

Frequency-Dependent Rheological Characterization of Viscoelastic Materials Using
Magnetic Nanoparticle Probes

by
Renee Myers

A THESIS

submitted to
Oregon State University
Honors College

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Honors Baccalaureate of Science in Chemical Engineering
(Honors Scholar)

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Commencement June 2020

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Skip Rochefort

Extending rheological characterization methods to very small length scales is of interest. AC susceptometry using magnetic nanoparticle probes has been proposed for measurement of frequency-dependent rheological properties at the nanoscale. As this technique has been primarily used for ideally Newtonian fluids, this research aimed to extend this technique to viscoelastic materials ranging from purely viscous (Newtonian) to purely elastic (Hookean). Polyethylene oxide, or PEO, was investigated as a representative viscoelastic material to be tested using the proposed AC susceptometry methods, and solutions of a high molecular weight PEO (POLYOX UCARFLOC 309) and a low molecular weight PEO (Sigma Aldrich, 200 K MW) were characterized. Frequency dependent properties of both solutions were obtained for both solutions using bulk-scale rheology techniques, and measurements of intrinsic viscosity were used to characterize the POLYOX 309 solution. VivoTrax magnetic tracer particles were also evaluated for their size distribution and mass dependence on magnetic susceptibility. Due to the inconsistencies observed in the frequency dependent measurements for the PEO 200K solution, additional study should be carried out to improve the characterization data. Further work to experimentally evaluate the frequency dependent behavior of polyethylene oxide using AC susceptometry methods is also necessary.

Key Words: rheology, polyethylene oxide, viscoelastic, magnetic susceptibility

Corresponding e-mail address: myersren@oregonstate.edu

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APPROVED:

Skip Rochefort, Mentor, representing Chemical Engineering

Travis Walker, Committee Member, representing Chemical Engineering

Trevor Carlisle, Committee Member, representing Chemical Engineering

Katrina Donovan, Committee Member, representing Materials and Metallurgical Engineering

Toni Doolen, Dean, Oregon State University Honors College

I understand that my project will become part of the permanent collection of Oregon State University, Honors College. My signature below authorizes release of my project to any reader upon request.

Renee Myers, Author

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1. Introduction

1.1. Introduction

Magnetic nanoparticle probes present a novel approach for extraction of the frequency-dependent properties of material samples at the nanoscale level. The use of small fluorescent particles as tracer probes has been used extensively at the microscale to extract information about the viscoelastic character of a sample; however, the use of light microscopy that is inherent to these measurements makes it difficult to extend these techniques to the nanoscale.¹ As nanoscale measurements offer an approach for gaining further insight into the properties of a sample at very small length scales, AC susceptometry using magnetic tracer particles as probes has been proposed as a viable measurement technique for conducting nanoscale frequency-dependent rheological measurements. Although this technique has been used in previous research to measure the frequency-dependent rheological properties of ideally Newtonian materials, extending this technique to viscoelastic materials, ranging from purely viscous (Newtonian) to purely elastic (Hookean), serves to broaden the scope of conventional rheology and to allow for analysis of materials across a wide range of length scales.

1.2. Research Outline

This project investigates and characterizes a well-studied viscoelastic polymer, polyethylene oxide, as a representative viscoelastic material to be tested using the proposed AC susceptometry “nanorheology” methods. Established bulk-scale rheological techniques were used to determine the frequency-dependent rheological properties of two polyethylene oxide solutions at varying concentrations, and measurements of intrinsic viscosity were used to further characterize the molecular properties of one of the polymer solutions. VivoTrax magnetic tracer probes were also investigated for their size distribution and mass-dependent susceptibility response to varying frequency. Finally, mathematical models were used to simulate the susceptibility response using the Newtonian, Maxwell, and Kelvin-Voigt constitutive fluid models.

2. Background

2.1. Introduction to Rheology

Rheology is the study of material deformation and flow behavior, and it is an interdisciplinary branch of physics encompassing materials science, physical chemistry, and transport phenomena. As most materials do not exhibit ideal flow behavior, knowledge of rheology is essential for understanding the material properties of common complex fluids, including polymers, adhesives, paints, printer inks, foods, and cosmetics. Rheology is of great interest to industrial manufacturers, as the rheological properties of a material dictate characteristics such as mouthfeel, consistency, leveling and sagging behavior, and spreadability, which are important to product consumers. In polymer processing, rheology offers valuable information about polymer flow characteristics to inform processing techniques such as injection molding, compression molding, and extrusion. In this discussion, specific attention will be given to frequency-dependent sample behavior, as these oscillatory measurements offer significant information regarding the material structure of a sample.

2.2. Viscoelastic Behavior

Viscoelastic materials display both viscous (“liquid-like”) and elastic (“solid-like”) characteristics. Ideally viscous flow, or the response of a fluid to continuous deformation, is modeled by Newton’s law as follows,

$$\sigma = \eta\dot{\gamma}, \quad (2.1)$$

where σ represents the shear stress, $\dot{\gamma}$ represents the shear rate, and η represents the viscosity of the fluid.² This equation shows that the shear stress is linearly proportional to the shear rate through viscosity as a material constant. Similarly, ideally elastic behavior, or the response of a solid to deformation, is modeled by Hooke’s law,

$$\sigma = G\gamma, \quad (2.2)$$

where σ again represents the shear stress, γ represents the shear strain, and G represents the shear modulus of the solid.²

Solids store energy, and energy that is applied to deform an ideal solid is completely stored within the material. Solid deformation is entirely reversible, and solids recover their initial shape following deformation from an applied force. In contrast, liquids lose energy, and the energy that is applied to deform an ideal liquid is dissipated through frictional losses at the molecular scale during the flow process. As the deformation energy applied to a liquid is completely lost, liquid deformation is irreversible.

The dashpot element and the spring element are used to model the behavior of ideally viscous and ideally elastic materials, respectively. As illustrated in Figure 2.1 (a), the dashpot element consists of a piston cylinder arrangement filled with viscous fluid.² Continuous force is applied to the piston, causing the piston to move through the liquid in the dashpot as long as force is applied. The spring element, as shown in Figure 2.1 (b), consists of a simple linear elastic spring. Force is applied to the spring, causing an instantaneous deformation proportional to the applied force.

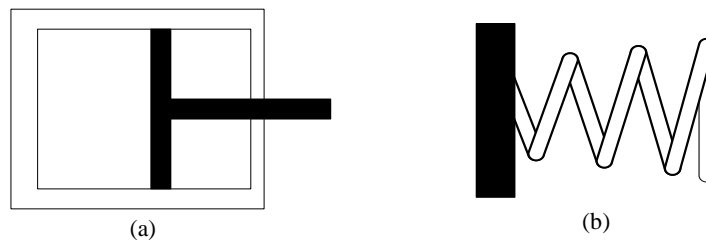


Figure 2.1 (a) Simplified cartoon of the dashpot element for ideally viscous behavior and (b) cartoon of the spring element for ideally elastic behavior.

As viscoelastic materials exhibit characteristics of both liquid and solid materials, the spring and dashpot elements are used in combination to model the response of a viscoelastic material to an applied force. These models can be combined in series (known as the Maxwell model) or in parallel (known as the Voigt-Kelvin model).² These configurations are illustrated in Figure 2.2 below.

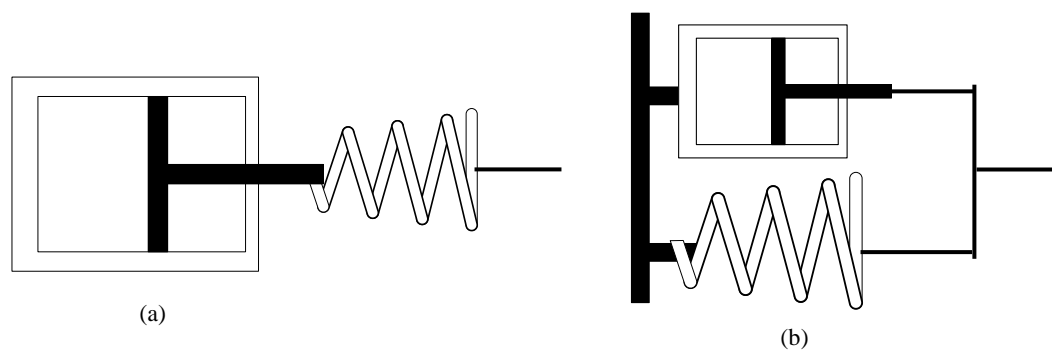


Figure 2.2 (a) Simplified cartoon of the Maxwell element for viscoelastic liquids and (b) cartoon of the Voigt-Kelvin element for viscoelastic solids.

The Maxwell model, Figure 2.2 (a), is used to model the behavior of viscoelastic liquids. In the Maxwell model, force causes an instantaneous deformation of the spring, which is then followed by movement of the dashpot piston. Upon removal of the load, the spring reforms completely (elastically), while the dashpot piston remains fixed in the final position. In the Voigt-Kelvin model, Figure 2.2 (b), which models viscoelastic solid behavior, force is applied to the spring and dashpot in parallel, and the deformation of the spring is delayed by the presence of the dashpot. When the applied force is removed, the dashpot slows the restoration of the spring until it makes a complete recovery.

Viscoelastic materials are unique in their ability to both store and dissipate energy, and most commercially available materials exhibit viscoelastic character and complex fluid behavior. As the degree of viscoelasticity and the viscous and elastic response is highly variable across materials, measurement of these parameters is useful in rheological characterization.

2.3. Dynamic Oscillatory Shear Rheology

Although rotational or “steady-shear” rheology offers useful information as to the flow properties of a sample, dynamic oscillatory shear rheology offers valuable clues about the inherent structure of a material. Because only small oscillations are applied to the sample, insight into the material structure of a sample can be gained without causing breakage or disruption.³ Therefore, oscillatory rheology is useful as a “molecular probe” to make determinations about the structure of a material,

and it can be applied across varying length scales to understand the structure at the bulk scale, microscale, and even nanoscale.

In dynamic oscillatory shear rheology, a sinusoidal oscillation in the form of imposed strain is applied to the sample at a set frequency. The sample then responds to the applied oscillation with a resultant stress, and the difference between the applied oscillation and the sample response gives information about the viscoelastic character of the sample. For conventional rheometry, this stress is measured as torque on the instrument. As shown in Figure 2.3 (a), the resultant stress curve exactly matches the applied strain for a purely elastic material. However, for a purely viscous material as shown in Figure 2.3 (b), the resultant stress curve is completely out of phase with the applied oscillation.

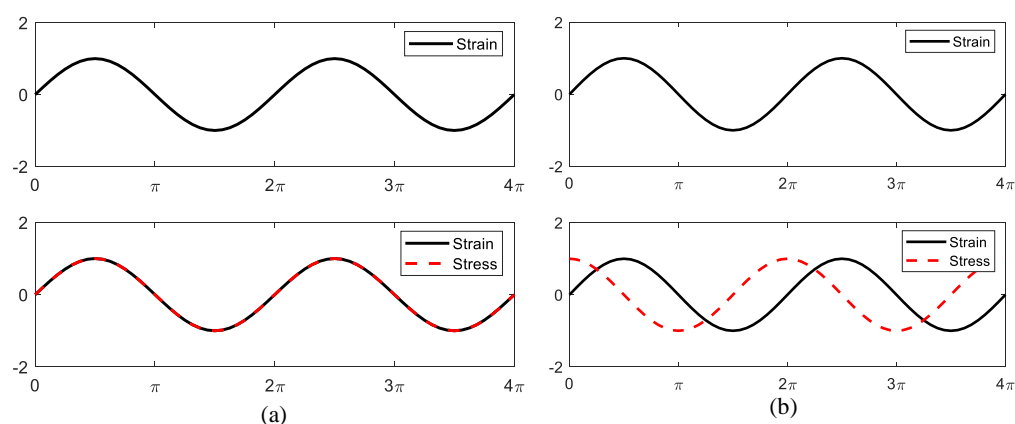


Figure 2.3. (a) Input (strain) and response (stress) curves for an ideally elastic material. No phase lag is observed between the input and the response. (b) Input and response curves for an ideally viscous material. The response curve is found to be $\pi/2$ radians (90°) out of phase.

For viscoelastic materials, the lag of the response curve is found to be between 0 and $\pi/2$ radians (0 and 90°). The lag between the two curves represents the phase angle, δ , and allows for quantitative determination of the viscoelastic character of the material. The elastic or solid character of a sample is represented by the storage modulus G' , while the viscous or liquid character of a sample is represented by the loss modulus G'' . The storage and loss moduli are derived from the complex modulus G^* , which is a ratio of stress to strain represented in the complex plane.² The storage and

loss moduli G' and G'' are related to G^* as follows, where G' represents the real part of the complex modulus, and G'' represents the imaginary part of the complex modulus:

$$G^* = G' + iG'' \tag{2.3}$$

$$G'' = G^* \cos(\delta), \text{ and} \tag{2.4}$$

$$G' = G^* \sin(\delta). \tag{2.5}$$

The tangent of the phase angle represents a ratio between G'' and G' :

$$\tan(\delta) = G''/G' \tag{2.6}$$

For materials where G'' is significantly greater than G' , the material is more likely to exhibit liquid-like structure. In contrast, materials where G' is significantly greater than G'' are more likely to exhibit solid or gel like structure.⁴

Amplitude sweeps are oscillatory tests that are conducted at constant frequency, and amplitude sweeps are often used to determine the range for which the sample remains in the linear viscoelastic region or LVE. The limit of the linear viscoelastic region represents the maximum strain, or deformation, at which tests can be completed without destroying the sample structure.² Amplitude sweeps can also offer information about the yield point of a material and the material “stiffness” or rigidity.

Frequency sweeps are another class of oscillatory tests, providing useful information about material structure. Frequency sweeps can be used to understand the short-term and long-term relaxation behavior of a sample and the networking or crosslinking that is present in a material. This test is particularly useful for understanding polymeric materials, as frequency sweeps can be used to distinguish between unlinked and cross-linked polymers.² For polymers, the relaxation time can be determined from the crossover point of the storage modulus and loss modulus, ω_c .⁵

$$\tau = \frac{1}{\omega_c}. \quad (2.7)$$

In a frequency sweep, the frequency of the sinusoidal oscillation is varied at a constant amplitude. The amplitude that is chosen should be within the linear viscoelastic region to ensure that the sample structure remains intact throughout the test. The storage modulus G' and loss modulus G'' are then plotted against frequency ω to assess the viscous and elastic character of the sample with varying frequency.

2.4. Microrheology

Although conventional “bulk-scale” rheology provides insight into material structure and viscoelastic response, extension of rheology to smaller length scales offers numerous advantages. Because of the limitations of inertial effects at high frequencies, rheology at the macroscale can only probe frequencies up to tens of Hz.⁶ Furthermore, bulk-measurement techniques can require up to 1-2 mL of sample, which may be prohibitive for measurements of costly or limited-quantity samples. Conventional rheology is also only capable of providing average measurements of the bulk-sample response, which may not be adequate for probing of inhomogeneous systems or understanding of localized behavior.⁶

Microrheology techniques offer solutions to many of the limitations that are presented by conventional rheology. Microrheology tracks the thermal motion, or “Brownian motion,” of microscopic tracer particles in solution.⁷ This allows for a local probe of viscous and elastic character and an understanding of the material response on a micrometer length scale. Microrheology also allows for analysis across a broader range of frequencies, allowing for analysis into the MHz regime.⁶ Both active microrheology, the manipulation of probes by external forces, and passive microrheology, the use of thermal energy alone to drive motion, are approaches for investigation of microscale rheological properties. Although the methods for conducting active and passive microrheology are numerous, the specifics of these techniques are beyond the scope of this paper.

2.5. Nanorheology

Extending rheological characterization to even smaller length scales beyond the microscale is of interest. Building upon the many characterization advantages afforded by microrheology, nanoscale rheology offers opportunities for study of the material properties of a sample at the length scale of the constituent units in the sample.¹ Furthermore, these measurements can be made at even higher frequencies than microrheology, with measurements typically in the range of MHz to GHz.⁸ While microrheology typically relates the translational motion of tracer probes within a fluid to the rheological properties of the fluid, tracking of the rotational Brownian motion of magnetic nanoparticles has been proposed as a means of obtaining rheological parameters at the nanoscale.¹

Previous research has employed AC susceptibility measurements for the extraction of frequency-dependent parameters in nanorheology. In this process, an oscillating magnetic field of small amplitude is applied to the sample at varying frequency. The magnetization response is given by

$$M = X'H_0 \cos(\omega t) + X''H_0 \sin(\omega t) \quad (2.8)$$

where M represents the magnetization response, X' represents the real or in-phase component of magnetic susceptibility, X'' represents the imaginary or out of phase component of magnetic susceptibility, H_0 represents the magnitude of the applied magnetic field, and ω represents the frequency of the magnetic-field oscillations.⁸

The imaginary and real components of the magnetic susceptibility X have been theorized to be analogous to the storage and loss moduli G' and G'' that are observed in macroscale rheology.

Roeben et al.⁹ has proposed the following relationship between these parameters:

$$G' = \frac{1}{K} \left(\frac{X'_N}{X'_N{}^2 + X''_N{}^2} - 1 \right), \text{ and} \quad (2.9)$$

$$G'' = \frac{1}{K} \left(\frac{X''_N}{X'_N{}^2 + X''_N{}^2} \right). \quad (2.10)$$

The constants are then broken down as follows, where X_0 is the magnetic susceptibility at a frequency of 0 Hz, X_∞ is the magnetic susceptibility at the limit of infinite frequency, and k_B is the Boltzmann constant:

$$K = \frac{4\pi a^3}{k_B T}, \quad (2.11)$$

$$X'_N = \frac{X' - X_\infty}{X_0 - X_\infty}, \text{ and} \quad (2.12)$$

$$X''_N = \frac{X''}{X_0 - X_\infty}. \quad (2.13)$$

This approach has thus far been used to measure the viscosity of fluids at the nanoscale for ideally Newtonian materials, and it has shown good agreement between the nanoscale and microscale viscosities for simple fluids.⁹ It is expected that this approach can be extended to viscoelastic fluids and other complex materials.

In this technique, magnetic nanoparticles are suspended in the fluid of interest and subjected to a constant temperature and constant amplitude of applied magnetic field. The magnetic field is oscillated sinusoidally, and the AC susceptibility is then measured across a range of frequencies. The in-phase and out of phase components of susceptibility (X' and X'') can then be plotted against frequency. Using particles with a narrow size distribution is recommended, as the polydispersity in the size distribution must be considered when determining the in phase and out of phase susceptibility parameters.

2.6. Mathematical Modeling of Nanorheology

Mathematical models can be used to make predictions about the in phase and out of phase susceptibility parameters X' and X'' for a number of constitutive fluid models. Assuming the

magnetic particles follow a lognormal size distribution, these models are derived from the Gement-DiMarzio-Bishop (GDB) model for magnetic susceptibility X^* :⁹

$$\frac{X^* - X_\infty}{X_0 - X_\infty} = \int_0^\infty \frac{1}{1 + K(D)G^*(\omega)} f(D)dD, \quad (2.14)$$

where

$$K(D) = \frac{\pi D^3}{2k_B T}, \text{ and} \quad (2.15)$$

$$f(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp\left[-\frac{(\log(D) - \mu)^2}{2\sigma^2}\right], \quad (2.16)$$

where X_0 represents the initial susceptibility at 0 Hz, X_∞ represents the high frequency limit of susceptibility, G^* represents the modulus, D represents the particle diameter, k_B represents the Boltzmann constant, and μ and σ represent the mean and variance of the particle size distribution respectively.¹⁰

The magnetic susceptibility X^* can be broken down into the in phase and out of phase susceptibility parameters X' and X'' as well as the storage and loss moduli G' and G'' using the relationship

$$X^* = X' - iX'', \text{ and} \quad (2.17)$$

$$G^* = G' - iG'', \quad (2.18)$$

These expressions can be substituted into Equation 2.12 so that,

$$\frac{X'}{X_0 - X_\infty} = \int_0^\infty \frac{1 + K(D)G''}{(1 + K(D)G')^2 + (K(D)G'')^2} f(D)dD + X_\infty, \text{ and} \quad (2.19)$$

$$\frac{X''}{X_0 - X_\infty} = \int_0^\infty \frac{K(D)G''}{(1 + K(D)G')^2 + (K(D)G'')^2} f(D)dD. \quad (2.20)$$

Constitutive fluid models can be used to determine expressions for the storage and loss moduli G' and G'' in terms of frequency, ω , relaxation modulus, G , and viscosity η . For a Newtonian fluid model,

$$G' = 0, \text{ and} \quad (2.21)$$

$$G'' = \omega\eta. \quad (2.22)$$

For a Maxwell viscoelastic fluid model, the storage and loss moduli can be represented by,

$$G' = \frac{G\omega^2\eta^2}{G^2 + \omega^2\eta^2}, \text{ and} \quad (2.23)$$

$$G'' = \frac{G^2\omega\eta}{G^2 + \omega^2\eta^2}, \quad (2.24)$$

and for a Kelvin-Voight viscoelastic fluid model, the moduli are represented by,

$$G' = G, \text{ and} \quad (2.25)$$

$$G'' = \omega\eta. \quad (2.26)$$

These expressions can then be substituted into Equations 2.17 and 2.18 to determine the susceptibility parameters for the constitutive model of choice.¹⁰

2.7. Dilute Solution Viscometry

Dilute-solution viscometry is an analytical technique that is frequently used alongside other methods for polymer characterization. For concentrated solutions where the concentration of polymer exceeds the coil overlap concentration c^* , entanglements dominate and only permit study of polymer-polymer interactions.³ However, within the dilute regime, the concentration is below the coil overlap concentration, allowing for investigation of the polymer-solvent interactions. This observation makes dilute solutions ideal for determination of solution viscosity and relative molecular weight.

The intrinsic viscosity $[\eta]$ of a polymer solution is the inverse of the coil overlap concentration c^* , allowing for the experimental determination of c^* for a given polymer-solvent system:⁵

$$[\eta] = \frac{1}{c^*} \quad (2.27)$$

The intrinsic viscosity of a polymer solution can also be related to the molecular weight of the polymer through a simple mathematical relationship, offering a fast and effective means of estimating average molecular weight. Intrinsic viscosity represents an extrapolation of the reduced viscosity η_{red} as concentration c goes to zero, such that

$$\eta_{red} = \frac{\eta - \eta_s}{\eta_s c}, \text{ and} \quad (2.28)$$

$$[\eta] = \lim_{c \rightarrow 0} \eta_{red}, \quad (2.29)$$

where η_s is the viscosity of the solvent and η is the viscosity of the solution.⁵ This expression can be related to the molecular weight of the polymer through the Mark-Houwink Sakurada equation as follows,

$$[\eta] = kM^a \quad (2.30)$$

where k is the proportionality constant of the polymer, a is a parameter based on the “goodness” of the polymer solvent, and M is the viscosity average molecular weight of the polymer.³ Although intrinsic measurements do not account for the molecular-weight distribution, or polydispersity, of the polymer, these measurements can be used in combination with absolute methods including gel permeation chromatography (GPC) and light scattering (MALLS) for complete characterization.⁵

3. Materials

3.1. Polyethylene Oxide

Polyethylene oxide, or PEO, is a flexible, non-ionic, water soluble polymer widely used in a variety of industrial and research applications.¹¹ Polyethylene oxide is water soluble, easily produced, and non-toxic, and is used in applications including drag reduction, electrospinning, flocculation, and polymer-based drug delivery. As it is available in a wide range of molecular weights with varying rheological properties, PEO serves as a useful representative viscoelastic material.

3.2. VivoTrax Magnetic Tracer Particles

VivoTraxTM magnetic tracer particles contain superparamagnetic iron oxide dextran nanoparticles (5.5 mg/mL) suspended in a PBS buffer solution. VivoTrax particles have been widely used for magnetic particle imaging applications as well as for cell tracking within the human body.¹¹

4. Experimental Methods

4.1. Preparation of Polymer Solution

Stock solutions of a high molecular weight polyethylene oxide (POLYOX UCARFLOC 309) and a lower molecular weight polyethylene oxide (200K MW, Sigma Aldrich) were prepared at concentrations of 5000 ppm and 15 wt% respectively. To prepare stock solutions, powdered polymer was added gradually to room temperature DI water on a stir plate set to medium stirring speed until all polymer was dissolved. Solutions were prepared over a three-day period, and the solutions were stirred continuously to limit the formation of aggregations in the solutions. A parafilm cover was used to minimize water evaporation between additions. After all powdered polymer was dissolved, the solutions were left stirring continuously overnight to ensure complete mixing. Stock solutions were stored in dark glass bottles and placed on a shaker table set to minimum speed for long-term storage.

4.2. Intrinsic Viscosity Measurements`

Intrinsic viscosity measurements were used to characterize the high molecular weight PEO solution (POLYOX 309). DI water was used as a solvent, and solutions at concentrations of 100 ppm, 75

ppm, 50 ppm, and 25 ppm were measured using a Ubbelohde dilution viscometer. Time was measured to hundredths of a second using a stopwatch timer, and trials were conducted at room temperature (21 °C).

4.3. Dynamic Light Scattering for VivoTrax Tracer Particles

Dynamic light scattering (DLS) was performed for one vial of VivoTrax magnetic tracer particles used in experiments. Samples were diluted with nanopure water in disposable cuvettes, and a Brookfield DLS analyzer was used to take measurements. Three runs were conducted at 3 minutes each. To assess the influence of particle settling on the DLS data, the cuvettes were allowed to rest for 9 total minutes and were then re-run again using the same experimental parameters.

4.4. Bulk Rheology Measurements - Dynamic Oscillatory Shear

Bulk scale rheology measurements were performed using an AR-G2 rheometer and 60 mm diameter 1° cone and plate geometry. All experiments were performed at a constant temperature of 20 °C using a raised Peltier plate control system.

Amplitude sweeps were conducted at a constant frequency of 1 Hz to determine the linear viscoelastic (LVE) range for each concentration measured. Frequency sweeps were conducted from 0.01 to 10 Hz at a constant strain % within the LVE for each concentration, and G' and G'' were measured across the frequency range.

4.5. VivoTrax Tracer Particles - Mass Studies

A DynaCool Physical Property Measurement System (PPMS) was used to measure the in phase and out of phase AC susceptibility (X' and X'') for pure, undiluted VivoTrax particles. Particle volumes of 10 μL , 20 μL , 50 μL , and 100 μL were tested undiluted in 1 mL ampoules. Frequency was swept from 500 to 3000 Hz for an amplitude of 5 Oe at a constant temperature of 300 K.

5. Results/Discussion

5.1. Dynamic Light Scattering

Dynamic light scattering was performed for one vial of VivoTrax magnetic tracer particles. Particle diameter is plotted against the probability density function $f(D)$ as shown in Figure 5.1.

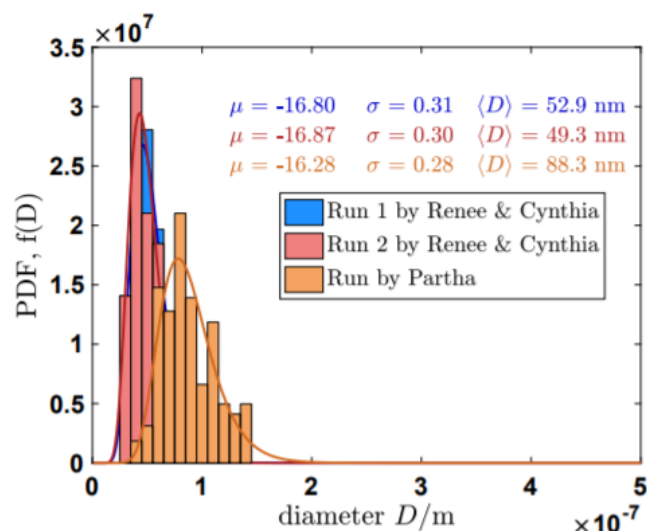


Figure 5.1. Plot of dynamic light scattering data for VivoTrax magnetic nanoparticles. (Credit: Mingyang Tan). Data from two runs is compared against data collected for VivoTrax particles by Partha Sarathi Paul.¹²

Data for two runs was compared to against data collected for a different vial of VivoTrax particles used in prior research¹² to assess the variability between vials of particles. As shown in Figure 5.1, the mean particle diameter was found to be consistent between both runs conducted for the same vial – however, the particle diameter was found to be significantly different for the runs conducted for different vials. As the particle diameters for the new particles were found to be 52.9 nm and 49.2 nm respectively compared to 88.3 nm for the previously studied particles, it is evident that particle diameter is not consistent between vials of particles. An average particle diameter should therefore not be assumed when conducting measurements using these particles, and dynamic light scattering should be performed on each vial of particles before use in experiments.

Both vials of particles displayed a range of particle diameters. Although the new vial of particles showed a narrower distribution compared to the particles used by Partha, diameter was still found

to vary between the particles in the samples studied. Furthermore, the variation in particle sizes observed suggests that a single particle diameter should not be assumed when taking measurements and developing models. As the distribution of particle sizes is reasonably narrow, however, VivoTrax particles are an appropriate choice of nanoparticle to use as tracers in these experiments.

5.2. Intrinsic Viscosity Measurements

Intrinsic viscosity measurements were used to characterize the POLYOX 309 PEO, allowing for determination of the coil overlap concentration and viscosity average molecular weight of the polymer. Intrinsic viscosity was measured at four concentrations of polymer as shown in Figure 5.2.

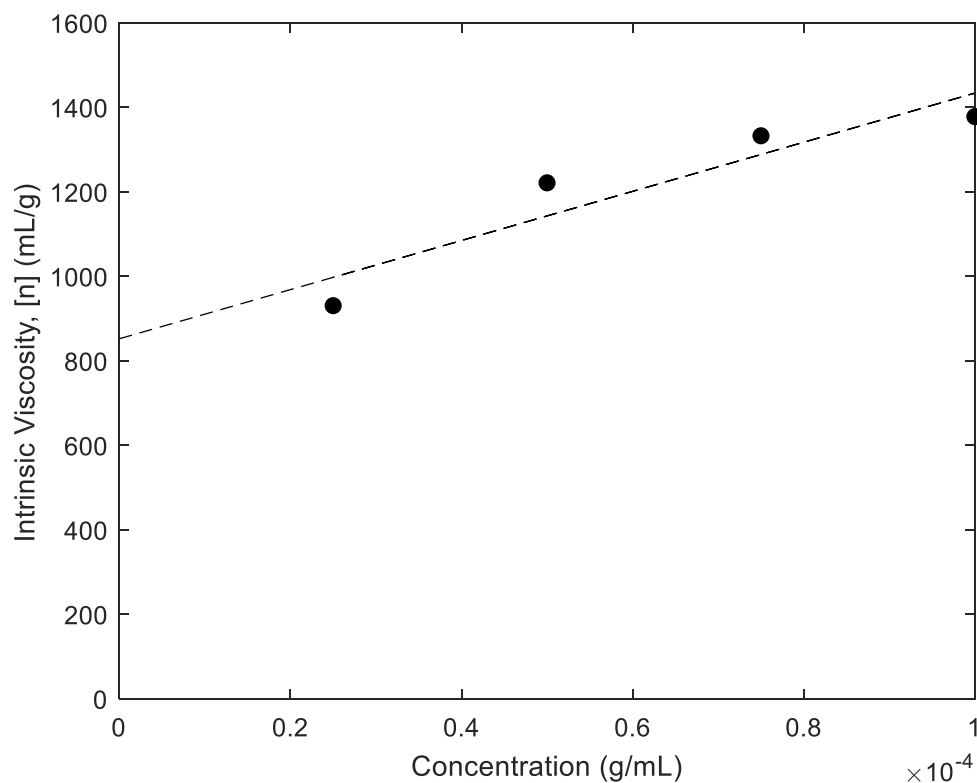


Figure 5.2. Plot of intrinsic viscosity against concentration for POLYOX 309 polyethylene oxide. Concentrations of 100 ppm, 75 ppm, 50 ppm, and 25 ppm were tested in a Ubbelohde dilution viscometer using DI water as a solvent. A linear regression trendline was used to fit the data and was found to be $y = 6 \times 10^6 x + 852.5$.

A linear regression trendline was used to fit the data and was found to be $y = 6 \times 10^6 x + 852.5$. As the intrinsic viscosity $[\eta]$ of the solution can be represented by the y intercept of this equation, $[\eta]$ was found to be 852.5 [mL/g]. The coil overlap concentration c^* , found from the inverse of intrinsic viscosity, was found to be $c^* = 0.00117$ [g/mL] or 1173 ppm. This was within a similar order of magnitude compared to literature values, where c^* was found to be 760 ppm for PEO with a molecular weight of 2×10^6 g/mol.¹³ This indicates that all concentrations above this value represent concentrated solutions, showing that the 5000 ppm stock solution prepared is sufficient for study of polymer-polymer interactions.

Mark-Houwink Sakurada parameters were determined from data tabulated by the American Polymer Standards Corporation¹⁴ and used to calculate the molecular weight. Parameters were found to be $k = 0.0125$ [mL/g] and $a = 0.78$, yielding a viscosity average molecular weight M_v of 1.57×10^6 g/mol. This order of magnitude makes sense, showing that the POLYOX PEO 309 has a molecular weight of around 2 million g/mol.

5.3. Bulk Rheology Characterization of Standard Solutions

Preliminary bulk rheology measurements were performed for standard solutions to evaluate the performance of the AR-G2 rheometer. To assess the validity of measurements compared to those taken by other instruments, a flow sweep was conducted for a low viscosity polydimethylsiloxane (PDMS) standard (Dow Corning, 350 CS) across shear rates of 0.01 to 1000 1/s using the AR-G2 rheometer. These results were compared to results obtained using a DHR-3 rheometer as shown in Figure 5.3.

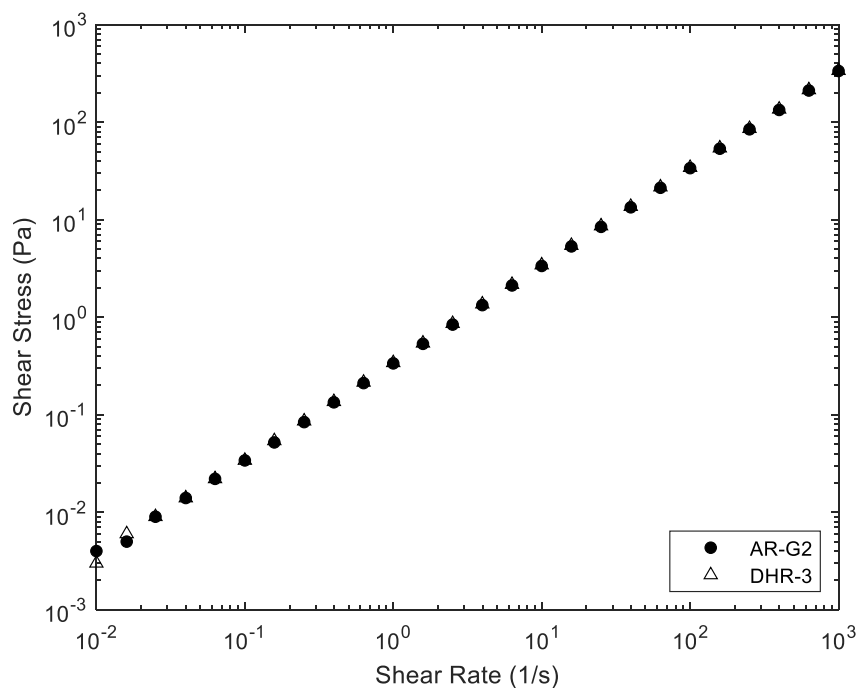


Figure 5.3. Flow sweep for polydimethylsiloxane (Dow Corning, 350 CS). Shear rate was swept from 0.01 to 1000 1/s, and shear stress was measured by the instrument. Measurements were taken using an AR-G2 rheometer (circles) and DHR-3 rheometer (triangles) using a 60 mm 1° cone and plate geometry. Measurements from both rheometers were found to overlap across the range of shear rates tested.

As illustrated in the figure, shear stress was found to increase linearly with shear rate for measurements taken by both rheometers. This indicates constant viscosity across the range of shear rates tested, which is in accordance with the results expected for this viscoelastic standard material. The results for both rheometers were found to overlap for all measurements taken, showing that consistent results were obtained by both instruments.

To evaluate the performance of the AR-G2 for dynamic oscillatory shear measurements, a frequency sweep from 0.1 to 10 Hz was used to characterize a high viscosity polydimethylsiloxane standard (Dow Corning, 30,000 CS) as shown in Figure 5.4.

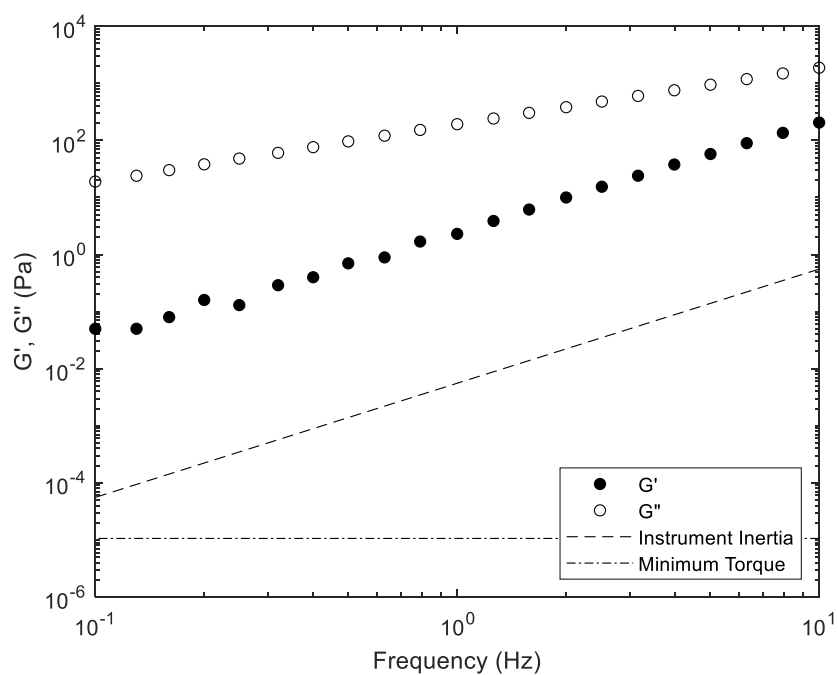


Figure 5.4. Frequency sweep plot for Dow Corning PDMS standard (30,000 CS). Frequency was swept from 0.1 to 10 Hz at a constant amplitude of 25 strain %. Instrument inertia and minimum torque G_{\min} are co-plotted against frequency.

As illustrated in the figure, the loss modulus G'' dominated behavior at both low and high frequencies, showing primarily viscous behavior for the standard solution. Both G' and G'' were found to increase with increasing frequency, which would be expected for this viscoelastic standard. No crossover frequency was observed across the frequency range tested. Results for the standard were found to lie outside the range of the instrument inertia limit as well as the instrument minimum torque, showing that these effects did not cause issues with the data collected for the standard solution.

A frequency sweep for 7 wt % polyisobutylene solution was performed to evaluate the rheometer response for a non-standard viscoelastic material. A frequency sweep from 0.01 to 10 Hz was conducted at a constant amplitude of 5 strain % as shown in Figure 5.5.

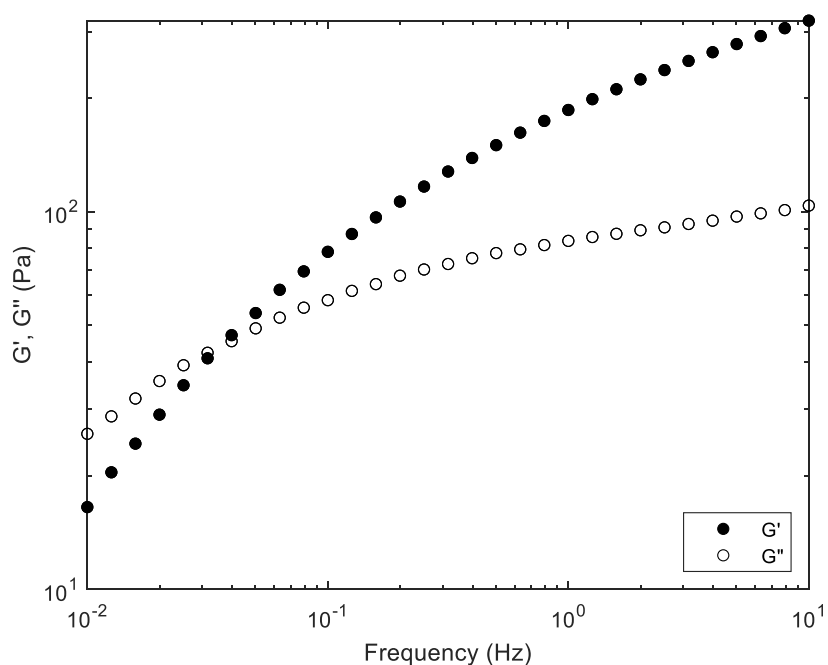


Figure 5.5. Frequency sweep plot for 7 wt% polyisobutylene solution. Frequency was swept from 0.01 to 10 Hz at a constant amplitude of 5 strain %.

As shown in the figure, the loss modulus G'' dominated behavior at low frequencies, showing primarily viscous behavior at long time scales. The crossover frequency ω_c was observed to be 0.04 Hz, after which the storage modulus G' was found to dominate behavior at higher frequencies and short time scales. The results obtained make sense for this material, as both the loss modulus G'' and the storage modulus G' vary with frequency as would be expected for a viscoelastic material.

5.4. Bulk Rheology Characterization of POLYOX 309

Bulk rheology measurements were used to characterize the average viscoelastic response of the POLYOX PEO 309 solution. Amplitude sweeps were conducted to assess the linear viscoelastic region (LVE) for the 5000 ppm stock solution, and frequency sweeps were conducted across a range of frequencies with the goal of drawing comparisons to nanoscale rheology data for the same solution.

An amplitude sweep for the POLYOX PEO 309 solution was conducted for the 5000 ppm stock solution to evaluate the linear viscoelastic region of the polymer solution (Figure 5.6).

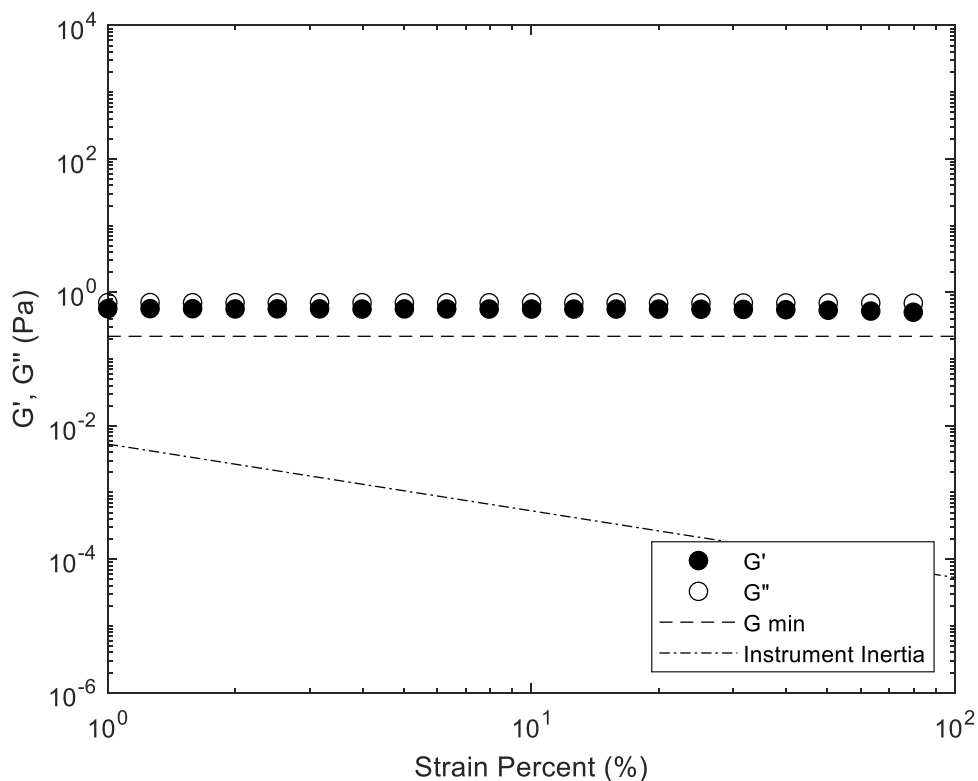


Figure 5.6. Amplitude sweep plot for POLYOX PEO 309 at 5000 ppm. Strain was swept from 1 to 100% strain at a constant frequency of 1 Hz. Instrument limits (instrument inertia and minimum torque G_{\min}) are co-plotted against strain %.

As illustrated in Figure 5.6, the values of the storage modulus G' and loss modulus G'' remained relatively constant across the range of strain percents tested, suggesting that the linear viscoelastic region extends across the range of strain percents tested. As the values of both moduli approach the limits of instrument inertia, however, it is expected that these values do not represent valid data, especially with the unusual overlapping of the moduli observed.

Frequency sweeps were used to characterize the viscoelastic behavior of the 5000 ppm POLYOX 309 solution. A strain of 10 % was chosen to ensure the sample would remain in the LVE for the duration of the test (Figure 5.7).

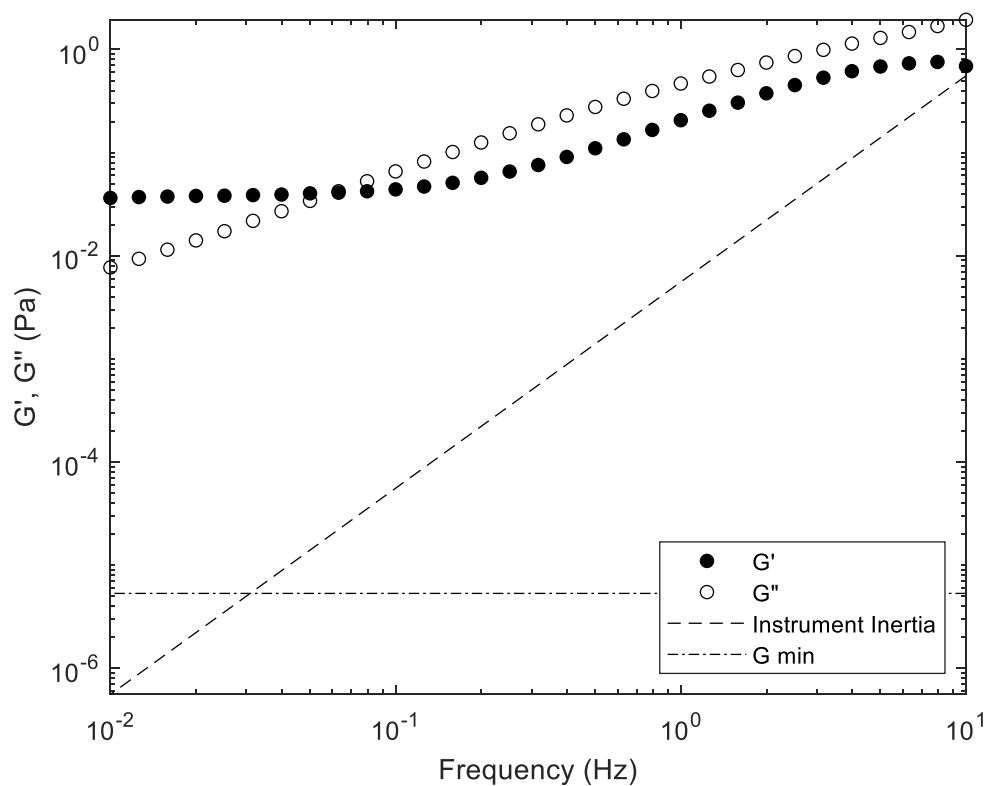


Figure 5.7. Frequency sweep plot for POLYOX 309 PEO at a concentration of 5000 ppm. Frequency was swept from 10 Hz to 0.01 Hz at a constant amplitude of 10 strain %. Instrument limits are co-plotted against frequency for a minimum torque G_{\min} of 5.30×10^{-6} Pa.

As shown in the figure, the loss modulus G'' crosses the storage modulus G' at a crossover frequency ω_c of 0.05 Hz, indicating a relaxation time τ of 20 seconds for the polymer. The storage modulus G' was found to dominate behavior at very low frequencies and very long time scales, while the loss modulus G'' was found to dominate at higher frequencies. Because the viscoelastic moduli were both found to vary with frequency, results suggested that the POLYOX 309 PEO exhibits viscoelastic character as expected. As the moduli lie well above the instrument limits for minimum torque and instrument inertia, it is also expected that this characterization serves as a reasonable depiction of polymer behavior.

5.5. Bulk Rheology Characterization of PEO 200K

Due to the difficulties presented by preparing POLYOX 309 PEO at high concentrations of polymer, it was hoped to attempt to characterize a material with a broader range of viscoelastic character. A lower molecular weight PEO, PEO 200K, was chosen with the goal of preparing solutions across a wide range of concentrations.

Amplitude sweeps were conducted for the 200K PEO for concentrations of 10 wt%, 1.25 wt%, and 0.5 wt% to compare the LVE across varying concentrations of polymer (Figure 5.8).

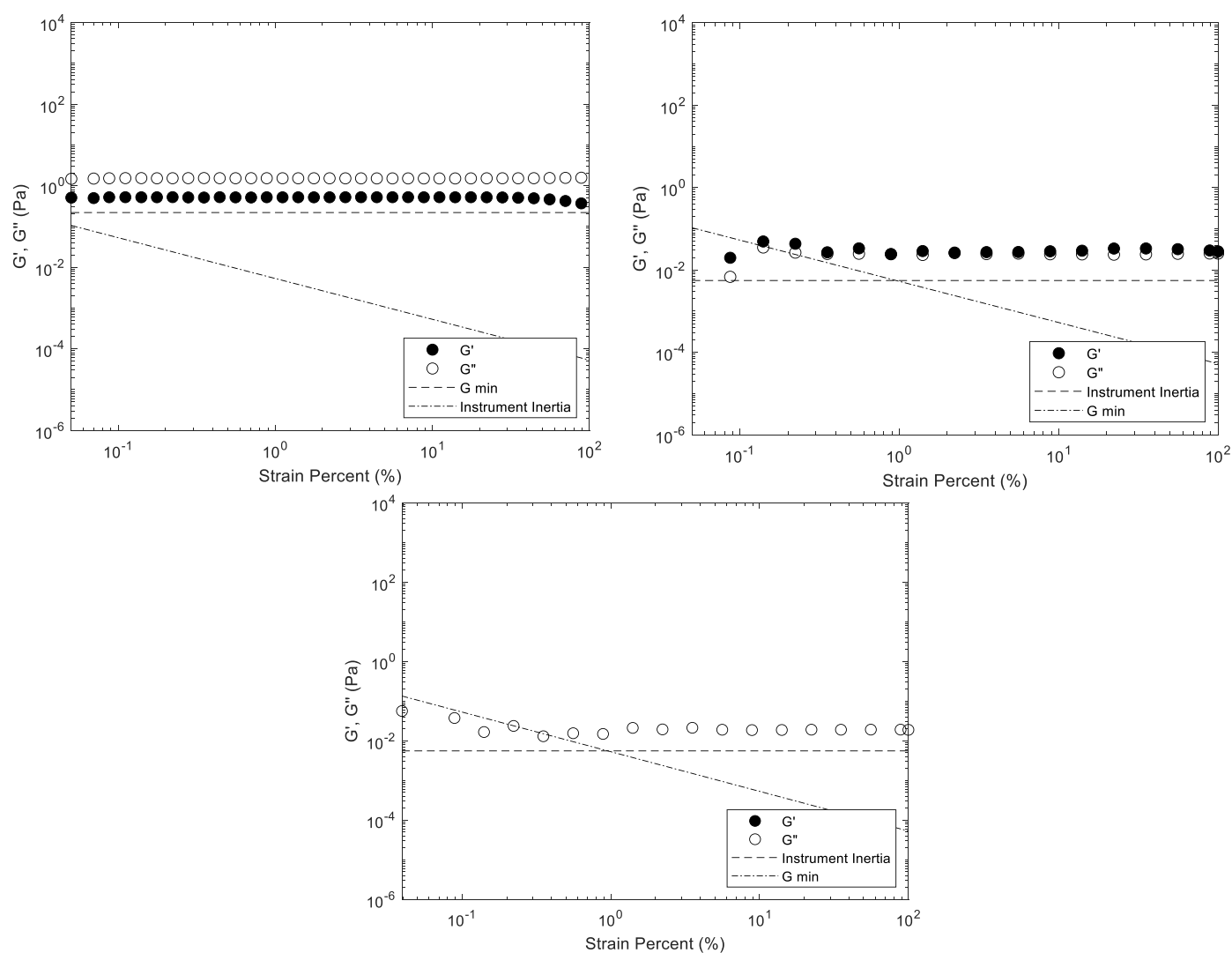


Figure 5.8. Amplitude sweep plot for 200K PEO at concentrations of (clockwise from top left) 10 wt%, 1.25 wt%, and 0.5 wt%. Strain was swept from 0.05 to 100% strain at a constant frequency of 1 Hz. Instrument limits (instrument inertia and minimum torque G_{\min}) are co-plotted against strain %.

While the 10 wt% solution shows that the storage modulus G' begins to decrease close to 100 strain %, the plots of 1.25 wt % and 0.5 wt% do not show any observable trends. For concentrations of 1.25 wt% and 0.5 wt%, the values below 1% strain fall below the minimum torque G_{\min} of the instrument. The values measured also fall close to the limits of instrument inertia, suggesting that they may be inconsistent with expected trends. For the solution of 0.5 wt% polymer, the data suggest that the rheometer was not sensitive enough to detect measurements of the elastic modulus G' at this concentration of polymer.

Frequency sweeps were conducted for concentrations of 0.5 wt%, 1.25 wt%, 2.5 wt%, 5 wt%, 10 wt%, and 15 wt% PEO 200K. For concentrations of 10 wt% and 15 wt%, a strain of 5 % was chosen, and sample frequency was swept from 0.01 to 10 Hz (Figure 5.9).

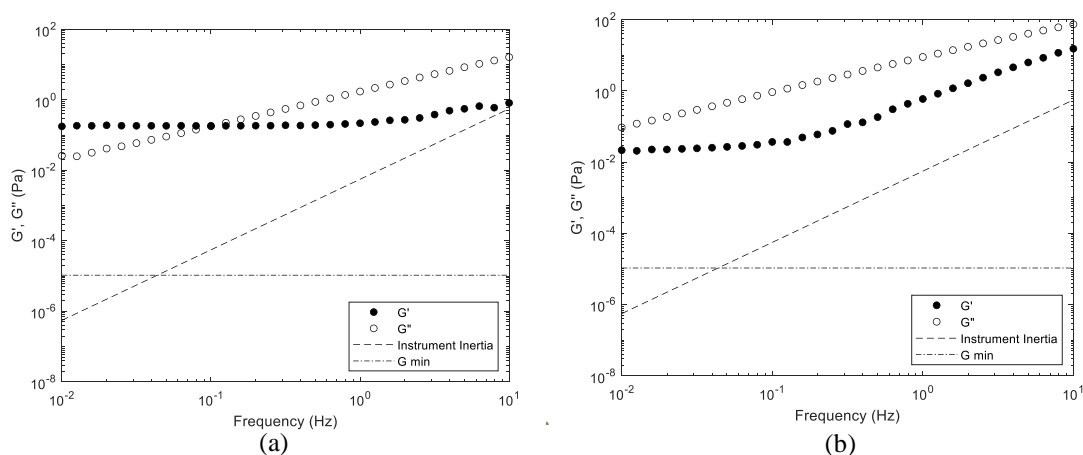


Figure 5.9. Frequency sweep data for PEO 200K solutions for concentrations of (a) 10 wt % and (b) 15 wt% PEO 200K. Frequency was swept from 0.01 to 10 Hz for a constant amplitude of 5 strain %. Instrument limits (instrument inertia, minimum torque G_{\min}) are co-plotted against frequency.

Although the data for the 15 wt% solution fell well above the limits of the instrument, no crossover frequency was observed across the frequency range tested. Both the storage modulus and loss modulus for the 15 wt% solution were found to vary with frequency, suggesting viscoelastic behavior. A crossover frequency was observed for the 10 wt% solution and was found to be 1 Hz. However, the plateau of the storage modulus in the 10 wt% solution does not make sense for this solution, as this would indicate that the storage modulus G' remained constant with frequency.

For concentrations of 0.5 wt%, 1.25 wt%, 2.5 wt%, and 5 wt%, a strain of 5 % was chosen, and sample frequency was swept from 0.01 to 10 Hz (Figure 5.10).

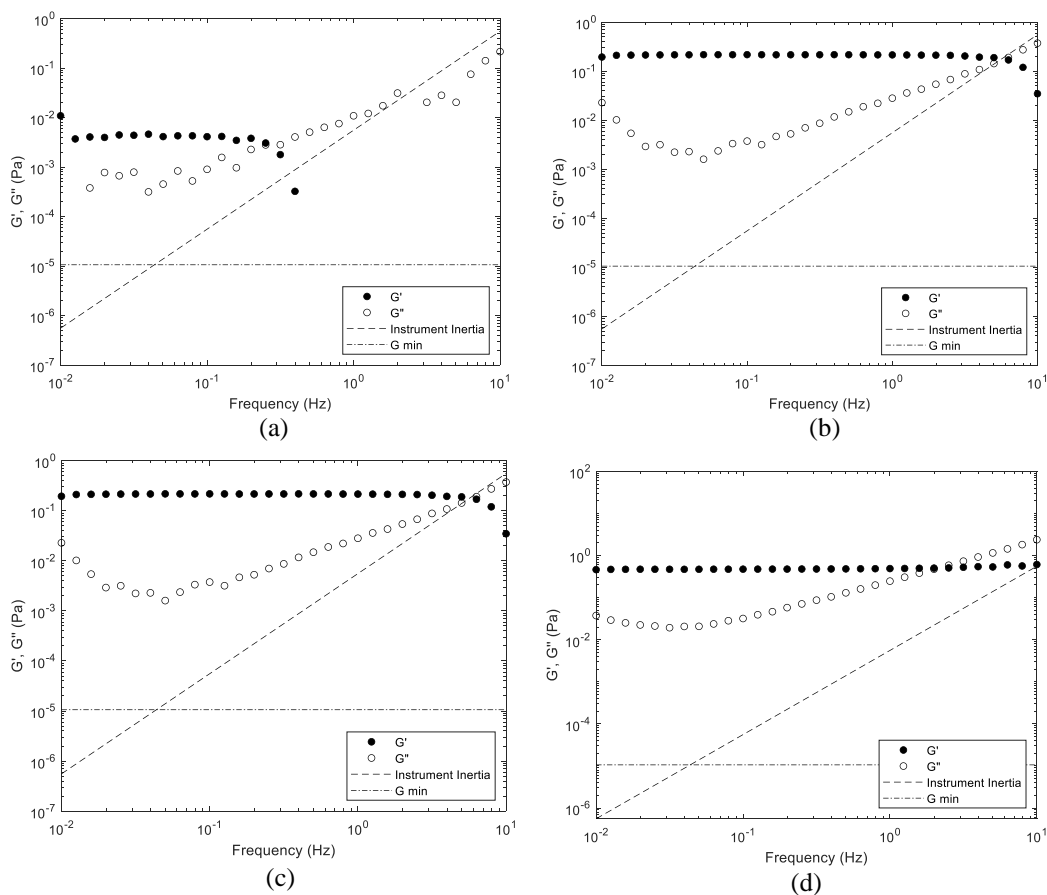


Figure 5.10. Frequency sweep data for PEO 200K solutions for concentrations of (a) 0.5 wt % , (b) 1.25 wt% , (c) 2.5 wt% , and (d) 5 wt% PEO 200K. Frequency was swept from 0.01 to 10 Hz for a constant amplitude of 5 strain %. Instrument limits (instrument inertia, minimum torque G_{\min}) are co-plotted against frequency.

As shown in the figure, the loss modulus G'' was found to fall on or below the limit for minimum torque for low concentration of polymer (0.5 wt % , 1.25 wt% and 2.5 wt%), and these effects were found to be more pronounced as concentration of polymer decreased. It was also observed that the storage modulus G' remained flat across the frequency range, while the loss modulus G'' showed variance with frequency. These results indicate that the sample exhibits primarily viscous character, with the data for the storage modulus G' potentially a result of surface tension effects rather than true elastic behavior. This suggests that the PEO 200K does not exhibit viscoelasticity at low

concentrations of polymer as expected, and that further study should be done to improve the characterization data and substantiate these results.

5.6. VivoTrax Tracer Particles - Mass Studies

The in phase and out of phase AC susceptibility parameters X' and X'' were measured for volumes of 10 μL , 20 μL , 50 μL , and 100 μL undiluted VivoTrax particles for an oscillating magnetic field swept from 500 to 3000 Hz. The susceptibility parameters were found to increase linearly with particle mass, which is consistent with expected results. As AC susceptibility was observed to vary with particle mass, these results suggest that particle mass should remain fixed in future tests.

5.7. AC Susceptibility Models

Mathematical models were used to simulate experimental results for the in phase and out of phase AC susceptibility parameters X' and X'' for polyethylene oxide. As experimental data for polyethylene oxide was not available, parameters from prior experiments using blood plasma were used to represent the behavior of polyethylene oxide as a viscoelastic material.¹⁰ Calibration curve data collected in prior research for VivoTrax particles in a Newtonian fluid was used to determine the susceptibility parameters X_∞ and X_0 at the limits of high and low frequency respectively.¹⁵

As shown in Figure 5.11, AC susceptibility was modeled from 0 to 3×10^6 Hz to model the susceptibility response over several orders of magnitude. Susceptibility parameters for the Newtonian, Maxwell, and Voigt-Kelvin constitutive fluid models were evaluated, and an assumed particle concentration of 3 mg/mL particles was used for all models.

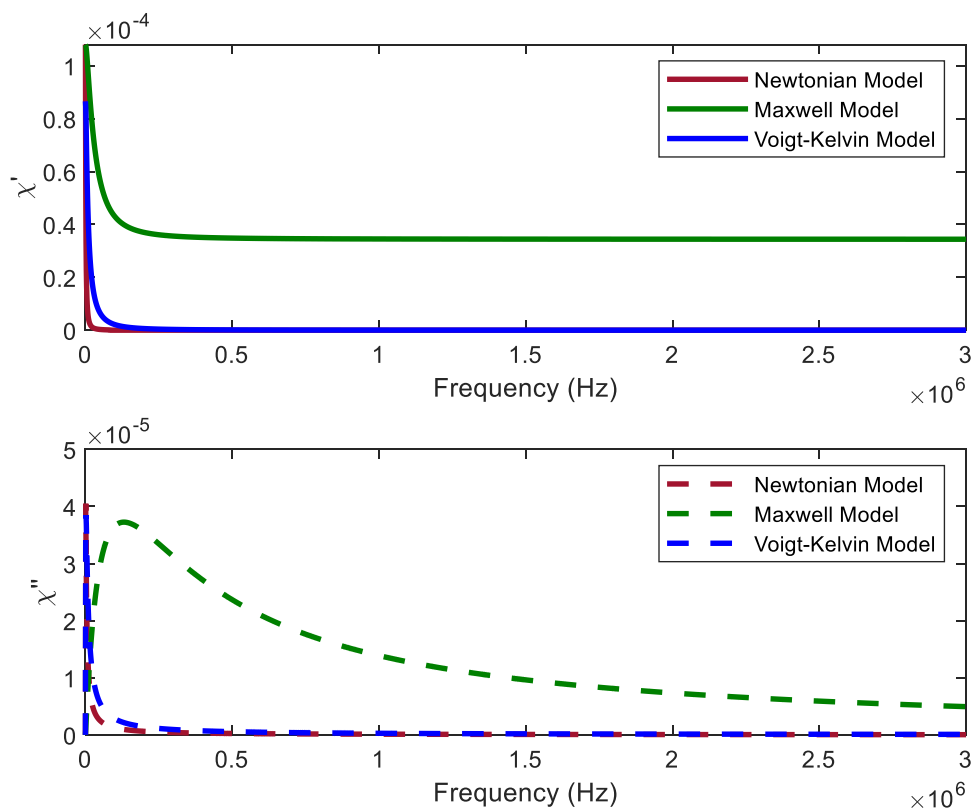


Figure 5.11. Magnetic susceptibility parameters X' and X'' against frequency for VivoTrax magnetic tracer particles. Data was fitted to the Newtonian, Maxwell, and Kelvin Voight constitutive fluid models for frequency ranging from 0 to 3×10^6 Hz to simulate the frequency dependent response of a viscoelastic material. Values for relaxation modulus G and viscosity η were determined from data collected for blood plasma by Mingyang Tan and Partha Sarathi Paul.¹⁵

As shown in Figure 5.11, the Maxwell model was shown to have higher values for the in-phase susceptibility X' when compared to the Newtonian and Voigt-Kelvin models. Similarly, the values of the out of phase susceptibility X'' were found to be higher for the Maxwell model compared to the other two models studied. The results obtained for the Newtonian model and Voigt-Kelvin models were found to follow similar trends for both the out of phase susceptibility X'' and in phase susceptibility X' . All of the models studied showed approached constant susceptibility at very high frequencies, and it was observed that both the Newtonian and Voigt-Kelvin models approached an asymptote of zero while the Maxwell model approached a non-zero asymptote.

To generate more appropriate models specific to polyethylene oxide, values of the relaxation modulus G and viscosity η should be determined experimentally for the two polyethylene oxide

solutions characterized in the bulk-scale rheology experiments. Additionally, the calibration curves relating particle concentration to the in phase and out of phase susceptibility parameters should be re-evaluated to ensure that particle mass is precisely controlled, as the high frequency limit X_{∞} was found to be highly sensitive to particle mass in prior experimentation.¹⁵ As the polyethylene oxide is a viscoelastic liquid, it is likely that the Maxwell model will be most appropriate for modeling of this solution – however, experimental measurements of the susceptibility parameters for both solutions of polyethylene oxide should be carried out across the frequency range to determine the model that most closely describes the material behavior.

6. Conclusions and Future Work

Through characterization of the VivoTrax magnetic tracer particles, it was observed that the particles showed a polydisperse size distribution with diameter highly variable between vials of particles used. It was also found that the AC susceptibility parameters X' and X'' vary linearly with particle mass, indicating that particle mass must be known precisely when taking measurements.

Bulk scale rheology was used to characterize two solutions of polyethylene oxide at different molecular weights. However, the overlap of the loss modulus with the minimum torque at low polymer concentrations for the PEO 200K solution suggests that further work should be done to eliminate these interferences and improve the characterization data. Additionally, the lack of viscoelastic character observed for low concentrations of polymer for the PEO 200K solution demonstrated that these concentrations of polymer are too low for use in this study and that higher concentrations should be studied in further research. As the goal of this project was to obtain data for a viscoelastic material across a broad range of concentrations to compare to nanoscale rheology characterization measurements, it is also suggested that other molecular weights of PEO should be investigated for use as better representative viscoelastic materials.

Mathematical models for three constitutive fluid models (Newtonian, Maxwell, and Kelvin-Voigt) were developed to describe the in phase and out of phase susceptibility response of a viscoelastic material to varied frequency. The Newtonian and Kelvin-Voigt model were found to yield similar results for both the in phase and out of phase susceptibility parameters X' and X'' , while the Maxwell model was found to yield higher values for both parameters. As these models relied on values derived for blood plasma as a viscoelastic material, modification of these models to use data collected for polyethylene oxide is of interest.

Further study is needed to evaluate the ability of nanorheology to study the frequency dependent behavior of polyethylene oxide polymer at varying concentrations, and it is hoped that these findings will be in accordance with the determined mathematical models. Further exploration into this technology would allow for connection of data collected at the macroscale, microscale, and nanoscale.

7. References

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