

Elasticity and Extensional Rheology of PEO-PEG-based Aqueous Boger Fluids

By

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THESIS

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This work is dedicated to my family, especially my parents, brother, wife and daughter. Without their support, encouragement and vision this work would not have come to fruition.

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List of Abbreviations

PEO	Polyethylene oxide
PEG	Polyethylene glycol
DoS	Dripping-onto-substrate
SOAS	Small amplitude oscillatory shear
LDPE	Low-density polyethylene
PAM	Polyacrylamide
CaBER	Capillary breakup extensional rheometer
TVEC	Terminal viscoelastocapillary
IC	Intericapillary
VC	Viscocapillary
EC	Elastocapillary
FE	Finite extensibility
EV	Excluded volume
HI	Hydrodynamic interactions

Summary

Elasticity influences flow behavior, processability, and applications of complex fluids. Elasticity can be characterized using torsional rheometers by measuring normal stresses in steady shear, elastic modulus in oscillatory shear, and stress relaxation after step-strain. Complex fluids display flow kinematics, as well as instabilities that are quite distinct from Newtonian fluids. However, determining the effects of elasticity are not straightforward, as most complex fluids that show measurable elasticity, also display rate-dependent viscosity. Simultaneous manifestation of these complex fluid phenomena leads to their conflation! To resolve this problem, David Boger developed a ‘purely elastic’ fluid that displays a constant viscosity. Such fluids, known as Boger fluids, are typically formulated by dissolving high molecular weight polymers in relatively high-viscosity solvents, to facilitate measurements with torsional rheometry. However, most Boger fluids are too viscous to emulate fluids used in coating flows. Though aqueous PEO-PEG Boger fluids allow access to these germane viscosities, but characterization of elasticity using state-of-the-art rheometers suffers due to the resolution limit of torque and normal force transducers, or due to elastic instabilities. Furthermore, many coating flows are susceptible to stream-wise velocity gradients associated with extensional flows, and hence characterization of extensional rheology response is necessary. In this contribution, we investigate the shear and extensional

rheology of PEO/PEG Boger fluids. We show that dipping-onto-substrate (DoS) protocols that rely on characterization of pinching dynamic allow measurement of both relaxation time and extensional viscosity. Even though most studies treat Boger fluids as experimental equivalents of Oldroyd-B fluids, the pinching dynamics displays terminal viscoelastocapillary regime, illustrating finite extensibility effects. The extensional relaxation time for aqueous PEO/PEG Boger fluids shows the concentration-dependent scaling also observed for aqueous PEO solutions, where measurements on torsional rheometers show no evidence of elasticity. Thus we show the possibility of utilizing aqueous polymer solutions as model Boger fluids, with elasticity quantified using DoS rheometry, and illustrate the extensional viscosity response exhibits strain-hardening, that could impact the coating flows, in addition to elastic effects.

1. Introduction

1.1 Preface

A Boger fluid is an elastic fluid with constant viscosity, often formulated by adding a dilute amount of high molecular weight polymer to a high viscosity fluid.[1,2] The influence of macromolecular dynamics in determining rheological response (i.e. response to imposed to deformation and flow) of polymer solutions and melts are detailed in many texts[3-5] and reviews[6-9]. Ever since their introduction, the Boger fluids are utilized for elucidating the impact of elasticity on both viscometric and processing flows and instabilities, and for comparison of experiments with theory and simulations.[2, 11-13] Newtonian fluids such as water, oils, and organic solvents that display a linear dependence on stress on deformation rate are often called simple fluids as their resistance to flow is characterized by single material property called viscosity.[14,16,101] For Newtonian fluids, extensional viscosity that characterizes resistance to extensional flows associated with stream-wise velocity gradients (say in contracting channels or in pinching necks formed during drop formation) is three times the shear viscosity that characterizes resistance to shear flows that typically arise next to walls.[14] In contrast, complex fluids can display non-Newtonian behavior in myriad ways, including by displaying rate-dependent viscosity, time-dependent viscosity, and by showing elasticity in response to applied stress or deformation.

Understanding the relative contribution of elasticity and rate-dependent viscosity is essential for developing materials and formulations with controlled flow behavior, determining optimal processing parameters, as well as for developing more realistic constitutive models to describe the response to imposed shear and extensional flow. However, discerning the influence of elasticity and rate-dependent viscosity is not obvious or straightforward, as the two phenomena are easily conflated. To resolve this dilemma, the Boger fluid, a highly elastic, constant-viscosity fluid was developed in 1977 by David Boger.[1] Using Boger fluids, direct comparisons of response can be made against a Newtonian fluid of matched viscosity, and the differences observed in kinematics, onset and growth of instabilities and in pattern formation can be attributed to elasticity.[2]

Instabilities of viscoelastic fluids impact and arise in a diverse range of instances/ application from nature to industry. Examples include beads-on-a-string structures formed by glue on spider webs[19,31], elastic instabilities that can influence rheological characterization[47] as well as channel flows[48], and capillarity-driven pinching flows that arise during drop formation in printing and dispensing operations[1-6]. Over time, various formulations of Boger fluids were developed, and used to probe influence of elasticity on onset and growth of instabilities and study viscoelastic kinematics and behavior predicted by different constitutive models.[2] However, the influence response to extensional flows

remains relatively less well-explored, due to the well-documented challenges of measuring extensional rheology response.[7-15] The formulations of particular interest and the primary focus of this dissertation research are the aqueous PEG/PEG Boger fluids that are particularly favored in model studies on coating instabilities due to the relatively low viscosity and weak elasticity of these fluids, that is comparable to coating fluids.[52-56] The PEO/PEG Boger fluids have shear viscosity that is at least an order of magnitude lower than most of the other Boger fluids.[2] High viscosity Boger fluids pose three challenges (detailed later in the document): (i) susceptibility to elastic instabilities, (ii) not representative of fluid viscosity and elasticity for many coating flows, and (iii) difficulty in extensional rheology characterization under flow rates encountered in processing flows. In this introductory chapter, we provide the definitions necessary for describing viscoelasticity and typical behavior of polymeric complex fluids, summarize the typical methods used for measuring the rheological response (i.e. response to deformation and flow) of viscoelastic fluids, and discuss the impact of non-Newtonian rheological response on representative hydrodynamic instabilities, with particular emphasis on deciphering influence of elasticity in response to shear deformations, as well as extensional rheology response, on flow behavior and instabilities rather than just the impact of rate-dependent steady shear viscosity.

The rheological characterization of PEO/PEG Boger fluids, along with a discussion of their influence and impact on characterizing viscoelastic instabilities are focus of Chapter 2. In this contribution, we utilize Dripping-onto-Substrate (DoS) rheometry protocols that involve visualization and analysis of capillarity-driven pinching of liquid filaments (or necks) created by dripping a fixed volume of a fluid onto a substrate. The DoS rheometry protocols characterize pinching dynamics as well as facilitate quantitative measurement of non-Newtonian extensional rheology response, even for PEO/PEG Boger fluids that show weak or no signature of viscoelasticity in conventional shear and extensional rheometry.

1.2 Viscoelasticity

The response of simple fluids to flow created by applied pressure gradients or by drag, next to moving surface, can be analyzed using constitutive equation known as Newton's law of viscosity^{14,16,101}, which states that stress $\boldsymbol{\tau}$ responds linearly to the deformation rate $\{\nabla\mathbf{v} + [\nabla\mathbf{v}]^\dagger\}$ and proportionally by a constant viscosity η

$$\boldsymbol{\tau} = \eta \{\nabla\mathbf{v} + [\nabla\mathbf{v}]^\dagger\} \quad (1.1)$$

Simple fluids like water, glycerol and organic solvents (like toluene) can be described using Newton's law of viscosity; however, complex fluids or non-

Newtonian fluids (like polymeric liquids) deviate can drastically deviate from this relation, instead manifesting their own genre of phenomena[14,16,101], shown schematically in Figure 1.

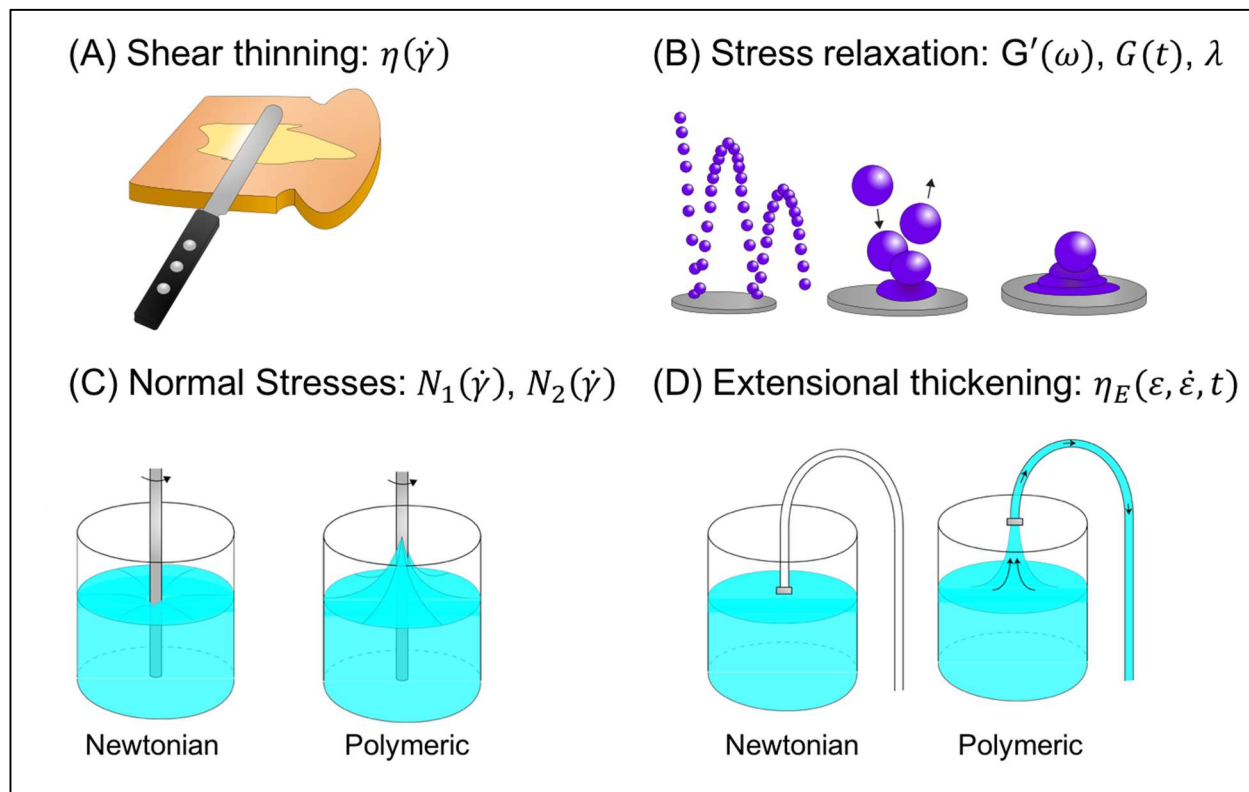


Figure 1. The four key rheological phenomena. Schematic illustrating examples of non-Newtonian fluid phenomena. (A) Shear thinning can be demonstrated by spreading mayonnaise on toast, which has a higher viscosity at rest versus when dragged by a knife. (B) Stress relaxation can be demonstrated by silly putty bouncing when thrown, such that stress is abruptly stored and released, and flowing when slowly moved, such that stress is low and dissipated via viscous flow. (C) Normal stress differences can be demonstrated via rotating a rod in a fluid, which proceeds to climb the rod, rather than forming a “whirlpool” around the rod. (D) Extensional thickening can be demonstrated by the self-siphoning process, where a fluid will continue to drain itself, against gravity, because of its enhanced resistance or “thickening” when encountering stretching, preventing the fluid column from breaking.

Many polymeric complex fluids exhibit shear thinning, i.e. steady shear viscosity decreases with increase in shear rate, $\dot{\gamma}$. Such fluids appear to become “thinner”, the faster they flow.[16] Apart from polymer solutions and melts, examples include mayonnaise (see figure 1 (A)), blood, foams, decorative architectural paints, cosmetics like nail polishes and shampoos, among others.[14,16] Since Newton’s law of viscosity is not applicable, often the deformation-rate-dependent viscosity is typically incorporated using Generalized Newtonian fluid models.[14] The simplest such constitutive equation is the power law model that characterizes a fluid using a pre-factor, m and power-law index, n

$$\eta(\dot{\gamma}) = m\dot{\gamma}^{n-1} \quad (1.2)$$

Generalized Newtonian fluid models like power law model are inadequate to describe elasticity. Deformations and recovery of elastic polymeric fluids in the limit of small deformations, known as linear viscoelastic response, can be considered somewhat analogous to Hooke’s law, and hence the simplest models for macromolecular dynamics considers polymer chains as elastic dumbbells: two Stokes beads connected by a Hookean spring.¹⁴ However, the response to large deformations leads to additional considerations for modeling nonlinear viscoelasticity including consideration of non-Hookean elastic response, finite extensibility, and conformation-dependent drag.[14,16,101] The textbook by Bird, Armstrong, and Hassager provides a comprehensive account of non-Newtonian

fluid mechanics and different constitutive models whereas Macosko's 1994 treatise provides a detailed discussion of the rheological characterization methods. In addition to rate-dependent viscosity response, modeling and characterization of complex fluids aims to describe the following three viscoelastic responses (shown schematically in Figure 1) discussed in context of polymeric complex fluids. (I) Stress relaxation describes the time-dependent variation in stress after step strain[14]. Newtonian fluids show nearly instantaneous transition to stress-free state, whereas the stress in viscoelastic fluids decreases or relaxes over time, often with a decay constant called shear relaxation time, (generally denoted by λ). Both elastic and viscous response can be characterized using small amplitude oscillatory shear at a range of frequencies, yielding a storage or elastic modulus (G') from stress-response in phase with oscillatory strain and a loss or viscous modulus (G'') that is $\pi/2$ out of phase.

(II) Normal stress differences in shear flow that arise due to entropic elasticity of polymer coils in response to perturbations by imposed nonlinear strong flows, result in both stream-wise stress $N_1 = \tau_{11} - \tau_{22}$ and transverse stress $N_2 = \tau_{22} - \tau_{33}$. [14] These normal stress differences are responsible for the rod climbing phenomena or “Weissenberg effect” depicted in figure 1 (C). (III) Extensional thickening that refers to increase in extensional viscosity as a function of extensional strain, ε and extensional deformation rate $\dot{\varepsilon}$, is associated with large

increase in drag associated with the dynamics of stretched polymer chains.[14] Extensional viscosity $\eta_E = \frac{\tau_{11}-\tau_{22}}{\dot{\epsilon}}$ is defined using the ratio of extensional stress to extension rate, and influences contraction channel flows as well as pinching dynamics. Though Newtonian fluids display an extensional viscosity that is three times the shear viscosity, relatively large values of extensional viscosity, even 10^3 - 10^5 times shear viscosity can be observed for polymeric fluids[29]. As illustrated in figure 1 (D), this enhanced resistance to stretching in fluid column prevents the breakup or thinning of the said column, allowing for self-syphoning or tubeless siphon, which Newtonian fluids are incapable of manifesting.

1.3 Typical Measured Responses of Polymeric Liquids

Most rheological measurements to characterize the properties responsible for the aforementioned fluid phenomena are performed in a torsional rheometer, in which a controlled strain is applied to sample and its stress is measured via torque transduction, or vice versa.[14] Through these measurements, shear viscosity is computed via the relation $\eta = \tau_{12}/\dot{\gamma}$. Archetypal Newtonian fluid and shear thinning polymeric liquid are displayed in figure 2. The red squares, representing the viscosity of glycerin, demonstrate a constant viscosity across a range of shear rates characteristic of a Newtonian fluid. Alternately, the blue triangles,

representing a concentrated polymer solution, demonstrate a decreasing viscosity with increasing shear rate, characteristic of a shear thinning response.

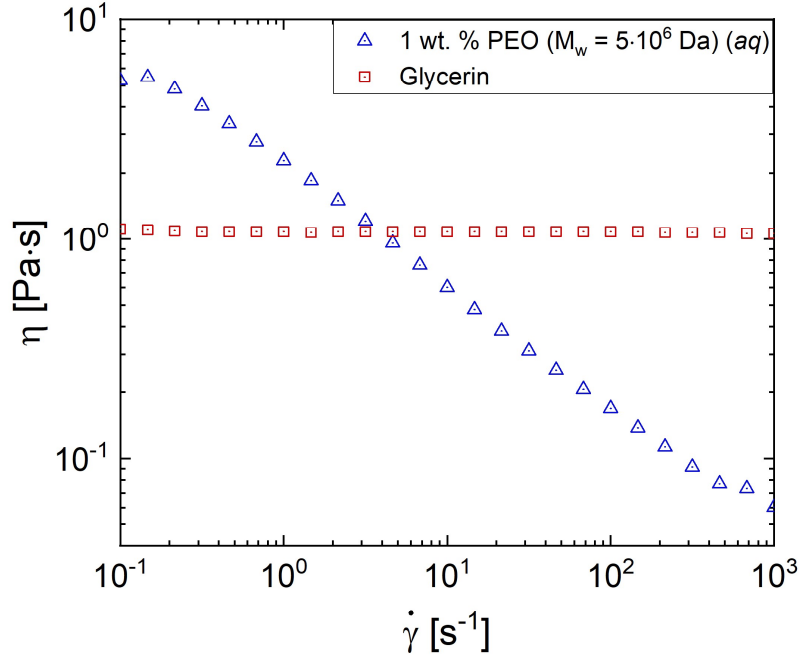


Figure 2. Archetypal viscosity measurement of a shear thinning fluid versus a Newtonian fluid. Flow curve for a concentrated polyethylene oxide (PEO) solution and glycerin; shear viscosity is plotted as a function of shear rate. Glycerin (red squares), a Newtonian fluid, shows a constant viscosity response, in contrast to the PEO solution (blue triangles), which demonstrates shear thinning or a decrease in viscosity with increasing shear rate. Measurements were made in a cone-and-plate flow cell on a rheometer at $T = 22^\circ \text{C}$.

Steady shear viscosity was measured as a function of shear rate by using cone-and-plate geometry on an Anton Paar MCR 302 rheometer. A fixed shear rate was applied to the fluid by controlling the differential angular velocity between the cone and the plate Ω , such that the shear rate $\dot{\gamma} = \Omega/\beta$, where β is the angle between the cone apex and plate.[16] The torque M transferred through the fluid

indicates the apparent shear stress $\tau_{12} = \frac{3M}{2\pi R^3}$, where R is the radius of the cone and the plate. Apparent shear viscosity (frequently referred to as just “viscosity”) is the ratio of shear stress to shear rate and is hence computed $\eta = \tau_{12}/\dot{\gamma}$. Since viscosity, as well as other rheological properties, are highly sensitive to temperature, temperature inside rheometer flow cells are controlled and in the case of the measurements reported in figure 2 are held at a constant $T = 22^\circ \text{C}$.

Measurement of viscoelastic behavior is also typically carried out using torsional rheometers. Linear viscoelastic response is characterized using small amplitude oscillatory shear (SAOS) whereas nonlinear viscoelasticity manifested as the first (and second) normal stress difference are measured using steady shear.[14] The SAOS protocol measures the torque or stress required to impose a small amplitude oscillatory strain for fixed amplitude for a range of angular frequencies. The oscillatory stress response is measured via torque transduction and the wave is decomposed into a real component, known as the storage modulus G' , which describes the stress stored by the fluid and an imaginary component, known as the loss modulus G'' , which describes the stress dissipated by viscosity. A requisite condition for using SAOS is a relatively high viscosity, sufficient for a clean stress signal. Polymer melts satisfy this requirement and a typical dataset is shown in figure 3 for a low-density polyethylene (LDPE) melt from literature.[17]

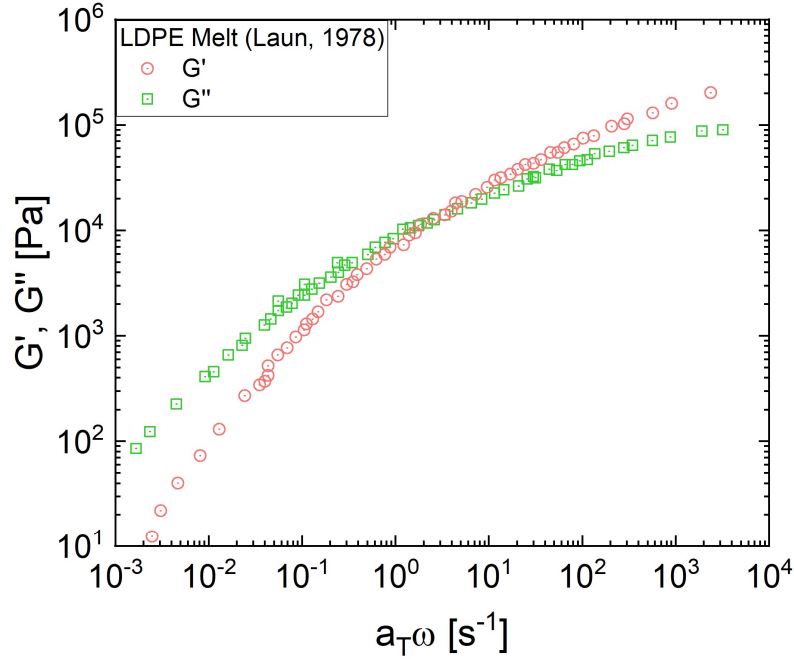


Figure 3. Archetypal measurement of elastic and loss moduli. Small amplitude oscillatory shear data for a low-density polyethylene melt, showing the elastic modulus G' (pink circles) and loss modulus G'' (green squares) as a function of reduced angular frequency $a_T \omega$. Both moduli increase with angular frequency, the elastic modulus increasing about 5 orders of magnitude and the loss modulus increasing about 4 orders of magnitude. Initially the loss modulus is larger than the elastic modulus, but becomes the lesser after $\omega \approx 3$ rad/s. Measurements were made using cone-and-plate geometry and time-temperature superposition to extend the angular frequency range. Data adopted from Laun. [17]

Measurements were made in cone-and-plate flow cell in a modified Weissenberg Rheogoniometer Model R 12/15 rheometer with temperatures ranging from $T = 112 - 190$ °C. The stress measurement is identical to that of viscosity measurement; however, instead of continuous rotation, the cone and plate oscillate differentially at an angular frequency ω . Since the LDPE polymer melt has a viscosity sufficiently high to challenge the maximum torque of the rheometer,

time-temperature superposition was used to access and broader range of angular frequencies. Since the viscosity and stress (torque) response are inversely proportional and related by the proportionality constant a_T ; thus, by increasing the melt temperature, the stress transduced by the melt is decreased and higher angular frequencies are achievable or *vice versa* with a temperature decrease. Fitting of the moduli data using appropriate constitutive model allows the computation of a shear relaxation time as a characteristic measure of viscoelasticity.

The first normal stress difference is measured by applying a steady shear to a fluid sample, much like that in steady viscosity measurements (which are typically performed simultaneously).[14] The force normal to the direction of flow is measured and translated to $N_1 = \tau_{11} - \tau_{22}$. For example, in the cone-and-plate and plate-and-plate geometries, the first normal stress difference applies a normal force which attempts to push the cone and plate or plate and plate apart. In figure 4, the same HDPE melt reported in figure 3 is characterized in the cone-and-plate flow cell with a steady rotation and normal force transduction. The normal force computed into the first normal stress difference is plotting as blue triangles in figure 4. Similarly, to SAOS, first normal stress measurements require a high enough viscosity, as well. The first normal stress difference can be sometimes determined from SAOS or viscosity data by approximation using several empirical expressions, including the AbNormal rule,¹⁵ Laun rule, [18] and Cox-Merz

rule.[19] In addition to the direct measurement of first normal stress difference for the LDPE melt (blue triangles) in figure 4, the values computed using the AbNormal rule (red squares) and the Laun rule (green dashed line) are shown for comparison. As useful as these approximations may be for melts and concentrated polymer solutions, such empirical relations cannot be used for determining N_1 in Boger fluids.[15]

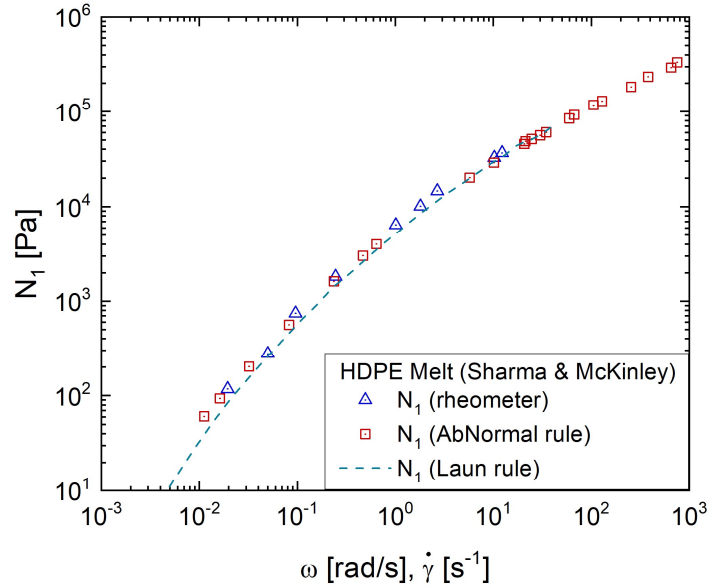


Figure 4. Archetypal measurement of the first normal stress difference and select approximations. First normal stress difference direct measurement (blue triangles), approximation via the AbNormal Rule (red squares), and via Luan rule (green dashed line) as a function of angular frequency and shear rate for a high-density polyethylene melt. Measurements were made using cone-and-plate geometry for steady shear flow in the case of direct measurement and AbNormal rule and via SAOS in the case of Laun rule. Data adopted from Sharma and McKinley. [20]

Strain hardening or extensional thickening is a phenomenon common to polymeric liquid where the extensional viscosity increases as a function of

extensional strain and/or extension rate,[14] the latter case which is displayed in figure 5, which data was obtained using the opposing jet extensional rheometry protocol. This extensional viscosity enhancement arises due to increase in drag correlated with dynamics of stretching chains.[7] Due to extreme sensitivity to entire deformation history and difficulty in reaching steady extensional rate, the characterization of extensional rheology response is considered quite challenging, and remains less well explored than shear rheometry. [7-15]

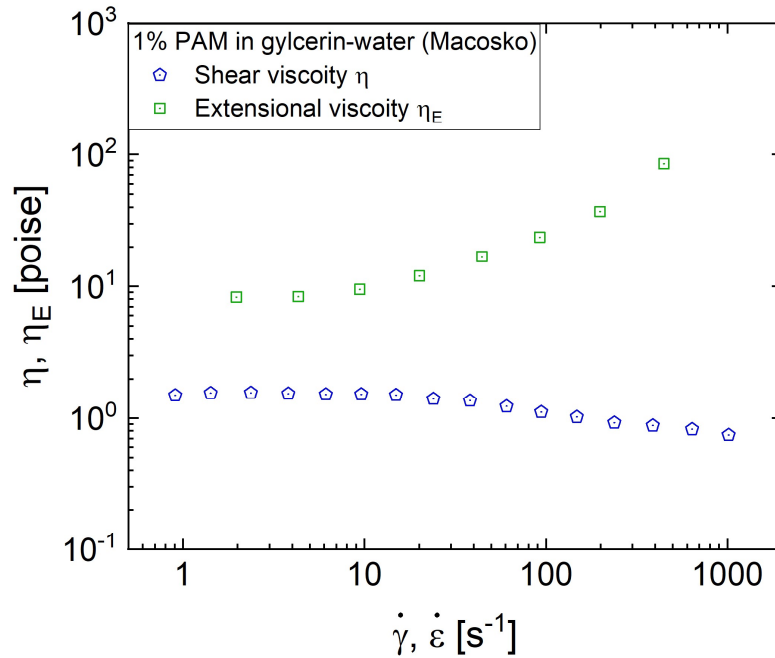


Figure 5. Archetypal measurement of extensional viscosity with strain hardening and shear viscosity. Shear viscosity (blue pentagons) and extensional viscosity (green squares) as function of shear rate $\dot{\gamma}$ and extension rate $\dot{\epsilon}$, respectively, for a solution of 1% polyacrylamide in glycerin-water. The shear viscosity exhibits slight shear thinning after $\dot{\gamma} \approx 40 \text{ s}^{-1}$. The extensional viscosity demonstrates strain hardening, as the extension viscosity increases with extension rate after $\dot{\epsilon} \approx 5 \text{ s}^{-1}$. Extensional viscosity measurement was made using the opposing jet extensional rheometry protocol. Data adopted from *Rheology Principles*. [16]

1.4 Free Surface Flows and Industrial Applications

A free surface flow is a flow in which the fluid is affected by a zero shear stress boundary condition, frequently about a liquid-gas interface.[21] Free surface flows are found in many industrial applications, including dripping, jetting, fiber spinning, and coating flows.[12, 22, 23] , as illustrated in figure 6 (B-D). In most of these free surface flow processes, the liquid interfaces with air, such that the interfacial tension shapes the fluid volume and controls the curvature. In the case of roll coating, slot coating and fiber spinning (as displayed in figure 6 (C)) the convexity is controlled, while in drop formation (as displayed in figure 6 (B)), drop pinch off is controlled. The fluid flowing about the interface experiences a stretching action, as displayed figure 6 (A), which produces extensional flows. The features of extensional deformation and curved streamlines make free surface flows highly potent at exacerbating viscoelasticity, because of strain hardening and normal stress behavior.[24] The augmentation of resistance to extensional flow will be demonstrated using dripping-onto-substrate (DoS) rheometry with the PEO/PEG Boger fluid and elastic instabilities about curved streamlines are discussed herein.

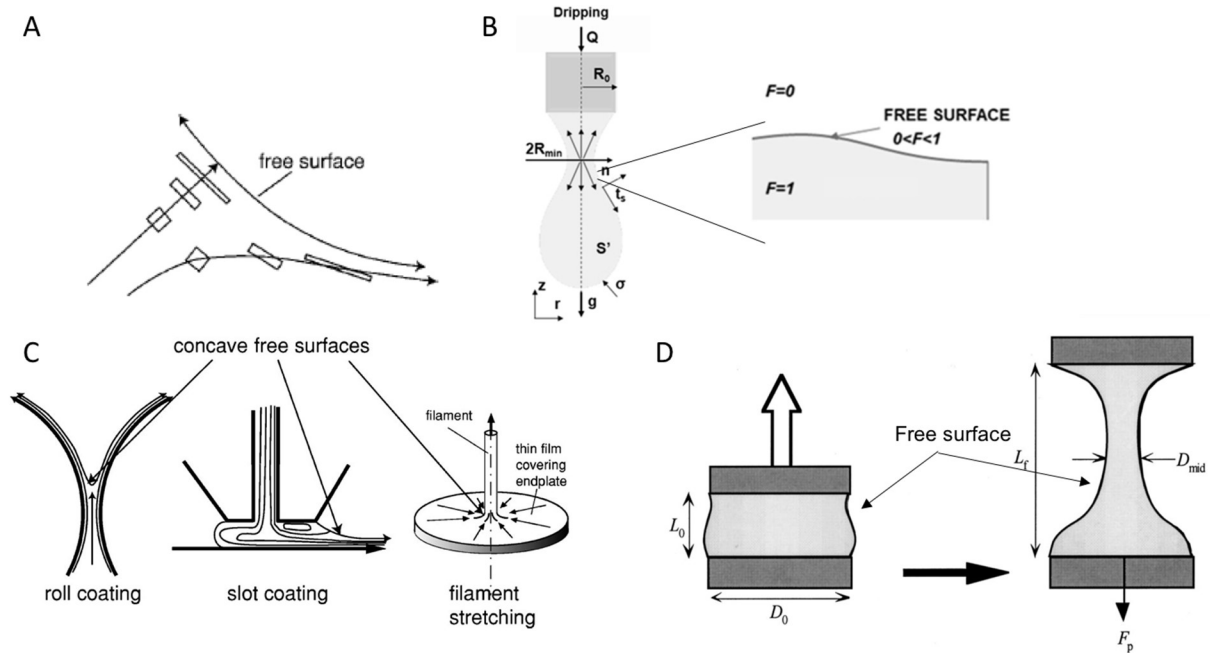


Figure 6. Examples of free surface flows with extensional deformations. Illustrations of various free surface flows, where a fluid flows against a zero shear stress boundary, such as a gas. (A) General schematic of elongation flow along a free surface where the fluid volumes are stretched. Figure adopted from Graham. [23] (B) Dripping schematic showing capillary thinning action as surface tension chokes the drop neck and the free surface of the liquid drop interfacing with air deforms. Figure adopted from Dinic and Sharma. [22] (C) Coating and filament spinning illustrations depicting the presence of free surfaces in roll coating, slot coating, and filament stretching, all of which involve an evolving liquid air-interface. Figure adopted from Graham. [23] (D) Schematic depicting the capillary break-up extensional rheometer (CaBER), within which a fluid volume is placed between two plates and stretched, placing the fluid in a uniaxial extensional flow, with a free surface evolving between the fluid and the air (similarly to figure 11 (B)). Figure adopted from Anna and McKinley. [25]

1.5 Hydrodynamic Instabilities

Hydrodynamic instabilities exist in nature as well as engineered systems[26] and can often manifest themselves as beautiful or menacing patterns, depending on their context. For example, the surface tension-driven instability called Plateau-

Rayleigh instability that leads to break-up of a fluid jet can be utilized in ink-jet printing, [2, 27] including emerging applications that use specialized inks that deliver DNA, cells, electronic materials or photonic devices. The same Plateau-Rayleigh instability is rather undesirable in application that require formation of filaments (like fiber spinning). Other common examples of hydrodynamic instabilities are: inertia-driven Taylor vortices in a Taylor-Couette flow cell[28] and elastic instabilities in certain polymeric flows.[29] Instabilities are often analyzed by experimentally and theoretically by recognizing the conditions or parameters that can be tuned to trigger growth of perturbations. The study of these unstable flows requires careful rheological considerations, especially when dealing with polymeric liquids with non-Newtonian behaviors.[24] The caveat of these non-Newtonian fluids is their readily unstable nature, which is desirable in instability experiments, but poses an impediment for rheological considerations.

1.5.1 Taylor Vortices

The appropriate place to start the discussion of PEO/PEG Boger fluids and their applicability to elastic instability studies is with Taylor vortices, which are analogous to elastic instabilities. Taylor vortices are an inertial instability which can occur in a Couette flow cell [30], which consists of concentric cylinders with fluid in-between, rotating at a differential rate and deforming the fluid by shear flow [28][16]. The Couette flow cell is a staple of viscometer and rheometer

manufacturers, but suffers from non-viscometric flow at high deformation rates, where inertia is the dominant force. The Reynolds number is the natural measure of inertial versus viscous force, which arises from the equation of motion,

$$Re = \frac{\rho v l}{\eta} \quad (1.3)$$

where v and l are characteristic velocity and length scales, respectively, and ρ and η are density and viscosity, respectively. [28] In pipe flows, turbulent secondary flows can occur at $Re \cong 2300$ [28]; however, the onset of these unstable secondary flows necessitates relatively large initial disturbance [30]. For this reason, G. I. Taylor sought to investigate and identify an inertial instability with more readily reproducible and regular behavior. In 1923, Taylor found such inertial instability in the Couette flow cell and characterized the phenomena by its production of streamwise vortices (later called “Taylor vortices”) and a steady secondary cellular structure [31], as seen in figure 7.

From the equation of motion, Taylor found the onset of instability was not solely driven by inertia, but the product of an inertial term and a geometric term which is a measure of streamline curvature. This quantity is currently referred to as the Taylor number

$$Ta = 2 \left(\frac{b}{r_{\text{inner}}} \right) Re^2 \quad (1.4)$$

where b is the gap length between the concentric cylinders, r_{inner} is the radius of the inner cylinder, and Re is Reynolds number. The Taylor number is proportional to streamline curvature, $Ta \sim \frac{1}{r_{inner}}$, and varies to the square of Reynolds number, $Ta \sim Re^2$. While the Taylor number serves as a good predictor of the onset of instability for viscous fluids in the Couette flow cell, it fails to do so with viscoelastic fluids, as discussed henceforth.

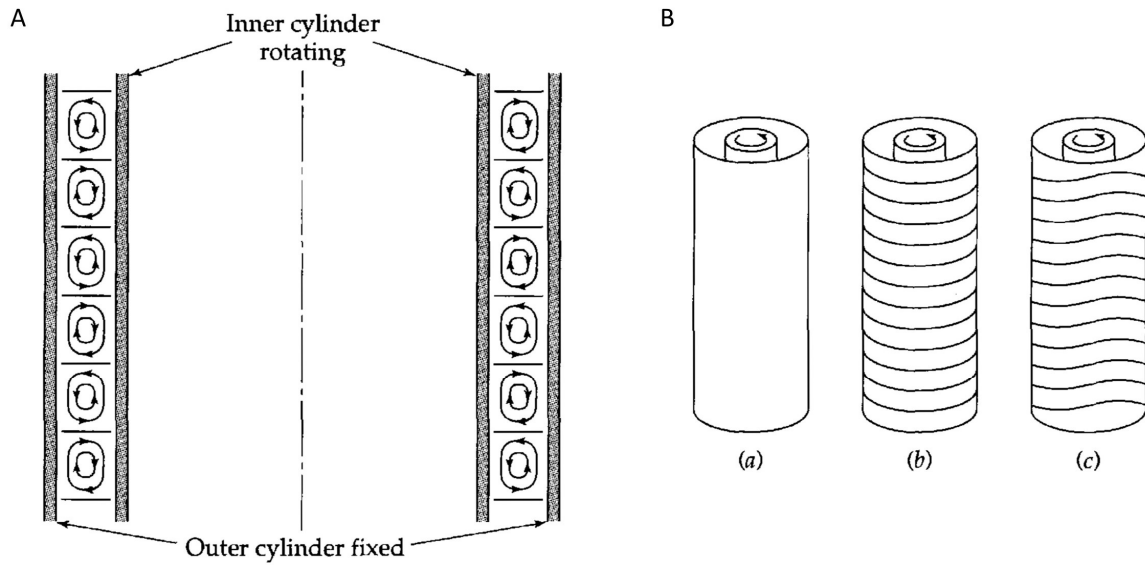


Figure 7. Inertial instability inside a Couette flow cell. (A) Cross-section schematic of the Couette flow cell with Taylor vortices in the fluid contained in the annular space between the concentric cylinders. (B) Drawings of flow phenomena in a Couette flow cell: (a) laminar flow in the tangential direction, (b) unstable flow with Taylor vorticity direction indicated by lines in the tangential direction, (c) unstable flow with secondary periodic structure. Figures adopted from *Transport Phenomena* by Bird, Stewart and Lightfoot [28].

1.5.2 Elastic Instability

Non-Newtonian fluids can produce complex responses to deformation shown in Figure 1, such as (1) rate-dependent shear viscosity, (2) stress storage/relaxation, (3) normal stress differences, and (4) rate- and history-dependent resistance to stretching¹⁴, the latter three behaviors of which are considered “elastic” because of their spring-like stress responses or fluid “memory.” Due to these rheological properties, viscoelastic fluids have different fluid mechanics than their Newtonian counterparts, which can be seen kinematically, for example, in the Couette flow cell. In 1989, Larson, Muller and Shaqfeh characterized the flow behavior of ideal elastic fluids (also known as “Boger fluids”) in the Couette geometry[29], and found hydrodynamic instabilities at negligible Taylor numbers (see figure 8). Larson *et al.* argued that the instability in the Couette flow cell is not driven by inertia; rather, the instability is driven by fluid elasticity. Larson *et al.* posited that the mechanism for this elastic instability can be attributed to a radial perturbation of the macromolecules transverse to the streamlines, leading to chain stretching, followed by recoil, which results in an unstable secondary flow.

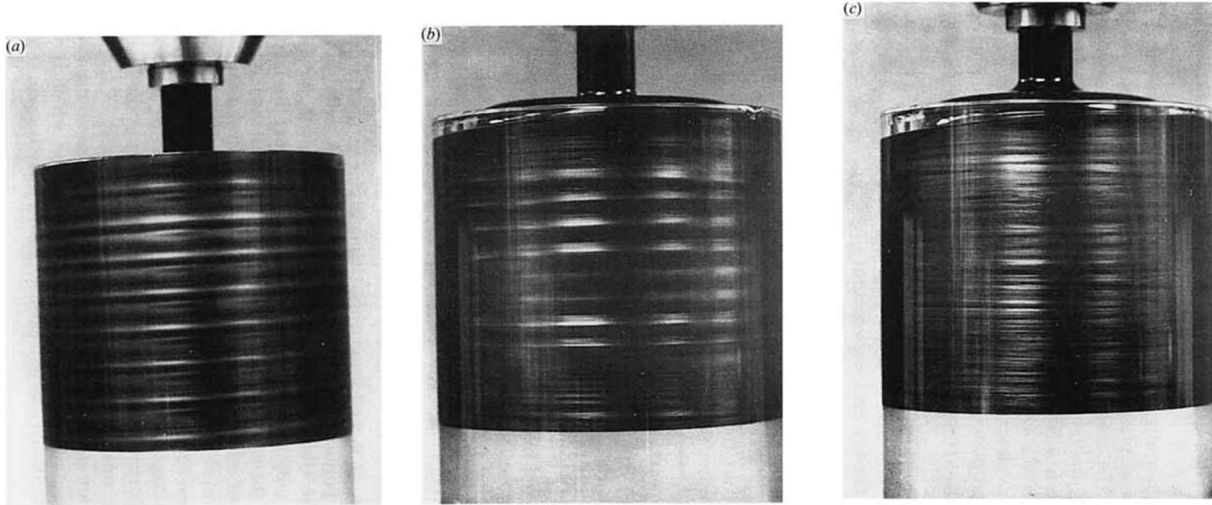


Figure 8. Elastic instability inside a Couette flow cell. Flow visualization in a transparent Couette flow cell. (a) Unstable Newtonian fluid at a high Taylor number, $Ta = 3800$, producing Taylor vortices. (b) Unstable viscoelastic fluid at a negligible Taylor number, $Ta = 9.6 \times 10^{-8}$, shortly after onset of instability. (c) Fully-developed flow of an unstable viscoelastic fluid at a negligible Taylor number. Figure adopted from Larson *et al.* [29].

Shortly thereafter in 1991, McKinley *et al.* published a similar study of elastic instabilities in cone-and-plate and parallel-plate flow cell geometries with viscoelastic fluids[32], rather than the Couette flow cell. It is noteworthy that like the Couette flow cell, the cone-and-plate and parallel plates flow cells are also prolific geometries used in viscometric and rheometric measurements[16]. By using a rheometer, McKinley *et al.* not only visualized the flow, but measured apparent viscosity and the apparent first normal stress difference of the fluids, which deviation indicated the onset of unstable and non-viscometric flows. McKinley *et al.* employed two dimensionless groups to characterize the onset of elastically unstable flow: the Weissenberg number, Wi , and the Deborah number,

De. The Weissenberg number is a dimensionless measure of elasticity scaled by deformation rate, which is generally expressed $Wi = \frac{\lambda}{t_{\text{deform}}}$, where λ is the fluid relaxation time (either in shear or extensional flows) and t_{def} is the deformation rate (also, either in shear or extensional flows). A high Weissenberg number ($Wi > 1$) indicates a predominantly elastic flow, as the fluid is deformed at a faster rate than it can relax. Similarly, Deborah number is a dimensionless measure of elasticity, but, scaled by process time t_{process} , generally expressed $De = \frac{\lambda}{t_{\text{process}}}$. In the cone-and-plate and parallel-plate geometries, the deformation time scale refers to the shear rate and the process time scale refers to the time over which a polymer coil stretches transversely to streamlines. Figure 3 displays a viscoelastic fluid in the parallel-plate flow cell at a lower Deborah number, prior to instability, and at a higher Deborah number, as the instability onsets and evolves temporally. McKinley *et al.* determined the onset of elastic instability in the cone-and-plate and parallel-plate geometries depended on the combination of Weissenberg and Deborah numbers.

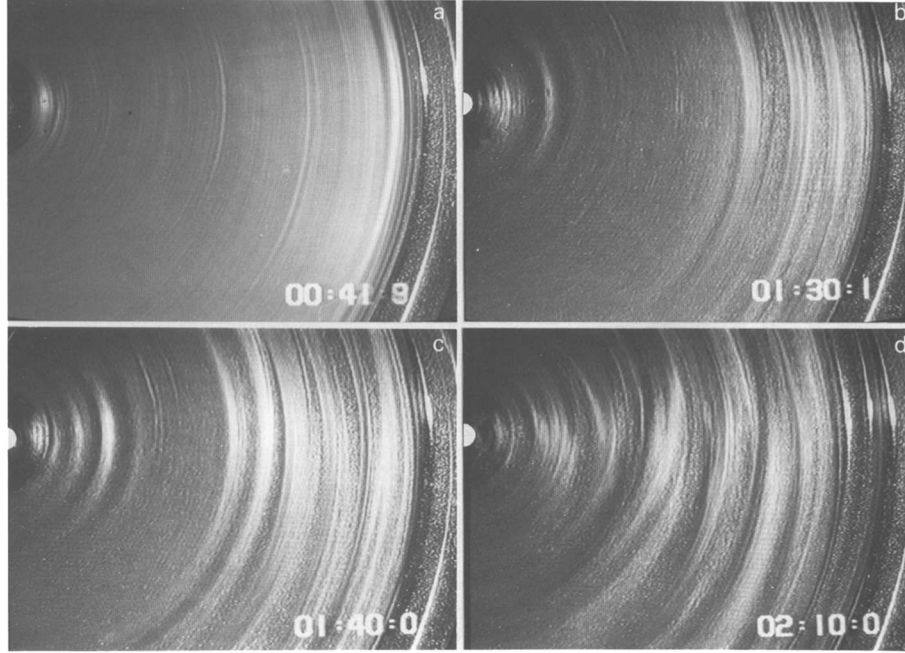


Figure 9. Elastic instability inside a plate-and-plate flow cell. Flow of a viscoelastic fluid in a parallel-plate flow cell with a transparent plate for imaging at different times. (1) Stable, viscometric flow at $De = 3.57$, (b) onset of elastic instability at $De = 4.81$ with cellular structure, (c) radial propagation of cellular structure, and (d) final stage of the instability with time-dependent 3-D flow. Figures adopted from McKinley *et al.* [32].

Further refinement of this instability criterion was made in 1996 by Pakdel and McKinley[24], who made the connection between the occurrences of elastic stabilities in geometries with curved streamlines and G. I. Taylor's work on inertial instabilities. The Taylor number, which predicts the onset of the inertial instability in the Couette flow cell, is the product of an inertial driving-force term (Re^2) and a geometric term ($2 \frac{b}{r_{inner}}$). Pakdel and McKinley postulated that the onset of elastic instability (hereafter referred to as the Pakdel-McKinley criterion) occurs when $M >$

M_{crit} , where M is the product of an elastic driving-force term (Wi with $t_{\text{deform}} = 1/\dot{\gamma}$ for a shear flow) and a geometric term (a modified De):

$$Wi De \geq M_{\text{crit}} \quad (1.5)$$

Unlike the general Deborah number, which is a ratio of time scales, Pakdel and McKinley define the Deborah number as a ratio of length scales, rendering the Deborah number a geometric measure:

$$De = \frac{\ell}{\mathcal{R}} = \frac{U\lambda}{\mathcal{R}} \quad (1.6)$$

where ℓ is the length required for a perturbed polymer chain to relax along a streamline of velocity U and $\mathcal{R}$ is the radius of curvature of the streamline. When the Deborah number is at or above unity, a perturbed polymer chain does not have sufficient length to relax within the streamline along which it is originally flowing, causing a transverse migration from said streamline. This transverse migration of the polymer causes tension of the chain between the streamlines, as figure 4 depicts and contrasts with a polymer traveling along a single streamline. The radial tension of the polymer chain results in a radial recoil (deviatoric normal stress), causing an unstable radial velocity component, secondary to the flow along the streamline. Pakdel and McKinley found good agreement of the Pakdel-McKinley criterion with 1-D and 2-D base flows in confined geometries. The typical

polymeric liquid exhibits shear thinning, which kinematic effects can be conflated with that of elasticity, when used in a process; thus, an initial conflict arises: how can purely viscoelastic kinematics be achieved to examine the impact of elasticity in a process?

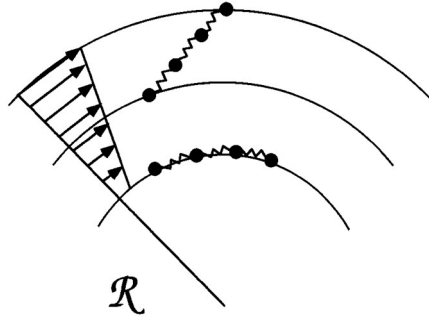


Figure 10. Elastic instability mechanism. Schematic of polymer coil (dumbbell model) tension and stretching across curved streamlines and a polymer coil traveling unperturbed along a streamline, all with radius of curvature $\mathcal{R}$. Figure adopted from Pakdel and McKinley [24].

1.6 The Applicability of Boger Fluids

Boger fluids are elastic fluids with constant shear viscosities.[33] David Boger formulated the first Boger fluid, polyacrylamide (PAM) solution in maltose syrup, achieving a nearly rate-independent viscosity and an appreciable first normal stress difference, as shown in figure 10.[34] The first Boger fluid had a relatively high viscosity (10^4 times water viscosity) and the stress vs. shear rate data showed nearly linear slope. Boger's pioneering study has inspired rheologists to create alternative formulations of Boger fluids, and a few representative examples are tabulated in table 1. A flexible polymer of relatively high molecular

weight (*e. g.* PAM) is dissolved in a solvent of relatively high viscosity (*e. g.*, maltose syrup), which suppresses shear thinning. These Boger fluids have been used to investigate viscoelastic constitutive equations (such as Oldroyd-B, Giesekus, and FENE-P) and the influence of elasticity on flow kinematics, including elastically unstable flows.[33] For a given flow process, elastic kinematics can be elucidated from viscous effects by comparing flow of a Boger fluid to a Newtonian (control) fluid of like viscosity; thus, the difference in kinematics between the Boger fluid and Newtonian fluid is attributable to elasticity. In the Table, Boger fluids formulated with dilute amount of high molecular weight PEO added to a highly concentrated aqueous solution of PEG (lower molecular weight PEO) .

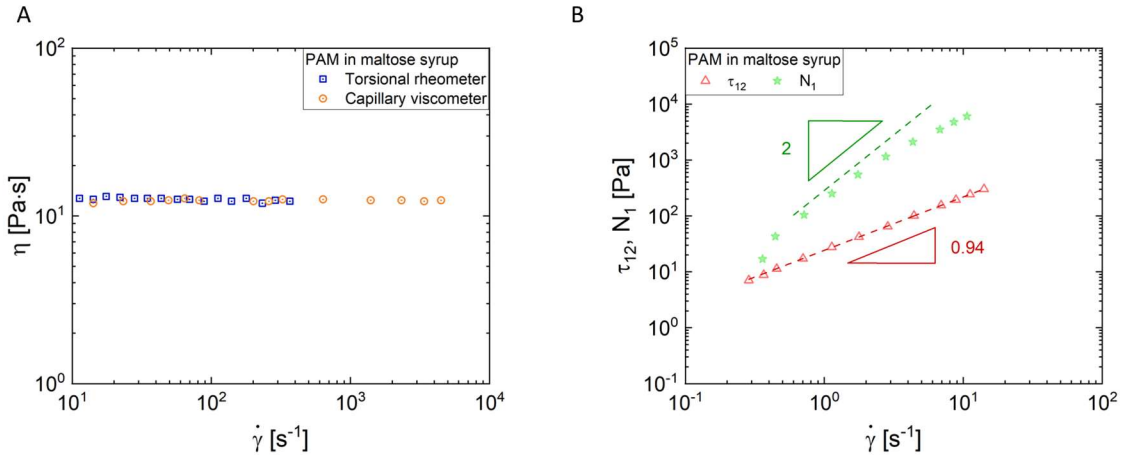


Figure 11. Rheology of the first Boger fluid. (A) Shear viscosity as function of shear rate for the original PAM-maltose syrup Boger fluid from 1977/1978. The viscosity appears independent of shear rate. (B) Shear stress and first normal stress difference as a function of shear rate for the Pam-maltose syrup Boger fluid. A shear stress response with power law index of $n = 0.94$ indicates virtually rate-independent viscosity and the first normal stress difference indicates the fluid

viscoelasticity with stresses up to nearly two orders of magnitude greater than shear viscosity. Figure adopted from Boger. [34]

Table 1. Recipes used to formulate Boger fluids and cursory properties describing viscoelastic properties.

High Polymer /Solvent	M_w	η_0 [Pa · s]	η_s [Pa · s]	λ_s [s]	Comments	Ref.
Polyacrylamide / maltose syrup		22.5	22	4.25	$N_1 \rightarrow$ Maxwell model	[34]
Polyisobutylene / polybutene		2.65	1	0.70	N_1 , $G' \rightarrow$ Oldroyd-B model	[35, 36]
Polystyrene oligomeric polystyrene /		4 – 12	2 – 9	0.3 – 2.5	$G' \rightarrow$ Oldroyd-B model	[37]
Polyethylene oxide / polyethylene glycol		0.02 – 0.3	0.003– 0.2	1.6 – 7.9	$G' \rightarrow$ Oldroyd-B model	[60]
Polystyrene dioctyl phthalate /		0.6-1	0.5	1-8	$N_1 \rightarrow$ Oldroyd-B model	[38]

The use of PEO/PEG Boger fluids facilitates the investigation of elastic instabilities and rheological response at relatively high deformation rates associated with many coating flows. This Boger fluid recipe was first described by Dontula *et al.*, reporting a rate-independent shear viscosity as shown in figure 12 (A), prior to apparent shear thickening characteristic of elastic instabilities, and elasticity measured by SAOS as shown in figure 12 (B).[67] This introduction opens the door to many possibilities and challenges, and a thorough examination of

the literature on PEO/PEG Boger fluids is presented in next chapter, along with experiments and analysis carried out as a part of this dissertation study. Even though elastic instabilities limit the characterization of elasticity in torsional rheometry, in the next chapter, we utilize understanding of capillarity-driven flows and instabilities to determine both relaxation time and extensional viscosity using the dripping-onto-substrate (DoS) rheometry protocols.

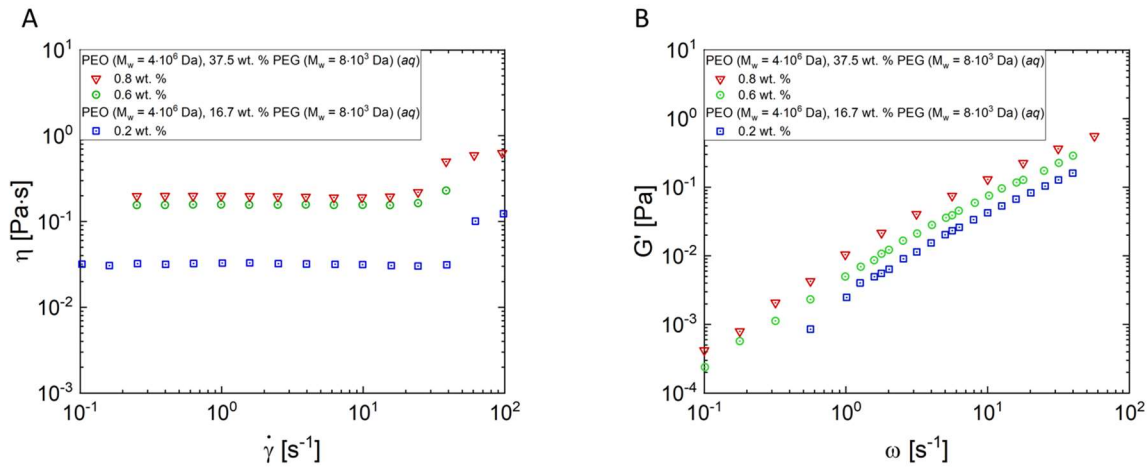


Figure 12. Original PEO/PEG solution rheology. (A) Viscosity as a function of shear rate for PEO/PEG solution, for 17.5 wt. % PEG with 0.2 wt. % PEO (blue squares) and 37.5 wt. % PEG with 0.6 (green circles) and 0.8 (red inverted triangles) wt. % PEO. There is a concentration dependence of viscosity on both PEO and PEG. The PEO/PEG solutions show a rate-independent shear viscosity, characteristic of Boger fluids, with apparent shear thickening at higher rates. (B) Elastic modulus as a function of angular frequency for PEO/PEG solution, for 17.5 wt. % PEG with 0.2 wt. % PEO (blue squares) and 37.5 wt. % PEG with 0.6 (green circles) and 0.8 (red inverted triangles) wt. % PEO. The elastic modulus is proportional to both PEO concentration.

1. Rheological and Polymer Physics Investigation into PEO-PEG-based Boger Fluids

Introduction

A Boger fluid is an elastic fluid with constant viscosity.[33, 39] Solutions and melts of linear, flexible and semi-flexible polymers typically exhibit shear thinning response, and show measurable value of first normal stress difference at higher rates.[40, 41] Stretching and orientation of polymer coils in response to applied shear flow results in decrease in shear viscosity whereas the drive to recover entropically-favored conformation of unperturbed coil leads to elastic effects including stress relaxation and normal stresses.[40-42] The role of macromolecular stretching, orientation, and relaxation in contributing to universalities exhibited by polymer solutions and melts in their shear rheology response are detailed in many texts[40-42] and reviews.[7, 43-45] In practice, significant challenges arise in decoupling the influence of elasticity, typically characterized in terms of first normal stress difference, from the effect of non-Newtonian, rate-dependent viscosity. Ever since their inception in 1977/1978 paper,[39] the eponymous Boger fluids have been utilized for determining and defining the impact of elasticity on torsional flows, instabilities in channel flows as well as free surface flows, influence of rate-dependent extensional viscosity in mixed flows,[46] and comparison of experiments with theory and simulations.[33, 47-49] Characterization of elasticity of Boger fluids has typically relies on either

the measurement of the first normal stress difference, $N_1(\dot{\gamma})$ in response to steady shear flow, or of elastic modulus, $G'(\omega)$ in response to small amplitude oscillatory shear (SAOS) using frequency sweep at fixed strain. However, the elasticity measurable with typical torsional rheometers is limited by the instrument design in terms of torque or normal force range of the transducers,[20, 50] and typical Boger fluids have shear viscosity 1 Pas and relaxation times, 1 s. High viscosity Boger fluids pose three challenges: (i) susceptibility to elastic instabilities, (ii) not representative of fluid viscosity and elasticity for many coating flows, and (iii) difficulty in extensional rheology characterization under flow rates encountered in processing flows.

A Boger fluid is said to be model elastic fluid that provides an experimental analog for viscoelastic fluids that can be described Oldroyd-B model.[33] One of the simplest constitutive equation for viscoelastic fluid, Oldroyd-B model, incorporates the polymeric contribution to the stress in response to applied flow through the upper-convective Maxwell model, and the solvent contribution using Newton's law of viscosity.[7, 48, 50-52] The upper-Oldroyd-B incorporates two material parameters: shear relaxation time and rate-independent shear viscosity, and can be derived by modeling polymer as an elastic dumbbell with Hookean spring connectors.[52] In addition to the role played by relaxation time, Oldroyd-B fluid allows exploration of elastic effects and predicts a finite first normal stress

difference as well as linear viscoelastic response in oscillatory shear.[33, 51, 52] However, the extensional viscosity values diverge for an Oldroyd-B fluid at dimensionless extensional rate or Weissenberg number, $Wi = \lambda \dot{\epsilon} = 1/2$ and also show an unlimited stress growth in response to applied extensional flows. The successes and limitations of Oldroyd-B models are discussed in many studies that seek a deeper understanding of nonlinear flows and elastic instabilities. For example, drop formation during dripping, jetting or spraying invariably involves creation of a liquid neck that undergoes capillarity-driven pinching, and stream-wise velocity gradients associated with extensional flows spontaneously arise in the pinching neck. According to Entov and Hinch,[53] among others,[54-56] the analysis of pinching dynamics with Oldroyd-B leads to an elastocapillary response characterized by an exponential decay in radius, with decay constant governed by relaxation time. However, in practice, the extensional relaxation time and extensional modulus extracted from fits to the radius evolution data are quite distinct from the shear relaxation time or modulus in Oldroyd-B model (or extracted using shear rheometry), and elastocapillary regimes truncates, eventually liquid neck pinches-off.[3, 4, 13, 54, 57-61] Models that incorporate conformation-dependent drag (for example the Giesekus model) or finite extensibility undergo finite time pinch-off, but also predict shear thinning.[13, 62-66] Furthermore, in the last stage before pinch-off, FENE-P fluids (described with Finitely Extensible

Nonlinear Elastic with Peterlin approximation dumbbels) exhibit a terminal viscoelastocapillary (TVEC) regime, with characterized with linear decrease in radius that yields measurement of steady, terminal extensional viscosity.[3, 13, 53, 60, 61, 66]

In this contribution, we investigate the elasticity, pinching dynamics and extensional rheology of relatively low viscosity Boger fluids. Boger fluids are often formulated by dissolving a flexible polymer of relatively high molecular weight in a relatively high viscosity Newtonian solvent. However, several Boger fluids are designed by dissolving a dilute amount of a high molecular weight polymer in a matrix phase that is itself a polymer solution, containing higher lower molecular weight fraction (see Table 1 for a representative list). [33, 39] Thus the inability to characterize elasticity using torsional rheometry restricts the choice of Boger fluids to relatively high viscosity systems, and simultaneously makes such fluids susceptible to various elastic instabilities than can manifest in secondary flows, apparent shear thickening, anti-thixotropic effect, and lead to non-viscometric flows. Recognizing that the high viscosity Boger fluids are not a good model for many processing operations that utilize polymeric fluids with lower viscosity $< 1 \text{ Pa}\cdot\text{s}$, Dontula *et al.* introduced high molecular weight PEO dissolved in aqueous PEG solutions [67] as model Boger fluids of low viscosity. These aqueous PEO/PEG Boger fluids have since been used in many studies of effect of

elasticity on coating flows, pattern formations and flow instabilities. Examples include slot coating,[68] viscoelastic liquid curtain,[69-72] fingering instability,[73] flows into capillaries,[74] extensional flows in contracting channels[75-78] and fluidic four-roll mill,[79] drops moving on hydrophilic or superhydrophobic surfaces,[80, 81], flows over wavy surfaces,[82] and liquid transfer from one surface to another.[83] Though several studies rely on relaxation time as an estimate for elastic effects by using values determined using CaBER,[71, 80, 81, 83], the extensional viscosity response is not discussed typically, concentration-dependent variation in viscoelastic parameters is not characterized or discussed and we found no mention of the finite extensibility regime.

The influence of macromolecular parameters and interactions on the response to extensional flows remains relatively less well-understood,[7, 11, 44, 45] due to the well-documented challenges of measuring extensional rheology response, [7-15] and the challenges involved in identifying constitutive models that correlates with experiments as well as dynamics of stretched and orientated chains[7, 8, 11, 44, 45, 84-86]. In a series of recent papers, Dinic *et al.*[1-6] have established Dripping-onto-Substrate (DoS) rheometry protocols that involve visualization and analysis of capillarity-driven pinching of liquid filaments (or necks) created by dripping a fixed volume of a fluid onto a substrate. The DoS rheometry protocols characterize pinching dynamics as well as facilitate

quantitative measurement of non-Newtonian extensional rheology response, even for complex fluids that show no signature of viscoelasticity in conventional shear and extensional rheometry.[1-6, 60] In this contribution, we utilize DoS rheometry to characterize the pinching dynamics and the extensional rheology of aqueous solutions of polyethylene oxide (PEO) in order to elucidate the influence of chemical structure (i.e., polymer choice and resulting macromolecular parameters). We contrast the concentration-dependent variation in extensional relaxation time measured for PEO/PEG Boger fluids against exponents obtained for dilute aqueous PEO solutions using DoS rheometry and dripping, and against PEO/PEG Boger fluids datasets acquired using alternative techniques including opposed nozzle, CaBER.[82]

2.1 Materials and Methods

2.1.1 The Boger Fluid

Poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) of $M_w = 5 \cdot 10^6$ Da and $8 \cdot 10^3$ Da, respectively, were used to prepare aqueous PEO-PEG solutions. PEO and PEG in crystalline form were purchased from Sigma-Aldrich and Research Product International, respectively, and each polymer was used without additional purification. PEO-PEG solutions were prepared by dissolving individual PEO and PEG stock solutions. Both polymer crystals were dissolved by slowly adding water and placing the mixture on a bottle roller to accelerate mixing. All deformation rates during mixing were kept minimal to avoid chain scission which

may occur during strong deformations. [87] Each stock solution is then mixed and diluted to desired concentrations before being placed back on the bottle roller for hastened blending. For the PEO-PEG solution, as with other Boger fluids, a high-viscosity solvent is used to suppress shear thinning, which is typically exhibited by high molecular weight polymers in solution or as melts.[33] Aqueous PEG serves as the solvent for the PEO-PEG solution, providing the high background viscosity. For our PEO-PEG system, aqueous PEG solution with $c_{\text{PEG}} = 30$ wt. % was employed as the solvent, producing a solvent viscosity η_s approximately 50x water viscosity, as demonstrated in figure 1 (A). The PEO concentrations used in the PEO-PEG solutions range from $c_{\text{PEO}} = 0.01$ wt. % to 0.09 wt. %, all of which augment the soliton viscosity no more than $2\eta_s$ are below c^* . [88] One exceptional quality of the water-based PEO-PEG system is a reactively low bulk viscosity of $O(10^{-2} \text{ Pa s})$ versus a typical Boger fluid viscosity of $O(1 \text{ Pa s})$. [33] Such a viscosity range of the PEO-PEG system allows for achievement of greater deformation rates, which is crucial for the study of elastic stabilities. [24]

2.1.2 Viscometry

The shear viscosity response of the PEO-PEG-based Boger fluids was characterized using a cone-and-plate (1° cone angle, 50 mm diameter) flow cell on an Anton Paar MCR 302 rheometer (torque range $10^{-5} - 200 \text{ mN}\cdot\text{m}$). Additionally, the Boger fluid solvent, aqueous 30 wt. % PEG ($M_w = 8,000 \text{ Da}$), was

characterized using a concentric cylinder (double gap) flow cell, as a control against the addition of high molecular weight PEO ($M_w = 5 \cdot 10^6$ Da). The steady shear viscosity, $\eta(\dot{\gamma}) \equiv \tau / \dot{\gamma}$ was calculated from the measured shear stress, τ from imposed shear rates in the range of $\dot{\gamma} = 0.01 - 10^3 \text{ s}^{-1}$.

2.1.3 Dripping-onto-substrate (DoS) extensional rheometry

The extensional rheology response of the aqueous Boger solutions was characterized using dripping-onto-substrate (DoS) rheometry. The experimental set-up comprises an imaging system, drop dispensing mechanism, and backlight. A finite volume of fluid is dispensed through a stainless-steel nozzle, and is deposited on a clean glass substrate at a height H below the nozzle. The radius of the nozzle is kept constant for all experiments, with outer diameter of $D_0 = 2R_0 = 1.27 \text{ mm}$ and inner diameter of $D_i = 0.838 \text{ mm}$. The fluid is pumped at a low and fixed flow-rate ($Q = 0.02 \text{ mL/min}$) using a syringe pump such that deformation within nozzle is minimized and an aspect ratio of $H/D_0 \approx 3$. The imaging system includes a light source, diffuser, and high-speed camera (Fastcam SA3 with A Nikkor 3.1 x zoom (18-55 mm) lens). Depending on the duration of pinch-off, frame rates ranging 500 – 3,000 FPS were used for the PEO-PEG-based Boger fluids. The DoS videos are analyzed with ImageJ and specially written MATLAB codes for determination of the minimum neck radius as a function of time.

DoS rheometry relies on the analysis of pinching dynamics using radius evolution data, in analogy with other capillarity-based techniques, including commercially-available technique called CaBER (Capillary break-up extensional rheometer) [12, 14, 89-91] that analyzes pinching dynamics of a neck created by applying step-strain to liquid confined between two parallel plates. Due to the finite time and large deformation associated with the application of the initial step-strain, the CaBER (and its variants) are often found to be unsuitable for measurements involving low viscosity ($\eta < 50 \text{ mPa}\cdot\text{s}$), or low elasticity (relaxation time, $\lambda < 1 \text{ ms}$) fluids, as pinching occurs before initial step-strain stage is completed.[14, 92] Likewise, the pinching dynamics for micro-structured materials like physical gels, wormlike micellar solutions and polymer-particle mixtures are influenced by the magnitude and time of step-strain.[91, 93, 94] Several papers, including our previous contributions,[1-6, 60, 95, 96] can be consulted for detailed account of the utility and application of DoS rheometry protocols for measurements of capillarity-driven pinching dynamics and extensional rheology response for a range of complex fluids, including polymer and polyelectrolytes solutions,[1-6, 60, 95-100] inks,[2, 27] micellar solutions,[2, 101-103] and yield stress fluids[2] including particle suspensions, Carbopol solutions, emulsions, foods (mayonnaise and ketchup), and cosmetics.[2]

2.2 Results and Discussion

Characterization of shear rheology response

Figure 1a shows the shear viscosity, $\eta(\dot{\gamma}) = \tau_{12} / \dot{\gamma}$ that is computed as the ratio of shear stress, τ_{12} measured in response to a applied shear deformation rate $\dot{\gamma}$, at a controlled temperature ($T = 22$ °C). The aqueous PEG solution, used as matrix or solvent in this study, shows a rate-independent viscosity value (solid black dots) of $\eta_s = 50$ mPa·s that is approximately 50 times the viscosity of water. Addition of high molecular weight PEO to the PEG solution in the concentration range (0.01-0.09 wt.%) creates solutions with nearly rate-independent shear viscosity in the range between 50-100 mPa·s, in agreement with previous studies.[70] However, for the three highest PEO concentration included in Figure 13 (A), an apparent shear thickening regime can be observed at high shear rates (>100 s⁻¹). Similar results were reported for several Boger fluids, including aqueous PEO/PEG Boger fluids and for PAM in glycerin.[104, 105] Figure 13 (B) and 13 (c) respectively show the stress and the first normal stress values as a function of shear rate for three polymer solutions. Though flow does not remain viscometric at highest shear rates show, the force transducer on the rheometer picks up a measurable normal force that shows quadratic dependence on shear rate. Figure 13 (D) shows that the first normal stress difference exceeds shear stress at high deformation rates.

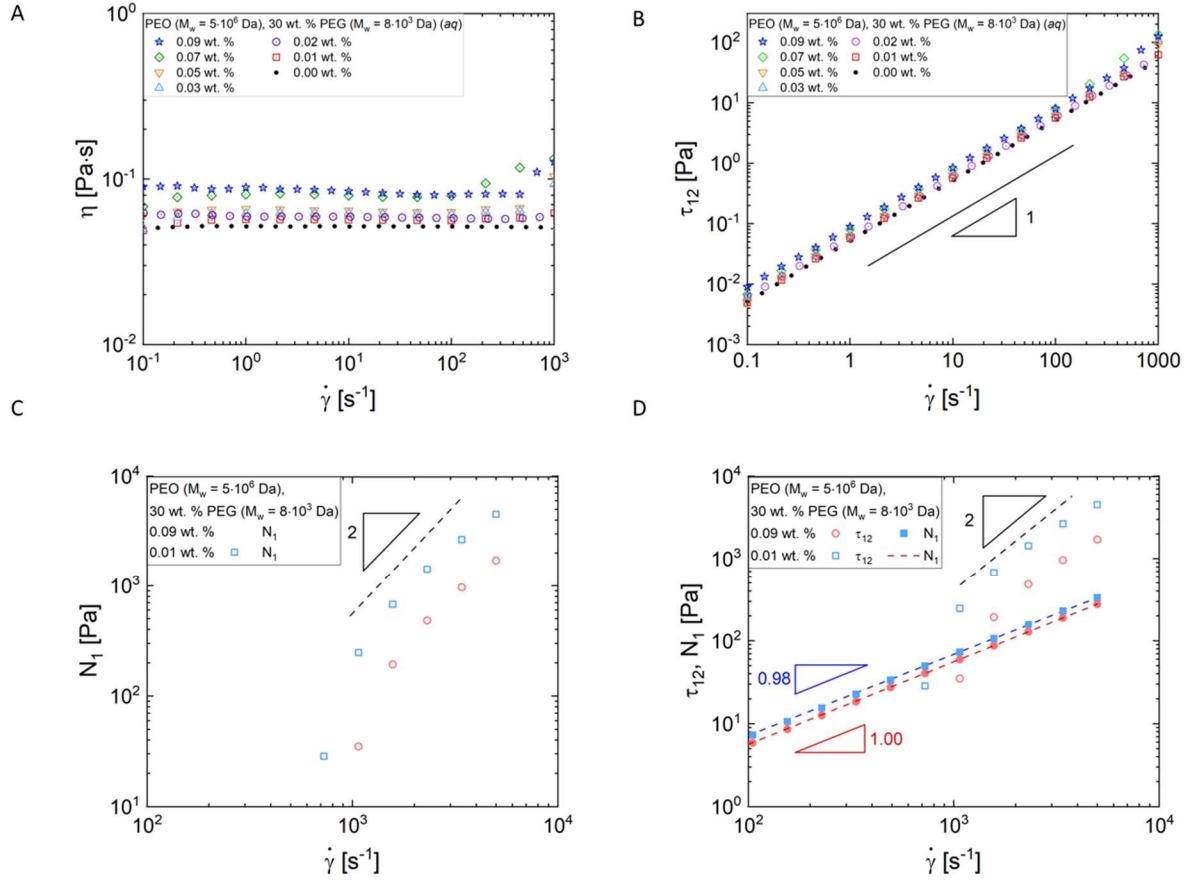


Figure 13. Steady shear rheological response of PEO/PEG solutions. (A) Apparent shear viscosity of PEO-PEG-based Boger fluids for a range of $c_{PEO} = 0.01 - 0.09$ wt. % and PEG-based solvent for a shear deformation rate range of $\dot{\gamma} = 0.1 - 10^3$ s⁻¹. The PEO-PEG-based Boger fluids (and PEG-based solvent) exhibit virtually rate-independent shear viscosity, a characteristic of Boger fluids. Apparent shear thickening occurs at higher PEO concentration Boger fluids at shear rates at or above approximately 100 s⁻¹, which is attributable to non-viscometric elastic instability. (B) Shear stress as a function of shear rate for a range of $c_{PEO} = 0.01 - 0.09$ wt. % and PEG-based solvent for a shear deformation rate range of $\dot{\gamma} = 0.1 - 10^3$ s⁻¹. The increase in shear stress with shear rate follows a slope of 1, indicating a constant shear viscosity. Additionally shear stress ranges from O(10⁻³ – 10² Pa). (C) First normal stress difference as a function of shear rate for the concentration extrema of the PEO-PEG-based Boger fluids, all measured with ramp down. There is a PEO concentration dependence on the normal stress. The data show a normal stress response of approximately 2 as a function of shear rate. (D) The magnitudes of the normal stress can manifest themselves over one order of magnitude greater than the shear stress at higher deformation rates.

Pinching dynamics and extensional rheology

The pinching dynamics and underlying extensional rheology response of the PEO/PEG solutions was characterized using DoS rheometry protocols shown schematically in Figure 14 (A) (see methods section for details). Figure 14 (B) shows two image sequences that contrast the neck shape and shape evolution captured for 0.03% and 0.09% PEO in PEG solution respective. The radius evolution data obtained by analyzing neck diameter as a function of time, t is displayed in Figure 14 (C) for concentrations ranging from 0.01–0.09 wt. % PEO dissolved in the PEG-based solvent. At least three distinct regimes can be identified. The initial radius evolution regime for viscoelastic fluids like polymer solutions, can be described by the same response as observed for Newtonian fluids: either dictated by a balance of inertial and capillary forces leading to the inertio-capillary (IC) response for low viscosity fluids or by a balance of viscous and capillary stress, that results in visco-capillary (VC) response [22]. The neck radius evolution for IC regime is captured by

$$\frac{R(t)}{R_o} = R_c \left(\frac{t_{ic} - t}{t_R} \right)^{2/3} \quad (2.1)$$

where t_{ic} is the time scale of a thinning process dominated by inertia, t_R is Rayleigh time $t_R = \sqrt{\rho R_o^3 / \sigma}$, where σ is surface tension, R_C is the critical radius, defined below. The VC regime shows a linear decrease in neck radius such that

$$\frac{R(t)}{R_o} = 0.07 \left(\frac{t_p - t}{t_{vc}} \right) \quad (2.2)$$

where t_p is the pinching process time and t_{vc} is the visco-capillary time $t_{vc} = (\eta_0 R_o) / \sigma$. The Rayleigh time on IC timescale, t_R does not depend on viscosity, whereas viscocapillary time, t_{vc} increases linearly with increase in upon the zero-shear viscosity. Both the matrix phase (PEG solution) and the PEO/PEG solutions exhibit an initial VC response, consistent with the relatively high viscosity of these solutions compared to solutions made in low viscosity solvent like water. The radius evolution data for PEO-PEG-solutions in Figure 14 (C) show a stark transition to a second regime that appears linear on a semi-log plot indicating an exponential thinning behavior, characteristic of elastocapillary response:

$$\frac{R(t)}{R_o} = \left(\frac{G_E R_o}{2\sigma} \right) \exp \left[-\frac{t - t_c}{3\lambda_E} \right] \quad (2.3)$$

where G_E is the extensional elastic modulus, λ_E is the largest extensional relaxation time and onset of elastocapillary regime occurs at $t = t_c$. The expression differs

from the most often cited Entov-Hinch expression[53] in utilizing λ_E and G_E rather than the values of the longest shear relaxation time, λ_s and shear modulus, G . Defining the IC/VC to EC transition at t_c and fitting the elastocapillary (EC) regime using a shifted timescale, $(t-t_c)$ provides more physically reasonable values for G_E . [3] Thus, the pre-factor in equation 2.1 corresponds to a critical radius $R_c \approx R_0 (G_E R_0 / 2\sigma)^{1/3}$ determined by interplay of viscoelasticity and capillarity. [3, 59]

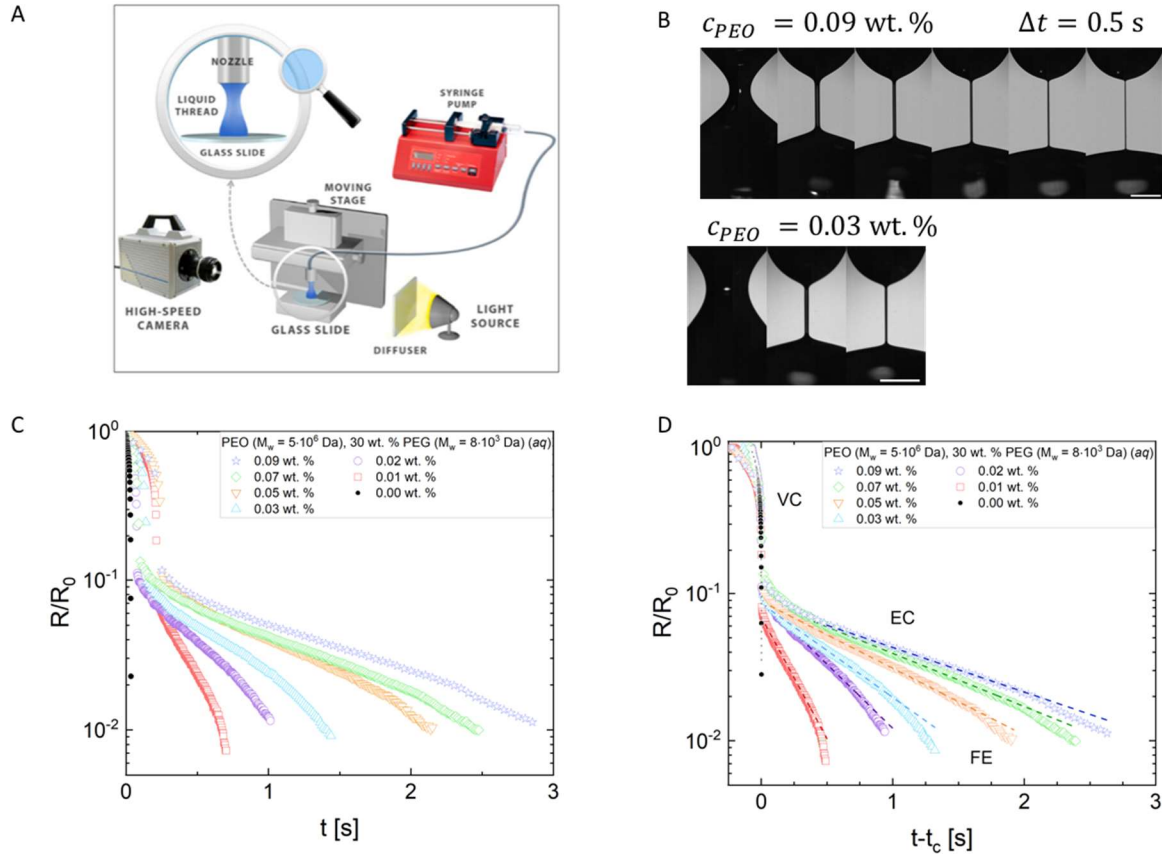


Figure 14. DoS measurement of the PEO/PEG solution. (A) Dripping-onto-substrate (DoS) setup, consisting of an imaging system, drop dispensing mechanism, and backlight. (B) Snapshots from an image sequence recorded using the DoS protocol for two PEO/PEG Boger fluids of a high and lower PEO concentration, the former solution which displays a greater resistance to filament

thinning. The first snapshot for both concentrations displays the VC regime, while the last snapshot for each concentration displays the FE regime, and all snapshots in-between show the EC regime. Scale bars indicate 2 mm. (C) Radius evolution profiles as a function of time for PEO/PEG Boger fluids for a range of $c_{PEO} = 0.01 - 0.09$ wt. % and PEG-based solvent. By adding high molecular weight PEO to the PEG solution, the pinching dynamics time scale changes from $O(10 \text{ ms})$ to $O(10^3 \text{ ms})$. (D) Radius evolution profiles as a function of time after the *critical time* for PEO-PEG-based Boger fluids for a range of $c_{PEO} = 0.01 - 0.09$ wt. % and PEG-based solvent. All solutions exhibit an initial VC regime. The PEG-based solvent shows no appreciable EC regime, while the PEO-PEG-based Boger fluids show broad EC regimes for $t > t_c$ and FE regimes.

In Figure 14 (D), the radius evolution data is replotted using a shifted time scale. All PEO/PEG solutions show an initial VC response similar to the PEG-based solvent, but in the second regime, the slope changes and filament lifespan increases, consistent with an increase in resistance to capillarity-driven pinching flows. By adding high molecular weight PEO to the PEG-based solvent (thus producing the PEO-PEG-based Boger fluid) an enhancement in resistance to pinch off and prolonged filament lifespan is observed. Furthermore, after the EC regime, the radius evolution profiles of the PEO/PEG Boger fluids exhibit the finite extensibility (FE) regime, where polymer chains cannot be stretched further [22].

The extensional viscosity of the fluid is characterized *via* the DoS rheometry protocol by using the elastocapillary balance between the extensional stress and capillary stress using the following equation:

$$\eta_E = \frac{\sigma}{R(t)\dot{\epsilon}} = -\frac{\sigma}{2\frac{dR}{dt}} \quad (2.4)$$

where $\dot{\varepsilon} = 2 \frac{d \ln R}{dt}$ is the extensional deformation rate. The extensional rate attains a constant value for neck pinching in the elastocapillary regime, and diverges in finite extensibility regime as pinch-off event is approached. Therefore, the extensional viscosity measured using capillarity-driven pinching flows is presented in Figure 15 (C) as a function of the Hencky strain, $\varepsilon = 2 \ln \left(\frac{R_0}{R(t)} \right)$ that steadily increases with decrease in neck radius. Extensional viscosity increases with increase in PEO concentration, and the absolute value of extensional viscosity is 3-4 orders of magnitude than the corresponding shear viscosity values. Extensional viscosity value progressively increases with strain in the elastocapillary regime, signifying increase in drag associated with the influence of stretched chains, and increased interchain overlap. The degree to which a polymer chain can be extended is finite because the polymer chain is of a finite length [106], thus the drag on the polymer chain approaches a maximum in the finite extensibility limit [22], as is seen in figure 15 (C) [88]. All extensional viscosity plots show the strain and strain-rate independent steady, terminal extensional viscosity, associated with the finite extensibility regime in radius evolution plots. From the finite extensibility regime, the filament lifespan time t_f of the filament is extrapolated and plotted in figure 15 (B) as a function of PEO concentration for the PEO-PEG-based Boger fluid. The filament lifespan time response to the addition of PEO scales $t_f \sim c_{\text{PEO}}^{0.66}$,

similarly to the scaling behavior of extensional relaxation time. The filament lifespan time serves as measure of extensibility of the solution. [107]

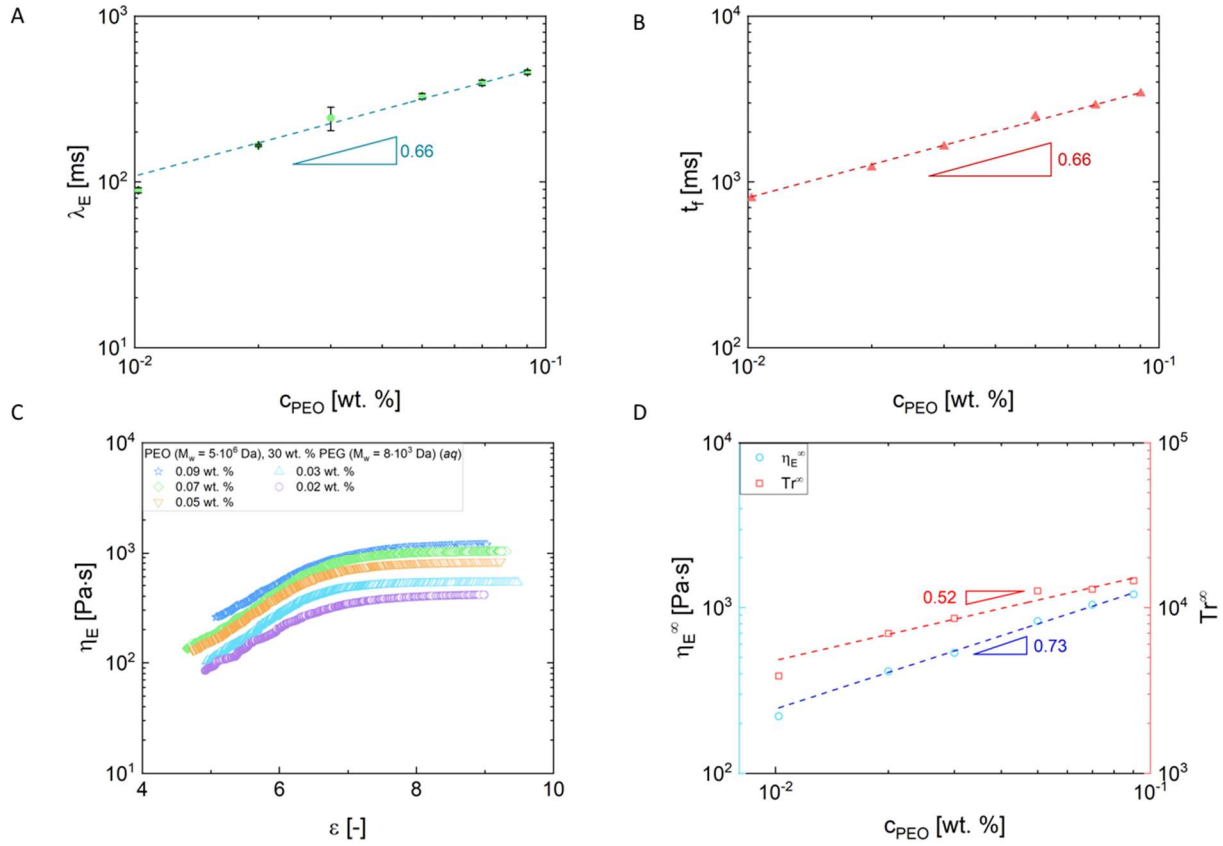


Figure 15. Extensional properties of the PEO/PEG solution obtained from DoS. (A) Extensional relaxation time as a function of PEO concentration for the PEO-PEG-based Boger fluid. The extensional relaxation time response to concentration follows $\lambda_E \sim c_{PEO}^{0.66}$ and ranges from 89 ms to 459 ms for a concentration range of 0.01 wt. % to 0.09 wt. %. (B) Filament lifespan as a function of PEO concentration for the PEO-PEG-based Boger fluid. Like extensional relaxation time, filament lifespan response to concentration follows $t_f \sim c_{PEO}^{0.66}$, ranging from 896 ms to 3418 ms over the aforementioned concentration range. (C) Extensional viscosity as a function of Hencky strain for PEO-PEG-based Boger fluids for a range of $c_{PEO} = 0.02 - 0.09$ wt. %. The magnitude of extensional viscosity is proportional to PEO concentration. Strain hardening is observed and a steady-state extensional viscosity is reached at large strains. (D) Steady-state extensional viscosity and terminal Trouton ratio as a function of PEO concentration are presented.

At sufficiently high strain the PEO/PEG fluids approach a strain-indent extensional viscosity, called the steady-state extensional viscosity or terminal extensional viscosity η_E^∞ , which is plotted in figure 15 (D) as a function of PEO concentration for the PEO/PEG solutions. The steady-state extensional viscosity increases $\eta_E^\infty \sim c_{PEO}^{0.73}$, which is a similar concentration dependence to the extensional relaxation time, as presented further in this work. The associated Trouton ratio where $\eta_E = \eta_E^\infty$ is defined $Tr^\infty = \eta_E^\infty / \eta$, which is also plotted as a function of concentration in figure 3 (D) for the PEO/PEG solution and increases $Tr^\infty \sim c_{PEO}^{0.52}$, indicating the maximum resistance to stretching of the polymer chains versus the resistance to shear flow increases approximately by the square root of PEO concentration. The magnitude of the steady-state Trouton ratio ranges from 10^3 to 10^4 .

The EC regime of the radius evolution profile (from figure 14 (D)) is further analyzed using equation 2.3 to determine the extensional relaxation time of the PEO/PEG solution, as shown in Figure 15 (A) and Figure 16 (A). Also shown is the data for extensional relaxation time for aqueous PEO ($M_w = 10^6$ Da) from Dinic *et al.*[1, 4, 61] for comparison in the latter figure. The extensional relaxation time values for the PEO/PEG solutions range from 89 ms to 459 ms, as compared to the aqueous PEO which ranges from 0.9 ms to 1.9 ms. To model the extensional relaxation time, consideration of both Rouse time and Zimm time must be made

[4]. Both Rouse time and Zimm time serve as time scales over which a polymer coil diffuses a distance of the order of its own length and both time scales involve the characteristic time scale over which its Kuhn monomer relaxes [41]

$$\lambda_0 \approx \frac{\zeta b^2}{kT} \quad (2.5)$$

where ζ is the Stokes drag on the polymer coil, b is the length of the Kuhn monomer, k is the Boltzman constant, and T is temperature. This Kuhn monomer relaxation time is a ratio of the drag force area on the polymer to the energy of Brownian motion. Where the Rouse time and Zimm time differ, is in Rouse time excluded volume (EV) and hydrodynamic interactions (HI) are screened, while in Zimm time excluded volume and hydrodynamic interactions are accounted. Deciding which time scale is appropriate depends on a screening length ξ , above which EV and HI are neglected and below which EV and HI are dominant. Within a blob, HI can play a role, leading to the relaxation time prediction $\lambda \approx \lambda_0 N^2 \phi^{(2-3v)/(3v-1)}$, where v is the solvent quality scaling exponent, N is the number of Kuhn monomers in the polymer, and ϕ is the polymer volume fraction in solution. Considering the extreme cases where EV interactions are included and where EV are screened renders the exponent $(2 - 3v)/(3v - 1)$ to equal 0.31 and 1, respectively. Jinic *et al.* predicted the EV interactions and HI to be only partially

screen, thus Rouse model is used and the aforementioned exponents are geometrically averaged, producing the extensional relaxation time prediction

$$\lambda_E \approx \lambda_0 N^2 \phi^{0.65} = \lambda_R \phi^{0.65} \quad (2.6)$$

where λ_R is Rouse time. This model predicts a concentration dependence on extensional relaxation time of $\lambda_E \sim c^{0.65}$, which is in close agreement with both the PEO/PEG Boger fluid and aqueous PEO solution in figure 15 (A) and figure 16 (A) for both the PEO-PEG-based Boger fluid and the aqueous PEO solution.

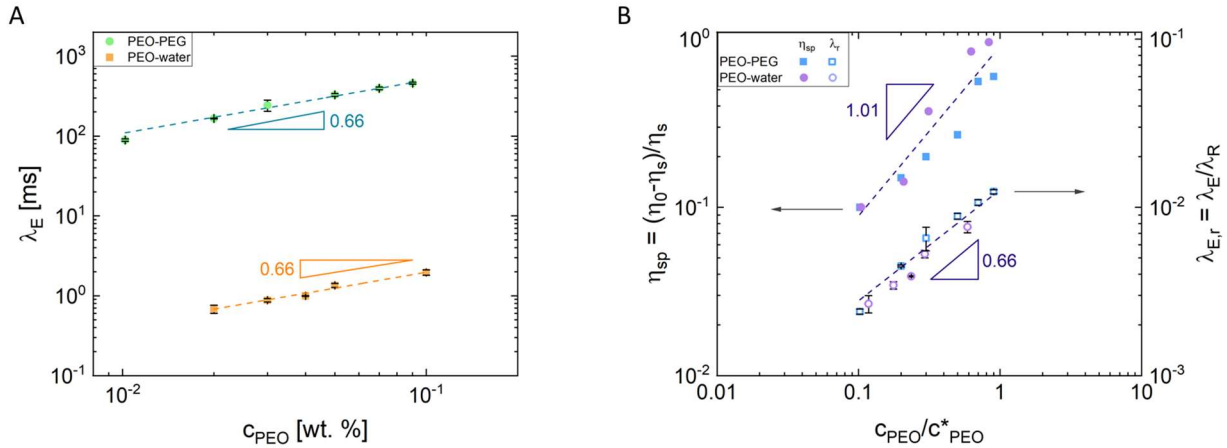


Figure 16. Generalization of rheological properties via scaling laws. (A) Extensional relaxation time as a function of PEO concentration for the PEO/PEG solutions and for aqueous PEO ($M_W = 1 \cdot 10^6$ Da), which is obtained from the fit of the EC regime of the radius evolution profiles. Both the PEO-PEG-based Boger fluids and aqueous PEO exhibit an identical extensional relaxation time concentration dependence of $\lambda_E \sim c_{PEO}^{0.66}$. (B) Specific viscosity and reduced extensional relaxation time as a function of PEO concentration scaled by c^* for the PEO/PEG-based solution and for aqueous PEO. The specific viscosity profiles of the PEO/PEG solution and aqueous PEO ($M_W = 5 \cdot 10^6$ Da) show identical dependencies on PEO concentration, with $\eta_{sp} \sim c_{PEO}^{1.01}$ indicating both solutions are in the dilute regime. The reduced extensional relaxation time data for both the PEO-PEG-based Boger fluids and aqueous PEO solutions collapse onto a single trend,

with a PEO concentration dependence of $\lambda_{E,r} \sim c_{\text{PEO}}^{0.66}$, indicating intrinsically semi-dilute behavior, [1] thus the excluded volume effects are screened when the solutions undergo extensional flow.

To model the shear and extensional rheological responses of PEO/PEG fluids, scaling relations for dimensionless polymeric viscosity contribution or specific viscosity, defined as

$$\eta_{sp} = \frac{\eta_0 - \eta_s}{\eta_s} \quad (2.7)$$

and reduced extensional relaxation time, defined as the measured extensional relaxation time scaled by Rouse time

$$\lambda_{E,r} = \frac{\lambda_E}{\lambda_R} \quad (2.8)$$

as function of PEO concentration scaled by the critical overlap concentration of PEO $c_{\text{PEO}}/c_{\text{PEO}}^*$.

The specific viscosity of the PEO-PEG-based Boger fluid and an aqueous PEO solution is plotted in figure 16 (B). The data for both solutions collapses onto a single curve with a specific viscosity response to PEO addition of $\eta_{sp} \sim c_{\text{PEO}}^{1.01}$, which scaling is commensurate with the behavior of a dilute polymer solution. [88] The reduced extensional relaxation time scales the measured extensional relation time with Rouse time, which accounts for the length of the high molecular weight

polymer (PEO in this case) and its monomer relaxation time, allowing for comparisons across molecular weights and solvent viscosities. Much like the specific viscosity data, the reduced extensional relaxation time data for both the PEO/PEG solutions and aqueous PEO solution collapse onto a single curve. The reduced extensional relaxation time response to the addition of PEO follow the scaling relationship $\lambda_{E,r} \sim c_{\text{PEO}}^{0.66}$, which does not change from the each solutions' respective extensional relaxation time scaling, shown in figure 16 (A).

When formulating a PEO-PEG-based Boger fluid, PEO molecular weight and concentration can be tuned, as well as the solvent viscosity (via selection of PEG molecular weight and concentration). Choices in formulation will determine the solution rheology, both in shear and extensional flows. The scaling relationships presented in figure 16 (B) for specific viscosity and reduced extensional relaxation time can be used as an empirical model for predicting the viscoelastic response of constant viscosity PEO-based fluid formulation, which was demonstrated from 30 wt. % to 0 wt. % PEG.

3. Conclusions and Outlook for Future Work

In this contribution, the elasticity, pinching dynamics and extensional rheology response of PEO-PEG Boger fluids are characterized. The aqueous Boger fluids have shear viscosity in the range from 50-100 mPa·s, making them suitable for characterizing effect of elasticity in coating flows (for typical coating fluids have viscosity in the range 0.001-1 Pa·s).[52-56] Although the PEO-PEG-based Boger fluid has been used for numerous applications, a sparse number of works characterized the extensional rheology, all of which using CaBER. [69, 82, 83, 108] Of those works which measured the extensional response, none show consistent access of the FE regime and none shows any scaling relationship of extensional rheological properties to PEO concentration. For these reasons, the present work offers new insight into controlling the shear and extensional rheological responses of PEO-PEG-based Boger fluids, which provides a toolkit with which past works may be reinterpreted, better constitutive equations may be derived, and elastic instabilities may be deciphered.

One avenue on which the PEO-PEG-based Boger fluid ought to be utilized is in viscoelastic fingering (VEF), which is one of the most relevant interfacial instabilities in both industry and academia occurs when an inner less viscous fluid η_{in} displaces an outer more viscous fluid η_{out} in quasi-two dimensional geometry such as Hele-Shaw cell seen Figure 17. Figure 17 (a) is the Hele-Shaw cell set-up

which consists of two transparent parallel plates separated by a gap of width, b . The displacement of a transparent more viscous fluid by a dyed less viscous fluid is captured using a digital camera and light source placed under the cell. Figure 17 (b) illustrates the top-down view of the Hele-Shaw cell which shows the formation of finger-like patterns that occur when their prerequisite conditions are met (principally, sufficient velocity, thin gap width, and large viscosity contrast); this is known as “Viscous fingering” or Saffman-Taylor Instability. [109] Due to its importance in pattern formation and other engineering applications such as enhanced oil recovery, carbon sequestration, and other situations that involve displacement and/or mixing of fluids with different viscosities, Saffman-Taylor instability became a subject of diverse inquiry. [110-115]

However, it was only recent that global features of fingers such as shape and shape evolution has started to emerge. Experimental studies showed that the inner to outer viscosity ratio η_{in}/η_{out} is a control parameter in setting the large-scale features of the fingers pattern. [116, 117] In radial Hele-Shaw cell (as seen in Figure 17), two main regions can be identified: a circular stable region, and an unstable region identified with fingers. Bischofberger et. al argued that the ratio between the lengths of stable and unstable regions is set by the viscosity ratio η_{in}/η_{out} , while the number of initially formed fingers is constant. Because the results correspond to Newtonian fluids, the main question that needs to be

addressed is will the use of complex fluids (in this case viscoelastic) have a role in determining the global features of the fingering instability when compared to Newtonian fluids. Although many studies have addressed the use of non-Newtonian fluids in fingering instability, [73, 118-121] sufficient understanding of the role of non-Newtonian effects on the large-scale structures and nonlinear growth of fingers is not well established. In addition, little or no attention has been given to cases where the inner or invading fluid is viscoelastic. Fortunately, Boger fluids can serve as a gateway to exploring the role of elasticity alone on interfacial instability. By utilizing their constant viscosity and high elasticity, which is the topic of this thesis, PEO-PEG aqueous solutions, can be useful in understanding how elasticity alters the fingering instability by emulating the experimental work done by Bischofberger et. al. By utilizing a viscous and a Boger fluid with equal viscosities, the effects that results from elasticity can be isolated and characterized carefully.

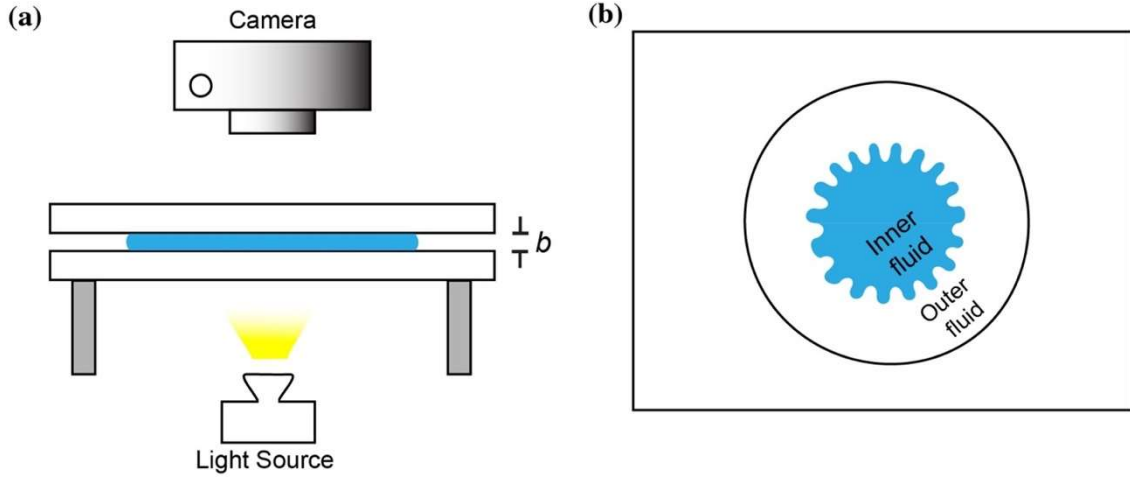


Figure 17. A schematic showing Hele-Shaw cell. The Hele-Shaw cell consists of (a) transparent parallel plates separated by a gap of width, b . A light source is placed under the cell and a digital camera on top. (b) Top view of the Hele-Shaw cell illustrating the invasion of a less viscous inner fluid η_{in} into a more viscous fluid η_{out} in confined geometry that can lead to an instability forming finger-like pattern known as “Viscous fingering” or Saffman-Taylor instability.

In figure 18, two montages show the comparison between viscous and viscoelastic fingering in radial Hele-Shaw cell is shown. In both cases, the outer fluid is pure glycerin and the viscosity ratio η_{in}/η_{out} and viscosity difference $\Delta\eta = \eta_{out} - \eta_{in}$ is nearly identical ($\eta_{in}/\eta_{out} \approx 0.08$ and $\Delta\eta = 1$). However, the red inner fluid is PEG-water solution and blue fluid is PEO/PEG solution. Next to the montage is an evolution map outlining the interfacial evolution. Despite the nearly equal η_{in}/η_{out} which has been suggested in previous works to control the instability, a large contrast in the overall pattern is observed when a Boger fluid is used as an inner fluid versus a Newtonian fluid. At the onset of the instability

where fingers start to form, viscoelastic fluids form much larger number of fingers with reduced size. At later stages, the total number of fingers formed by a Boger fluid is larger and fingers are thinner.

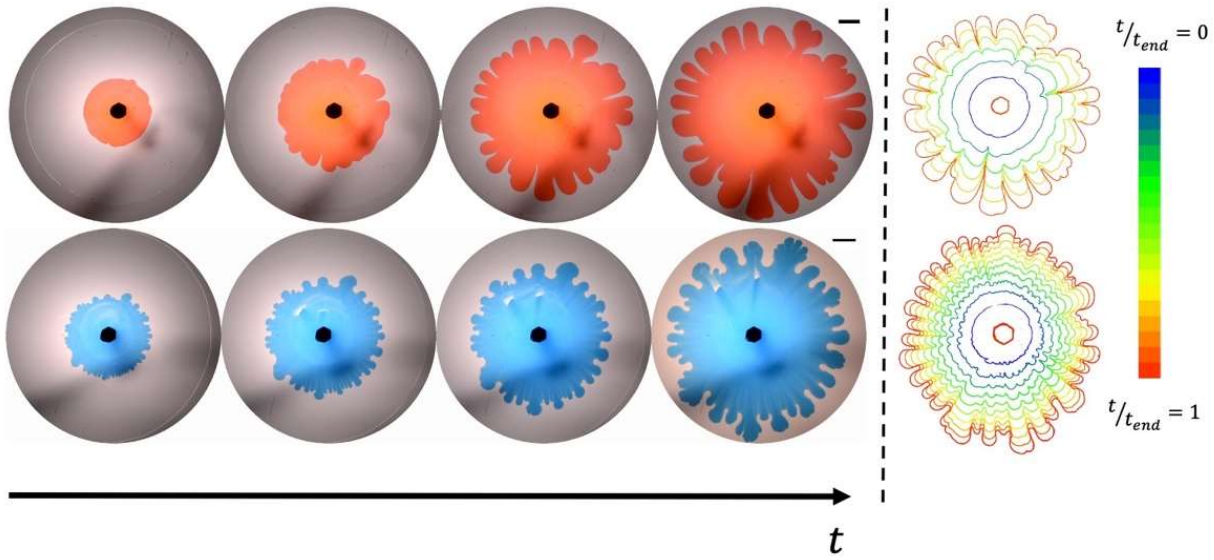


Figure 18. Comparison between Viscous and Viscoelastic Fingering. Montages on the left showing the onset and growth of fingers over time. The column on the right is an evolution map of the fingers outlined at each $\Delta t = 2 \text{ s}$. Dyed in red is 35 wt. PEG aqueous solution ($\eta_{in} = 0.095 \text{ Pa} \cdot \text{s}$) displacing pure glycerin ($\eta_{out} = 1.1 \text{ Pa} \cdot \text{s}$), and 0.15 wt. PEO ($M_w = 5 \text{ million Da}$) in 30 wt. PEG (8000 Da) (aq) was used as viscoelastic inner fluid ($\eta_{in} = 0.091 \text{ Pa} \cdot \text{s}$) and pure glycerin was used as outer fluid. A noticeable contrast between both patterns is observed, which can be seen in the number of initially formed fingers, the reduction in the finger's width, and increase in the number of fingers at the later stages of the instability. Injection rate, $Q=100 \text{ mL/min}$, cell gap width, $b = 1.4 \text{ mm}$, and scale bar is 2cm.

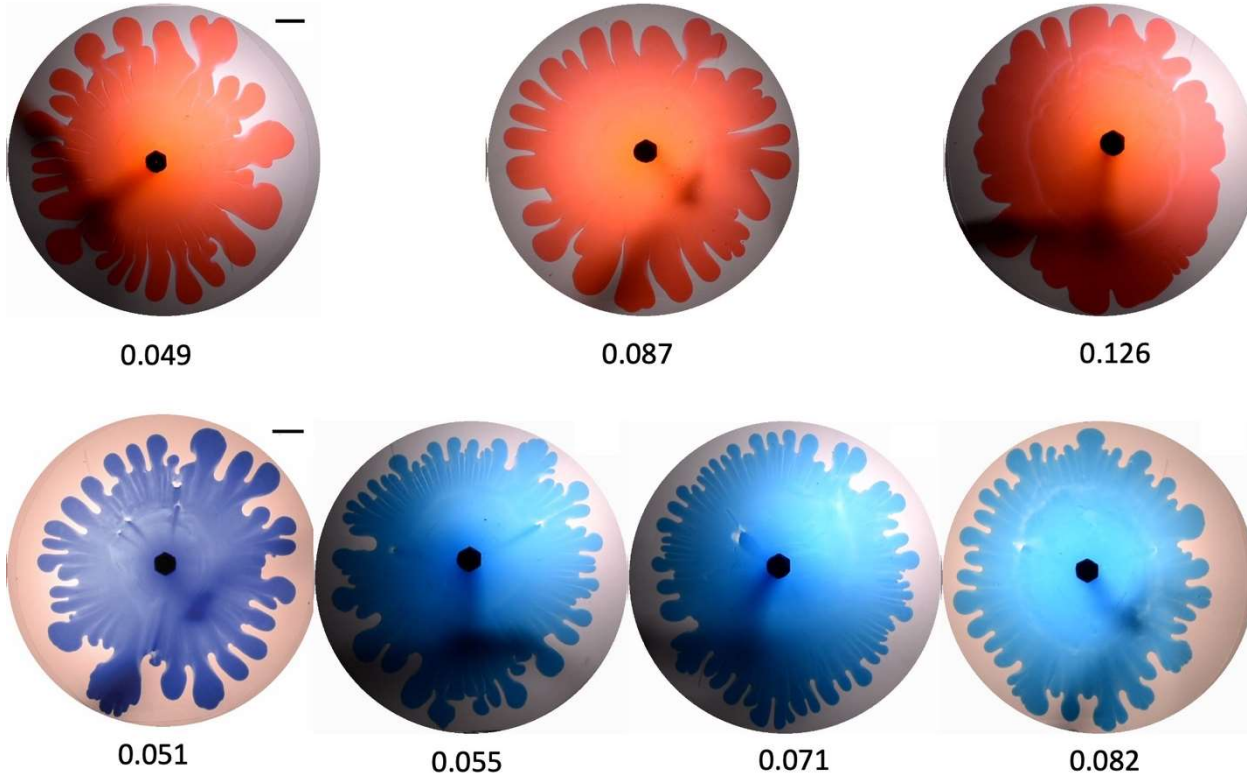


Figure 19. Comparison between viscous and viscoelastic fingering with varying η_{in}/η_{out} . Snapshots show the dependence of the fingers pattern on η_{in}/η_{out} when the inner fluid is viscous (red) and viscoelastic (blue). Pure glycerin was used as outer fluid in all experiments. The numbers below the snapshots correspond to η_{in}/η_{out} values ($\eta_{in}/\eta_{out} = 0.049$ to 0.126 for PEG-water solutions and $\eta_{in}/\eta_{out} = 0.051$ to 0.082 for PEO-PEG aqueous solutions). Injection rate, $Q=100$ mL/min, cell gap width, $b = 1.4$ mm, and scale bar is 2cm.

When η_{in}/η_{out} is varied, purely viscous fingering changes in fingers size while the overall number of fingers is nearly constant. However, the tendency of how fingering pattern vary with η_{in}/η_{out} for viscoelastic is different than viscous. A comparison between the two cases is presented in Figure 19. PEG-water system, shown in red, transitions from formation of long fingers or twigs to reduction in finger length as η_{in}/η_{out} increases while the number of fingers is nearly constant.

Shown in blue is PEO/PEG solution used as inner fluid with viscosity ratio ranging from $\eta_{in}/\eta_{out}= 0.051$ to 0.082 . In PEO/PEG system, as viscosity ratio η_{in}/η_{out} is increased by adding more PEO, elasticity which can be characterized by extensional relaxation time is also enhanced. At low η_{in}/η_{out} , the fingering pattern is somewhat similar to those in PEG-water aqueous. When more PEO is added, the number of fingers increases, and finger narrowing behavior is observed. This suggests that other non-Newtonian, in this case elasticity, can effectively play a role in altering the fingering growth, and produce patterns that are not explained by η_{in}/η_{out} alone. Further detailed studies on the use of Boger fluids in viscous fingering instability can reveal more insights about the role of non-Newtonian effects on interfacial instabilities.

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5. Vita

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Education

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Work Experience

Chemist II in Drug Dissolution

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Characterize drug release via USP *in vitro* experimental methods and modeling. CFD with mass transfer in dissolution flow cells. Semi-empirical drug release modeling for *a priori* prediction.

Skills

Numerically solving PDEs and ODEs, torsional rheometry, extensional rheometry, polymer physics, non-Newtonian fluids, CFD, heat and mass transfer, data fitting and modeling, image analysis, HPLC, moisture analysis, USP App. I, II, GMP documentation

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