7.3. The magnetic field strength, $H$, and shear rate, $\dot{\gamma}$, were varied over the range 0-40 kA/m and 0.1-1000 s$^{-1}$, respectively. The variables $\alpha$, $\beta$, $\zeta$, $c$ and $c_1$ were treated as fitting parameters since their values could not be directly measured and were therefore determined through optimization of the model’s viscosity predictions for each fluid. These values are also reported in Table 7.3.

Substitution of the values in Table 7.3 into Equation (7.35) results in predictions of viscosity as a function of the magnetic field strength and shear rate for each of the four MR fluids investigated in this paper. Three-dimensional plots of the model predictions for magnetic field strengths in the range 0-40 kA/m and shear rates 0.1-1000 s$^{-1}$ for all four fluids are shown in Figure 7.9. From these plots it is apparent that the model qualitatively captures the rheological properties of the fluids observed in the experimental measurements. First, when there is no magnetic field present ($H = 0$) the model predicts each of the fluids to be shear thinning with a high shear Newtonian plateau. The plateaus of the MR350 fluids is greater than the MR10 fluids as was observed in the experimental measurements. Second, all fluids are predicted to increase in viscosity with increasing magnetic field strength and decrease in viscosity with increasing shear rate. A Newtonian plateau at high shear rates is predicted only when the magnetic field strength is zero.
Having validated the qualitative nature of the model we now seek to validate it’s quantitative accuracy. Figure 7.10-7.14 are comparisons of the experimentally measured values of steady state shear viscosity with model predictions for the fluids MR350L and MR10S over the shear rate range 0.1-1000 s^{-1} at a constant magnetic cell coil electric current values of 0A, 0.25A, 0.5A, 0.75A and 1.0A. The corresponding magnetic field strengths at these currents for each fluid are given in Table 7.2. Figure 7.10 demonstrates good agreement between the model predictions of the high shear Newtonian plateau and the experimentally measured values. Model predictions for MR10S are accurate over the entire range of shear rates tested while those for MR350L begin to deviate at low shear rates. The predicted viscosities are less than the experimentally observed values however they are still on the same order of magnitude.

In Figure 7.11-7.14 we see changes in the model’s accuracy with changing magnetic field strength. In the first step increase in magnetic field strength (Figure 7.11) it is apparent that the model overpredicts the viscosities of both the MR350L and MR10S fluids at all shear rates however the slopes of the experimental values and model predictions are nearly identical. As magnetic field increases the viscosity predictions for MR350L continue to be overpredicted however the magnitude of that overprediction decreases. Similarly, the MR10S predictions become more accurate with increasing magnetic field strength, however at the highest magnetic field strengths the viscosity is underpredicted. The slopes of the curves for both fluids at all magnetic field strengths are nearly identical.
An additional method to analyze the accuracy of the model is to compare model predictions with experimental data when the shear rate is held constant and the magnetic field is varied. Figure 7.15 is a plot of the experimentally measured and model predicted values of viscosity as functions of magnetic field strength at a constant shear rate of 500 s\(^{-1}\). As was seen in Figure 7.11-7.14 the qualitative behavior of increasing viscosity with increased magnetic field strength is captured by the model. Additionally, the model is able to predict the viscosity of MR10S to be greater than MR350L for equivalent magnetic field strengths and shear rates, with the exception of a magnetic field strength of 0 kA/m. The model does not provide an exact quantitative match to the experimental results however, they are relatively close and on the same order of magnitude.

7.6 Conclusions

The effects of carrier fluid viscosity, particle size, and magnetic field strength on the rheological properties of magnetorheological fluids under steady state shear and small amplitude oscillatory shear were investigated. It was found that in the absence of a magnetic field all of the MR fluids tested were shear thinning and reached a plateau at high shear rates. As the strength of an applied magnetic field was increased, the viscosities of the MR fluids also increased while maintaining a shear thinning character. Additionally, there was no significant difference between the rheological behaviors of fluids containing either large or small iron particles.

The MR fluids containing a lower viscosity carrier fluid displayed a stress response independent of shear rate but increased with increasing magnetic field strength.
The stress response of the MR fluids with the lower viscosity carrier fluid was greater than the stress response of the MR fluids with the higher viscosity carrier fluid for all magnetic field strengths and shear rates investigated except when no magnetic field was applied. The MR fluids exhibited a yield stress that increased exponentially with increasing magnetic field strength. The linear viscoelastic response of the MR fluids was measured and it was found that when a magnetic field was applied, $G'$ was always much greater than $G''$, indicating a solid-like material. $G'$ was also independent of frequency but increased with increasing magnetic field strength.

A model for predicting the flow behavior of magnetorheological fluids subjected to an external magnetic field was derived from first principles by adapting the kinetic theory of polymers. The proposed model accounts for the various forces transmitted through the fluid such as viscous drag on spherical particles, external magnetic field forces, Brownian motion, and attractive forces between the particles. The model was used to predict the steady state shear rheology of four MR fluids that differed in the viscosity of the carrier fluid and size of the carbonyl iron particles. We found the model was capable of predicting the shear thinning behavior of the fluids that occurred at all magnetic field strengths tested and the high shear viscosity plateau that occurred when no magnetic field was applied. The model also predicted the experimentally observed behavior of MR10 fluids having a greater viscosity at similar magnetic field strengths than the MR350 fluids. This model provides improved predictions of the rheological behavior of the MR fluids studied in this paper compared to previously proposed models which predict Newtonian viscosity in the absence of a magnetic field. From our analysis
of the model’s predictions we conclude that this new model provides accurate qualitative and quantitative predictions of the steady state shear rheology of the MR fluids investigated in this study and could be adapted in the future to model more complicated flow behaviors.
Table 7.1  Summary of fluid compositions used in the experimental study.

<table>
<thead>
<tr>
<th>Fluid Name</th>
<th>Silicone Oil Viscosity (cSt)</th>
<th>Silicone Oil Viscosity (Pa.s)</th>
<th>Carbonyl Iron Particle Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR10S</td>
<td>10</td>
<td>0.00935</td>
<td>2.0-5.0</td>
</tr>
<tr>
<td>MR10L</td>
<td>10</td>
<td>0.00935</td>
<td>4.0-7.0</td>
</tr>
<tr>
<td>MR350S</td>
<td>350</td>
<td>0.34055</td>
<td>2.0-5.0</td>
</tr>
<tr>
<td>MR350L</td>
<td>350</td>
<td>0.34055</td>
<td>4.0-7.0</td>
</tr>
</tbody>
</table>
Table 7.2  Applied currents and the corresponding magnetic field strengths for each MR fluid.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>10L</th>
<th>10S</th>
<th>350L</th>
<th>350S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current (A)</td>
<td>H (kA/m)</td>
<td>H (kA/m)</td>
<td>H (kA/m)</td>
</tr>
<tr>
<td>0.05</td>
<td>2.14</td>
<td>2.09</td>
<td>2.53</td>
<td>2.15</td>
</tr>
<tr>
<td>0.10</td>
<td>4.18</td>
<td>4.08</td>
<td>4.99</td>
<td>4.25</td>
</tr>
<tr>
<td>0.15</td>
<td>6.14</td>
<td>5.99</td>
<td>7.39</td>
<td>6.30</td>
</tr>
<tr>
<td>0.20</td>
<td>8.02</td>
<td>7.82</td>
<td>9.72</td>
<td>8.30</td>
</tr>
<tr>
<td>0.25</td>
<td>9.81</td>
<td>9.56</td>
<td>12.00</td>
<td>10.24</td>
</tr>
<tr>
<td>0.50</td>
<td>17.63</td>
<td>17.11</td>
<td>22.48</td>
<td>19.21</td>
</tr>
<tr>
<td>0.75</td>
<td>23.79</td>
<td>22.97</td>
<td>31.57</td>
<td>26.93</td>
</tr>
<tr>
<td>1.00</td>
<td>28.58</td>
<td>27.42</td>
<td>39.37</td>
<td>33.47</td>
</tr>
</tbody>
</table>
Table 7.3  Model parameters fit to the rheological data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MR10L</th>
<th>MR350L</th>
<th>MR10S</th>
<th>MR350S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_s$</td>
<td>0.00973</td>
<td>0.34</td>
<td>0.00973</td>
<td>0.34</td>
</tr>
<tr>
<td>$n$</td>
<td>2.12E+20</td>
<td>3.00E+21</td>
<td>3.90E+21</td>
<td>3.90E+21</td>
</tr>
<tr>
<td>$k$</td>
<td>1.38E-23</td>
<td>1.38E-23</td>
<td>1.38E-23</td>
<td>1.38E-23</td>
</tr>
<tr>
<td>$T$</td>
<td>298</td>
<td>298</td>
<td>298</td>
<td>298</td>
</tr>
<tr>
<td>$\chi$</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>$c$</td>
<td>7.55E+04</td>
<td>1.56E+04</td>
<td>5.00E+04</td>
<td>1.56E+04</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>3.00E+07</td>
<td>5.00E+05</td>
<td>3.50E+06</td>
<td>2.10E+05</td>
</tr>
<tr>
<td>$c_1$</td>
<td>0.008</td>
<td>0.0054</td>
<td>0.0005</td>
<td>0.0054</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.02</td>
<td>0.4</td>
<td>0.02</td>
<td>0.4</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>91.2</td>
<td>49.5</td>
<td>30.3</td>
<td>12.6</td>
</tr>
</tbody>
</table>
Figure 7.1  SEM micrograph of the FE042 carbonyl iron particles.
Figure 7.2  Magnetic field strength (H) measured as a function of magnetic flux density (B) for fluid MR10L.
Figure 7.3 Steady state shear viscosity vs. shear rate for (a) MR10L, (b) MR10S, (c) MR350L and (d) MR350S at different magnetic field strengths. The magnetic field strength is indicated in the legend.
Figure 7.3 continued

(c)

(d)
Figure 7.4  Steady state shear stress vs. shear rate for (a) MR10L, (b) MR10S, (c) MR350L and (d) MR350S.
Figure 7.4 continued

(c)

(d)
Figure 7.5  Yield stress as a function of magnetic field strength (H) for fluid MR350S.
Figure 7.6  Strain sweeps of fluid MR350S at an angular frequency of 10s$^{-1}$ at magnetic field strengths of (a) 0 kA/m and (b) 33.47 kA/m.
Figure 7.7  \( G' \) vs. frequency for MR350S at different magnetic field strengths.
Figure 7.8  The particle pair model.
Figure 7.9  Model predictions of steady state shear viscosity as a function of magnetic field strength (H) and shear rate for the fluids (a) MR10L, (b) MR10S, (c) MR350L and (d) MR350S. The model was solved using the parameter values found in Table 7.3.
Figure 7.9 continued
Figure 7.10 A comparison of the experimentally measured values of steady state shear viscosity (symbols) with model predictions (lines) for the fluids MR350L and MR10S over the shear rate range 0.1-1000 s$^{-1}$ at a constant magnetic field strength of 0 kA/m.
Figure 7.11 A comparison of the experimentally measured values of steady state shear viscosity (symbols) with model predictions (lines) for the fluids MR350L and MR10S over the shear rate range 0.1-1000 s$^{-1}$ at constant magnetic field strengths of 12.00 kA/m and 9.56 kA/m, respectively.
Figure 7.12 A comparison of the experimentally measured values of steady state shear viscosity (symbols) with model predictions (lines) for the fluids MR350L and MR10S over the shear rate range 0.1-1000 s\(^{-1}\) at constant magnetic field strengths of 22.48 kA/m and 17.11 kA/m, respectively.
Figure 7.13 A comparison of the experimentally measured values of steady state shear viscosity (symbols) with model predictions (lines) for the fluids MR350L and MR10S over the shear rate range 0.1-1000 s$^{-1}$ at constant magnetic field strengths of 31.57 kA/m and 22.97 kA/m, respectively.
Figure 7.14 A comparison of the experimentally measured values of steady state shear viscosity (symbols) with model predictions (lines) for the fluids MR350L and MR10S over the shear rate range 0.1 - 1000 s\(^{-1}\) at constant magnetic field strengths of 39.37 kA/m and 27.42 kA/m, respectively.
Figure 7.15 Comparison of experimental measurements (symbols) to model predictions (lines) of the dependence of steady state shear viscosity on magnetic field strength for fluids MR350L and MR10S at a constant shear rate of 500 s$^{-1}$. 
8.1 Introduction

Carbon nanotubes (CNTs) have tremendous potential to be used in a wide range of applications because their tensile strength, electrical conductivity and thermal conductivity are among the greatest of all known materials. The performance properties currently achieved in macroscopic assemblies of CNTs are significantly less than those of individual nanotubes and are highly dependant upon processing conditions. There is a need to understand the principals controlling the behavior of carbon nanotube assemblies in order to realize the full potential of these materials and create marketable products. The objective of this project is to develop a multi-scale structural model that explains differences in the observed bulk phase performance properties of CNT materials. In order to do this several different properties of CNTs and CNT structures were measured in an attempt to identify the significant differences which result in the observed behaviors.

8.2 Materials and Sample Preparation

Several different nanotubes were studied in this research. Three primary sources were used for all experiments. The first nanotube lot, with an average diameter of 0.8 nm,
was made by the HiPco process by Carbon Nanotechnologies, Inc. (CNI) and will hereafter be referred to as CNI, the second nanotube lot, with an average diameter of 1.5 nm, was made by the chemical vapor decomposition (CVD) process by Thomas Swann and will hereafter be referred to as Swann, and the third nanotube lot, with an average diameter of 1.5 nm, was also made by the CVD process by Unidym and will hereafter be referred to as Unidym. Three CNI samples, one containing 4wt% iron catalyst, another containing 21wt% iron catalyst and a super purified version; a nanotube referred to as P2, and a final nanotube sample referred to as B High P arc P2 (which hereafter will be referred to as B) were also used in various experiments.

Bucky papers were prepared by combining 10 mg of carbon nanotubes and 10 ml of chlorosulfonic acid (CSA) in a 4 dram glass vial and mixing with a magnetic stir bar for either 16 or 24 hours. Only one sample of the CNI nanotubes was stirred for 16 hours, while all other nanotubes were mixed for 24 hours. After mixing the nanotube solution was filtered with a 0.02 µm pore Anodisc filter. After the acid was removed the bucky papers were washed twice, while still on the filter, with 25 ml of diethyl ether. The bucky papers were allowed to dry in air for 24 hrs before further testing.

Nanotubes and nanotube films were characterized with a LabRAM Aramis Raman spectrometer using laser wavelengths of 532, 633 and 785 nm. No additional sample preparation was necessary. All samples were tested at room temperature.

The nanoscale features of carbon nanotube films such as bundle size, orientation, the presence of amorphous carbon and CNT length, were characterized using an FEI Nova nanoSEM scanning electron microscope (SEM) operating at 5 keV with a spot size
of 2.0. Samples were prepared by cutting a film into a 1.5 mm wide strip then applying stress in an axial direction until fractured, similar to a tensile test. This was done in order to determine if there were differences between the films at the location of tensile failure as well as at undeformed locations far away from the failure. Films made from the CNI 24hr, Elicarb, Unidym, CNI 4wt% Fe and CNI 21wt% Fe nanotubes were imaged with the SEM.

The tensile strength and modulus properties of the SWNT films were measured with an RSAIII. Tests were conducted at 25°C at a strain rate of $3 \times 10^{-4}$ s$^{-1}$ on films cut into strips 1.0 mm wide by 15 mm long by 15 µm thick (as measured by optical microscopy and confirmed with calipers), with each sample being tested at least four times. Experiments were performed on CNI16hr, CNI24hr, Swann and Unidym films.

Creep experiments were performed on CNI16hr, CNI24hr, Swan, and Unidym film samples cut 1.5 mm wide and ~20 mm long. One end of the film was fixed in a clamp using a fast drying epoxy to ensure a no slip occurred within the clamp. The other end of the film was secured in a second clamp, also with epoxy, which was attached to a 30 g mass and a linear variable displacement transducer (LVDT) probe. The 30 g mass was added to the system to provide the constant stress needed to measure the creep response of the films. The displacement of the film is detected through the use of the LVDT. The LVDT probe slides freely in a coil assembly which has an electric current flowing through it. Small changes in the position of the probe result in changes to the magnetic field created by the current flowing through the coil assembly. The changes in the magnetic field are detected and converted to a position of the probe.
8.3 Results

8.3.1 Raman Characterization

Several nanotube films and powders were characterized using Raman spectroscopy using laser wavelengths of 532, 633, and 785 nm. There are several regions of interest in the Raman spectra of carbon nanotubes. The radial breathing mode, which occurs between 100-300 cm$^{-1}$, is affected by the diameter of the nanotubes; the D-band, which occurs around 1300 cm$^{-1}$, is sensitive to defects in the sidewall of the nanotube or the presence of impurities; and the G-band which occurs around 1600 cm$^{-1}$, and arises due to the symmetry and order of the nanotube atomic structure. The first samples characterized were CNI16hr, CNI24hr, Swann, and Unidym films. We will first examine the Raman spectra collected for these samples using a 633 nm laser, shown in Figure 8.1, there are several observations that can be made. Using this data the films can be ranked in order of smallest to largest D-band intensity as follows: Unidym, CNI16hr, CNI24hr, Elicarb which means the Elicarb sample had the most impurities and/or sidewall defects; the Raman spectra alone cannot distinguish between the two. The CNI samples indicate that longer mixing times in the CSA can induce more defects, most likely in the sidewall. This is supported by the upshift in G-band (~1600 cm$^{-1}$) that occurs between the CNI16hr and the CNI24hr samples which is indicative of p doping or oxidation (electrons are removed) [163]. This is could be due to the nanotubes reacting with the CSA to bond negatively charged groups to the surface of the tube which would also explain the increase in the D-band.
The radial breathing modes of these samples are all very different as well which is caused by differences in the diameter distributions of the nanotubes. The RBM peaks of the CNI16hr and CNI24 hr films, shown in Figure 8.2, occur at nearly the same frequencies, which is due to the samples having the same CNT diameter distribution, however, there is an upshift in the peak position in the CNI16hr sample compared to the CNI24hr sample. The upshift in the peak location is attributed to higher van der Waal’s forces due to larger CNT bundles [79,164]. This is interpreted as longer mixing times in the CSA leads to more effective debundling of the nanotubes and thus smaller bundle sizes.

When the 785 nm laser was used, two unique peaks appeared in the Unidym sample that were not seen in any of the other three films which were located at ~1750 and ~1860 cm\(^{-1}\). This spectra is shown in Figure 8.3. Dresselhaus et al. [80] referred to the peak at ~1750 cm\(^{-1}\) as the M-band and attributed it’s presence as being due to overtones of the out-of-plane, infrared-active mode at 867 cm\(^{-1}\) in graphite. They attributed the second band to a combination of two intravalley phonons, one from the in-plane transverse optical branch and the second phonon from the longitudinal acoustic branch. There is no further discussion of these peaks by Dresselhaus et al. or in any other papers. At the present there is no explanation for why the Unidym film was the only sample to display these peaks. The raw Unidym nanotubes were characterized by Raman spectroscopy with the same 785 nm laser to determine if the peaks were present due to some sort of unique structure that resulted from the process of making the thin film. Tests
on the raw nanotubes revealed the same peaks therefore they were not caused by something unique to the film formation process.

Several other nanotube samples were characterized with Raman spectroscopy in an attempt to find tubes that displayed an M-band when excited with a 785 nm laser: three CNI samples, one containing 4wt% iron catalyst, another containing 21wt% iron catalyst and a super purified version; a nanotube referred to as P2, and a final nanotube sample referred to as B High P arc P2 (which hereafter will be referred to as B). Only the B sample displayed the same M-band peaks as Unidym sample when excited with a 785 nm laser. The spectrum is shown in Figure 8.4. The B sample has very similar peaks compared to the Unidym samples therefore these nanotubes are most likely the same.

8.3.2 Scanning Electron Microscopy Characterization

The structural information gathered by Raman spectroscopy was expanded through direct observation of both the microscale and nanoscale features of the nanotube films using scanning electron microscopy (SEM). The CNI24hr, Swann and Unidym films were observed using this method using the sample preparation method described in Section 8.2. A low magnification (~2000 – 2500x) image of the films at the location of tensile failure is shown in Figure 8.5. In the images it is apparent that the CNI and Swann films have a much different structure than the Unidym films at the microscale. The CNI and Swann films appear to have a layered structure, almost as if the film was formed by multiple thin films sandwiched together, while the Unidym film appears to be very uniform and continuous with no noticeable agglomerates or imperfections. The CNTs in
the Unidym sample at the location of the fracture are also much longer than in either the CNI or Swann. This seems to suggest that either the CNI and Swann nanotubes are inherently shorter than the Unidym tubes or when the samples are fractured the CNI and Swann nanotubes are broken while the Unidym tubes slide past each other and are unbroken. All samples however show the nanotubes to be aligned in the immediate area where the break occurred.

High magnification (80,000x) images taken farther away from the fracture are shown in Figure 8.6. From these images nanoscale differences between the samples can be seen. As predicted from the Raman spectroscopy data, the Unidym sample shows very little, if any, amorphous carbon or other impurities while they are quite prevalent in both the CNI and Swann samples. It appears that there are more impurities in the Swann sample as it is very difficult to distinguish individual nanotube bundles whereas many nanotube bundles can be seen in the CNI film.

The average bundle sizes present in the CNI, Swann, and Unidym samples were measured using SEM images taken at both the fracture location and far away from the fracture (see Figure 8.6). The images were imported to AutoCAD and lines were drawn across the diameter of the bundles. An AutoLISP program was used to compile the measured bundle diameters which were then averaged. The results of these measurements are shown in Table 8.1. It should be noted that there was not a significant difference between the bundle sizes at the fracture and away from the fracture. The bundle size measurements reveal that the Elicarb film had the largest bundles which were twice as large as the bundles in the CNI 24hr film. The Unidym film had bundles slightly larger
than those in the CNI 24hr film. Since all of the films were created by identical means the size of the bundles must be affected by something other than the processing methods. Possible variables include the diameter of the tubes, their atomic structure, the presence of impurities, and how bundled they were prior to mixing with CSA. The diameters of the Swann and Unidym tubes were identical but perhaps the Unidym tubes had a higher affinity for the CSA which would help them debundle to a greater degree. The CNI nanotubes had the smallest diameter and were also the smallest bundles but their chemical structure is different from both the Unidym and Swann tubes so a quantitative relationship between bundle size and nanotube diameter cannot be deduced. The Unidym tubes may have also been more debundled before mixing with acid which could be the most important factor. SEM images of the virgin nanotubes are needed to determine the initial degree of bundling.

8.3.3 Tensile Strength and Modulus

The tensile strength and modulus of CNI16hr, CNI24hr, Swann, and Unidym films were experimentally measured at room temperature following the procedure described in Section 8.2. From the stress-strain curves presented in Figure 8.7, it is apparent that the CNI16hr, CNI24hr and Swann films exhibit a different type of failure than the Unidym films. The stress-strain curves for the CNI16hr, CNI24hr and Swann films show an instantaneous failure which is indicative of brittle failure. The Unidym samples fail in a ductile manner which is indicated by a more gradual decrease in strain with increasing stress before complete failure. In polymer systems, the transition from
ductile to brittle failure is caused by several factors, such as molecular weight and cross link density, but is primarily related to the ability of the polymer chains to slide past one another. The more mobile the polymer chains the more likely the material is to exhibit ductile failure. From this analogy we can conclude that the Unidym nanotubes are able to dissipate an applied stress by untangling and sliding past one another. The reasons why this occurs in only the Unidym samples are not immediately obvious. Several researchers have shown that the tensile strength and modulus of a nanotube film depend on factors such as bundle size, defects in the nanotube structure, nanotube length, the concentration of impurities such as amorphous carbon and residual catalyst. It is also possible that the CNI and Swann nanotubes have more defects than the Unidym tubes and thus a lower tensile strength. When stress is applied to these tubes the force needed to untangle the tubes is greater than the strength of the tubes and therefore the tubes break resulting in the brittle failure mode.

If nanotube fracture was the source of failure of the CNI and Elicarb samples in tension the tensile strength and modulus of the material is expected to be much greater because the tensile strength and modulus of an individual CNT has been reported to be approximately 37 GPa and 640 GPa, respectively [127]. The greatest tensile strength and modulus experimentally measured were 70 MPa and 4.3 GPa, respectively, which are significantly less than the theoretical maximum value. Several reasons exist that could explain this behavior. First, the random orientation of the nanotubes in the bucky papers has the effect of distributing an applied load to fewer CNTs. The stress will be felt primarily by those CNTs aligned with the direction of strain. Also the tensile strength and
modulus of a bucky paper or CNT fiber are calculated based on the width and thickness (or diameter) of the sample. As the SEM images show, the structure formed by the nanotubes is not a continuous structure, there are void spaces present which means the true area the tensile force is distributed over is less than the area calculated from measurements of the samples dimensions. The density of the bucky papers then becomes an important parameter. A denser structure would have more closely packed CNTs and more area for external forces to be distributed over leading to higher tensile strengths.

The Swann sample shows a much larger amount of deformation before breaking than the other samples. In polymer samples deformation occurs due to bond stretching or angle deformation, viscous flow of the chains past one another, and reorientation or the molecules. Since the bonds in CNTs do not significantly stretch and the brittle failure seems to indicate they do not easily flow past one another, the most likely deformation mechanism is reorientation of the nanotube bundles which is possible because of the large amounts of void space in the film. SEM images reveal very little curl or waviness of the nanotube bundles in the Swann sample so it is unlikely that the straightening of these bundles can explain the large strain deformation of the Swann sample before rupture occurs.

The average tensile strength at break and tensile modulus results are shown in Figure 8.8. From this data we have evidence of the role of nanostructure in the properties of a nanotube film. If we examine the CNI 24hr and 16hr samples we see that the CNI 24hr samples have a greater tensile strength and modulus and because they were made from the same nanotube source the only difference between these two samples is the
length of time they were mixed. Evidence for the difference in bundle sizes can be seen in Raman spectrographs from the two samples as was discussed previously. This evidence suggests that smaller CNT bundles provide increased tensile strength although the bundle sizes of our samples have not yet been quantitatively measured. It is possible that there are other differences that result from longer mixing times like shorter CNT lengths, more or less amorphous carbon, or more CNT sidewall defects. As discussed in Section 8.3.1, if anything, the Raman spectra show evidence that the CNI24hr film has more defects than the CNI16hr film, therefore the decreased bundle size was able to outweigh the potentially increased number of defects. The effects of CNT length are on tensile strength and modulus of a nanotube film have never been studied because of the difficulty in obtaining carbon nanotubes with a uniform length distribution. It is also difficult to know how long the nanotubes or nanotube bundles are in our samples because the entire length of the bundle cannot be seen in the SEM images we obtained.

8.3.4 Creep

The long time deformation of the CNI 16hr, CNI24hr, Swann, and Unidym nanotube films under a constant stress, also known as creep, was experimentally measured following the procedure described in Section 8.2. The creep compliance of the sample is found by dividing the strain, which is the change in length of the sample divided by the original sample length, by the applied stress. Larger amounts of deformation lead to larger values of creep compliance. Figure 8.9 shows the experimentally measured values of creep compliance as a function of time for all four
samples as well as a plot of strain as a function of time. As Figure 8.9a shows, the shapes of the creep curves of all samples are very similar. The creep curves of both CNI samples are nearly identical indicating high similarity of the structures which has been confirmed through Raman spectroscopy.

If we look at Figure 8.9b it is apparent that the Swann film has the greatest amount of initial deformation and has the highest creep rate of any sample tested. The initial deformation corresponds well to the strain before break seen in the tensile strength experiments where the Swann film also had the largest deformation. This would suggest that these two properties are related and could be caused by the free volume in the sample allowing motion for the nanotube bundles. Also in Figure 8.9b we see that the Unidym and CNI samples have almost identical creep rates, which is the rate the nanotube bundles detangle and slide past one another. This raises the question, if the CNI and Unidym bundles detangle and slide past one another at the same rate why do only the Unidym films show ductile failure and why wouldn’t the Swann films have ductile failure since their creep rate is the highest of any? This could be explained by the time scale of the experiments. The creep rate of the Swann films is $2.3 \times 10^{-3}$ hr$^{-1}$ which is equal to $6.4 \times 10^{-7}$ s$^{-1}$ while the strain rate in the tensile test was $3 \times 10^{-4}$ s$^{-1}$, three orders of magnitude greater than the fastest creep rate. Since the tensile strength experiments occurred at a much shorter time scale than the process of the nanotube bundles sliding past each other, if the nanotubes are weakened, perhaps by sidewall defects, it is likely that the bundles would not have enough time dissipate stress by sliding and would therefore break. This could explain why the CNI and Elicarb tubes, which were revealed
to have large amounts of defects through Raman spectroscopy, displayed brittle failure while the Unidym film, which had almost no defects, could break in a ductile manner.

Previous researchers [165] have theorized that capillary forces play an important role in the creep behavior of nanotube films. Evidence for this was seen by Whitten et al. [165] who exposed nanotube bucky papers to different liquids which created different levels of capillary force holding the nanotubes together. They found that bucky papers made by identical methods from the same nanotubes possess very different responses to constant stress, particularly the amount of initial strain and the strain rate. One possible explanation for the differences in the creep behavior of our nanotube films (Figure 8.9), in addition to nanostructural differences, is that they possess different moisture contents resulting in differences in capillary forces between nanotubes.

The effect of moisture content on the creep behavior of the nanotube films was tested by performing the standard creep experiment at ~72°F and 50% relative humidity for ~100 hrs, then enclosing the creep apparatus with a large plastic bag which was secured to the bench top with masking tape, creating an airtight seal. Within the plastic bag, a tray containing 200g of desiccant was added in order to remove any moisture from the air and nanotube film. The creep strain as a function of time for a Unidym film using this procedure is shown in Figure 8.10. As this figure demonstrates, when the sample is exposed to 50% RH air there is a steady creep response with the film continuing to increase in length. Within several hours of introducing the desiccant the creep in the film ceases. It is possible that the desiccant removes water that has been absorbed by the nanotubes, bringing them in closer contact with each other thus increasing the force
needed to cause the tubes and bundles to slide past each other. Further experimentation exposing the films to different chemical species will be done in order to get a better understanding of the role of capillary forces on the properties of nanotube films.

8.4 Conclusions

Three primary nanotube sources have been used in this study, HiPco CNI, CVD Swann and CVD Unidym. Raman spectroscopy of these samples showed significant differences between all three nanotube types. The Unidym sample displayed very unique peaks at ~1750 and ~1860 cm\(^{-1}\) in its Raman spectra which have been rarely reported to date. The reasons why these were the only tubes to display these peaks and their significance is presently unknown and requires further investigation.

Tensile strength and modulus measurements of the nanotube films revealed more behavior unique to the Unidym film. The Unidym film showed ductile behavior while the other two films tested were brittle. SEM images showed the difference was not caused by the bundle size distribution as the Unidym and CNI films were equivalent. The strength of the carbon nanotubes could be the source of this difference. Both the CNI and Swann tubes were shown by Raman spectroscopy to contain many defects which would weaken the tensile strength of the nanotubes while the Unidym tubes possessed very few defects. When the tensile stress was applied the defect weakened CNI and Swann tubes broke resulting in a brittle failure while the Unidym tubes held together and simply untangled from one another resulting in the observed ductile behavior. The breakage of the CNI and Swann nanotubes is supported by SEM images which show these nanotubes to be
significantly shorter at the location of the tensile break compared to the Unidym nanotubes.

Creep experiments demonstrated the importance of capillary forces on the behavior of the nanotube films. All nanotube films tested under constant stress at ~72°F and 50% relative humidity were found to increase in length with increasing time although the rate at which this occurred varied from one sample to the next. When these films were enclosed in an airtight chamber and desiccant was added to remove moisture from the surrounding air the films ceased to be creep. It is likely that when the moisture in the air was removed it was also removed from the sample causing the nanotubes and nanotube bundles to be drawn closer together thus increasing the force needed to create sliding of the nanotubes and bundles. The nanotube films will be exposed to different chemical compounds to determine their effects on the creep rate.
Table 8.1 Average bundle diameters in three different nanotube film samples as measured from SEM images.

<table>
<thead>
<tr>
<th>Nanotube Sample</th>
<th>Avg. Bundle Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNI 24hr</td>
<td>9.1</td>
</tr>
<tr>
<td>Swann</td>
<td>18.2</td>
</tr>
<tr>
<td>Unidym</td>
<td>11.3</td>
</tr>
</tbody>
</table>
Figure 8.1 Raman spectra of (a) CNI16hr (b) CNI24hr (c) Swann and (d) Unidym films using a 633 nm laser.
Figure 8.1 continued
Figure 8.2 Raman spectra in the RBM region for (a) CNI16hr and (b) CNI24hr films using a 633 nm laser.
Figure 8.3  Raman spectra for the Unidym sample using the 785 nm laser.
Figure 8.4  Raman spectra for the B nanotube sample using the 785 nm laser.
Figure 8.5  Low magnification SEM image of the CNI24hr, Swann, and Unidym films at the location of tensile failure.
Figure 8.6  High magnification SEM images of the CNI24hr, Swann, and Unidym films at a location near the middle of the sample, far from the tensile failure.
Figure 8.7 Stress-strain curves for the CNI16hr, CNI24hr, Swann and Unidym films tested at an extension rate of $3 \times 10^{-4} \text{ s}^{-1}$. 
Figure 8.8 The (a) tensile strength at break and (b) tensile modulus of CNI16hr, CNI24hr, Swann and Unidym films.
Figure 8.9 The (a) creep compliance and (b) creep strain as functions of time for CNI16hr, CNI24hr, Swann and Unidym films.
Figure 8.10 Creep response of a Unidym film exposed to air at 50% relative humidity followed by sealing of the film in an airtight chamber containing desiccant to remove the moisture in the air.
CHAPTER 9

FUTURE WORK AND RECOMMENDATIONS

There are several experiments that could be performed that follow naturally from the work presented here. A new method of measuring the orientation of nanofibers during flow was presented in Chapter 5 and applied to composites under uniaxial extensional flow. This method could be used to experimentally measure the orientation evolution of carbon nanofibers during shear flow which could then be used to improve the predictions of the constitutive model. Similarly, the behavior of polystyrene/carbon nanofiber composites during flow reversal was studied in Chapter 4 and the effect of flow reversal on nanofiber orientation was unknown. The orientation measurement method could be applied to this case to determine how nanofiber orientation changes when shear flow is reversed or if orientation changes during a rest time following the application of a shear flow.

The constitutive model presented in Chapters 3 to 6 was used to predict the flow behavior of polymer nanocomposites under steady state and transient shear flows as well as extensional flows. This model could be adapted to predict the flow behavior of these composites under small amplitude oscillatory shear. The addition of nanoparticles to a polymer matrix was experimentally shown to result in an increase in the storage and loss
modulus of the composite with increasing nanoparticle concentration and the slope of the storage and loss modulus were shown to decrease with increasing nanoparticle concentration. By changing the definition of the shear rate in the constitutive model it would be possible to predict the linear viscoelastic behavior of these composites.

Finally, it would be beneficial to devise a way to characterize the mechanical and electrical properties of the carbon nanofiber/polystyrene composites that contain different fiber orientations. If composites containing different nanofiber orientation distributions could be created and their properties characterized, models could be developed that connect their performance properties to the properties (strength, conductivity, aspect ratio, concentration, orientation) of the nanoparticles. If the performance properties model and the model of the rheological properties and nanoparticle orientation evolution during flow presented in this work were used together, a polymer processing operation, such as injection molding, could be simulated using software such as MoldFlow using the rheological models in order to accurately predict the orientation of the carbon nanofibers which would then allow the properties of the composite to be predicted using the performance property model. This combination of models would enable the optimization of composite formulation and processing operations to create a final product with the desired performance properties.
REFERENCES


APPENDIX A: MATLAB Program for Solving the Constitutive Model for Transient Shear Flow

The following is the program written in MATLAB used to solve the constitutive model presented in Chapter 4 for the transient shear viscosity and CNF orientation tensor:

```matlab
function transient_ver2
x=1;
total12=0;
y=zeros(1,3);
tp=zeros(1,6);
re=44.0; %CNF aspect ratio
global alpha lambda etap chi r CI
chi=1.0*(re^2-1)/(re^2+1); %another form of aspect ratio
rf=1750.0; %fiber density
rs=1000.0; %polymer density
etap=[6012.077,16631.960,10326.558,17206.151,1165.003];
lambda=[0.130,5.736,30.503,1.039,0.011];
alpha=[0.999,0.999,0.999,0.758,0.277];
sigma=1.0;
t=0.0; %initial time
mass=[2.0/100.0, 5.0/100.0, 10.0/100.0, 0.0];

%ALTER PROGRAM BELOW
modes=5;
r=0.01; %shear rate, change this manually
CI=((-0.011*log(r)+0.0379)/0.1876)^(1/0.5006) %change this manually
tstep=.01;
c=1; %1 = .02wt, 2=.05wt, 3=.1wt, 4=.00wt
tspan=(t:tstep:1000.01);

phi=1.0*rs*mass(c)/(rf+(rs-rf)*mass(c));
Ap=1.0*re^2/(3*log(sqrt(1.0*pi/phi)));

while x<modes+1
    disp (x)
    [to,yo]=ode45('modetransientsub',tspan,[.33, 0, .33]); %braceted term is the initial values of a11, a12 and a22
    total12=total12+to(1,2);
end
```

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disp('orientation calculation done')

[toutp, youtp]=ode45('modepolymersub',tspan,tp);
disp('polymer stress calculation done')
tau12=youtp(:,2);
total12=total12+tau12;
x=x+1;
end

all=yo(:,1);
al2=yo(:,2);
a22=yo(:,3);
et=total12./r;
coef=2.0*eta*phi;
tfl2=(coef*Ap*r).*((27.0*(a11.*a22.*(1-a11-a22)-a12.^2.*(1-a11-a22))).*(-1.0/35.0+1.0/7.0*(a11+a22))+(a12.^2).*(-27.*(a11.*a22.*(1-a11-a22))+27.0*a12.^2.*(1-a11-a22)));
etac=tf12/r+eta;
disp('finished.')

answer = input('Do you want to plot? Y/N ', 's');
if answer==('Y')||answer==('y')
    %!!ONLY UNCOMMENT ONE GRAPH AT A TIME OR ELSE OVERWRITE WILL OCCUR!!!

    %ORIENTATION GRAPH, UNCOMMENT TO MAKE
    %semilogx(to,yo)
    %xlabel('Time (sec)');
    %ylabel('Orientation %');
    %legend('11', '12', '22');
    %title('Orientation Change Over Time');

    %STRESS GRAPH, UNCOMMENT TO MAKE
    %loglog(toutp, tau12/r)
    %xlabel('Time (sec)');
    %ylabel('Tau 12');
    %title('Stress Change Over Time');

    %VISCOCITY GRAPH, UNCOMMENT TO MAKE
    loglog(toutp,etac)
    xlabel('Time (sec)');
    ylabel('Viscosity (Eta C)(Pa-s)');
    title('Viscosity vs Time');
else
    disp('Done Plotting')
end
datafinal = zeros(44,6);
The following is the subroutine ‘modetransientsub’ found in the main body of the program:

```matlab
function dyo = modetransientsub(t,y)
    global CI x;
    global r;
    global chi;
    dyo=zeros(3,1);
    dyo(1,1)=r*y(2)+2*CI*r*(1.0-3.0*y(1))+chi*r*y(2)-
       2*chi*r*(3.0/7.0*y(2)*(27.0*y(1)*y(3)*(1-y(1)-y(3))-27.0*(y(2)^2)*(1-y(1)-y(3)))
      +1.0-27.0*y(1)*y(3)*(1-y(1)-y(3)))+27.0*(y(2)^2)*(1-y(1)-y(3)))*y(1)*y(2));
    dyo(2,1)=1.0/2.0*r*y(2)-
       1.0/2.0*r*y(1)+chi*((1.0/2.0*r*y(3)+1.0/2.0*r*y(1))-1.0/2.0*r*y(1)+
       (chi*2.0*r)*((27.0*y(1)*y(3)*(1-y(1)-y(3))-27.0*(y(2)^2)*(1-y(1)-y(3)))*(-1.0/35.0+1.0/7.0*y(1)+1.0/7.0*y(3))
      +(1.0-27.0*y(1)*y(3))*(1-y(1)-y(3))+27.0*(y(2)^2)*(1-y(1)-y(3)))
      +1.0-27.0*y(1)*y(3)*(1-y(1)-y(3)))+27.0*(y(2)^2)*(1-y(1)-y(3)))*y(1)*y(2));
    dyo(3,1)=r*y(2)+2*CI*r*(1.0-3.0*y(1))+chi*r*y(2)-
       2*chi*r*(3.0/7.0*y(2)*(27.0*y(1)*y(3)*(1-y(1)-y(3))-27.0*(y(2)^2)*(1-y(1)-y(3)))
      +1.0-27.0*y(1)*y(3)*(1-y(1)-y(3)))+27.0*(y(2)^2)*(1-y(1)-y(3)))*y(1)*y(2));
    %y(1) = temp1, y(2)=temp2, y(3)=temp4, temp6=1-y(1)-y(3)
end
```
The following is the subroutine ‘modepolymersub’ found in the main body of the program:

```matlab
function dyp = modepolymersub(t,tp)
global r x;
global alpha;
global etap;
global lambda;
dyp=zeros(6,1);
dyp(1,1)=-alpha(x)*(tp(1)^2+tp(2)^2+tp(3)^2)/etap(x)-
       tp(1)/lambda(x)+2*r*tp(2);
dyp(2,1)=-alpha(x)*(tp(1)*tp(2)+tp(2)*tp(4)+tp(3)*tp(5))/etap(x)-
       tp(2)/lambda(x)+etap(x)*r/lambda(x)+r*tp(4);
dyp(3,1)=-alpha(x)*(tp(1)*tp(3)+tp(2)*tp(5)+tp(3)*tp(6))/etap(x)-
       tp(3)/lambda(x)+r*tp(5);
dyp(4,1)=-alpha(x)*(tp(2)^2+tp(4)^2+tp(5)^2)/etap(x);
dyp(5,1)=-alpha(x)*(tp(2)*tp(3)+tp(4)*tp(5)+tp(5)*tp(6))/etap(x)-
       tp(5)/lambda(x);
dyp(6,1)=-alpha(x)*(tp(3)^2+tp(5)^2+tp(6)^2)/etap(x)-
       tp(6)*1.0/lambda(x);
```
APPENDIX B: MATLAB Program for Solving the Constitutive Model for Transient Extensional Flow

The following is the program written in MATLAB used to solve the constitutive model presented in Chapter 6 for the transient extensional viscosity and CNF orientation tensor:

```matlab
function transient_ver2
global x;
x=1;
totall2=0;
y=zeros(1,3);
 tp=zeros(1,3);
 re=44.0; %aspect ratio
 global alpha lambda etap chi r CI
 chi=1.0*(re^2-1)/(re^2+1); %another form of aspect ratio
 rf=1750.0; %fiber density
 rs=1000.0; %polymer density
 etap=[30966.807,31289.859,356.399,7850.120,3653.067];
 lambda=[1.000,0.990,13.989,98.852,110.277];
 alpha=[0.830,0.811,0.999,0.999,0.001];
 sigma=1.0;
t=0;
 mass=[2.0/100.0, 5.0/100.0, 10.0/100.0, 0.0];

%ALTER PROGRAM BELOW
CI=0.029;
r=1; %shear rate, change this manually
 tstep=0.01;
c=1; %1 = .02wt, 2=.05wt, 3=.1wt, 4=.00wt
 tspan=(t:tstep:1000.01);

phi=rs*mass(c)/(rf+(rs-rf)*mass(c))
Ap=re^2/(3*log(sqrt(pi/phi)))

while x<6 %<----- FOR NEW AMOUNT OF MODES CHANGE HERE!! IMPORTANT:
#=modes+1
 disp(x)
```

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[to, yo] = ode45('modeextensionalsub', tspan, [.586, .207, .207]); % braceted term is the initial values of a1, a22 and a33
disp('orientation calculation done')
[toutp, youtp] = ode45('modeexpolymersub', tspan, tp);
disp('polymer stress calculation done')
tau11 = youtp(:, 1);
tau22 = youtp(:, 2);
tau12 = tau11 - tau22;
total12 = total12 + tau12;
x = x + 1;
end

all = yo(:, 1);
a22 = yo(:, 2);
a33 = yo(:, 3);
et = total12 ./ r;
coef = 2.0 * eta * phi;
etac = tf12 / r + eta;
disp('finished.')

% answer = input('Do you want to plot? Y/N ', 's');
answer = 'n';
if answer == ('Y') || answer == ('y')
    % !!! ONLY UNCOMMENT ONE GRAPH AT A TIME OR ELSE OVERWRITE WILL OCCUR!!!

    % ORIENTATION GRAPH, UNCOMMENT TO MAKE
    semilogx(to, yo)
    xlabel('Time (sec)');
    ylabel('Orientation %');
    legend('11', '22', '33');
    title('Orientation Change Over Time');

    % STRESS GRAPH, UNCOMMENT TO MAKE
    loglog(toutp, tau12 / r)
    xlabel('Time (sec)');
    ylabel('Tau 12');
    title('Stress Change Over Time');

    % VISCOSITY GRAPH, UNCOMMENT TO MAKE
    loglog(total12, etac)
    xlabel('Time (sec)');
    ylabel('Viscosity (Eta C) (Pa-s)');
    title('Viscosity vs Time');
else
    disp('Done Plotting')
 end
datafinal = zeros(41,6);
a=1;
x=1;

while x<=41
    datafinal(a,1)= toutp(points(x));
    datafinal(a,2:4) = [yo(points(x),1), yo(points(x),2),
    yo(points(x),3)];
    datafinal(a,5)= total12(points(x))/r;
    datafinal(a,6)= etac(points(x));
    a=a+1;
    x=x+1;
end
disp 'Done sorting'
disp 'Writing...
xlswrite('MultiMode', datafinal, 'NEWDATA','A2:F42');

disp 'Finished, Terminating Program'
disp 'Terminated'
end

The following is the subroutine ‘modeextensionalsub’ found in the main body of
the program:

function dyo = modeextensionalsub(t,y)
global CI;
global r;
global chi;
global etap;
global alpha lambda x;
global alpha lambda x;
dyo=zeros(3,1);
dyo(1,1)=CI*2*3^(.5)*r*(1-3*y(1))+2*chi*r*y(1)-
    2*chi*r*(27*y(1)*y(2)*y(3)*(-2/35+(10*y(1)-y(2)-y(3))/14)+1-
    27*y(1)*y(2)*y(3))*(y(1)^2-(y(1)*y(2)+y(1)*y(3))/2));
dyo(2,1)=CI*2*3^(.5)*r*(1-3*y(2))-chi*r*(27*y(1)*y(2)*y(3)*(-2/35+(10*y(1)-y(2)-y(3))/14)+1-
    27*y(1)*y(2)*y(3))*(y(1)*y(2)-y(1)^2+y(2)^2+y(3)^2)/2));
dyo(3,1)=CI*2*3^(.5)*r*(1-3*y(3))-chi*r*y(3)-
    2*chi*r*(27*y(1)*y(2)*y(3)*(-2/35+(10*y(1)-y(2)-y(3))/14)+1-
    27*y(1)*y(2)*y(3))*(y(1)*y(3)-y(1)^2+y(2)^2+y(3)^2)/2));
y(1) = temp1, y(2)=temp4, y(3)=temp6, temp6=1-y(1)-y(2)
End
The following is the subroutine ‘modeexpolymersub’ found in the main body of
the program:

```matlab
function dyp = modeexpolymersub(t,tp)
global r;
global alpha x;
global etap;
global lambda;
global sigma;
global a11;
dyp=zeros(3,1);
dyp(1,1)=2*r*etap(x)/lambda(x)-tp(1)/lambda(x)-alpha(x)/etap(x)*tp(1)^2+2*r*tp(1);
dyp(2,1)=-r*etap(x)/lambda(x)-tp(2)/lambda(x)-alpha(x)/etap(x)*tp(2)^2-r*tp(2);
dyp(3,1)=-r*etap(x)/lambda(x)-tp(3)/lambda(x)-alpha(x)/etap(x)*tp(3)^2-r*tp(3);
```
APPENDIX C: Expansion of the Constitutive Model Equations

In order to solve the constitutive model presented in Chapters 3, 4, and 6 with MATLAB, the model equations must be expanded to solve for each component using each closure model of interest. This expansion will be presented for transient shear flow and transient extensional flow. The constitutive model is composed of the following equations:

\[ \tau_{ij}^c = -p\delta_{ij} + 2\eta_p D_{ij} + \tau_{ij}^p + \tau_{ij}^{CNF}, \]  \hspace{1cm} (C.1)

\[ \sigma\tau_{ij}^p + \lambda \frac{D\tau_{ij}^p}{Dt} + \frac{\alpha\lambda}{\eta_p} (\tau_{ik}^p \tau_{kj}^p) + \frac{m(1-\sigma)}{2} (a_{ik} \tau_{ij}^p + \tau_{ik}^p a_{ij}) = 2\eta_p D_{ij}, \]  \hspace{1cm} (C.2)

\[ \tau_{ij}^{CNF} = 2[\eta_s + \eta] \phi \left[ AD_{ik} a_{ijkl} + B (D_{ik} a_{kj} + a_{ik} D_{kj}) + CD_{ij} + 2Fa_{ij} D_{ij} \right], \]  \hspace{1cm} (C.3)

\[ \frac{da_{ij}}{dt} = (W_{ik} a_{kj} - a_{ik} W_{kj}) + \chi (D_{ik} a_{kj} + a_{ik} D_{kj} - 2D_{ik} a_{ik}) + 4C_i \Gamma^{ij} \left( \delta_{ij} - ma_{ij} \right) \]  \hspace{1cm} (C.4)

Transient shear flow will be evaluated first. The stress tensor for this flow is given by a 3×3 matrix which is written in shorthand as \( \tau_{ij} \) in the model equations. This tensor is symmetric and has four non-zero components: \( \tau_{11}, \tau_{22}, \tau_{33}, \tau_{12} = \tau_{21} \). This means that for each of the 4 equations that make up the constitutive model there are four equations that can be written, one for each unique component of the 3×3 matrix.
First we will evaluate the modified Giesekus model (Equation C.2) and simplify each of the four possible equations so that they are expressed as the derivative of the stress component with time. Expression of the equations in this manner allows them to be easily solved by MATLAB. In shear flows, the skew and symmetric parts of the Eulerian velocity gradient are given by

\[
W_{ij} = \begin{bmatrix}
0 & \dot{\gamma}/2 & 0 \\
-\dot{\gamma}/2 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]  
(C.5)

\[
D_{ij} = \begin{bmatrix}
0 & \dot{\gamma}/2 & 0 \\
\dot{\gamma}/2 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]  
(C.6)

respectively. The upper convected time derivative, \( \frac{D\tau_{ij}^p}{Dt} \), is defined as:

\[
\frac{D\tau_{ij}^p}{Dt} = \frac{d}{dt} \tau_{ij}^p - W_{ik} \tau_{kj}^p + \tau_{ik}^p W_{kj} - D_{ik} \tau_{kj}^p - \tau_{ik}^p D_{kj}
\]  
(C.7)

Solving for each of the four components leads to:

\[
\frac{D\tau_{11}^p}{Dt} = \frac{d}{dt} \tau_{11}^p - W_{12} \tau_{21}^p - \tau_{12}^p W_{21} - D_{12} \tau_{21}^p - \tau_{12}^p D_{21}
\]  
(C.8)

\[
= \frac{d}{dt} \tau_{11}^p - \frac{\dot{\gamma}}{2} \tau_{21}^p - \tau_{12}^p \frac{\dot{\gamma}}{2} - \frac{\dot{\gamma}}{2} \tau_{21}^p - \tau_{12}^p \frac{\dot{\gamma}}{2}
\]  
(C.9)

\[
= \frac{d}{dt} \tau_{11}^p - 2\dot{\gamma}\tau_{12}^p
\]  
(C.10)
\[
\frac{D\tau_{22}^p}{Dt} = \frac{d}{dt} \tau_{22}^p - W_{21} \tau_{12}^p + \tau_{21}^p W_{12} - D_{21} \tau_{12}^p - \tau_{21}^p D_{12} \quad (C.11)
\]

\[
= \frac{d}{dt} \tau_{22}^p + \frac{\dot{\gamma}}{2} \tau_{12}^p + \tau_{21}^p \frac{\dot{\gamma}}{2} - \frac{\dot{\gamma}}{2} \tau_{12}^p - \tau_{21}^p \frac{\dot{\gamma}}{2} \quad (C.12)
\]

\[
= \frac{d}{dt} \tau_{22}^p \quad (C.13)
\]

\[
\frac{D\tau_{33}^p}{Dt} = \frac{d}{dt} \tau_{33}^p - W_{3k} \tau_{k3}^p + \tau_{3k}^p W_{k3} - D_{3k} \tau_{k3}^p - \tau_{3k}^p D_{k3} \quad (C.14)
\]

(in this case \(W\) and \(D = 0\) for all \(k\)’s)

\[
= \frac{d}{dt} \tau_{33}^p \quad (C.15)
\]

\[
\frac{D\tau_{12}^p}{Dt} = \frac{d}{dt} \tau_{12}^p + \tau_{11}^p W_{12} - \tau_{11}^p D_{12} - W_{12} \tau_{22}^p - D_{12} \tau_{22}^p \quad (C.16)
\]

\[
= \frac{d}{dt} \tau_{12}^p + \tau_{11}^p \frac{\dot{\gamma}}{2} - \tau_{11}^p \frac{\dot{\gamma}}{2} - \frac{\dot{\gamma}}{2} \tau_{22}^p - \frac{\dot{\gamma}}{2} \tau_{22}^p \quad (C.17)
\]

\[
= \frac{d}{dt} \tau_{12}^p - \dot{\gamma} \tau_{22}^p \quad (C.18)
\]

The simplified forms of \(\frac{D\tau_{ij}^p}{Dt}\) are substituted into Equation (C.2) which is then simplified:

\[
\sigma \tau_{11}^p + \lambda \left( \frac{d}{dt} \tau_{11}^p - 2\dot{\gamma} \tau_{12}^p \right) + \frac{\alpha \lambda}{\eta_p} \left( \tau_{11}^2 + \tau_{12}^2 + \tau_{13}^2 \right) + \frac{3(1-\sigma)}{2} \left( 2\tau_{11}^p a_{11} + \tau_{12}^p a_{12} + \tau_{13}^p a_{13} \right) \quad (C.19)
\]

\[
= 2\eta_p D_{11}
\]
\begin{align}
\frac{d}{dt} \tau_{11}^p - 2\gamma \tau_{12}^p &= -\sigma \tau_{11}^p - 3(1-\sigma)\left(\tau_{11}^p a_{11} + \tau_{12}^p a_{12} + a_{13} \tau_{13}^p \right) - \frac{\alpha}{\eta_p} \left( \tau_{11}^2 + \tau_{12}^2 + \tau_{13}^2 \right) \\
&= \frac{-\sigma \tau_{11}^p - 3(1-\sigma)\left(\tau_{11}^p a_{11} + \tau_{12}^p a_{12} \right)}{\lambda} - \frac{\alpha}{\eta_p} \left( \tau_{11}^2 + \tau_{12}^2 \right) + 2\gamma \tau_{12}^p \\
\frac{d}{dt} \tau_{22}^p &= \sigma \tau_{22}^p + \lambda \left( \frac{d}{dt} \tau_{22}^p \right) + \frac{\alpha \lambda}{\eta_p} \left( \tau_{22}^2 + \tau_{23}^2 + \tau_{33}^2 \right) + \frac{3(1-\sigma)}{2} \left( 2[\tau_{12}^p a_{12} + \tau_{22}^p a_{22} + \tau_{32}^p a_{32}] \right) \\
&= 2\eta_p D_{22} \\
\frac{d}{dt} \tau_{33}^p &= \sigma \tau_{33}^p + \lambda \left( \frac{d}{dt} \tau_{33}^p \right) + \frac{\alpha \lambda}{\eta_p} \left( \tau_{33}^2 + \tau_{23}^2 + \tau_{33}^2 \right) + \frac{3(1-\sigma)}{2} \left( 2[\tau_{13}^p a_{13} + \tau_{23}^p a_{23} + \tau_{33}^p a_{33}] \right) \\
&= 2\eta_p D_{33} \\
\frac{d}{dt} \tau_{12}^p &= \sigma \tau_{12}^p + \lambda \left( \frac{d}{dt} \tau_{12}^p - \gamma \tau_{12}^p \right) + \frac{\alpha \lambda}{\eta_p} \left( \tau_{11} \tau_{12} + \tau_{12} \tau_{22} + \tau_{13} \tau_{23} \right) + \frac{3(1-\sigma)}{2} \left( a_{11} \tau_{12} + a_{12} \tau_{22} + a_{13} \tau_{13} \right) - 2\eta_p D_{12} \\
\frac{d}{dt} \tau_{12}^p &= \frac{\eta_p \dot{\gamma}}{\lambda} - \frac{\sigma \tau_{12}^p}{\lambda} - \frac{3(1-\sigma)}{2\lambda} \left( a_{11} \tau_{12} + a_{12} \tau_{22} + a_{13} \tau_{13} + a_{22} \tau_{12} \right) \\
&= \frac{\eta_p \dot{\gamma}}{\lambda} - \frac{3(1-\sigma)}{2\lambda} \left( a_{11} \tau_{12} + a_{12} \tau_{22} + a_{13} \tau_{13} + a_{22} \tau_{12} \right) - \frac{\alpha}{\eta_p} \left( \tau_{11} \tau_{12} + \tau_{12} \tau_{22} \right) + \gamma \tau_{12}^p
\end{align}
Only the $\tau_{12}^{CNF}$ component in Equation (C.3) must be solved because that is the only component needed to calculate the viscosity of the composite, $\frac{\tau_{12}}{\dot{\gamma}}$, using Equation (1):

$$\tau_{ij}^{CNF} = 2[\eta_s + \eta] \phi \left[ AD_{i\lambda} a_{j\lambda} + B \left( D_{i\lambda} a_{j\lambda} + a_{i\lambda} D_{j\lambda} \right) + CD_{ij} + 2Fa_{ij}D_r \right] \quad (C.28)$$

(Note: $\eta_s = 0$)

$$\tau_{12}^{CNF} = 2\eta \phi \left[ AD_{12} a_{12} + B(D_{12} a_{12} + a_{12} D_{12}) + CD_{12} + 2Fa_{12} \left( C_i \dot{\gamma} \right) \right] \quad (C.29)$$

$$\tau_{12}^{CNF} = 2\eta \phi \left[ A(D_{12} a_{12} + D_{22} a_{12}) + B(D_{12} a_{22} + a_{11} D_{12}) + CD_{12} + 2Fa_{12} \left( C_i \dot{\gamma} \right) \right] \quad (C.30)$$

$$\tau_{12}^{CNF} = 2\eta \phi \left[ A\dot{\gamma} a_{12} + B \left( \frac{\dot{\gamma}}{2} a_{22} + \frac{\dot{\gamma}}{2} a_{11} \right) + C\dot{\gamma} + 2Fa_{12} \left( C_i \dot{\gamma} \right) \right] \quad (C.31)$$

The final form of Equation (C.3) depends on what closure approximation is chosen to solve for $a_{1212}$:

**Hybrid:**

$$\tau_{12}^{CNF} = 2\eta \phi \left[ A\dot{\gamma} + \frac{27a_{11}a_{22}a_{33} - a_{12}^2 a_{33}}{\frac{-1}{35} + \frac{a_{11} + a_{22}}{7}} \right]$$

$$+ a_{12}^2 \left( 1 - 27a_{11}a_{22}a_{33} + 27a_{12}^2 a_{33} \right) + B \left( \frac{\dot{\gamma}}{2} a_{22} + \frac{\dot{\gamma}}{2} a_{11} \right) + C\dot{\gamma} + 2Fa_{12} \left( C_i \dot{\gamma} \right) \quad (C.32)$$

**Quadratic:**

$$\tau_{12}^{CNF} = 2\eta \phi \left[ A\dot{\gamma} a_{12}^2 + B \left( \frac{\dot{\gamma}}{2} a_{22} + \frac{\dot{\gamma}}{2} a_{11} \right) + C\dot{\gamma} + 2Fa_{12} \left( C_i \dot{\gamma} \right) \right] \quad (C.33)$$

**Linear:**
\[ \tau_{12}^{\text{CNF}} = 2\eta \phi \left[ A\dot{\gamma} \left( -\frac{1}{35} + \frac{a_{11} + a_{22}}{7} \right) + B \left( \frac{\dot{\gamma}}{2} a_{22} + \frac{\dot{\gamma}^2}{2} a_{11} \right) + C\dot{\gamma} + 2Fa_{12}(C_i\dot{\gamma}) \right] \]  

(C.34)

The solution to Equation (C.4) also depends on the choice of closure approximation.

Hybrid:

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

(C.35)

\[ \frac{da_{12}(t)}{dt} = \frac{\dot{\gamma}}{2} \left[ a_{22}(t) - a_{11}(t) \right] - 6C_i\dot{\gamma}a_{12}(t) \]

(C.36)

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

(C.37)
\[
\frac{da_{33}(t)}{dt} = 2C_{ij} \dot{\gamma} \left[1 - 3a_{33}(t)\right] - 2\chi \ddot{\gamma} \left\{ \frac{1}{7} \left[ 27a_{11}(t)a_{22}(t)a_{33}(t) - 27a_{12}^2(t)a_{33}(t) \right]a_{12}(t) + \left[ 1 - 27a_{11}(t)a_{22}(t)a_{33}(t) + 27a_{12}^2(t)a_{33}(t) \right]a_{12}(t)a_{33}(t) \right\}
\]

(C.38)

**Quadratic:**

\[
\frac{da_{11}(t)}{dt} = \dot{\gamma}a_{12}(t) + 2C_{ij} \dot{\gamma} \left(1 - 3a_{11}(t)\right) + \chi \ddot{\gamma}a_{12}(t) - 2\chi \ddot{\gamma}a_{12}a_{12}(t)
\]

(C.39)

\[
\frac{da_{12}(t)}{dt} = \frac{\dot{\gamma}}{2} \left[ a_{22}(t) - a_{11}(t) \right] - 6C_{ij} \dot{\gamma} a_{12}(t) + \chi \ddot{\gamma} \left[ a_{22}(t) + a_{11}(t) \right] - 2\chi \ddot{\gamma}a_{12}^2(t)
\]

(C.40)

\[
\frac{da_{22}(t)}{dt} = -\dot{\gamma}a_{12}(t) + 2C_{ij} \dot{\gamma} \left(1 - 3a_{22}(t)\right) + \chi \ddot{\gamma}a_{12}(t) - 2\chi \ddot{\gamma}a_{12}a_{12}(t)
\]

(C.41)

\[
\frac{da_{33}(t)}{dt} = 2C_{ij} \dot{\gamma} \left(1 - 3a_{33}(t)\right) - 2\chi \ddot{\gamma}a_{33}(t)a_{12}(t)
\]

(C.42)

**Linear:**

\[
\frac{da_{11}(t)}{dt} = \dot{\gamma}a_{12}(t) + 2C_{ij} \dot{\gamma} \left(1 - 3a_{11}(t)\right) + \frac{1}{7} \chi \ddot{\gamma}a_{12}(t)
\]

(C.43)

\[
\frac{da_{12}(t)}{dt} = \frac{\dot{\gamma}}{2} \left[ a_{22}(t) - a_{11}(t) \right] - 6C_{ij} \dot{\gamma} a_{12}(t) + \chi \ddot{\gamma} \left[ a_{22}(t) + a_{11}(t) \right] - 2\chi \ddot{\gamma} \left\{ -\frac{1}{35} + \frac{1}{7} \left[ a_{11}(t) + a_{22}(t) \right] \right\}
\]

(C.44)

\[
\frac{da_{22}(t)}{dt} = -\dot{\gamma}a_{12}(t) + 2C_{ij} \dot{\gamma} \left(1 - 3a_{22}(t)\right) + \frac{1}{7} \chi \ddot{\gamma}a_{12}(t)
\]

(C.45)

\[
\frac{da_{33}(t)}{dt} = 2C_{ij} \dot{\gamma} \left(1 - 3a_{33}(t)\right) - \frac{2}{7} \chi \ddot{\gamma}a_{12}(t)
\]

(C.46)
The following is the expansion of Equations (C.1)-(C.4) for extensional flow:

Extensional flow is defined as:

\[ \eta_E^+ = \frac{\tau_{11} - \tau_{22}}{\dot{\varepsilon}} \]  \hspace{1cm} (C.47)

Thus, Equation (C.1) is written as:

\[ \eta_E^+ = \frac{\tau_{11}^c - \tau_{22}^c}{\dot{\varepsilon}} = \frac{\left(\tau_{11}^p + \tau_{11}^{CNF}\right) - \left(\tau_{22}^p + \tau_{22}^{CNF}\right)}{\dot{\varepsilon}} \]  \hspace{1cm} (C.48)

In extensional flow there are only three non-zero components of the stress tensor: \(\tau_{11}, \tau_{22}\) and \(\tau_{33}\), therefore for each of the three remaining equations (Equations C.2-C.4) that make up the constitutive model there are three equations that can be written

For extensional flow:

\[ W = 0 \]  \hspace{1cm} (C.49)

\[ D_0 = \begin{bmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon}/2 & 0 \\ 0 & 0 & -\dot{\varepsilon}/2 \end{bmatrix} \]  \hspace{1cm} (C.50)

Equation (C.2):

\[ \sigma \tau_{ij} + \lambda \frac{D \tau_{ij}}{Dt} + \frac{\alpha \lambda}{\eta_p} (\tau_{ik} \tau_{kj}) + \frac{3(1-\sigma)}{2} (a_{ik} \tau_{kj} + \tau_{ik} a_{kj}) = 2\eta_p D_{ij} \]  \hspace{1cm} (C.51)

\[ (\tau_{ik} \tau_{kj}): \]

For

\[ i,j = 1,1: (\tau_{ik} \tau_{kj}) = (\tau_{11}^2) \]  \hspace{1cm} (C.52)

\[ i,j = 2,2: (\tau_{ik} \tau_{kj}) = (\tau_{22}^2) \]  \hspace{1cm} (C.53)
\( i,j = 3,3: (\tau_{ik} \tau_{kj}) = (\tau_{33}^2) \)  
(C.54)

\( (a_{ik} \tau_{kj} + \tau_{ik} a_{kj}) \):

For
\( i,j = 1,1: (a_{ik} \tau_{kj} + \tau_{ik} a_{kj}) = (2a_{11} \tau_{11}) \)  
(C.55)
\( i,j = 2,2: (a_{ik} \tau_{kj} + \tau_{ik} a_{kj}) = (2a_{22} \tau_{22}) \)  
(C.56)
\( i,j = 3,3: (a_{ik} \tau_{kj} + \tau_{ik} a_{kj}) = (2a_{33} \tau_{33}) \)  
(C.57)

\[ \begin{align*}
\frac{D \tau_{ij}}{Dt} : \\
\text{For} \\
\text{i,j} = 1,1: & & \frac{D \tau_{ij}}{Dt} = \frac{d}{dt} \tau_{11} - 2D_{11} \tau_{11} = \frac{d}{dt} \tau_{11} - 2 \dot{\epsilon} \tau_{11} \\
\text{i,j} = 2,2: & & \frac{D \tau_{ij}}{Dt} = \frac{d}{dt} \tau_{22} - 2D_{22} \tau_{22} = \frac{d}{dt} \tau_{22} + \dot{\epsilon} \tau_{22} \\
\text{i,j} = 3,3: & & \frac{D \tau_{ij}}{Dt} = \frac{d}{dt} \tau_{33} - 2D_{33} \tau_{33} = \frac{d}{dt} \tau_{33} + \dot{\epsilon} \tau_{33}
\end{align*} \]  
(C.58-60)

\( \sigma \tau_{11} + \lambda \left( \frac{d}{dt} \tau_{11} - 2 \dot{\epsilon} \tau_{11} \right) + \frac{\alpha \lambda}{\eta_p} \left( \tau_{11}^2 \right) + \frac{3(1 - \sigma)}{2} (2a_{11} \tau_{11}) = 2 \eta_p D_{11} \)  
(C.61)

\[ \frac{d}{dt} \tau_{11} = \frac{2 \eta_p \dot{\epsilon} \lambda}{2} - \frac{\sigma \tau_{11} \lambda}{2} - \frac{3(1 - \sigma)}{2} (2a_{11} \tau_{11}) - \frac{\alpha}{\eta_p} \left( \tau_{11}^2 \right) + 2 \dot{\epsilon} \tau_{11} \]  
(C.62)
\[ \sigma \tau_{22} + \lambda \left( \frac{d}{dt} \tau_{22} + \dot{\tau}_{22} \right) + \frac{\alpha \lambda}{\eta_p} \left( \dot{\tau}_{22}^2 \right) + \frac{3(1 - \sigma)}{2} (2a_{22}\tau_{22}) = 2\eta_p D_{22} \] (C.63)

\[ \frac{d}{dt} \tau_{22} = -\frac{\eta_p \dot{\tau}_{22}}{\lambda} - \frac{\sigma \tau_{22}}{\lambda} + \frac{3(1 - \sigma)}{\lambda} (a_{22}\tau_{22}) - \frac{\alpha}{\eta_p} \left( \tau_{22}^2 \right) - \dot{\tau}_{22} \] (C.64)

\[ \sigma \tau_{33} + \lambda \left( \frac{d}{dt} \tau_{33} + \dot{\tau}_{33} \right) + \frac{\alpha \lambda}{\eta_p} \left( \dot{\tau}_{33}^2 \right) + \frac{3(1 - \sigma)}{2} (2a_{33}\tau_{33}) = 2\eta_p D_{33} \] (C.65)

\[ \frac{d}{dt} \tau_{33} = -\frac{\eta_p \dot{\tau}_{33}}{\lambda} - \frac{\sigma \tau_{33}}{\lambda} - \frac{3(1 - \sigma)}{\lambda} (a_{33}\tau_{33}) - \frac{\alpha}{\eta_p} \left( \tau_{33}^2 \right) - \dot{\tau}_{33} \] (C.66)

In Equation (C.3):

\[ \tau_{11}^{CNF} : D_{kl}a_{ijkl} = D_{11}a_{1111} + D_{22}a_{1122} + D_{33}a_{1133} \] (C.67)

\[ \tau_{22}^{CNF} : D_{kl}a_{ijkl} = D_{11}a_{2211} + D_{22}a_{2222} + D_{33}a_{2233} \] (C.68)

Solving Equation (C.3) with the Quadratic closure approximation:

\[ \tau_{11}^{CNF} : D_{kl}a_{ijkl} = \dot{\tau}_{11} \left( a_{11}^2 - \frac{a_{11}a_{22} + a_{11}a_{33}}{2} \right) \] (C.69)

\[ \tau_{22}^{CNF} : D_{kl}a_{ijkl} = \dot{\tau}_{22} \left( a_{11}a_{22} - \frac{a_{22}^2 + a_{22}a_{33}}{2} \right) \] (C.70)

\[ \tau_{11}^{CNF} - \tau_{22}^{CNF} = 2\eta_p A \dot{\tau}_{11} \left[ a_{11}^2 + a_{22}^2 + 3a_{11}a_{22} - a_{11}a_{33} + a_{22}a_{33} \right] \] (C.71)

Linear:

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\[ \tau_{11}^{\text{CNF}} : D_{kl}a_{ijkl} = \frac{\dot{\epsilon}}{7} \left( -\frac{2}{5} - 2a_{11} - \frac{a_{22} + a_{33}}{2} \right) \]  
(C.72)

\[ \tau_{22}^{\text{CNF}} : D_{kl}a_{ijkl} = \frac{\dot{\epsilon}}{7} \left( \frac{1}{5} + a_{11} + a_{22} - \frac{a_{33}}{2} \right) \]  
(C.73)

\[ \tau_{11}^{\text{CNF}} - \tau_{22}^{\text{CNF}} = 2\eta \phi A \dot{\epsilon} \left[ \frac{3}{7} \left( -\frac{1}{5} - a_{11} - \frac{a_{22}}{2} \right) \right] \]  
(C.74)

**Hybrid:**

\[ \tau_{11}^{\text{CNF}} : D_{kl}a_{ijkl} = \dot{\epsilon} \left[ 27a_{11}a_{22}a_{33} \left( -\frac{2}{35} + \frac{10a_{11} - a_{22} - a_{33}}{14} \right) + \left( 1 - 27a_{11}a_{22}a_{33} \right) \left( \frac{a_{11}a_{22} + a_{11}a_{33}}{2} \right) \right] \]  
(C.75)

\[ \tau_{22}^{\text{CNF}} : D_{kl}a_{ijkl} = \dot{\epsilon} \left[ 27a_{11}a_{22}a_{33} \left( \frac{1}{35} + \frac{2a_{11} - 5a_{22} - a_{33}}{14} \right) + \left( 1 - 27a_{11}a_{22}a_{33} \right) \left( a_{11}a_{22} - \frac{a_{22}^2 + a_{22}a_{33}}{2} \right) \right] \]  
(C.76)

\[ \tau_{11}^{\text{CNF}} - \tau_{22}^{\text{CNF}} = 2\eta \phi A \dot{\epsilon} \left[ 27a_{11}a_{22}a_{33} \left( -\frac{3}{35} + \frac{4a_{11} + 2a_{22}}{7} \right) + \left( 1 - 27a_{11}a_{22}a_{33} \right) \left( \frac{a_{11}^2 - 3a_{11}a_{22} - a_{11}a_{33} + a_{22}^2 + a_{22}a_{33}}{2} \right) \right] \]  
(C.77)

**Equation (4) with Quadratic Closure:**

\[ \frac{da_{11}}{dt} = 2\sqrt{3} C \dot{\epsilon} (1 - 3a_{11}) + 2\chi \dot{\epsilon} a_{11} - 2\chi \left( \frac{\dot{\epsilon} a_{11}^2 - \frac{\dot{\epsilon}}{2} a_{11}a_{22} - \frac{\dot{\epsilon}}{2} a_{11}a_{33}}{2} \right) \]  
(C.78)

\[ \frac{da_{22}}{dt} = 2\sqrt{3} C \dot{\epsilon} (1 - 3a_{22}) - \chi \dot{\epsilon} a_{22} - 2\chi \left( \frac{\dot{\epsilon} a_{11}a_{22} - \frac{\dot{\epsilon}}{2} a_{22}^2 - \frac{\dot{\epsilon}}{2} a_{22}a_{33}}{2} \right) \]  
(C.79)
\[
\frac{da_{33}}{dt} = 2\sqrt{3}C_i \dot{\epsilon}_i (1 - 3a_{33}) - \chi\dot{\epsilon}_{a_{33}} - 2\chi \left( \dot{\epsilon}a_{11}a_{33} - \frac{\dot{\epsilon}}{2}a_{22}a_{33} - \frac{\dot{\epsilon}}{2}a_{33}^2 \right) \quad (C.80)
\]

Equation (4) with Linear Closure:

\[
\frac{da_{11}}{dt} = 2\sqrt{3}C_i \dot{\epsilon}_i (1 - 3a_{11}) - 2\chi\dot{\epsilon}_{a_{11}} - 2\chi \left( \frac{2}{35} - \frac{1}{2} - \frac{1}{2}a_{22} + a_{33} \right) \quad (C.81)
\]

\[
\frac{da_{22}}{dt} = 2\sqrt{3}C_i \dot{\epsilon}_i (1 - 3a_{22}) - 2\chi\dot{\epsilon}_{a_{22}} - 2\chi \left( \frac{1}{35} + \frac{1}{14}a_{11} + a_{22} - \frac{1}{14}a_{33} \right) \quad (C.82)
\]

\[
\frac{da_{33}}{dt} = 2\sqrt{3}C_i \dot{\epsilon}_i (1 - 3a_{33}) - 2\chi\dot{\epsilon}_{a_{33}} - 2\chi \left( \frac{1}{35} + \frac{1}{14}a_{11} - \frac{1}{14}a_{22} + a_{33} \right) \quad (C.83)
\]

Equation (4) with Hybrid Closure:

\[
\frac{da_{11}}{dt} = 2\sqrt{3}C_i \dot{\epsilon}_i (1 - 3a_{11}) - 2\chi\dot{\epsilon}_{a_{11}} - 2\chi \dot{\epsilon}_{a_{11}} - 2\chi \dot{\epsilon}_{a_{11}} \left( \frac{27a_{11}a_{22}a_{33}}{35} + \frac{10a_{11} - a_{22} - a_{33}}{14} \right) \quad (C.84)
\]

\[
\frac{da_{22}}{dt} = 2\sqrt{3}C_i \dot{\epsilon}_i (1 - 3a_{22}) - 2\chi\dot{\epsilon}_{a_{22}} - 2\chi \dot{\epsilon}_{a_{22}} \left( \frac{27a_{11}a_{22}a_{33}}{35} + \frac{10a_{11} - 5a_{22} - a_{33}}{14} \right) \quad (C.85)
\]

\[
\frac{da_{33}}{dt} = 2\sqrt{3}C_i \dot{\epsilon}_i (1 - 3a_{33}) - 2\chi\dot{\epsilon}_{a_{33}} - 2\chi \dot{\epsilon}_{a_{33}} \left( \frac{27a_{11}a_{22}a_{33}}{35} + \frac{10a_{11} - 5a_{22} - 5a_{33}}{14} \right) \quad (C.86)
\]