December 2013

Rheology of Solutions of Polyisophrene and Polyisoprene-Carbon Nanotube Composites

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Graduate Program in Physics

A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

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RHEOLOGY OF SOLUTIONS OF POLYISOPRENE AND POLYISOPRENE-
CARBON NANOTUBE COMPOSITES

(Thesis format: Integrated Article)

by

Ruiping Ge

Graduate Program in Physics

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

The School of Graduate and Postdoctoral Studies
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Abstract

The addition of a small amount of carbon nanotubes to a polymer matrix can result in large changes in its mechanical properties. In this work, we study the rheological behavior of solutions of polyisoprene (PI) in chloroform and suspensions of multi-walled carbon nanotubes (MWCNT) and single-walled carbon nanotubes (SWCNT) in these PI solutions using shear rheometry. We perform rheological measurements to study the viscoelastic properties of solutions of trans-PI in chloroform for polymer concentrations ranging from 1.0 wt% to 10.0 wt%. Oscillatory strain sweep tests show a concentration-and-frequency independent critical strain of $\gamma_c \approx 60\%$ that defines the limit of the linear viscoelastic region. Frequency sweep tests performed in the linear viscoelastic regime give $G' \propto \omega^2$ and $G'' \propto \omega^1$ for low concentrations, as predicted by the Maxwell model. The zero-shear viscosity $\eta_0$ of the PI solutions, determined by three methods in this work, has a dependence on polymer concentration $c$ of $\eta_0 \propto c^5$, which implies that the polymer molecules in our solutions are entangled.

CNTs are dispersed in the PI solutions using a water-bath sonicator to obtain suspensions of MWCNTs and SWCNTs. Sonication times of many hours are required to obtain stable dispersions. We observe that the viscosity of the PI/CNT composites is a factor of 10 lower than that of the pure PI solution at the same polymer concentration, and independent of shear rate over the range studied. Films of PI/CNT composites are formed by evaporating the solvent from the suspensions. The well-dispersed state of CNTs in our PI/CNT systems is verified by scanning electron microscopy of the films and by the stability and reproducibility of our steady-state-shear flow measurements.

We discuss the mechanisms invoked in the literature to explain viscosity reductions observed in other systems and introduce a new mechanism that we believe that applies to our PI/CNT systems. We propose that the adsorption of polymer chains onto the CNT surface reduces the amount of polymer in solution and thus leads to a decrease in viscosity. Shear alignment of the CNTs may also enhance alignment of the PI chains remaining in solution, causing a further reduction in viscosity and eliminating shear-
thinning behavior of the CNT-filled PI solutions.

Keywords
Rheology, carbon nanotubes, polyisoprene, particle-filled nanocomposites, entangled polymers, decrease in viscosity, polymer adsorption.
Acknowledgements

I would first like to acknowledge my supervisor Dr. John R. de Bruyn, without whom the completion of my thesis would not have been possible. I thank you for your patience in helping me, your constant guidance and advice, your valuable comments and suggestions, and your encouragement during my study period. I am really very happy to have had a dedicated supervisor like you, and I appreciate your openness and trustworthiness. You have always helped me to solve all possible problems with your nice and friendly supervision.

I would like to extend my sincerest thanks and appreciation to my supervisory committee, Dr. Lyudmila Goncharova and Dr. Peter J. Simpson, who have also given me lots of support and assistance.

My special gratitude goes to members of Dr. de Bruyn's research group, past and present: Nan Yang, Felix Oppong, Maryam Mozaffari, Tahani Aldahri, Yang Liu, Cameron Hopkins, Maria Goiko, and Nirosh Gatangama. I would also like to thank Brad Kobe and Dr. Maxim Paliy for their help in performing SEM measurements and in discussing various aspects of physics involved in my research. The time spent with them in learning and discussions was really enjoyable.

I would like to thank the wonderful office staffs that have helped me to navigate classes, registration, and finally graduation: Clara, Jodi, Jackie, Lisa, and Nelia. I would also like to thank the Natural Sciences and Engineering Research Council of Canada and the University of Western Ontario for funding this research.

Finally, I would like to thank my parents for loving me and believing in me, and thank my three older sisters and my little brother for their endless support and encouragement. I also appreciate the help I have received from my mother-in-law during my studies. I am highly grateful to my husband Zhiqiang Wang for his love and understanding. Thank you for your patience and constant encouragement to my study and my life. Finally, I thank my lovely son Ethan X. Wang, who brings me so much love, happiness and joy to my life.
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Chapter 1

1 Introduction

1.1 Rheology

1.1.1 What is Rheology?

The word rheology comes from the Greek verb ῥέω, to flow. Rheology is the study of flow and deformation. It is largely concerned with the study of the fundamental constitutive relationships between deformation and stress in materials, primarily liquids [1].

![Figure 1.1 Schematic plots of (a) the stress as a function of deformation for an elastic solid governed by Hooke’s law, and (b) the stress as a function of rate of deformation for a viscous liquid governed by Newton’s law.](image)

The simplest, and probably the first, constitutive equation relating deformation and stress is Hooke’s law, which describes a simple elastic solid. Hooke’s law states that the stress is proportional to the deformation, as shown in Fig. 1.1 (a), or

\[ \sigma = G\gamma, \]  

(1.1)

where \( \sigma \) is the force per unit area or stress, \( \gamma \) is the relative length change or strain, and \( G \) is the elastic modulus, an intrinsic property of the solid [2]. This law is the basic constitutive equation for solid mechanics, and most metals and ceramics are ideally elastic at small strain.
For viscous liquids, the constitutive equation is Newton’s law of viscosity, which states that the stress is proportional to the rate of strain, \( \dot{\gamma} = d\gamma / dt \), as shown in Fig. 1.1 (b). Mathematically,

\[
\sigma = \eta \dot{\gamma},
\]

where \( \eta \) is a property of the material called the Newtonian viscosity. Fluids obeying Newton’s law are called Newtonian fluids, and are the subject of classical fluid mechanics. Gases and small-molecule liquids like water and oils are Newtonian.

Although many real materials obey these idealized laws, many important materials such as blood, polymers, and foods have behavior that is “in between” the ideal elastic solid and the ideal viscous fluid. In these viscoelastic materials, both viscous and elastic properties coexist and the simple constitutive equations given above do not hold. One major goal of rheology is to determine more complex constitutive equations that correctly describe the behavior of viscoelastic materials. These are often based on combinations and generalizations of the above equations.

### 1.1.2 Rheology Theory

Viscoelastic materials under shear show a time-dependent response \([1, 3, 4]\). They behave as solids on short time scales or at high frequencies and as viscous liquids at long times or low frequencies. When a shear stress is applied to a viscoelastic material, an instantaneous elastic deformation, as expected for a Hookean solid, is followed by a continuous viscous deformation, as expected for a Newtonian fluid. When the stress is removed, the elastic deformation recovers but the viscous deformation is irreversible.

#### 1.1.2.1 Maxwell Model

Mechanical models consisting of a combination of springs obeying Hooke’s law and viscous dashpots obeying Newton’s law can duplicate the mechanical properties of simple viscoelastic materials. Maxwell’s model consists of a spring connected in series with a dashpot, as shown in Fig. 1.2 (a). In this case, the strain, or equivalently the strain rate, is additive. Hence, the total rate of strain for this system is the sum of the rates of strain of the two elements, which gives

\[
\dot{\gamma} = \dot{\gamma}_E + \dot{\gamma}_V.
\]
Here $\dot{\gamma}_e = \dot{\sigma}/G$ represents the rate of strain of the elastic spring as given by Eq. (1.1) and $\dot{\gamma}_v = \sigma/\eta$ represents the rate of strain of the viscous dashpot (Eq. (1.2)). This leads to

$$\dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta}. \quad (1.4)$$

Rearranging Eq. (1.4), we get

$$\sigma + \lambda \frac{\partial \sigma}{\partial t} = \eta \dot{\gamma}, \quad (1.5)$$

where $\lambda = \eta/G$ has units of time and characterizes the relaxation of the material in response to an external deformation. Eq. (1.5) is the differential form of the Maxwell model.

To solve Eq. (1.5), we multiply both sides by $e^{t/\lambda}$ to obtain

$$\frac{1}{\lambda} e^{t/\lambda} \sigma + e^{t/\lambda} \frac{\partial \sigma}{\partial t} = \frac{d}{dt} \left( e^{t/\lambda} \right) \sigma = \frac{\eta}{\lambda} e^{t/\lambda} \dot{\gamma}. \quad (1.6)$$

Integration over all past times up to the time of interest $t$ yields

$$\int_{-\infty}^{t} \frac{d}{dt} \left( e^{t/\lambda} \sigma(t') \right) \frac{\dot{\gamma}(t')}{\lambda} dt' = \frac{\eta}{\lambda} \int_{-\infty}^{t} e^{t/\lambda} \dot{\gamma}(t') dt' \quad (1.7)$$

and

$$e^{t/\lambda} \sigma(t') \bigg|_{-\infty}^{t} = \frac{\eta}{\lambda} \int_{-\infty}^{t} e^{t/\lambda} \dot{\gamma}(t') dt'. \quad (1.8)$$

For a finite stress at $t = -\infty$, the left-hand side of Eq. (1.8) can be simplified to yield the integral form of the Maxwell model as

$$\sigma = e^{t/\lambda} \frac{\eta}{\lambda} \int_{-\infty}^{t} e^{t/\lambda} \dot{\gamma}(t') dt' = \frac{\eta}{\lambda} \int_{-\infty}^{t} e^{\frac{t-t'}{\lambda}} \dot{\gamma}(t') dt'. \quad (1.9)$$

This model describes the low frequency behavior of linear polymer solutions or melts quite well. For many materials, however, this model with a single Maxwell element is insufficient. Thus we can consider a number $N$ of discrete Maxwell elements with different relaxation times $\lambda_k$ and viscosities $\eta_k$ connected in parallel as in Fig. 1.2 (b), and add the stresses of the individual elements to obtain

$$\sigma = \sum_{k=1}^{N} \frac{\eta_k}{\lambda_k} \int e^{\frac{t-t'}{\lambda_k}} \dot{\gamma}(t') dt'. \quad (1.10)$$
This is referred to as the generalized Maxwell model.

Figure 1.2 Maxwell model. (a) One Maxwell element containing a spring and a dashpot connected in series. (b) Several Maxwell elements connected in parallel.

1.1.2.2 Oscillatory Shear

Small-amplitude oscillatory shear (SAOS) is a common deformation mode for investigating linear viscoelastic behavior. The Maxwell model can be used to describe the response of a material to SAOS.

Consider an oscillatory strain written as

\[ \gamma(t') = \gamma_0 \exp(i \omega t'), \quad \text{(1.11)} \]

where \( i = \sqrt{-1}, \omega \) is the oscillatory frequency and \( \gamma_0 \) is the strain amplitude which is small enough that the response of the system remains linear. The strain rate is then given by

\[ \dot{\gamma}(t') = i \omega \gamma_0 \exp(i \omega t'). \quad \text{(1.12)} \]

We substitute this into the generalized Maxwell constitutive equation Eq. (1.10) to obtain

\[ \sigma = \sum_{k=1}^{N} \frac{i \omega \gamma_0 \eta_k}{\lambda_k} \int_{-\infty}^{t'} \exp \left[ -\frac{(t-t')}{\lambda_k} \right] \exp(i \omega t') dt'. \quad \text{(1.13)} \]

If we introduce \( \xi = t - t' \) and substitute it into Eq. (1.13), we obtain

\[ \sigma = \sum_{k=1}^{N} \frac{i \omega \gamma_0 \eta_k}{\lambda_k} \int_{0}^{\infty} \exp \left[ \frac{(1 + i \omega \lambda_k) \xi}{\lambda_k} \right] d\xi \]
\[ \sigma = \sum_{k=1}^{N} \frac{i \omega \eta_k}{1 + i \omega \lambda_k} \gamma(t). \quad (1.15) \]

We can define a complex shear modulus \( G^* \), through the equation \( \sigma = G^*(\omega)\gamma(t) \). From Eq. (1.15) we see that

\[ G^*(\omega) = \sum_{k=1}^{N} \frac{i \omega \eta_k}{1 + i \omega \lambda_k} \left( \sum_{k=1}^{N} \frac{\eta_k \lambda_k \omega^2}{1 + \lambda_k^2 \omega^2} \right) + i \left( \sum_{k=1}^{N} \frac{\eta_k \omega}{1 + \lambda_k^2 \omega^2} \right). \quad (1.16) \]

Then we can write

\[ G^*(\omega) = G'(\omega) + i G''(\omega), \quad (1.17) \]

where \( G'(\omega) \) is referred to as the storage modulus and \( G''(\omega) \) is referred to as the loss modulus. \( G' \) is the coefficient of the real part of Eq. (1.15) that is in phase with the applied strain, and is thus a measure of the stored elastic energy per cycle of deformation. Similarly, the imaginary part of Eq. (1.15) is in phase with the rate of strain and \( G'' \) is a measure of the dissipated energy per cycle of deformation. From Eqs. (1.16) and (1.17) we obtain

\[ G'(\omega) = \sum_{k=1}^{N} \frac{\eta_k \lambda_k \omega}{1 + \lambda_k^2 \omega^2} \quad (1.18) \]

and

\[ G''(\omega) = \sum_{k=1}^{N} \frac{\eta_k \omega}{1 + \lambda_k^2 \omega^2}. \quad (1.19) \]

These expressions capture important features of material behavior. Particularly, for \( \omega \to 0 \) we have

\[ \lim_{\omega \to 0} G'(\omega) \propto \omega^2 \quad (1.20) \]

and
\[
\lim_{\omega \to 0} G''(\omega) \propto \omega.
\] (1.21)

These power law relationships have been experimentally verified for some viscoelastic systems \([5 - 10]\). In many materials, however, measurements cannot be carried to low enough frequencies to obtain this behavior \([3]\). In general, oscillatory shear measurements probe the response of the material on the time scale of \(1/\omega\). SAOS experiments distinguish the low frequency response of viscoelastic solids (i.e., gels) from that of viscoelastic liquids. A viscoelastic solid has \(G' > G''\) at low \(\omega\), with \(G'\) approximately independent of frequency, while a viscoelastic liquid has \(G'' > G'\) dominating at low \(\omega\), with \(G''\) becoming proportional to frequency in the low-frequency limit.

1.2 Rheology of Polymer Materials

The rheology of polymers, melts and solutions, is studied extensively, not only because the subject is extremely important in industry, but also because of the wide range of rheological phenomena exhibited by polymer materials. Polymer materials can be studied by performing rheological measurements such as steady-state shear flow and oscillatory shear flow. The general rheological behavior of polymer systems, and polymer solutions in particular, will be introduced below, accompanied by a description of how the molecular properties of the polymer are revealed through their macroscopic behavior.

1.2.1 Shear Viscosity of Polymer Materials

Most polymer materials are non-Newtonian and exhibit strong viscoelastic effects. Polymers typically show a decrease in viscosity with increasing shear rate in a steady simple shear flow. This behavior is referred to shear thinning. Fig. 1.3 shows the general shape of the plot of viscosity \(\eta\) against shear rate \(\gamma\) for a shear-thinning polymer. \(\eta\) is a constant and equal to \(\eta_0\) at very low shear rates, while in the limit of high shear rates it approaches \(\eta_\infty\). These two regimes are referred to as the first and second Newtonian regimes, and \(\eta_0\) and \(\eta_\infty\) are known as the zero-shear viscosity and the infinite-shear viscosity. In practice, the second Newtonian regime is hard to reach due to experimental
limitations. The shear-thinning behavior of polymers observed between these two limits is attributed to the disentanglement and alignment of the long polymeric chains under shear.

![Figure 1.3](image)

**Figure 1.3** A graph of viscosity against shear rate for a typical polymer material.

1.2.2 The Dependence of viscosity on Molecular Weight and Concentration

The complex rheological properties of polymers are due to the long-chain molecules, which make up the materials. The length of the chain, which is often expressed in terms of the molecular weight $M$, is the main factor that determines the polymer rheology at a given temperature. A material consisting of short-chain polymer molecules containing very few monomers will show Newtonian behavior, similar to small-molecule liquids. However, when the polymer chain becomes long enough, the polymer molecules start to interact. When the length and concentration are high enough, entanglement occurs and the polymer system starts to show elastic behavior. Several papers and books have shown that the zero-shear viscosity for a linear polymer melt increases linearly with $M$ at low molecular weight, then starts to increase proportionally to $M^{3.4}$ once $M$ becomes greater
than a critical molecular weight $M_c$ [1, 3, 4, 11 - 13]. The abrupt change in dependence of $\eta_0$ on $M$ is due to the formation of entanglements between molecules.

In a linear polymer solution with $M > M_c$, the viscosity of the solution shows a power law dependence on the concentration $c$ of the polymer. At very low concentrations, there are no strong interactions between the polymer molecules and the viscosity of the solution increases linearly with $c$. As $c$ is increased, the polymer molecules start to interact and the viscosity of the solution increases at a faster rate. At high concentrations the viscosity varies as $c^\alpha$, with the power law exponent $\alpha$ being about 3 or even higher [11, 14, 15]. For example, $\alpha = 3.9$ for a solution of polystyrene (PS) in toluene and $\alpha = 4.7$ for poly(ethylene oxide) in water [11]. Graessley et al. [14] reported an exponent of $\alpha = 5.0$ for the dependence of $\eta_0$ on polymer concentration for solutions of linear polyisoprene in tetradecane. Kulicke et al. [15] found an increase in the logarithmic slope of the specific viscosity $\eta_s p$ from 1 to 4.55 for PS in toluene and from 1 to 6.30 for PS in t-decalin. Here $\eta_s p = (\eta - \eta_s) / \eta_s$, where $\eta_s$ is the viscosity of the solvent. As above, the change in slope of $\eta$ vs. $c$ is associated with the formation of polymer entanglements, and the concentration $c_e$ at which the slope changes is referred to as the entanglement concentration.

### 1.2.3 Rheological Regimes of Polymer Solutions

Based on the dependence of the rheological behavior on the molecular weight and concentration of the polymers as discussed above, Graessley identified five different regimes in terms of $M$ and $c$, as shown in Fig. 1.4 [16]. There are well-established models for the rheological behavior of polymer solutions located in these regions: the Zimm model for dilute solutions, the Rouse model for semidilute unentangled solutions, and the reptation model for entangled solutions.
A. Dilute Solutions

In dilute solutions, polymer molecules behave as individual chains. The chains can be looked on separately, and only polymer-solvent and inter-monomer interactions need to be considered. The dynamics of dilute polymer solutions are described by the Zimm model, which considers hydrodynamic interactions between monomers in the polymer chain and between monomer and solvent within the volume occupied by the chain [1 – 4, 11, 17].

When a monomer moves, it drags some of the surrounding solvent with it. The Zimm model treats the polymer chain as a solid object of size $R = bN^\nu$ moving through the surrounding solvent, where $b$ is the segment length, and $N$ is the number of segments [11, 17]. The longest relaxation time $\tau_Z$ of a chain diffusing a distance of order of its own size is given by $\tau_Z = \tau_0 N^{3\nu}$, where $\tau_0$ is the segment relaxation time, and $\nu = 0.588$ for a good solvent or 0.5 for a theta solvent [11].
B. Semidilute Unentangled Solutions

As polymer concentration is increased, the individual chains start to overlap each other at a concentration $c^*$, where $c^* \approx N^{1-3\nu}$. Polymer solutions with $c^* < c < c_e$, where $c_e$ is the entanglement concentration, are semidilute unentangled solutions. In this regime, the Zimm model in combination with the Rouse model describes the dynamics of the polymer chains.

In the Rouse model, small beads used to represent the sites of fluid friction are connected by a length of frictionless polymer chain [4, 14, 18]. The longest relaxation time in the Rouse model, called Rouse time $\tau_R$, is given by $\tau_R \approx \tau_0 N^2$ [11].

A correlation length $\xi \approx b c^{\nu/(1-3\nu)}$, which is the distance between two adjacent overlapping chains, delineates the domains of applicability of the Rouse and Zimm models. On length scales smaller than $\xi$, the monomers come from a single chain and hydrodynamic interactions dominate. On these scales the Zimm model describes the dynamics. On length scales greater than $\xi$, the hydrodynamic interactions are screened and polymer-polymer interactions dominate. In this case, the Rouse model is used to describe the dynamics.

Rubinstein and Colby [11] showed that $G'(\omega)$ and $G''(\omega)$ have a similar power-law dependence on frequency at high frequencies in both the Zimm and Rouse models, with $G'(\omega) \sim G''(\omega) \sim \omega^{\mu}$, where $\mu = 2$ for the Rouse model and $\mu = 3\nu$ for the Zimm model.

C. Entangled Solutions

When the concentration becomes larger than $c_e$, chain entanglement becomes important. Polymer chains in entangled solutions form networks, and the motions of these networked chains are topologically constrained by each other because they cannot cross. These topological constraints are called entanglements.

Edwards [19] treated the motion of a chain as being confined to a tube-shaped region due to the topological constraints imposed by its neighboring chains. The diameter of this tube $a$, which can be interpreted as the end-to-end distance of an entanglement strand of $N_c$ monomers, is the dynamic length scale relevant to entangled polymer systems and is
significantly larger than the correlation length $\xi$\[11\]. For an entangled polymer solution, $a$ is given by $a \approx b\sqrt{N_e}e^{1/(1-3\eta)}$\[11\].

Using Edwards’ tube concept, de Gennes\[20\] built the reptation model, in which an entangled chain diffuses along the confining tube in a way similar to a snake’s motion. In this model, the reptation time $\tau_{rep}$, defined as the time for the chain to escape from the tube, is $\tau_{rep} \approx \tau_e \left( N/N_e \right)$, where $\tau_e \approx \tau_0 N_e^2$ is the Rouse time of an entanglement strand.

The reptation model describes the dynamics of entangled polymer systems for lengths larger than the tube diameter, as discussed above. The dynamics on length scales smaller than $a$ can be described by the Rouse model. On the length scales smaller than $\xi$, the hydrodynamic interactions again become important and the Zimm model applies.

$G'$ and $G''$ of a typical entangled solution of linear polymers with $N > N_e$ are shown as a function of frequency in Fig. 1.5. A characteristic of the rheological behavior of entangled polymers is the appearance of a constant storage modulus over a wide region of frequency. This constant modulus is called the plateau modulus $G_e$. $G'$ and $G''$ cross over at a high frequency $1/\tau_0$, beyond which the Zimm model describes the dynamics.

Power law dependence $G' \sim G'' \sim \omega^{1/2}$ is shown in the region $1/\tau_e < \omega < 1/\tau_0$, as predicted by the Rouse model. The plateau modulus $G_e$ spans the frequency range $1/\tau_{rep} < \omega < 1/\tau_e$, corresponding to relaxation on length scales between $\xi$ and $a$, as discussed above. The third crossover of $G'$ and $G''$ is located at $\omega = 1/\tau_{rep}$. The reptation time $\tau_{rep}$ represents the longest relaxation time of the system, and is the time taken by the chains to diffuse a distance equal to the tube length in the reptation model. At frequencies below $1/\tau_{rep}$, $G'$ and $G''$ show the power law relationships predicted by the Maxwell model.
1.3 Rheology of Particle-filled Polymer Liquids

The use of suspended nanoparticles as fillers in polymers has become a common way to impart desirable mechanical and electrical properties to polymers or to reduce the cost of polymer processing. Typical filler materials include silica, calcium carbonate, clays, glass fibers, carbon black, and carbon nanotubes. These particles have shapes ranging from spheres to long fibers. The presence of fillers magnifies the complexities of the rheological behavior of the polymer and changes their linear viscoelastic properties.

There are a number of factors that determine the rheological properties of filled polymers, with the concentration, shape, dimensions, and size distribution of the filler, and the polymer matrix being most important. Metzner [21] and Barnes [22] have reviewed the effects of these factors on the rheological behavior of suspensions in polymeric liquids, while Shenoy gave a very detailed discussion of the rheology of filled polymer systems in his book [23].

1.3.1 Effect of Concentration of Fillers

Several theoretical and empirical relationships have been proposed to describe the concentration dependence of the viscosity of particle suspensions. Einstein was the first
to study the viscosity of a dilute suspension of neutrally buoyant rigid spheres in a Newtonian liquid. He [24, 25] made the assumption that the particles are far enough apart to be treated independently of each other and derived the classic expression

$$\eta_r = 1 + 2.5\phi,$$

(1.22)

where the relative viscosity $\eta_r$ is the ratio of the viscosity of the suspension to that of the background fluid, and $\phi$ is the volume fraction of the suspended spheres. Batchelor and Green [26] took into account the interactions between two adjacent particles, which becomes important as $\phi$ increases, into account and extended this expression to second order:

$$\eta_r = 1 + 2.5\phi + 6.2\phi^2.$$  

(1.23)

There are also many empirical equations developed to describe the concentration dependence of the viscosity of more concentrated suspensions. For example, Thomas [27] suggested a power series type of expression,

$$\eta_r = 1 + 2.5\phi + 10.05\phi^2 + A \exp(B\phi),$$

(1.24)

where $A = 0.00273$ and $B = 16.6$, and Mooney [28] proposed an Arrhenius type of equation,

$$\eta_r = \exp\left(\frac{2.5\phi}{1 - \alpha_c \phi}\right),$$

(1.25)

where $\alpha_c = 1.35 \sim 1.91$.

A commonly used empirical expression is

$$\eta = \eta_0 \left(1 - \frac{\phi}{\phi_m}\right)^2.$$  

(1.26)

This expression originated with Maron and Pierce [29] and was carefully evaluated by Kitano and co-workers [30, 31]. $\phi_m$ is defined as the maximum attainable concentration, and is normally determined from experimental data [23]. Eq. (1.26) provides a good description of the concentration dependence of the viscosity of irregular-shaped particle suspensions in both viscous liquids and viscoelastic polymer liquids [21 - 23].
1.3.2 Effect of Shape, Dimension and Size Distribution of Fillers

When the filling particles are not spherical but rod-shaped, having an aspect ratio greater than 1, the viscosity of suspensions in both Newtonian liquids [23, 32] and non-Newtonian polymer liquids [31] was found to be increased. Regarding the effect of particle size on viscosity, Metzner [21] quoted Thomas’ work [27] and concluded that for suspensions in a viscous liquid at a given $\phi$ the particle size has no effect as long as the particles are small compared to the characteristic length of the measuring instrument. On the other hand, Jeffery [33] indicated that the consistency of viscosities reported in [27] for suspensions with different particle size was due to compensation by the author for the factors other than $\phi$ to extract an “average” curve of $\eta$, against $\phi$, and thus does not reveal the true effect of those other factors, including particle size. In fact, it has been found that decreasing the size of the suspended particles in a polymeric liquid at a fixed particle volume fraction increased the steady shear viscosity [34, 35]. Both Metzner [21] and Shenoy [23] indicated that the distribution of particle sizes has little effect on the viscosity of filled polymer systems at $\phi < 20$ vol%. At higher $\phi$, however, the effect is dramatic, with a broadening of distribution leading to a decrease in the relative viscosity compared to a unimodal particle distribution. Detailed reports studying the effect of particle size distribution on viscosity can be found in [36].

1.3.3 Effect of Polymer Matrix

The chemical nature and viscoelastic characteristics of the pure polymer with no nanoparticles filled determine the effect of the polymer matrix on the viscosity of filled systems [23]. An unfilled polymeric liquid typically shows Newtonian behavior at low shear rates, followed by shear thinning at higher shear rates, as discussed in Section 1.2.1. The addition of filler particles usually causes an increase in viscosity, but does not alter the general shape of the viscosity curve [1, 22, 23]. The general expectation is, therefore, that the viscosity of a suspension should increase with increasing $\phi$. Barnes [22] actually concluded in his review that there is always a
considerable increase in the dynamic moduli of particle-filled viscoelastic systems, which implies an increase in dynamic viscosity. Recently, however, there have been a few papers that report a decrease in viscosity in particle-filled polymer melts [37 - 44], and a number of different mechanisms have been proposed to explain this phenomenon. This will be discussed in Chap. 4. In this thesis, we studied the rheology of suspensions of carbon nanotubes (CNTs) in trans-polyisopene (PI) solutions. We observe that the PI/CNT systems have a lower viscosity than that of the neat polymer solutions. We will discuss our results in terms of the previously-proposed mechanisms, and propose a new mechanism that we believe explains our data. As a background, we briefly review the rheological behavior of CNT-filled polymeric composites in Section 1.4.

1.4 Rheology of CNT-filled Polymer Nanocomposites

CNTs are novel nanomaterials having exceptional thermal, electrical, and mechanical properties, which make them promising fillers for multifunctional polymer composites. There has been a great deal of work presented in the literature on the rheological properties of polymer/CNT composites for different suspending materials [45 - 54]. In general, the addition of CNTs into a polymer matrix is found to cause a more dramatic enhancement of the low-shear-rate viscosity than fiber suspensions at similar concentrations [45, 46]. Some authors explained this by the comparatively high aspect ratio of CNTs [47] and the interconnection of CNT aggregates [48]. For example, Song [49] reported that increasing the weight percent of added CNTs from 0.5% to 1.5% to a poly(ethylene oxide) (PEO) melt increases the viscosity and causes the disappearance of the Newtonian region at low $\dot{\gamma}$.

In practice, the concentration of CNTs in a composite is a main factor that determines its rheological behavior. A higher concentration implies smaller inter-CNT spacing and enhanced interactions between CNTs. There is a critical concentration of CNTs above which an interconnecting network of CNTs is formed, resulting in a dramatic increase in viscosity. This effect can be revealed in low-frequency oscillatory measurements as a transition from a liquid-like response to a solid-like response [50]. The onset of solid-like behavior corresponds to the rigidity or rheological percolation threshold, and typically
occurs at a CNT concentration smaller than 1 wt% [45].
Other factors such as the dispersion state and alignment of CNTs can also influence the rheological behavior of polymer/CNT composites. Huang and coworkers [51 - 53] observed that the rheological behavior of CNT-filled polydimethylsiloxane composites depended on the dispersion state. They found a critical dispersion time beyond which a stable rheology was established. Moniruzzaman and coworkers [54] found that the CNT concentration at the rheological percolation threshold decreased when the quality of dispersion was improved. It was found that alignment of the CNTs resulted in a decrease of the storage modulus [50].

1.5 Outline of the Thesis

As discussed above, CNTs are ideal candidates as nanoparticle fillers for polymer nanocomposites. However, CNTs tend to agglomerate and form clusters due to attractive Van der Waals forces. This makes it difficult to disperse the filler uniformly in the polymer matrix and prevents optimal transfer of the CNT’s superior properties to the nanocomposites. The objective of this thesis is to obtain stable and well-dispersed suspensions of CNTs in polymer solutions and to study the linear viscoelastic properties of these dispersions.

In chapter 2, the materials and experimental techniques used in this work will be introduced. Our results will be presented and discussed in Chapters 3 and 4. In Chapter 3, we study the dependence of the linear viscoelastic properties of solutions of PI in chloroform on polymer concentration. In Chapter 4, we disperse CNTs in solutions of PI in chloroform and characterize the viscoelastic properties of the suspensions using rheological techniques. The effect of the CNTs on the viscosity of PI/CNT nanocomposites and the quality of the CNT suspensions are also discussed in Chapter 4. Finally, Chapter 5 presents a general discussion and the conclusions of this work.
Bibliography


Chapter 2

2 Experiment

In this work, we studied the rheology of carbon nanotube-filled PI solutions. This chapter is devoted to a brief introduction to the materials and the experimental techniques we used. CNTs and PI are described in Section 2.1. Rheological measurements performed with a stress-controlled rheometer were used to characterize the viscoelastic properties of PI solutions and suspensions of CNTs in PI solutions, while scanning electron microscopy (SEM) was used to study the morphology of PI/CNT films made from these solutions. In Sections 2.2 and 2.3, we give a brief description of shear rheometry and SEM, respectively.

2.1 Materials

2.1.1 Carbon Nanotubes

Carbon nanotubes are long cylindrical tubes consisting of covalently bonded carbon atoms. There are two types of CNTs: multi-walled CNTs and single-walled CNTs. MWCNTs, discovered by Iijima [1] in 1991, consist of several concentric cylinders of graphene. SWCNTs, discovered by Iijima and coworkers [2] at NEC and Bethune and coworkers [3] at IBM in 1993, can be considered as a single seamless rolled up sheet of graphene. Most CNTs typically have a diameter of a few nanometers, while the tube length can be many thousands of times longer.

CNTs have extraordinary thermal, mechanical and electrical properties, which suggest a variety of applications such as nanoelectronics or high performance nanocomposites [4, 5, 6]. The bonding in a CNT is similar to that in graphene, in which each carbon atom is bonded to three other atoms. Fig. 2.1 shows the orbitals of graphene atoms. Each carbon atom has six electrons, with electronic structure $1s^22s^22p^2$. In a graphene sheet, the 2s orbital hybridizes with two 2p orbitals to form three $sp^2$ orbitals oriented at $120^\circ$ to each other in the plane of the sheet. These are referred to as $\sigma$-bonds. They bind the atoms in
the plane and result in the high stiffness and high strength of a CNT. The remaining \( p \) orbital forms \( \pi \)-bonds, which are out of plane. In graphite, these \( \pi \)-bonds interact with the \( \pi \)-bonds on the neighboring layers.

\[ \text{Figure 2.1 Schematic illustration of the orbitals of graphene atoms. The carbon nuclei are shown as filled red circles.} \]

Depending on the rolling angle of the graphene layer, CNTs can have three chiralities, referred to as armchair, zigzag, and chiral [4, 7 - 9]. To explain these three chiralities, Fig 2.2 defines the roll-up vector \( \vec{r} \) as a linear combination of the basis vectors \( \vec{a} \) and \( \vec{b} \) of the hexagonal lattice: \( \vec{r} = n\vec{a} + m\vec{b} \), where \((n, m)\) are integers. The armchair chirality results when \( n = m \), zigzag when \( m = 0 \), and chiral otherwise.

The MWCNTs and SWCNTs used in our work were supplied by US Research Nanomaterials, Inc. The material properties provided by the supplier are shown in Table 2.1.

\[ \text{Figure 2.2 Definition of roll-up vector as linear combinations of base vectors } \vec{a} \text{ and } \vec{b} \text{, and chiral angle } \theta. \]
Table 2.1 Physical properties of MWCNTs and SWCNTs used in this thesis.

<table>
<thead>
<tr>
<th></th>
<th>Purity</th>
<th>OD* (nm)</th>
<th>ID* (nm)</th>
<th>Length (µm)</th>
<th>SSA* (m²/g)</th>
<th>Density (g/cm³)</th>
<th>EC* (S/cm)</th>
<th>MM*</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs</td>
<td>&gt; 95%</td>
<td>5-15</td>
<td>3-5</td>
<td>~ 50</td>
<td>&gt; 233</td>
<td>~ 2.1</td>
<td>&gt; 100</td>
<td>CVD</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>&gt; 90%</td>
<td>1-2</td>
<td>0.8-1.6</td>
<td>5-30</td>
<td>&gt; 380</td>
<td>~ 2.1</td>
<td>&gt; 100</td>
<td>CVD</td>
</tr>
</tbody>
</table>

* OD: outside diameter; SSA: specific surface area; EC: electrical conductivity; MM: manufacturing method; CVD: chemical vapor deposition.

2.1.2 Polyisoprene

Polyisoprene, a type of rubber, is used extensively in many applications and products, either alone or in combination with other materials. It has a highly regular structure consisting primarily of linear sequences of cis- and trans- units. The cis-chains, which are the main component of natural rubber, form CH₂ bonds on the same side of the double bonds, while the trans-chains form CH₂ bonds on opposite sides of the double bonds, as shown in Fig. 2.3.

![Chemical structures of Polyisoprene](image)

Figure 2.3 Chemical structures of (a) Cis-PI, and (b) Trans-PI.

The different structures of cis-PI and trans-PI lead to different physical properties. Table 2.2 lists the properties of these two polymers at 25 °C. Trans-PI has a higher mechanical strength than cis-PI. This is attributed to the fact that at room temperatures trans-PI exists as a semi-crystalline polymer, while cis-PI is noncrystalline.

In addition to its excellent mechanical properties, trans-PI is electrically insulating, has low water and oil adsorption, and has good adhesion and thermoplastic properties. Because of this and its abundance in natural and synthetic forms, trans-PI has numerous applications.
In this thesis, we studied the rheology of pure and CNT-filled solutions of trans-PI in chloroform. The raw trans-PI was supplied by Sigma-Aldrich. It has a density of 0.904 g/ml at 25 °C and average molecular weight $M_w$ ca. 400,000 g/mol. PI was used without further purification.

<table>
<thead>
<tr>
<th>---</th>
<th>cis-PI</th>
<th>trans-PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness, Shore A$_2$</td>
<td>30-35</td>
<td>95 +</td>
</tr>
<tr>
<td>Tensile strength, kg/cm$^2$ (psi)</td>
<td>21 (300)</td>
<td>352 (5000)</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>1200</td>
<td>475</td>
</tr>
</tbody>
</table>

### 2.2 Shear Rheometry

In shear rheometry, materials are investigated in simple shear flows. The shear can be generated either by a pressure difference along a closed channel, or between moving and fixed solid surfaces. Rheometers based on the former are called capillary rheometers [10]. Capillary rheometers typically provide data on viscosity and melt flow as material passes through the instrument and are useful for studying flow at high shear rates. In contrast, rotational rheometers, which operate at relatively low shear rates, produce shear by drag flows. They are the preferred choice when the requirement is to obtain information about the molecular structure and viscoelastic properties of a material [11]. Because a stress-controlled rotational rheometer was used to perform rheological measurements on our materials, only drag-flow rheometers will be discussed in this chapter. In the following subsections, we will describe the basic components of a stress-controlled rheometer, then describe the common deformation geometries and explain their working equations.

#### 2.2.1 Description of a Stress-controlled Shear Rheometer

In stress-controlled measurements, the stress applied to the sample is controlled, and the resulting deformation of the sample is measured directly. In this work, we used an AR 1500ex stress-controlled rheometer, manufactured by TA Instruments (New Castle, DE). A schematic diagram of the main instrument components is shown in Fig. 2.4. The head
of the rheometer, which is mounted on the upper part of the column, can move vertically. A motor inside the head rotates a spindle, which is supported by an air bearing in the head. An encoder inside the head determines the angular position of the spindle. During a measurement, the sample is contained between the lower plate, on the base of the rheometer, and a removable upper fixture (a plate is shown in the figure) attached to the rotating spindle. A stress is applied to the sample by applying a torque to the upper plate, and the angular position or velocity of the spindle is measured and recorded by a computer. The lower plate contains a device that uses the Peltier effect to accurately control its temperature between -20 °C and 200 °C. A cooling system, which is not shown in the figure, pumps water through the lower plate to remove excess heat. A transducer built into the head of the rheometer is used to measure normal forces, generated by the sheared viscoelastic samples.

Figure 2.4 Schematic of the AR 1500ex rheometer.
2.2.2 Measurement Geometries

Four fixture geometries are commonly used with drag flow rheometers: sliding plates, concentric cylinders, cone-and-plate, and parallel plates. The cone-and-plate and parallel plate geometries were used in our measurements, and will be introduced below. On the other hand, parallel sliding plates are perhaps the simplest way to generate a shear flow in a fluid placed between them. This geometry has the simplest working equations and its analysis provides an elementary introduction to the concepts of shear stress, shear strain and shear rate. It will thus be discussed first.

A. Sliding Plate Geometry

Fig. 2.5 shows a schematic representation of a liquid subjected to a simple shear flow between two parallel sliding plates. The lower plate is held stationary and the top plate slides at a constant velocity \( v_0 \) in the \( x \) direction. The liquid is contained between the two parallel plates, which are a distance \( h \) apart. At sufficiently low velocities the liquid will everywhere flow parallel to the plates and the local velocity \( v_x \) of any liquid element will vary linearly across the gap. The shear strain \( \gamma \), defined as the ratio of the distance moved by topmost liquid element to the thickness of the liquid, is given by \( v_0 t / h \). The shear rate \( \dot{\gamma} \), given by the velocity gradient \( dv_x / dy \) in the \( y \) direction, is equal to \( v_0 / h \), which is constant throughout the liquid for the homogeneously uniform liquid.

To generate the flow, a shear force \( F_x \) has to be applied to the top plate, as shown in the figure. The shear stress \( \sigma_{xy} \), defined as the shear force per unit area, is given by \( F_x / LW \), where \( L \) and \( W \) are dimensions of the plates. The subscript \( x \) specifies the direction of the force and the subscript \( y \) is the direction normal to the plane in which the force is applied.

A major practical problem which this geometry is edge effects, which become more severe as the strain increases, making it difficult to achieve steady shear over long times. Thus, most shear rheological measurements are done with rotating geometries that have closed circular stream lines [10].
B. Cone-and-Plate Geometry

A sketch of the cone-and-plate geometry is shown in Fig. 2.6. The studied fluid fills the space between the upper cone and lower plate. For this geometry, spherical coordinates are the proper ones for analyzing the shear flow, as indicated in the figure. Simple shear flow is produced in the $\phi$ direction when the upper cone is rotated at a constant angular velocity $\Omega$ and the lower plate is fixed. The corresponding velocity components are

$$v = \begin{pmatrix} 0 \\ 0 \\ v_\phi(r, \theta) \end{pmatrix}.$$

(2.1)

We can write the velocity in the form

$$v_\phi(r, \theta) = A(r) \theta + B(r),$$

(2.2)

where $A(r)$ and $B(r)$ are parameters to be determined from the boundary conditions. As the lower plate is fixed while the upper cone is rotating, the no-slip boundary condition gives

$$v_\phi(r, \theta = \frac{\pi}{2}) = 0$$

(2.3)

on the plate, and
\[ v_\varphi(r, \theta = \frac{\pi}{2} - \alpha) = \Omega r \sin \left( \frac{\pi}{2} - \alpha \right) = \Omega r \]  

(2.4)
on the cone, where \( \alpha \) is the cone angle as indicated in the figure. \( \alpha \) is usually smaller than 6°, hence \( \sin(\frac{\pi}{2} - \alpha) \approx 1 \). Applying these boundary conditions to Eq. (2.2) yields

\[ v_\varphi(r, \theta) = A(r)\theta + B(r) = \Omega r \left( \frac{\pi/2 - \theta}{\alpha} \right), \]  

(2.5)

where \( A(r) = -\left( \frac{\Omega}{\alpha} \right) r \) and \( B(r) = \left( \frac{\pi/2}{\alpha} \right) r \).

The shear rate is given by [10]

\[ \dot{\gamma} = \frac{1}{r} \frac{\partial v_\varphi}{\partial \theta} - \frac{v_\varphi}{r} \cot \theta, \]  

(2.6)

where \( (\pi/2 - \alpha) \approx \alpha \) and \( \cot \theta = \cot(\pi/2 - \alpha) = \tan \alpha = \alpha \) as \( \alpha \) is small. This leads to

\[ \dot{\gamma} = \frac{\Omega}{\alpha} \left( 1 + \alpha^2 \right) = \frac{\Omega}{\alpha}. \]  

(2.7)

The shear strain can be calculated from the shear rate as

\[ \gamma = \int_0^t \dot{\gamma} dt = \frac{\Omega t}{\alpha} = \frac{q}{\alpha}. \]  

(2.8)

As defined in subsection A, the shear strain \( \gamma \) is also given by the ratio of the deformation of the sample at the surface of the upper cone over the time \( t \), to the undeformed thickness of the sample in the \( z \) direction. The former is \( \Omega rt = qr \), while the latter is \( r \sin \alpha = r \alpha \) for small \( \alpha \). Hence the shear strain is given by \( \gamma = q/\alpha \), as in Eq. (2.8).

The total torque acting on the top cone can be calculated as

\[ M = \int_A \left( \text{stress} \right) (\text{lever arm}) dA = \int_0^{2\pi} \int_0^R (\sigma_{\varphi r})_{\theta=\alpha} r dr d\varphi. \]  

(2.9)

Since the shear rate is constant, the shear stress is also constant and can be removed from the integral, leading to

\[ M = \frac{2\pi R^3}{3} \sigma_{\varphi r} \bigg|_{\theta=\alpha}, \]  

(2.10)

so the shear stress is given by
\[ \sigma_{\theta \theta} = \sigma_{\theta \phi} \bigg|_{\theta = \alpha} = \frac{3M}{2\pi R^3}. \tag{2.11} \]

If the test fluid is Newtonian, the viscosity of the fluid is given by

\[ \eta = \frac{\sigma_{\theta \phi}}{\dot{\gamma}} = \frac{3M}{2\pi R^3} \frac{\Omega}{\alpha} = \frac{3M\alpha}{2\pi R^3 \Omega}. \tag{2.12} \]

Figure 2.6 Schematic of the cone and plate geometry.

In addition to the continuous rotation mode discussed above, the cone-and-plate geometry can be used for oscillatory shear measurements. In this case, a sinusoidally varying torque drives the upper cone, while the lower plate is fixed. The amplitude of the sinusoidal deformation of the sample is measured by the rheometer. For the cone-and-plate geometry, the shear rate and the shear strain are both independent of position and can be easily calculated. For this reason, it is the most commonly used geometry for studying complex fluids.

C. Parallel-Plate Geometry

The parallel-plate geometry is sketched in Fig. 2.7. The fluid fills the gap between the parallel plates. For this geometry, we use cylindrical coordinates to analyze the shear flow, as indicated in the figure. Simple shear flow is produced in the \( \theta \) direction when the upper plate is rotated at a constant angular velocity \( \Omega \) and the lower plate is fixed.
Figure 2.7 Schematic of the parallel plate geometry.

The corresponding velocity components are

\[ v = \begin{pmatrix} 0 \\ v_\theta(r, z) \\ 0 \end{pmatrix} \]  \quad (2.13)

With the top plate rotating at angular velocity \( \Omega \) and the bottom plate stationary, and assuming no slip at the surfaces, the velocity is given by

\[ v_\theta(r, z) = \frac{r\Omega z}{h} \]  \quad (2.14)

Thus

\[ \dot{\gamma} = \frac{dv_\theta}{dz} = \frac{r\Omega}{h} \]  \quad (2.15)

where \( h \) is the gap between the parallel plates. Instead of being homogeneous as in cone-and-plate geometry, Eq. (2.15) indicates that the shear rate goes from zero at the center to a maximum of \( \dot{\gamma}_\text{max} = \dot{\gamma}_R = \frac{R\Omega}{h} \) at the edge of the plates.

The shear strain is given by

\[ \gamma = \int_0^t \dot{\gamma} dt = \frac{r\Omega t}{h} = \frac{r\theta}{h} \]  \quad (2.16)

which similarly depends on position.

To calculate the shear stress with this geometry, we consider the total torque at the top plate, which can be calculated as
\[ M = \int_A (\text{stress}) (\text{lever arm}) dA = 2\pi \int_0^R r\sigma_{\theta_c}rdr. \quad (2.17) \]

Using Eq. (2.15) and defining \( \dot{\gamma}_R = R\Omega/h \), we have
\[
\dot{r} = \frac{h}{\Omega} \dot{\gamma} = \frac{R}{\dot{\gamma}_R} \dot{\gamma} \quad (2.18)
\]
and
\[
\dot{\gamma} = \frac{R}{\dot{\gamma}_R} \dot{\gamma}_R. \quad (2.19)
\]

Applying Eqs. (2.18) and (2.19) to Eq. (2.17), we have
\[
M = 2\pi \int_0^R \left( \frac{R}{\dot{\gamma}_R} \right)^3 \dot{\gamma}_R^2 \sigma_{\theta_c} d\dot{\gamma}_R. \quad (2.20)
\]

We rearrange the above equation to get
\[
\frac{M}{2\pi R^3 \dot{\gamma}_R^3} = \dot{r} \int_0^R \dot{\gamma}_R^2 \sigma_{\theta_c} d\dot{\gamma}_R. \quad (2.21)
\]

Leibnitz’s rule states that
\[
\frac{d}{dx} \int_0^{f(x)} g(t) dt = g(f(x)) f'(x), \quad (2.22)
\]
so we differentiate both sides of Eq. (2.21) with respect to \( \dot{\gamma}_R \) to eliminate the integral and use Leibnitz’s rule to obtain the shear stress:

\[
\frac{d}{d\dot{\gamma}_R} \left( \frac{M}{2\pi R^3 \dot{\gamma}_R^3} \right) = \frac{d}{d\dot{\gamma}_R} \int_0^R \dot{\gamma}_R^2 \sigma_{\theta_c} d\dot{\gamma}_R
\]
\[
\frac{3M}{2\pi R^3 \dot{\gamma}_R^3} + \frac{\dot{\gamma}_R^3}{2\pi R^3} \frac{dM}{d\dot{\gamma}_R} = \dot{\gamma}_R^2 \sigma_{\theta_c}(\dot{\gamma}_R). \quad (2.23)
\]

Thus
\[
\sigma_{\theta_c}(\dot{\gamma}_R) = \frac{3M}{2\pi R^3} + \frac{\dot{\gamma}_R}{2\pi R^3} \frac{dM}{d\dot{\gamma}_R} = \frac{M}{2\pi R^3} \left( 3 + \frac{dM}{d\dot{\gamma}_R} \right) = \frac{M}{2\pi R^3} \left( 3 + \frac{d\ln M}{d\dot{\gamma}_R} \right). \quad (2.24)
\]

The viscosity is given in terms of the torque on the upper plate and the maximum shear rate as
\[ \eta(R) = \frac{\sigma_{\theta\gamma}(R)}{\dot{\gamma}_R} = \frac{M}{2\pi R^3 \dot{\gamma}_R} \left( 3 + \frac{d \ln M}{d \ln \dot{\gamma}_R} \right). \] (2.27)

Compared with the cone-and-plate geometry, it can be easier to load and unload viscous or soft solid samples using the parallel-plate geometry. Since the shear rate can be increased by either increasing the rotation rate or decreasing the gap, as indicated by Eq. (2.15), this geometry is useful for obtaining viscosity data at high shear rates. As for the cone-and-plate geometry, the parallel-plate geometry can also be used in small-amplitude oscillatory shear measurements to study the viscoelastic functions of complex materials, which are obtained directly from the controlling software in practice.

### 2.3 Scanning Electron Microscope

The scanning electron microscope produces images of a sample by scanning it with a focused beam of electrons. It is a relatively rapid and basically non-destructive technique for surface analysis. A SEM can produce high-resolution images of a sample surface with excellent depth of field, and under optimal conditions can reveal details as small as one to five nanometers in size.

A schematic illustration of a typical SEM is shown in Fig. 2.8. An electron beam is thermionically emitted from an electron gun. The energy of the electrons typically ranges from 0.2 keV to 40 keV. The beam is focused by one or two condenser lenses to a spot on the surface of the specimen about 0.4 nm to 5 nm in diameter. The spot is scanned across the surface in a pattern of parallel lines. The high-energy electrons in the primary beam collide with specimen atoms at or near the sample’s surface, and lose energy through repeated random scattering and absorption within a teardrop-shaped interaction volume. Energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, the emission of secondary electrons by inelastic scattering, and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The intensity of the secondary electrons is largely governed by the surface topography of the sample. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. The intensity of backscattered electrons
can be correlated to the atomic number of the elements within the interaction volume, providing qualitative, spatially-resolved information about the elemental composition of the sample. The analysis of characteristic X-rays emitted from the sample gives more quantitative elemental information.

In this work, the SEM images were obtained using a Hitachi S-4500 field emission SEM at an electron beam voltage of 5 kV.

**Figure 2.8** A sketch of the electron path in a scanning electron microscope.
Bibliography

Chapter 3

3 Rheology of Solutions of Polyisoprene in Chloroform

3.1 Introduction

Polymers are the basic materials of the rubber and plastic industries and are important to the textile, petroleum, automobile, paper, and pharmaceutical industries as well. They are non-Newtonian and exhibit viscoelasticity to a pronounced degree. A main task in polymer rheology is to understand polymer flow on both the macroscopic and molecular scales, that is, to relate the rheological behavior on the macroscopic scale to the corresponding microscopic structure. A lot of research has been done to understand the rheological behavior of polymer solutions and polymer melts [1 - 5].

Polyisoprene, a type of rubber, is used extensively in many applications and products, either alone or in combination with other materials. Its natural forms, Hevea rubber (cis-polyisoprene) or gutta-percha (trans-polyisoprene), are abundant in nature, and for technological purposes, synthetic forms are easily industrially polymerized from isoprene [6]. The rheological properties of polyisoprene solutions and melts have been studied in some detail [7 - 13]. Graessley et al. [7] studied the effect of molecular branching on the shear rate dependence of the viscosity of solutions of star branched polyisoprene in tetradecane in steady shear flow and found that the viscosity was highly sensitive to both concentration and branch length. They reported that the zero-shear-rate viscosity of entangled linear polyisoprene solutions is proportional to $c^{5.0}$, where $c$ is the concentration of polyisoprene. Philips and Wang [8] prepared entangled polyisoprene solutions at concentrations of 10 and 20 wt% in a short-chain polymer solvent of phenyl-terminated oligomeric polybutadiene and found that the solutions displayed the same flow response to controlled-rate and controlled-stress shear. Watanabe et al. [9] compared the viscoelastic and dielectric behaviors of polyisoprene solutions in butadiene oligomer to characterize the chain dynamics, specifically, the correlation of subchain motion in each chain at short time scales. They found that the subchain motion became
coherent to some extent as the polyisoprene concentration was increased above the entanglement concentration $c_e = 0.19\,\text{g/ml}$. Poh et al. [10] studied the viscoelastic behavior of guest polyisoprene in natural rubber networks and found that the longest mechanical relaxation time of the guest polyisoprene was governed by the molecular weight between entanglements and the molecular weight between crosslinks.

As background to help us understand the viscoelastic properties of carbon-nanotube-filled polyisoprene nanocomposites, in this chapter we use rheological techniques to study the viscoelastic properties of solutions of trans-polyisoprene in chloroform as a function of polymer concentration. We begin by describing the experimental details in Section 3.2. The results are presented and discussed in Sections 3.3 and 3.4, respectively. Finally, the conclusions are summarized in Section 3.5.

### 3.2 Experiment

#### 3.2.1 Materials

We studied trans-polyisoprene dissolved in chloroform at different concentrations. PI with a density of 0.904 g/ml and average molecular weight $M_w$ of approximately 400,000 g/mol was purchased from Sigma-Aldrich. Chloroform with a density of 1.480 g/ml and viscosity 0.56 mPas at 20 °C was purchased from Fisher Scientific. Materials were used without further purification. Solutions of PI in chloroform having concentrations $c$ ranging from 1.0 wt% to 10.0 wt% were prepared by dissolving the required amount of polymer in chloroform at 25 °C. The PI took up to several days to dissolve completely. The actual compositions of the samples are given in Table 3.1. To minimize evaporation of the solvent, polymer solutions were stored in glass vials with caps having a Teflon-lined seal until the rheological measurements were performed.
Table 3.1 Compositions of the PI solutions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PI (± 0.001 g)</th>
<th>Chloroform (± 0.001 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI 1.0 wt%</td>
<td>0.250</td>
<td>24.750</td>
</tr>
<tr>
<td>PI 1.5 wt%</td>
<td>0.270</td>
<td>17.730</td>
</tr>
<tr>
<td>PI 2.0 wt%</td>
<td>0.280</td>
<td>13.720</td>
</tr>
<tr>
<td>PI 2.5 wt%</td>
<td>0.274</td>
<td>10.685</td>
</tr>
<tr>
<td>PI 3.5 wt%</td>
<td>0.270</td>
<td>7.444</td>
</tr>
<tr>
<td>PI 4.5 wt%</td>
<td>1.044</td>
<td>22.156</td>
</tr>
<tr>
<td>PI 5.5 wt%</td>
<td>0.794</td>
<td>13.642</td>
</tr>
<tr>
<td>PI 6.5 wt%</td>
<td>1.608</td>
<td>23.130</td>
</tr>
<tr>
<td>PI 7.5 wt%</td>
<td>0.793</td>
<td>9.780</td>
</tr>
<tr>
<td>PI 8.5 wt%</td>
<td>2.413</td>
<td>25.975</td>
</tr>
<tr>
<td>PI 10.0 wt%</td>
<td>3.750</td>
<td>33.750</td>
</tr>
</tbody>
</table>

3.2.2 Rheological Measurements

The rheological properties of our PI solutions were measured with an AR-1500ex stress-controlled rheometer (TA Instruments). A 40 mm cone-plate tool with a cone angle of 4° was used for solutions with c from 2.0 to 8.5 wt% and the approximate loaded sample volume was about 1.2 ml. A 40 mm parallel plate tool was used for the 1.0 wt%, 1.5 wt% and 10.0 wt% PI solutions and the approximate loaded sample volume was about 2.5 ml, while the gap was 200 µm. The rheological experiments were performed at 25 °C. The evaporation rate of chloroform is very high. We therefore used a home-made environmental housing containing a piece of chamois cloth soaked with buffer solvent to enclose the rheometer tool. This ensured that the atmosphere around the sample was saturated with chloroform vapor and minimized evaporation of the solvent from the sample during the experiments.
The viscoelastic properties of the polymer solutions were investigated by measuring the response to an applied oscillatory shear. To confirm that the properties of the polymer solutions did not vary over time when the home-made housing was used, time sweep experiments were done at a fixed frequency of 1 rad/s and a fixed applied strain amplitude of 5% for 60 min. To determine the linear viscoelastic regime of the solutions, strain sweep measurements were performed at a fixed frequency of 1 rad/s as the applied strain amplitude varied from 0.01% to 100%. Frequency sweep measurements were performed at a strain amplitude of 5%, which we confirmed was within the linear regime, over a frequency range from 0.01 rad/s to 100 rad/s. Steady-state flow measurements were performed to study the dependence of viscosity on shear rate by sweeping the shear rate from 0.01 s\(^{-1}\) to 100 s\(^{-1}\). Finally, creep-recovery measurements were carried out on solutions of PI with \(c = 2.0 - 10.0\) wt% by suddenly applying a constant stress \(\sigma = 10\) Pa to the samples for 600 s. The shear stress was then removed to allow the samples to recover for up to 600 s.

### 3.3 Results

Time sweep tests were performed for solutions of PI at different concentrations. Fig. 3.1 shows the storage modulus \(G'\) as a function of time for \(c = 2.0, 3.5,\) and 4.5 wt% at a frequency of 1 rad/s and a strain amplitude of 5%. For these measurements, the home-made housing was used to enclose the rheometer tool. Also shown are measurements for \(c = 6.5\) at a frequency of 5 rad/s and a strain amplitude of 1% with no housing. In the tests when the housing was used, the storage moduli remained relatively constant. The changes in \(G'\) over 60 min are -15%, +6%, and -13% for \(c = 2.0, 3.5,\) and 4.5 wt%, respectively. In contrast, the change in \(G'\) for \(c = 6.5\) is as large as +34% over only 15 min when no housing was used. This indicates that our home-made housing effectively reduces the solvent evaporation rate. Based on these results, the time required for the rheological measurements discussed below was limited to less than 60 minutes to guarantee that the viscoelastic properties of the PI solutions did not change appreciably over the duration of the experiments.

Figure 3.1 The storage modulus $G'$ as a function of time at 25°C for $c = 2.0$, 3.5, and 4.5 wt% at a frequency of 1 rad/s and a strain amplitude of 5% while the homemade housing was used to enclose the rheometer tool, and for $c = 6.5$% at a frequency of 5 rad/s and a strain amplitude of 1% with no housing.

Strain sweep measurements were performed at a frequency $\omega$ of 1 rad/s for all solutions in order to determine the linear viscoelastic regime, in which the storage modulus $G'$ and the loss modulus $G''$ are independent of strain $\gamma$. Fig. 3.2 shows $G'$ and $G''$ for PI solutions as a function of PI concentration and strain amplitude. Both moduli decrease as the PI content is increased from 2.0 wt% to 10.0 wt%. $G'$ and $G''$ are independent of the strain for all PI concentrations until $\gamma$ reaches a critical strain $\gamma_c \approx 60\%$. For $\gamma > \gamma_c$, both $G'$ and $G''$ decrease, but the storage modulus decreases more quickly. Similar measurements at higher frequencies for the 2.0 wt% PI solution are shown in Fig. 3.3, and indicate that the critical strain is independent of frequency.
Figure 3.2 The storage modulus $G'$ (closed symbols) and the loss modulus $G''$ (open symbols) at $\omega = 1 \text{ rad/s}$ as a function of the strain amplitude for PI solutions at different concentration. The dashed line indicates the critical strain $\gamma_c \approx 60\%$.

Frequency sweep tests were performed at a strain amplitude of 5%, which is less than $\gamma_c$ and so within the linear viscoelastic regime. Fig. 3.4 shows the storage and loss moduli of PI solutions at 2.5 wt%, 4.5 wt%, and 10.0 wt% as a function of frequency. The results for other concentrations fall between the plotted data as expected and are not shown.

For all concentrations, both $G'$ and $G''$ increase as the frequency increases. At low frequencies, all solutions show a predominantly viscous character, with $G' < G''$. $G'$ increases more rapidly than $G''$, and the $G'$ curve crosses the $G''$ curve at a crossover frequency $\omega_c$. At this frequency, $G' = G''$ and the solution displays equal viscous and elastic characters. For $\omega > \omega_c$, $G' > G''$, and the solutions are predominantly elastic. In the linear viscoelastic approximation, $\omega_c$ corresponds to the longest relaxation time $\tau_c$ of the material. This represents the characteristic time for relaxation of molecular entanglements. $\tau_c$ is given by $\tau_c = 2\pi / \omega_c$. For $\omega < \omega_c$, the relaxation time of the
solution is shorter than the process time and the solution has sufficient time to relax. It thus shows more viscous behavior. When \( \omega > \omega_c \), the process time is shorter than the solution’s relaxation time and there is not sufficient time for it to relax, resulting in a more elastic behavior.

Figure 3.3 The storage modulus \( G' \) at \( \omega = 1 \) rad/s, 10 rad/s and 20 rad/s as a function of the strain amplitude for the 2.0 wt% PI solution. The critical strain \( \gamma_c \approx 60\% \), marked by the dashed line, is independent of the frequency.
Figure 3.4 Frequency dependence of the storage modulus $G'$ (closed symbols) and the loss modulus $G''$ (open symbols) at $\gamma = 5\%$ for PI solutions at different concentrations. The solid lines represent the low frequency limiting behavior of $G'$. The arrows and large squares denote the crossover frequencies $\omega_c$.

Both the crossover frequency $\omega_c$ and the storage modulus $G'_c$ at $\omega_c$ are dependent on concentration. The measured values of $\omega_c$, $\tau_c$ and $G'_c$ are summarized in Table 3.2. In general, the crossover frequency decreases with $c$ due to the fact that when the concentration is high there is more entanglement of the polymer chains and the material takes much longer to relax after a stress is applied. The concentration dependences of $\omega_c$ and $G'_c$ are shown in Fig. 3.5. We find that $\omega_c$ is proportional to $c^{-3.5 \pm 0.1}$, which means the relaxation time $\tau_c$ is proportional to $c^{3.5 \pm 0.1}$, as shown in Fig. 3.7 below, and $G'_c$ is proportional to $c^{1.5 \pm 0.2}$. Based on these results, we estimate that the zero-shear viscosity $\eta_0$ should have a concentration dependence given by $\eta_0 = G'_c / \omega_c \sim c^{5.0}$. This will be verified by the steady state flow measurements presented below.
Figure 3.5 The crossover frequency $\omega_c$ and the storage modulus $G_c'$ at $\omega_c$ as a function of the PI concentration ranging from 2.5 wt% to 10.0 wt%. The solid lines are power law fits to the data, which indicates that $\omega_c$ is proportional to $c^{-3.5 \pm 0.1}$, and $G_c'$ is proportional to $c^{1.5 \pm 0.2}$.

As shown in Fig. 3.4, $G'$ and $G''$ show a power law dependence on $\omega$ at low frequencies. This can be described as $G' \propto \omega^n$ and $G'' \propto \omega^m$ with $n$ and $m$ being power law indices. The values of $n$ and $m$ are also summarized in Table 3.2. The fitting results show that $n = 2.1 \pm 0.4$ and $m = 0.96 \pm 0.02$ for the 1.0 wt% PI solution, in the agreement with the predictions of the Maxwell model that $G' \propto \omega^2$ and $G'' \propto \omega$ at low enough frequencies [14]. As $c$ increases from 1.0 wt% to 10.0 wt%, the power law indices for both $G'$ and $G''$ decrease, with $n = 0.51 \pm 0.01$ and $m = 0.35 \pm 0.01$ for the 10.0 wt% PI solution.

Fig. 3.6 shows the viscosity $\eta$ of the PI solutions as a function of shear rate $\dot{\gamma}$ for $c$ ranging from 1.0 wt% to 10.0 wt% at 25°C. The viscosity of the solutions increases with
polymer concentration at a given shear rate. For example, at $\dot{\gamma}=1 \text{ s}^{-1}$, $\eta$ increases by a factor of $10^4$ from 0.04 Pas for the 1.0 wt% PI solution to 453.7 Pas for the 10.0 wt% PI solution. The viscosity of the solutions for $c \leq 2.0$ wt% is more-or-less independent of shear rate, while more obvious shear-thinning is observed at higher PI concentrations. In general, $\eta$ decreases slightly with increasing $\dot{\gamma}$ at low shear rates, but more rapidly at high shear rates.

Table 3.2 Crossover frequencies $\omega_c$, relaxation time $\tau_c$, the storage modulus $G'_c$ at $\omega_c$, and power law indices $n$ and $m$ for PI solutions as functions of $c$.

<table>
<thead>
<tr>
<th>$c$ (wt%)</th>
<th>$\omega_c$ (rad/s)</th>
<th>$\tau_c$ (s)</th>
<th>$G'_c$ (Pa)</th>
<th>$n$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>2.1 ± 0.4</td>
<td>0.96 ± 0.02</td>
</tr>
<tr>
<td>1.5</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1.6 ± 0.1</td>
<td>1.00 ± 0.03</td>
</tr>
<tr>
<td>2.0</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1.84 ± 0.04</td>
<td>0.962 ± 0.007</td>
</tr>
<tr>
<td>2.5</td>
<td>73 ± 3</td>
<td>0.086 ± 0.003</td>
<td>26 ± 1</td>
<td>1.37 ± 0.01</td>
<td>0.79 ± 0.01</td>
</tr>
<tr>
<td>3.5</td>
<td>23 ± 2</td>
<td>0.27 ± 0.02</td>
<td>45 ± 2</td>
<td>1.03 ± 0.02</td>
<td>0.65 ± 0.01</td>
</tr>
<tr>
<td>4.5</td>
<td>9 ± 1</td>
<td>0.70 ± 0.07</td>
<td>49 ± 2</td>
<td>0.90 ± 0.02</td>
<td>0.56 ± 0.01</td>
</tr>
<tr>
<td>5.5</td>
<td>4.8 ± 0.5</td>
<td>1.26 ± 0.07</td>
<td>63 ± 2</td>
<td>0.82 ± 0.02</td>
<td>0.52 ± 0.01</td>
</tr>
<tr>
<td>6.5</td>
<td>2.6 ± 0.2</td>
<td>2.4 ± 0.2</td>
<td>95 ± 3</td>
<td>0.65 ± 0.01</td>
<td>0.42 ± 0.01</td>
</tr>
<tr>
<td>7.5</td>
<td>2.6 ± 0.1</td>
<td>2.24 ± 0.09</td>
<td>114 ± 2</td>
<td>0.64 ± 0.01</td>
<td>0.40 ± 0.01</td>
</tr>
<tr>
<td>8.5</td>
<td>1.9 ± 0.1</td>
<td>3.3 ± 0.2</td>
<td>202 ± 6</td>
<td>0.64 ± 0.02</td>
<td>0.39 ± 0.01</td>
</tr>
<tr>
<td>10</td>
<td>0.51 ± 0.04</td>
<td>12.3 ± 0.9</td>
<td>222 ± 6</td>
<td>0.51 ± 0.01</td>
<td>0.35 ± 0.01</td>
</tr>
</tbody>
</table>
Figure 3.6 Viscosity $\eta$ as a function of shear rate $\dot{\gamma}$ determined from steady-state flow measurements for PI solutions with a range of concentrations: symbols refer to the data and lines show fits to the Cross model as described in the text.

To parameterize this behavior and to extract the zero-shear-rate viscosity from the steady-state flow measurements, the shear rate dependent viscosity was fitted to the Cross model [15], according to which the viscosity is given by

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty) / (1 + (k \dot{\gamma})^l).$$  \hspace{1cm} (5.1)

Here $\eta_0$ and $\eta_\infty$ refer to the zero-shear-rate viscosity and the infinite-shear-rate viscosity respectively, $k$ is related to the time scale for relaxation of entanglements and $l$ is a dimensionless power law index.
The concentration dependence of the relaxation time $\tau_c$ derived from frequency sweep measurements, and $k$ obtained from the Cross model fits. The solid lines are power-law fits to the data, which indicate that $\tau_c \propto c^{3.5 \pm 0.1}$ and $k \propto c^{3.6 \pm 0.3}$. $\tau_c$ and $k$ thus show the same power law dependence on $c$ within error.

The Cross model fits for all concentrations are also shown in Fig. 3.6 and the fit parameters are summarized in Table 3.3. The infinite-shear-rate viscosity $\eta_\infty$ increases with $c$, while the power law index $l$ is roughly equal to 0.76 for all $c$. The relaxation time $k$ shows a power law dependence on $c$ of $k \propto c^{3.6 \pm 0.3}$, which is in good agreement with the concentration dependence of $\tau_c$, obtained from the crossover frequency, as shown in Fig. 3.7. The zero-shear-rate viscosity $\eta_0$ is plotted as a function of PI concentration in Fig. 3.8. Over the entire concentration range measured, $\eta_0$ increases with concentration and is approximately proportional to $c^{5.0 \pm 0.2}$, in good agreement with the prediction derived from the frequency sweep measurements.
Table 3.3 Cross model parameters for PI solutions at different concentrations.

<table>
<thead>
<tr>
<th>( c ) (wt%)</th>
<th>( \eta_0 ) (Pas)</th>
<th>( \eta_\infty ) (Pas)</th>
<th>( k ) (s)</th>
<th>( l )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.044 ± 0.006</td>
<td>0.034 ± 0.003</td>
<td>0.5 ± 0.6</td>
<td>0.7 ± 0.8</td>
</tr>
<tr>
<td>1.5</td>
<td>0.282 ± 0.002</td>
<td>0.05 ± 0.01</td>
<td>0.023 ± 0.002</td>
<td>0.86 ± 0.07</td>
</tr>
<tr>
<td>2.0</td>
<td>1.2 ± 0.1</td>
<td>0.3 ± 0.1</td>
<td>1.8 ± 0.9</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>2.5</td>
<td>2.82 ± 0.02</td>
<td>0.24 ± 0.05</td>
<td>0.19 ± 0.01</td>
<td>0.76 ± 0.03</td>
</tr>
<tr>
<td>3.5</td>
<td>23.6 ± 0.4</td>
<td>0.6 ± 0.3</td>
<td>1.47 ± 0.09</td>
<td>0.64 ± 0.03</td>
</tr>
<tr>
<td>4.5</td>
<td>65 ± 1</td>
<td>3 ± 1</td>
<td>1.4 ± 0.1</td>
<td>0.83 ± 0.06</td>
</tr>
<tr>
<td>5.5</td>
<td>116 ± 2</td>
<td>2 ± 1</td>
<td>2.2 ± 0.2</td>
<td>0.80 ± 0.05</td>
</tr>
<tr>
<td>6.5</td>
<td>350 ± 10</td>
<td>4 ± 2</td>
<td>4.7 ± 0.5</td>
<td>0.75 ± 0.04</td>
</tr>
<tr>
<td>7.5</td>
<td>486 ± 6</td>
<td>6 ± 3</td>
<td>6.0 ± 0.3</td>
<td>0.76 ± 0.03</td>
</tr>
<tr>
<td>8.5</td>
<td>1556 ± 20</td>
<td>13 ± 5</td>
<td>14.8 ± 0.6</td>
<td>0.75 ± 0.02</td>
</tr>
<tr>
<td>10</td>
<td>5960 ± 70</td>
<td>30 ± 10</td>
<td>27 ± 1</td>
<td>0.79 ± 0.01</td>
</tr>
</tbody>
</table>

Creep-recovery measurements provide an alternative way to derive the zero-shear viscosity \( \eta_0 \) [16, 17, 18]. In a long-time creep test in which a stress \( \sigma_0 \) is applied to a viscoelastic material, the effect of elasticity decreases with time so that after a sufficiently long period, the rheological behavior is dominated by viscous flow and the deformation of the material becomes proportional to the time with a slope of \( \sigma_0 / \eta_0 \). When the stress is removed at a time \( t_1 \), the deformation starts to decrease until it approaches a final value of \( \gamma_r = \sigma_0 t_1 / \eta_0 \), as shown in Fig. 3.9. Thus, \( \eta_0 \) can be calculated from both the creep and recovery curves.

Fig 3.10 shows the strain as a function of time for (a) creep and (b) recovery tests for solutions of PI with \( c \) ranging from 2.0 to 10.0 wt\%. A stress of 10 Pa is applied at \( t = 0 \) and removed at \( t = 600 \) s. The strain increases dramatically over a very short time range, then the increase slows, becoming proportional to time at long times. As the concentration of PI increases, the strain at a given time decreases. This reflects the fact that the viscosity increases with polymer concentration. The strain recovery shown in Fig. 3.10 (b) is not obvious due to the wide range of strain plotted. The zero-shear viscosities
$\eta_0^c$ and $\eta_0^r$ are calculated from the creep and recovery curves, respectively, and summarized in Table 3.3. $\eta_0^c$ is plotted in Fig. 3.8 for comparison with the values of $\eta_0$ derived from the Cross model fits to the steady-state flow results. They are similar, with $\eta_0^c$ increasing with $c$ as $\eta_0^c \propto c^{5.7}$.

Table 3.4 Zero-shear viscosities derived from creep-recovery tests and Cross model fits to the steady-state flow for PI solutions.

<table>
<thead>
<tr>
<th>$c$ (wt%)</th>
<th>$\eta_0^c$ (Pas)</th>
<th>$\eta_0^r$ (Pas)</th>
<th>$\eta_0$ (Pas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.2185 ± 0.0003</td>
<td>0.2080 ± 0.0001</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>2.5</td>
<td>0.6558 ± 0.0003</td>
<td>0.6531 ± 0.0001</td>
<td>2.82 ± 0.02</td>
</tr>
<tr>
<td>3.5</td>
<td>6.726 ± 0.009</td>
<td>6.4705 ± 0.0006</td>
<td>23.6 ± 0.4</td>
</tr>
<tr>
<td>4.5</td>
<td>26.8 ± 0.1</td>
<td>24.084 ± 0.006</td>
<td>65 ± 1</td>
</tr>
<tr>
<td>5.5</td>
<td>81.1 ± 0.1</td>
<td>79.59 ± 0.02</td>
<td>116 ± 2</td>
</tr>
<tr>
<td>6.5</td>
<td>269.7 ± 0.4</td>
<td>263.9 ± 0.4</td>
<td>350 ± 10</td>
</tr>
<tr>
<td>7.5</td>
<td>307.5 ± 0.4</td>
<td>299.0 ± 0.4</td>
<td>486 ± 6</td>
</tr>
<tr>
<td>8.5</td>
<td>1469 ± 6</td>
<td>1380 ± 10</td>
<td>1560 ± 20</td>
</tr>
<tr>
<td>10</td>
<td>7582 ± 30</td>
<td>9295 ± 300</td>
<td>5960 ± 70</td>
</tr>
</tbody>
</table>

The full creep-recovery curves for $c = 2.0$ wt% and 10 wt% are plotted in Fig. 3.11 with $\eta_0^c$ and $\eta_0$ shown. The shear rates $\dot{\gamma} = d\gamma / dt$ in the terminal region of the creep curves were determined from the derivatives of the curves and are also shown in the figure. It shows that $\eta_0^c = 0.2185 \pm 0.0003$ Pas at $\dot{\gamma} = 47.5 \pm 0.5$ s$^{-1}$ for the PI solution at 2.0 wt% and $\eta_0^c = 7580 \pm 30$ Pas at $\dot{\gamma} = 0.0012 \pm 0.0001$ s$^{-1}$ for the PI solution at 10 wt%. The shear rates at which the low shear viscosities were obtained from the creep curves for other concentrations fall between these values, and they decrease with concentration. The viscosities at comparable shear rates in the steady-state shear flow experiments were
extracted from Fig. 3.6 for comparison with $\eta_0^c$ and, as shown in Fig. 3.12, they show good agreement. This reflects the fact that the viscosities extracted from the creep experiments under a constant load are not exactly zero-shear-rate viscosities, particularly for low concentrations, and also explains why the concentration dependence of $\eta_0^c$ has a higher power-law index than does $\eta_0$ from the Cross model fits.

Figure 3.8 Concentration dependence of the zero-shear-rate viscosity $\eta_0$ of PI solutions determined from steady shearing and creep measurements. The lines are power-law fits to the data. $\eta_0$ obtained from Cross-model fits is approximately proportional to $c^{5.0}$, while $\eta_0^c$ from the creep measurements is approximately proportional to $c^{5.7}$. 
Figure 3.9 A schematic drawing of the creep and recovery curves for a viscoelastic material when a stress is applied to the material at \( t_0 = 0 \) s and removed at \( t_1 \).

Figure 3.10 (a) Creep curves for an applied stress of 10 Pa. (b) Recovery curves following removal of the applied stress.
Figure 3.11 Creep and recovery curves for the solution of PI at (a) 2.0 wt% and (b) 10 wt%. A stress of 10 Pa was applied to the sample for 600 s and the stress then removed and the recovery monitored for 600 s.

Figure 3.12 A comparison of $\eta_0^c$ derived from the creep experiments and $\eta$ derived from the shear flow measurements at similar shear rates. The solid line is to guide the eye.
3.4 Discussion

Graessley identified five different regimes that characterized the behavior of polymer solutions in terms of the concentration and molecular weight of the polymers, as shown in Fig. 3.13 [19]. The molecular weight of the PI studied in our work is 400,000 g/mol, and the concentration of PI in chloroform ranges from 14.7 to 139.3 g/dl. All of our PI solutions are located in the “concentrated entangled” regime as marked in Fig. 3.13.

![Figure 3.13 Classification of polymer solutions in terms of concentration and molecular weight. The dashed lines indicate the molecular weight of our polymer and the lowest concentration studied. All of our solutions are in the concentrated entangled regime. Figure modified from [19].]
Colby [20] reported the overlap concentration \( c^* \sim N^{1-3\nu} \) and the entanglement concentration \( c_e \sim 10c^* \sim 10N^{(1-3\nu)} \) for neutral polymers in good solvent, where \( N \) is the number of segments per chain and \( \nu = 0.588 \) for good solvent. For a molecular weight of 400,000 g/mol and the molar mass of 113 g/mol for a segment [19], \( N \) is about 3600. This gives \( c_e \sim 1.9 \) wt\%, lying at the low concentrations studied in this work. This again indicates that our PI solutions are entangled.

The concentration dependence of zero-shear viscosity \( \eta_0 \) derived from steady state flow tests is a power law, \( \eta_0 \propto c^{5.0} \), as shown in Fig. 3.8, which is in good agreement with Graessley’s result for entangled polymer solutions [7]. This again indicates that our solutions are all entangled [7, 19, 21, 22], consistent with the prediction from Graessley’s classification discussed above.

![Figure 3.14](image)

**Figure 3.14** Comparison of the shear viscosity \( \eta \) measured in steady-shear flow to the magnitude of the complex viscosity \( |\eta^*| \) obtained from small amplitude shear measurements for solutions of PI at low concentrations.
The viscosities of the lowest concentration PI solutions are too small to be measured in our steady-state shear flow experiments at low shear rates $\dot{\gamma}$. For example, the viscosity of the 1.0 wt% PI solution could only be measured for $\dot{\gamma} > 1.0 \text{ s}^{-1}$, as shown in Fig. 3.6. To explore a possible way to extend the measurable shear rate range to lower values at low concentrations, we examine the so-called Cox-Merz rule. Cox and Merz [23] observed that for many polymeric systems, there was a correspondence between the steady state shear viscosity $\eta$ plotted against shear rate $\dot{\gamma}$, and the magnitude of the complex viscosity $|\eta^*|$ plotted against angular frequency. The complex viscosity $\eta^*$ is defined by $\eta^* = G^* / i\omega$, where $G^* = G' + iG''$ is the complex modulus. $|\eta^*|$ is then given by $|\eta^*| = |G^*| / \omega$. $\eta$ obtained from steady state shear flow measurements is compared with $|\eta^*|$ obtained from small amplitude oscillatory shear measurements at high frequencies in Fig. 3.12 for $c$ from 1.0 to 2.5 wt%. Good agreement is found at low shear rates, suggesting that this may be a useful way to measure low viscosities at low shear rates. On the other hand, obvious differences between $\eta$ and $|\eta^*|$ are found at higher concentrations and at higher shear rates (data not shown), so the Cox-Merz rule is not universally applicable to these solutions.

3.5 Conclusion

Rheological measurements were performed on solutions of polyisoprene in chloroform at concentrations ranging from 1.0 wt% to 10.0 wt%.

A concentration and frequency independent critical strain $\gamma_c \approx 60\%$, below which the viscoelastic properties of the solutions are independent of the strain, was found from strain-sweep tests. Frequency-sweep tests in the linear viscoelastic regime showed typical behavior of entangled polymers in the terminal region. The power law relationships $G' \propto \omega^2$ and $G'' \propto \omega$ predicted by the Maxwell model were found for low concentration solutions. The crossover frequency $\omega_c$ at which $G' = G''$ is proportional to $c^{-3.5}$. The decrease of $\omega_c$ is due to the fact that there is more entanglement between polymer chains.
at high concentrations, so the molecules take longer to relax when perturbed. The relaxation time $\tau_c$ given by $\tau_c = 2\pi / \omega_c$ is thus proportional to $c^{3.5}$. The concentration dependence of the relaxation time $k$ derived from fits of Cross model to the shear flow curves was the same within error.

The zero-shear viscosities of the PI solutions were derived by fitting the steady-state flow curves to the Cross model and from creep-recovery tests. A power law relationship, $\eta_0 \propto c^{5.0}$, was found.

Graessley’s classification of polymer solutions and the calculated entanglement concentration for our solutions indicate that all PI solutions tested in this work should be entangled solutions. This is consistent with the strong concentration dependence of the zero-shear viscosity measured in our experiments.
Bibliography

Chapter 4

4 Viscoelastic Behavior of PI/CNT Composites in Chloroform

4.1 Introduction

It is well known that the presence of various types of fillers incorporated into a polymer can improve its mechanical, thermal and electrical properties. The use of fillers thus provides a means of imparting certain desirable properties to polymeric materials and broadening their applications. The presence of the fillers, on the other hand, affects the rheological characteristics of the polymer system and increases the complexity of the rheological behavior, which has consequences for their industrial manufacturing and processing [1]. An understanding of the effects of any specific filler on the rheology and dynamics of polymeric materials is therefore important. A large variety of nanoparticles are commonly used commercially, including for example clays, quantum dots, metals, silica, carbon black, and carbon nanotubes, and there is an extensive literature on the rheology of polymer nanocomposites incorporating these nano-scale fillers [2 - 24]. Carbon nanotubes can be produced in high yield and reasonable quality by several techniques [17, 18]. These one-dimensional nanostructures have superior mechanical and electronic properties, which makes them an ideal candidate as a nanoparticle filler for polymer nanocomposites. However, the large-scale synthesis of CNTs usually results in clusters on the order of several hundred microns in size formed by thousands of individual nanotubes held together by physical entanglements and Van der Waals forces. This makes it difficult to disperse the filler uniformly in the polymer matrix and prevents optimal transfer of the CNT’s superior properties to the nanocomposites. In fact, overcoming the difficulties involved in obtaining a well-dispersed, stable dispersion of CNTs in the polymer matrix is a long-standing problem that has hindered the development of polymer-CNT nanocomposites. Star et al. [19] pointed out that polymeric molecules could wrap themselves around the surfaces of single-walled CNTs (SWCNTs)
and disrupt the van der Waals force. They successfully prepared poly(metaphenylenevinylene) (PmPV)-wrapped SWCNT suspensions in chloroform in a water-base sonicator, and found that the PmPV wrapped around the exterior of SWCNT bundles with diameters of a few nanometers. The polymer-wrapped SWCNT structures are then prevented from further aggregating into larger diameter ropes. Huang et al. [20, 21, 22] prepared multi-walled-CNT-filled polydimethylsiloxane nanocomposites at different stages of dispersion and subsequent tube re-aggregation over time. They analyzed the rheology of the nanocomposites in terms of the state of dispersion. They found that a critical mixing time, which is a function of nanotube concentration and the shear stress in the mixing device, was necessary to obtain a consistent and reproducible dispersion of carbon nanotubes in a polymer melt.

Recently, nanocomposites prepared from PI and CNTs were investigated, and found to have highly improved mechanical and electrical properties [23, 24]. However, the rheological properties of CNT-filled PI systems have been rarely studied. In this chapter we present measurements of the viscoelastic properties of the PI/MWCNT and PI/SWCNT nanocomposites, and discuss the interesting behavior we observe. We use a water-bath sonicator to disperse MWCNTs or SWCNTs in solutions of PI in chloroform. The viscoelastic properties are then characterized by rheological techniques. The effect of added CNTs on the viscosity of PI/CNT nanocomposites and the quality of the CNT suspensions are discussed in relation to the rheological behavior. We begin by describing the experimental details in Section 4.2. The results are presented and discussed in Sections 4.3 and 4.4, respectively. Finally, the conclusions are summarized in Section 4.5.

4.2 Experiment

4.2.1 Materials

The multi-walled carbon nanotubes and single-walled carbon nanotubes used in our work were supplied by US Research Nanomaterials, Inc. The MWCNTs had a tap density of 0.27 g/ml and a true density of 2.1 g/ml, and had outside diameter of about 5–15 nm, inside diameter of 3 - 5 nm, and were 50 µm long. The SWCNTs, with a tap density of
0.14 g/ml and a true density of 2.1 g/ml, were about 1.1 nm in diameter and 5 - 30 µm long. The properties and suppliers of polyisoprene and chloroform were described in Chapter 3. Materials were used without further purification. We prepared suspensions of MWCNTs and SWCNTs in solutions of PI in chloroform, and their viscoelastic behavior was studied as a function of concentration of CNTs $\phi$ at different polymer concentrations $c$. Firstly, PI is dissolved in chloroform to form 4.0 wt%, 5.0 wt% and 6.0 wt% PI solutions as described in Chapter 3. The required amount of MWCNTs or SWCNTs is dispersed in chloroform and sonicated in an ultrasonic bath with a frequency of 40 kHz for 3 hours. The dispersions of CNTs were then mixed with the polymer solutions and further sonicated until no CNT clusters were visible to the eye. This method produced suspensions of CNTs in PI solutions with $c = 2.0$ wt%, 2.5 wt%, and 3.0 wt%. The sonication time required to achieve a well-dispersed suspension was up to several days. All the samples were prepared at 25°C. A temperature controlled water bath was used to keep the temperature constant during the sonication process. The amount of MWCNTs or SWCNTs in the PI solutions ranged from 0.003 wt% to 0.124 wt%, which corresponds to volume fraction from 0.002 vol% to 0.086 vol%. The actual compositions and sonication times for the samples are given in Table 4.1. To minimize evaporation of the solvent during sample preparation, the suspensions of CNTs were stored in glass vials with caps having a Teflon-lined seal until the rheological measurements were performed.
Table 4.1 Compositions of the PI/CNT composites.

<table>
<thead>
<tr>
<th>Solution</th>
<th>MWCNTs</th>
<th>SWCNTs</th>
<th>Sonication time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(wt%)</td>
<td>(wt%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(vol %)</td>
<td>(vol %)</td>
<td></td>
</tr>
<tr>
<td>PI 2.0 wt%</td>
<td>0.003</td>
<td>0.002</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>0.012</td>
<td>0.008</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>0.026</td>
<td>0.018</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>0.062</td>
<td>0.043</td>
<td>134</td>
</tr>
<tr>
<td>PI 2.5 wt%</td>
<td>0.003</td>
<td>0.002</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>0.012</td>
<td>0.009</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>0.026</td>
<td>0.018</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>0.124</td>
<td>0.086</td>
<td>127</td>
</tr>
<tr>
<td>PI 3.0 wt%</td>
<td>0.004</td>
<td>0.002</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>0.013</td>
<td>0.009</td>
<td>130</td>
</tr>
</tbody>
</table>

4.2.2 Rheological Measurements

The rheological properties of our CNT-loaded PI solutions were measured with an AR-1500ex stress-controlled rheometer (TA Instruments). A 40 mm cone-plate tool with a cone angle of 4° was used and the approximate loaded sample volume was about 1.2 ml.
The rheological experiments were performed at a temperature of 25 °C. The evaporation rate of chloroform is very high, and we therefore used a home-made environmental housing containing a piece of chamois cloth soaked with chloroform to enclose the rheometer tool. This ensured that the atmosphere around the sample was saturated with chloroform vapor and minimized evaporation of the solvent from the sample during the experiments.

Both oscillatory shear and steady-state flow measurements were performed for each sample. To determine the linear viscoelastic regime of the solutions, strain sweep measurements were performed at a fixed frequency of 1 rad/s as the applied strain amplitude varied from 1% to 1000%. Frequency sweep measurements were performed at strain amplitude of 5%, which we confirmed was within the linear regime, for frequencies ranging from 0.1 rad/s to 1000 rad/s. Steady-state flow measurements were performed to study the dependence of viscosity on shear rate by sweeping the shear rate from 0.1 s\(^{-1}\) to 1000 s\(^{-1}\).

**4.2.3 SEM Imaging**

In order to examine the microstructures of PI/CNT composites, films were formed by removing the solvent by evaporation from samples at \(c = 2.5\) wt% at room temperature. A Hitachi S-4500 field emission scanning electron microscope was used to image the films. The films were freeze-fractured in liquid nitrogen to obtain a cross section. Both the firm surface and the cross section were viewed under SEM.

**4.3 Results**

**4.3.1 PI/MWCNT Composites**

Strain sweep measurements were performed on suspensions of MWCNTs in PI solutions at polymer concentrations \(c = 2.0\) wt%, 2.5 wt%, and 3.0 wt% to determine the linear viscoelastic regime. The weight fraction of MWCNTs \(\phi\) ranged from 0.003 wt% to 0.062 wt% in the 2.0 wt% PI solution, from 0.003 wt% to 0.124 wt% in the 2.5 wt% PI
solution, and was 0.003 wt% in the 3.0 wt% PI solution. Measurements were done at 25 °C and at a frequency of 1 rad/s.

Fig 4.1 shows the storage modulus $G'$ and the loss modulus $G''$ for the suspensions as a function of MWCNT concentration and strain amplitude. The moduli for pure PI solutions are also shown to illustrate the effect of the dispersed MWCNTs on the rheological properties of the polymer solutions. Fig 4.1 demonstrates that $G''$ remains constant over the entire strain range for all of the studied samples. $G'$ for the pure PI solutions starts to decrease when the strain amplitude is increased above $\gamma_c = 60\%$, whereas $G'$ for the suspensions remains independent of strain over the range examined for $\phi$ up to 0.124 wt%. For $\phi = 0.124$ wt% in the 2.5 wt% PI solution, $G'$ decreases steadily as $\gamma$ is increased. In most cases, both $G'$ and $G''$ decrease as $\phi$ is increased, becoming as much as 100 times less than for the pure PI solution at the highest concentration of MWCNTs. $G'$ is less than $G''$, and can get as low as $10^{-5}$ Pa. This is at the sensitivity limit of our rheometer, as shown as the noise in the data at low strain in Fig. 4.1.

**Table 4.2 Power law index $m$ for the suspensions of MWCNTs in PI solutions.**

<table>
<thead>
<tr>
<th>$c$ (wt%)</th>
<th>$\phi$ (wt%)</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.003</td>
<td>1.03 ± 0.03</td>
</tr>
<tr>
<td>PI 2.0</td>
<td>0.026</td>
<td>1.01 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>0.062</td>
<td>1.01 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>0.003</td>
<td>1.02 ± 0.01</td>
</tr>
<tr>
<td>PI 2.5</td>
<td>0.012</td>
<td>1.01 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>0.026</td>
<td>1.03 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>0.124</td>
<td>1.09 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>0.004</td>
<td>1.01 ± 0.01</td>
</tr>
<tr>
<td>PI 3.0</td>
<td>0.013</td>
<td>1.05 ± 0.01</td>
</tr>
</tbody>
</table>

Frequency sweep tests were performed at a strain amplitude of 5%, which is within the linear viscoelastic regime. Fig. 4.2 shows the storage and loss moduli of the suspensions
as a function of frequency. For the pure PI solutions, both $G'$ and $G''$ increase as the frequency increases. $G'$ is smaller than $G''$ at low frequencies but crosses over $G''$ at high frequencies, as discussed in Chapter 3. Adding MWCNTs to the PI solutions reduces both $G'$ and $G''$, and $G''$ remains greater than $G'$ over the whole measured frequency range, as shown in Fig. 4.2. This indicates that the suspensions show predominantly viscous behavior. For several of the composites, $G'$ is too small to be measured accurately. For all polymer concentrations studied, $G''$ decreases as $\phi$ is increased at constant polymer concentration. $G''$ shows a power law dependence on $\omega$ at low frequencies, which can be described as $G'' \propto \omega^m$. The power law index $m$ up to a frequency of 60 rad/s is summarized in Table 4.2. The fitting results show that $m = 1$ within error for all suspensions studied. This is in good agreement with the index of 1 predicted by Maxwell at low frequencies [25].

Fig. 4.3 shows the viscosity $\eta$ of the suspensions as a function of shear rate $\dot{\gamma}$ for $c = 2.0$ wt%, 2.5 wt%, and 3.0 wt% and $\phi$ ranging from 0.003 wt% to 0.124 wt%. The viscosity decreases with increasing MWCNT loading for all PI concentrations examined. For example, at $\dot{\gamma} = 10$ s$^{-1}$, $\eta$ decreases from 0.45 Pas for the pure 2.0 wt% PI solution to 0.014 Pas for the suspension with $\phi = 0.062$ wt%, while $\eta$ decreases from 1.23 Pas at $\phi = 0$ to 0.035 Pas at $\phi = 1.80$ mg/ml in the 2.5 wt% PI solution. The viscosities of the pure PI solutions, without MWCNTs, show obvious shear-thinning over the range of shear rates examined. On the other hand, $\eta$ is more-or-less independent of $\dot{\gamma}$ for the MWCNT suspensions.

Fig. 4.4 shows $\eta$ plotted against shear rate for the MWCNT suspensions in 2.5 wt% PI at different sample ages. The viscosities remain almost unchanged after the sample has been allowed to stand for several days. This stable and reproducible rheological response indicates that the MWCNTs are well-dispersed in the solutions.

We made films of the PI/MWCNT composites about 20 $\mu$m in thickness by placing about 2 ml of the material on the lower plate of our rheometer and allowing the solvent to evaporate at room temperature. Optical microscopy cannot be used directly to observe the bulk dispersion of MWCNTs within the PI matrix, since the films are optically non-transparent and the CNTs are extremely small. SEM provides a way to observe the inside
of the sample, though. Fig. 4.5 is a SEM image of the surface of a film formed from a suspension with $\phi = 0.003$ wt% and $c = 2.5$ wt%. It shows dispersed MWCNTs present in the polymer matrix. SEM images of the cross section of the films formed from suspensions with several values of $\phi$ and $c = 2.5$ wt% are shown in Fig. 4.6. Fig. 4.6 (a) shows that for $\phi = 0.003$ wt% the MWCNTs are well-dispersed, with no MWCNT clusters found. Some MWCNT clusters around 2 $\mu$m in size are seen for $\phi = 0.012$ wt% (Fig. 4.6 (b)). The clusters become bigger in Fig. 4.6 (c) as $\phi$ is increased to 0.026 wt%. Previous work has reported cluster sizes of about 6 $\mu$m for well-dispersed MWCNTs in poly(dinethyl siloxane) (PDMS) solutions [26] or up to 10 $\mu$m in PDMS/MWCNT composites [27]. Comparison with our results indicates that the dispersion of the MWCNTs in our films is excellent. The high-magnification SEM images in Fig 4.6 show that the diameters of the MWCNTs in the composites are around 20–50 nm, which is greater than the diameter of 5–15 nm specified by the supplier. This could be due to the coating of a layer of PI around the MWCNTs [28], as discussed in Section 4.4, or due to the bundling of the nanotubes.
Figure 4.1 The storage modulus $G'$ (red symbols) and loss modulus $G''$ (blue symbols) at $\omega = 1$ rad/s as a function of the strain amplitude for MWCNT suspensions in (a) 2.0 wt%, (b) 2.5 wt%, and 3.0 wt% PI solutions. The lines are to guide the eye.
Figure 4.2 Frequency dependence of the storage modulus $G'$ (red symbols) and the loss modulus $G''$ (blue symbols) at $\gamma = 5\%$ for MWCNTs suspensions in (a) 2.0 wt%, (b) 2.5 wt%, and (c) 3.0 wt% PI solutions. The solid black lines represent the low frequency limiting behavior of $G''$ predicted by the Maxwell model. The red and blue lines are to guide the eye.
Figure 4.3 Viscosity $\eta$ as a function of shear rate $\dot{\gamma}$ determined from steady-state flow measurements for suspensions of MWCNTs in (a) 2.0 wt%, (b) 2.5 wt%, and (c) 3.0 wt% PI solutions. The lines are to guide the eye.
Figure 4.4 Viscosity $\eta$ as a function of shear rate $\dot{\gamma}$ suspensions of MWCNTs in the 2.5 wt% PI solution at different sample ages, with (a) $\phi = 0.003$ wt%, (b) $\phi = 0.012$ wt%, and (c) $\phi = 0.026$ wt%.
Figure 4.5 SEM image of the surface of a PI/MWCNT film formed by evaporating the solvent from a suspension of MWCNTs with $\phi = 0.003$ wt% and $c = 2.5$ wt%. The scale is given by the dotted bar at the bottom right of the image.
Figure 4.6 SEM images of the cross-sections of films formed by evaporating the solvent from suspensions of MWCNTs at $\phi$ equal to (a) 0.003 wt%, (b) 0.012 wt%, and (c) 0.023 wt% in the 2.5 wt% PI solution. The magnification of the right-hand images is 10 times higher than the left-hand images.
4.3.2 PI/SWCNT Composites

SWCNTs were dispersed in 2.5 wt% PI solution at $\phi = 0.003$ wt%, 0.012 wt%, 0.028 wt%, and 0.124 wt%, as shown in Table 4.1. Fig 4.7 shows the results of strain sweep measurements performed at $\omega = 1$ rad/s for these suspensions. The storage modulus $G'$ and the loss modulus $G''$ are plotted against the strain amplitude. The moduli for the pure PI solution are also shown in the figure. Both $G'$ and $G''$ are smaller than the moduli of the 2.5 wt% PI solution with no added SWCNTs. $G' < G''$ for all samples, indicating viscous behavior. $G'$ for $\phi = 0.003$, 0.012, and 0.028 wt% are below the specified sensitivity of our rheometer, while $G'$ for $\phi = 0.124$ wt% is greater and independent of strain when $\gamma < 60\%$. $G''$ increases with increasing SWCNT concentration for all suspensions studied, but remains below the viscous modulus for the pure polymer. $G''$ is independent of $\gamma$ over the examined strain range.

Frequency sweep tests were performed at a strain amplitude of 5%, which is within the linear viscoelastic regime. Fig. 4.8 shows $G'$ and $G''$ of the suspensions as a function of frequency. $G'$ and $G''$ both increase with frequency and $G''$ remains greater than $G'$ over the examined frequency range. $G'$ is too small to be measured accurately for $\phi = 0.003$, 0.012, and 0.028 wt%. Both moduli are lower for the PI/SWCNT composites than for the pure 2.5 wt% PI solution. As seen in Fig. 4.8, $G''$ increases with $\phi$ while remaining below the value for $\phi = 0$. This is different from what we found for the PI/MWCNT suspensions, for which $G''$ decreased as the concentration of MWCNTs increased. $G'' \propto \omega^1$ at low frequencies for $\phi = 0.003$, 0.012, and 0.028 wt%, in good agreement with the predictions of the Maxwell model. For $\phi = 0.124$ wt%, $G''$ shows a weaker power law dependence, $G'' \propto \omega^{0.70 \pm 0.05}$, while $G'$ becomes independent of $\omega$ at low frequencies. The data suggest that $G'$ will become larger than $G''$ at a lower frequency, below the studied range. This flattening of $G'$ for $\phi = 0.124$ wt% indicates a transition from liquid-like to solid-like rheological behavior at low frequencies due to the formation of an elastic network at high CNT concentration [29, 30].
Fig. 4.9 shows the viscosity $\eta$ as a function of shear rate $\dot{\gamma}$ for the pure 2.5 wt% PI solution and the PI/SWCNT suspensions. The viscosities of the composites are lower than that of the pure PI solution, but $\eta$ increases with SWCNT loading once they are dispersed into the solution. This is consistent with the results of the oscillatory measurements discussed above.
Figure 4.7 (a) The storage modulus $G'$ and (b) the loss modulus $G''$ at $\omega = 1$ rad/s as a function of strain amplitude for SWCNT suspensions in the 2.5 wt% PI solution.
Figure 4.8 Frequency dependence of the storage modulus $G'$ (red symbols) and the loss modulus $G''$ (blue symbols) at $\gamma = 5\%$ for SWCNTs suspensions in the 2.5 wt% PI solution.
Figure 4.9 Viscosity $\eta$ as a function of shear rate $\dot{\gamma}$ determined from steady-state flow measurements for SWCNT suspensions in the 2.5 wt% PI solution.

4.4 Discussion

Einstein showed that the viscosity of a dilute suspension of neutrally buoyant rigid spheres in a Newtonian liquid was given by

$$\eta = \eta_0 \left(1 + 2.5\phi\right),$$  \hspace{1cm} (4.1)

where $\eta$ is the viscosity of the suspension, $\phi$ the volume fraction of the suspended particles, and $\eta_0$ the viscosity of the background liquid [31, 32]. The predicted increase in viscosity with $\phi$ has been experimentally verified many times since then [33 - 39]. As the filler concentration is increased, hydrodynamic interactions between the particles lead to an increase in dissipation and thus an increase in viscosity. The viscosity of a dilute suspension of rod-shaped fillers is predicted to be higher than that of a suspension of
spherical particles at the same volume fraction due to the increasing aspect ratio [1]. Surprisingly, however, we observe a decrease in viscosity for our CNT-filled PI solutions. A few recent papers have shown that the viscosity of polymeric melts can be reduced by the addition of nanoparticles [40, 42 - 49]. To date, four different mechanisms have been proposed in the literature to explain this phenomenon. We will introduce these four mechanisms and discuss their ability to explain the decrease in viscosity we observe in our PI/CNT systems.

A. Increased free volume

Mackay et al. [40] investigated the effect of polystyrene (PS) nanoparticles on the flow properties of linear PS melts. They found the terminal viscosities of the systems always decreased upon nanoparticle addition. This paralleled the observed reduction of the glass transition temperature $T_g$. The authors attributed this viscosity reduction to an increase in the free volume available to the polymer molecules introduced by the PS nanoparticles. They estimated this increase in free volume for a polymer melt containing 10 vol% PS nanoparticles with a diameter of $a = 3$ nm. They showed that if there was a spherical shell of excluded volume of thickness $\Delta = 0.1$ nm around each nanoparticle, then the fractional free volume would be increased by about 10%. Wang et al. [41] observed a similar decrease in viscosity for calcium carbonate blended polycarbonate (PC) melts and Jin et al. [42] observed it for MWCNT-filled PC melts. Both of these groups used a similar free volume argument to explain their results.

Our CNT suspensions are very dilute, with the nanoparticle volume fraction ranging from 0.002 vol% to 0.086 vol%, as shown in Table 4.1. If a single CNT is assumed to be a rod with a diameter of $a$ and a length of $L$, and a shell of excluded volume of thickness $\Delta$ is assumed around each CNT, the excluded free volume $v_f$ introduced by each nanotube is then given by

$$v_f = (\pi a L) \Delta,$$  \hspace{1cm} (4.2)

and the total number $N'$ of CNTs in a unit volume of a suspension at $\phi$ is give by

$$N' = \frac{\phi}{\pi \left(\frac{a}{2}\right)^2 L} = \frac{4\phi}{\pi a^2 L}.$$  \hspace{1cm} (4.3)
Hence, the total extra free volume $V_f$ introduced by CNTs in a suspension of a unit volume is given from Eqs. (4.2) and (4.3) by

$$V_f = v_f N' = \frac{4\phi \Delta}{a}.$$  \hspace{1cm} (4.4)

If we consider the CNT suspension at $\phi = 0.086$ vol\% and $c = 2.5$ wt\% = 4.03 vol\%, and assume $a = 10$ nm, $L = 50$ µm, and $\Delta = 0.1$ nm, the increased free volume in this suspension with a volume of 1 cm$^3$ is estimated to about $3.4 \times 10^{-5}$ cm$^3$, which is about 1 \% increase [43]. This is a much smaller change than in Ref. [40], and seems unlikely to be able account for the 97\% decrease in viscosity we observed for this suspension.

Mackay and his coworkers reported in their later work [44] that a decrease in viscosity was only observed for entangled and confined systems with $h < R_g$, where $h$ is the average interparticle half-gap and $R_g$ is the radius of gyration of a polymer.

We can estimate these parameters for our PI/CNT system. $R_g$ for a linear polymer chain can be calculated as [45]

$$R_g = b \sqrt{\frac{N}{6}},$$  \hspace{1cm} (4.5)

where $b$ is the segmental length and $N$ is the number of monomer units per chain. For our PI, $b$ is 0.82 nm [45] and $N$ is about 3600 obtained in Chap. 3. Eq. (45) thus gives $R_g = 20$ nm. The volume of a single MWCNT with $a = 10$ nm and $L = 50$ µm is given by

$$\pi \left(\frac{a}{2}\right)^2 L \approx 4.0 \times 10^{-15} \text{ cm}^3.$$  

For our highest volume fraction of $\phi = 0.086$ vol\%, there are thus about $N' \approx 8.6 \times 10^4 / 4.0 \times 10^{-15} \approx 2.2 \times 10^{11}$ MWCNTs per cm$^3$ of suspension.

To simplify the calculation of $h$, we assume a simple model in which the CNTs are evenly separated and arranged in a cubic box of side $M = 1$ cm as shown in Fig. 4.10. The perpendicular distance between two CNTs in adjacent columns is $2h$. The distance between the ends of two adjacent CNTs in the same column is assumed equal to $2R_g = 40$ nm, which is negligible in comparison to $L$. $h$ is then given by

$$h \approx \frac{1}{2} \left(M / \sqrt{\frac{N'}{M/L}}\right) = 150 \text{ nm}.$$  \hspace{1cm} (4.6)

This is about 7 times greater than $R_g$. Thus, our polymer molecules are not confined by
the nanoparticles, although as discussed in Chapter 3 they are entangled. We thus conclude that the increase in free volume introduced by our CNTs would have a negligible effect on the viscosity in our systems.

![Diagram of CNT arrangement](image)

**Figure 4.10** A schematic model of the arrangement of CNTs in a cubic box with a volume of $1 \text{ cm}^3$.

**B. Selective adsorption**

Jain et al. [46] reported that the melt viscosity of isotactic polypropylene (PP) blended with silica nanoparticles decreased by as much as a factor of 10. The viscosity decreased as the silica content was increased up to 0.5 wt%, then increased as silica content was further increased. To explain this, the authors postulated that the polymer chains with the highest molar mass were selectively adsorbed on the nanoparticle surface; while those with lower molar mass remained in the surrounding matrix. The adsorption of polymer on the silica surface resulted in particles with a core-shell morphology, with silica as the core and the adsorbed PP chains as the soft shell. The composite then consisted of these decorated particles embedded in a matrix of low molar mass PP chains, which led to a decrease in melt viscosity. A further increase in silica nanoparticle concentration resulted in a decrease of the interparticle distance until it became on the order of $R_g$ of the PP, at which point the chains became strongly confined. This led to an increase in the viscosity.
at high silica concentration. This mechanism depends strongly on the properties of the components and the atomic-scale interactions at the nanoparticle-polymer interfaces. The interactions between PI chains and CNT surfaces will be discussed in subsection E.

C. Size effect of a monomer-scale particle

Roberts et al. [47] blended silica clusters with two different radii in PDMS. They found that the viscosity increased on addition of particles with a radius of 2.2 nm, which is comparable to the gyration radius of PDMS, as predicted by Eq. (4.1). On the other hand, a viscosity reduction was found when the PDMS melt was filled by particles with a diameter of 0.35 nm, which is comparable to the length scale of an individual monomer. They suggested that the larger particles acted as a reinforcing agent for the polymer whereas the smaller particles behaved more like a “solvent”.

In our work, $R_g$ is about 20 nm, as calculated in subsection A, while the fillers are rod-shaped CNTs with a length up to 50 microns, a factor of $10^3$ greater than $R_g$. Thus, this mechanism does not seem suitable to explain the viscosity reduction in our systems.

D. “Ball bearing” effect

The fourth possible mechanism has been referred to as the “ball bearing” effect [48]. A schematic illustration is given in Fig. 4.11. This effect is based on the idea that when a polymer containing spherical particles is subjected to a shear flow, a high local shear is developed in the narrow gap between two nearby spherical particles, which may cause them to rotate and lead the chains between them to disentangle.

Xie et al. [48] observed a decrease in viscosity when CaCO$_3$ nanospheres were added to poly(vinyl chloride) melts. The authors introduced this “ball bearing” effect to explain their observation. Similarly, Chen et al. [49] observed a decrease in viscosity when they added micron-sized glass-beads to pure PC, while Lai et al. [50] observed a viscosity reduction for barium sulfate filled PC melts. These results were also interpreted in terms of the “ball bearing” effect.

This mechanism does not seem to explain our PI/CNT systems due to the rod-shaped geometry of CNTs, instead of the spherical geometry.
Figure 4.11 A schematic illustration of the “ball bearing” effect.

E. Proposed mechanism for our PI/CNT systems

Baskaran et al. [28] verified that PI chains adsorb onto untreated CNT surfaces due to attractive interactions between CH groups on the polymer chains and π-bonds on the CNTs. They indicated that the adsorbed polymer formed an amorphous layer around the CNTs. This is consistent with our SEM results shown in Fig 4.6, suggesting that adsorption of PI chains onto the CNT surfaces also happens in our systems.

We can use a simple model to estimate the amount of PI adsorbed on the CNTs. Based on our SEM results, we assume that there is an adsorbed PI layer with a thickness of $\Delta = 5$ nm around each CNT. As above, we take $a = 10$ nm and $L = 50 \mu$m, and consider a suspension with $\phi = 0.124$ wt$\%$ = 0.086 vol$\%$ and $c = 2.5$ wt$\%$ = 4.03 vol$\%$. The surface area of each CNT is about $S_0 = 3.14 \times 10^6$ nm$^2$, and its volume is about $V_0 = 3.9 \times 10^6$ nm$^3$.

In a total volume of 1 cm$^3$, the volume of CNTs is about $V = 8.6 \times 10^{17}$ nm$^3$, and the volume of PI chains is about $V_p = 4.03 \times 10^{19}$ nm$^3$. The number of CNTs $N'$ is then given by $N' = V / V_0 = 2.2 \times 10^{11}$ and the total CNT surface area is $S = N'S_0 = 6.9 \times 10^{17}$ nm$^2$.

Accordingly, the volume of PI adsorbed on the surface of the CNTs is given by $V'_p = S \times \Delta = 3.45 \times 10^{18}$ nm$^3$, so about $V'_p / V_p \times 100\% = 8.6\%$ of the PI chains in the suspension would be adsorbed. This decreases the concentration of the PI chains in the
surrounding solvent and leads to a decrease in viscosity. Since our data show that $\eta \propto c^5$, a decrease in $c$ by 8.6% would lead to a decrease in $\eta$ of about 40%, which is consistent with our data.

![Schematic illustration of the proposed mechanism for the decrease in viscosity for our PI/CNT systems.](image)

**Figure 4.12** A schematic illustration of the proposed mechanism for the decrease in viscosity for our PI/CNT systems.

In addition, it is well known that shearing flow tends to align suspended micron-sized fibers in the flow direction [51]. A suspension of aligned fibers exhibits a lower viscosity than a randomly-orientated fiber suspension as the fibers experience less resistance. This phenomenon could be extended to the nano-scale in our polymer/CNT suspensions [52]. The alignment of CNTs under shear would enhance the alignment of the PI chains remaining in solution, further reducing the viscosity. The enhanced alignment of the PI chains in CNT-filled PI solutions eliminates the shear-thinning behavior happening for the pure PI solutions at high shear rates. Fig. 4.12 shows a schematic illustration of the proposed mechanism for the viscosity reduction in our PI/CNT systems.

### 4.5 Conclusions

Suspensions of MWCNT and SWCNT in solutions of PI in chloroform were prepared using an ultrasonic bath sonicator. Rheological properties of CNT-loaded PI solutions were examined as a function of CNT content $\phi$. Films of PI/MWCNT composites were
formed by evaporating the solvent from the suspensions and then examined by SEM. SEM images showed that the MWCNTs were well-dispersed in the PI solutions. The viscosity of the CNT suspensions as a function of age verified the stability of the dispersions. The viscoelastic properties of the PI/CNT suspensions were independent of strain within the studied strain range, while the pure PI solutions had a critical strain $\gamma_c \approx 60\%$. Frequency-sweep tests in the linear viscoelastic regime showed liquid-like behavior in the terminal region. We found $G'' \propto \omega^1$ for $\phi < 0.124$ wt%, while $G'$ was too small to measure accurately. For a SWCNT suspension with $\phi = 0.124$ wt% in a 2.5 wt% PI solution, a transition from liquid-like to solid-like rheological behavior was observed due to the formation of an elastic network of SWCNTs at high concentration.

The addition of CNTs leads to a decrease in viscosity of the PI solutions. $\eta$ decreased with increasing $\phi$ for the MWCNT suspensions. For the SWCNT suspensions, $\eta$ remained smaller than the viscosity of the pure PI solution, but increased with increasing $\phi$. The mechanisms that have been invoked to explain viscosity reduction in different systems reported in the literature were discussed, and we introduced a new mechanism, which we believe applies to our PI/CNT systems. We proposed that the polymer chains are adsorbed onto the CNT surface due to interactions between CH groups donated by PI chains and $\pi$ bonds donated by CNTs, reducing the amount of polymer in solution and thus leading to a decrease in viscosity. Shear alignment of the CNTs may also enhance alignment of the PI chains remaining in solution, further reducing $\eta$ and eliminating shear-thinning behavior of the CNT-filled PI solutions.
Bibliography


Chapter 5

5 Summary and Future Work

5.1 Summary

The use of fillers incorporated into polymers provides a mean of imparting desirable physical properties to the polymeric materials, but also increases the complexity of their rheological behavior and, as a result, affects their industrial manufacturing and processing. An understanding of the effect of specific fillers on the rheology and dynamics of polymeric materials is therefore important. CNTs have extraordinary thermal, mechanical, and electrical properties, which make them an ideal candidate as a nanoparticle filler for polymer nanocomposites. In this thesis, we used solutions of PI in chloroform as a polymer matrix for suspensions of CNTs. We studied the rheology of the PI solutions and suspensions of CNTs in these PI solutions.

5.1.1 Rheology of PI Solutions in Chloroform

We studied the viscoelastic properties of solutions of trans-PI in chloroform for polymer concentrations, ranging from 1.0 wt% to 10.0 wt%. Using oscillatory strain sweep tests, we found a critical strain of \( \gamma_c \approx 60\% \), which defines the limit of the linear viscoelastic region. \( \gamma_c \) was independent of both concentration and frequency. Frequency sweep tests were performed in the linear viscoelastic regime and showed \( G' \propto \omega^2 \) and \( G'' \propto \omega^1 \) as predicted by the Maxwell model for low concentrations. Both the crossover frequency \( \omega_c \) at which \( G'=G'' \) and the storage modulus \( G'_c \) at \( \omega_c \) showed a power law dependence on concentration, with \( \omega_c \propto c^{-3.5 \pm 0.1} \) and \( G''_c \propto c^{1.5 \pm 0.2} \). The zero-shear viscosity \( \eta_0 = G'_c / \omega_c \) of the PI solutions thus had a concentration dependence of \( \eta_0 \propto c^5 \). \( \eta_0 \) was also derived by fitting the steady-state flow curves to the Cross model and from creep-recovery tests.
All of these methods gave power-law exponents around 5. These results showed that the polymer molecules in our solutions are entangled.

5.1.2 Rheology of CNT-filled PI Solutions

We used a water-bath sonicator to prepare suspensions of MWCNTs and SWCNTs in solutions of PI in chloroform. SEM was used to examine films of PI/CNT composites formed by evaporating the solvent from the suspensions, and the results indicated that the CNTs were well-dispersed. The viscoelastic properties of CNT-filled PI solutions were characterized by rheological techniques. The good dispersion of the CNTs was confirmed by stability and reproducibility of our steady-state-shear flow measurements.

The viscous and elastic moduli of the CNT suspensions were independent of strain over the studied range. Frequency sweep tests showed liquid-like behavior in the terminal region. $G''$ was proportional to $\omega$ for $\phi < 0.124 \text{ wt\%}$, while $G'$ was too small to measure accurately. For a SWCNT suspension with $\phi = 0.124 \text{ wt\%}$ in a 2.5 wt\% PI solution, a transition from liquid-like to solid-like rheological behavior was observed due to the formation of an elastic network of SWCNTs.

We found that the viscosity of the CNT suspensions decreased compared to the pure PI solutions. The mechanisms that have been invoked in the literature to explain viscosity reductions in the other systems reported were discussed, but were found to be unlikely to explain our results. We proposed that in our system the polymer chains are adsorbed onto the CNT surface, reducing the amount of polymer in solution and thus leading to a decrease in viscosity. Shear alignment of the CNTs may also enhance alignment of the PI chains remaining in solution, causing a further reduction in viscosity and eliminating shear-thinning behavior of the CNT-filled PI solutions.

5.2 Future Work

Our work raises several questions that are worthy of further investigation:

(1) Although we found that both MWCNT and SWCNT suspensions had lower
viscosities than the pure PI solutions, we observed that their viscosities showed different concentration dependence. A continuous decrease in $\eta$ with increasing $\phi$ for MWCNT suspensions, but an increase of $\eta$ with increasing $\phi$ for SWCNT suspensions. Further experiments and theoretical work are required to explain this behavior.

(2) Jain and his co-workers [1] reported that the decrease of the melt viscosity of PP/silica nanocomposites was reversed when the silica content was increased over 0.5 wt%, as discussed in Chap. 4. Their explanation for this increase in viscosity at high silica concentration was a confinement of the PP chains. It would be interesting to perform experiments on our PI/CNT system to determine whether a similar increase in viscosity occurs at high $\phi$.

(3) It would be interesting to study the rheological behavior of suspensions of CNTs in other polymers to investigate whether the unusual reduction in viscosity we observed is a general phenomenon or specific to PI. Such measurements may lead to a better understanding of the mechanism of viscosity reduction for other polymer-nanoparticle systems.
Bibliography

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