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DESIGN OF EQUIPMENT FOR THE STUDY OF NON-ISOTHERMAL FLOW IN POLYMER FLUID

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Opeoluwa Oluwaseun Kolawole
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Dedication

This thesis is dedicated to my God and family, who have encouraged me and exemplified endless love and support; without their support and patience, I would not be where I am today.

I will specially dedicate this to my loving father, Samuel Ereola Kolawole R.I.P, who did all he could to get me the best support to advance my education to the highest degree.

Acknowledgement

I give all glory to God, through all the hardship and stress, for bringing me to this point and seeing me through the rigors and hard work of graduate school.

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Abstract

The polymer industry is an ever growing industry, and, as it grows, companies are continuously looking for ways to study and understand the behaviors of polymers in relation to the processing and production. This is to ensure the production of high quality products and to improve existing products.

An important parameter during polymer processing is temperature. Temperature control affects several rheological parameters such as viscosity, and in turn the quality of the final products. Frictional or viscous heating is a very important part of polymer processing and occurs in almost every polymer processing operation.

The objective of this research is to design the apparatus and setup the equipment to examine the validity of the *Theory of Purely Entropic Elasticity* (PEE) on non-isothermal flow of concentrated polymeric solutions under a wide range of shear rates. A basic rheological study of the polymer in use is performed. PEE once played an important role in polymer processing. PEE is the assumption that the internal energy of a polymeric material is solely dependent on temperature, and specifically is not dependent on the polymer deformation, as developed by Astarita and co-workers [1-3, 16].

The design and results are presented. Potential improvements and future considerations are also presented.

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Chapter 1

Introduction

1.1 Characteristics and Importance of Polymers

Polymers are large macromolecules that can form long, extended chains of covalently bonded atoms [14]. The polymer industry is an ever growing industry, and, as it grows, companies are continuously looking for ways to study and understand the behaviors of polymers in relation to the processing and production. This is to ensure the production of high quality products and to improve existing products.

Polymers are commonly used in almost everything we encounter in our daily lives. They are everywhere around us in everyday use: in rubber, in plastics, in resins and in adhesives and adhesive tapes. Materials that were once produced using wood and metals are now being replaced by polymers. An example of this is in the automobile industries where cars used to be made primarily of metals but due primarily to cost, high weight, and energy consumption, polymers and plastics are now replacing metals parts to make cars lighter and more fuel efficient.

The extensive use of polymers in the manufacturing industry has led to further issues that need to be understood to be able to attain optimum efficiency in the production of polymeric products. An important parameter during polymer processing is temperature. Temperature control affects several rheological parameters such as viscosity, and in turn the quality of the

final products. Therefore, a study of thermal and thermodynamic characteristics of polymers is necessary. Frictional or viscous heating is a very important part of polymer processing and occurs in almost every polymer processing operation.

Polymers are characterized as viscoelastic materials which have complex internal microstructures. Viscoelastic materials also display complex non-Newtonian properties under the application of external forces such as a pressure gradient, shear stress, and extensional strain.

1.2 Direction of Current Work

In this thesis work, the design of an apparatus to study the thermodynamic aspects of polymeric liquids subjected to non-isothermal shearing flow is examined from theoretical and experimental perspectives. In most rheological modeling and experimental studies, isothermal conditions are usually assumed, but in reality this is far from the case. The reason for this assumption is because the study in the area of non-isothermal phenomena is not as advanced as it should be. It is just in the last 10 years that this area has seen significant attention paid to it due to its enormous importance in polymer processing, and in turn the importance of polymers to the society in general.

The expanding polymer industry demanded quantitative information about the material properties of these fluids under processing conditions, and these are all related in one way or another to the relaxation spectrum. It was thus of immediate importance to take measurements of the relaxation rates of polymeric fluids over extensive ranges of deformations [8]. An understanding early on after the large-scale development of high molecular weight polymers that solutions or melts of these materials, after removal of an applied load, would undergo a long-

time viscoelastic relaxation back to the undeformed state, which could be quantified with a spectrum of relaxation modes, each with a characteristic relaxation time [10].

The *Theory of Purely Entropic Elasticity* (PEE) once played an important role in polymer processing. PEE is the assumption with respect to polymeric fluids, developed by Astarita and co-workers [1-3, 16], that the material is incompressible and internal energy is a unique function of only temperature, U = U(T), and independent of deformation. Several decades ago, it was not possible to solve the complicated partial differential equations (PDE) arising in non-isothermal flow processes, and the PEE assumption enabled simple solutions to be obtained. However, this theory does not work for most polymers, as has been proven by several authors including Ionescu *et al.* [11]. These authors used the non-isothermal flow theory of Dressler *et al.* [8, 9] to derive an extended model of non-isothermal flows (described in some detail below), which was able to describe fully the complicated interplay of all relevant process variables (deformation rate, temperature, and microstructural evolution) within a new model that captured the available experimental data completely [11]. Still, more work and experiments are needed to examine the validity and effectiveness of this theory.

The objective of this research is to design the apparatus and set up the equipment to examine the validity of non-isothermal flow of concentrated polymeric solutions under a wide range of processing conditions (in this case shear flow). Similar works in this area have been done by others, including that of Ionescu *et al.* [11]**,** mentioned above. This work examined the effect of elongation flow on polymers from an experimental, simulation and theoretical perspective. The present study is very similar to that one, except that the set up will be for the study involving shear flow and not elongational flow. Furthermore, a key new aspect of non-isothermal flows is herein considered: the effect of a stationary or translating temperature probe.

In other words, we design and set up apparatus and equipment to perform two sets of experiments, one in which the temperature probe is stationary in an Eulerian sense (i.e., fixed in space), and another one in which the temperature probe is translated with the fluid at the local flow rate (Lagrangian description).

This research focuses on the design of the equipment for the study of non-isothermal deformation of the polymeric material, Hydroxypropyl Cellulose (HPC) at various concentrations. The design is such that the material is subjected to steady shear flow using the two temperature measurement methods just described. The temperature measurements using both the Eulerian and Lagrangian methods are then compared to determine the effects, if any, upon the measured temperature from the stationary and translating probes.

In Chapter 2, we will go into depth regarding the theory of PEE and review previous works that have been performed in this area. In Chapter 3, the methodology and materials used in this research are presented and discussed. In Chapter 4, a presentation and discussion of the experimental results is given. In Chapter 5, a basic summary, conclusion to our observations and experimental and future directions of the work will be presented.

Chapter 2

Background

As mentioned in Chapter 1, polymers are a very important aspect of the world we live in. There are in used in almost, if not all, major sectors of the economy. Due to this fact, studying the subject has been given an increased significance to be able to attain as much knowledge as possible about polymers. The expanding polymer industry demands quantitative information about the material properties of these fluids under processing conditions [8]. This has lead to increased study of non-isothermal conditions in polymer flow. Since mechanical properties such as viscosity and relaxation time are strongly temperature dependent, accurate knowledge of the thermal properties of polymers is essential for the development of accurate process models [20].

The thermodynamic aspects of polymeric liquids subjected to non-isothermal shearing flow are examined from theoretical and experimental perspectives. In most rheological modeling and experimental studies, isothermal conditions are usually assumed, but in reality this is far from the case.

2.1 General Equations

In an engineering analysis of a polymeric isothermal flow, one has a set of equations to solve to describe the basic characteristics of the polymer. These equations are the conservation of mass, momentum and a constitutive equation that relates stress to strain rate. In the case of

Upper-Convected Maxwell model (UCMM) the equation set is [8, 9]

$$\rho \frac{D\,\mathrm{v}}{Dt} = -\nabla p - [\nabla . \tau] + \rho g \tag{2.1}$$

$$\frac{\partial \rho}{\partial t} = -(\nabla . \rho \mathrm{v}) = 0 \tag{2.2}$$

$$\overset{\vee}{\tau}_{\alpha\beta} + \frac{1}{\lambda}\tau_{\alpha\beta} = G(\nabla_\alpha v_\beta + \nabla_\beta v_\alpha) \tag{2.3}$$

where **v** is the velocity vector field, $\boldsymbol{\rho}$ is the fluid mass density, $\boldsymbol{p}$ is the hydrostatic pressure, g is the acceleration due to gravity, $\boldsymbol{\tau}$ is the extra stress tensor field, $\boldsymbol{G}$ is the elastic modulus, $\boldsymbol{\lambda}$ is the relaxation time and D/Dt is the material time [4]. The superimposed reverse hat represents the upper-convected time derivative. Equation 2.2 and 2.3 represent the continuity and constitutive equations respectively.

Due to the fact that a non-isothermal case is under consideration, in this thesis work, the energy conservation equation has to be taken into account along with the above set of equations:

$$\rho \frac{D\hat{U}}{Dt} = -(\nabla . q) - p(\nabla . \mathrm{v}) + (\tau : \nabla \mathrm{v}) \tag{2.4}$$

where $\hat{U}$ denotes the internal energy per unit mass and $\boldsymbol{q}$ is the heat flux vector field. The UCMM constitutive equation has additional terms under non-isothermal conditions [8, 9].
For an incompressible fluid,

$$(\nabla \cdot \mathrm{v}) = 0 \tag{2.5}$$

which allows the equation set (eqn. 2.1-2.3) to be solved under appropriate initial and boundary conditions

2.2 Polymeric Materials with Purely Entropic Elasticity

In equation 2.4, internal energy, on the left side, is not a measurable quantity. It is deduced using the Helmholtz free energy. Helmholtz free energy is then a measure of the amount of energy you have to put in to create a system once the spontaneous energy transfer to the system from the environment is accounted for [17]. It is represented by

$$A \equiv U - TS \tag{2.6}$$

where U is the internal energy, S is entropy, and A is the Helmholtz free energy.

We define the rate of Helmholtz free energy change $\dot{A}$ as,

$$\dot{A} \equiv \dot{U} - \dot{T}S - T\dot{S} \tag{2.7}$$

and we define the "rate of accumulation of elastic energy" $\dot{E}$ as,

$$\dot{E} = \dot{A} + S\dot{T} \tag{2.8}$$

Then the "rate of accumulation of elastic energy" becomes

$$\dot{E} = \dot{U} - T\dot{S} \tag{2.9}$$

The rate of Helmholtz energy change identifies the rate of accumulation of energy in an isothermal process. The superimposed dots are representative of time derivative of the individual quantities.

It is necessary to consider both ends of the rheological spectrum. When structureless, isotropic fluids are subjected to deformation, the entropy of the configuration does not change when deformations stops, provided that the flow is incompressible [19]. Therefore, it would be

safe to assume that purely viscous fluids can accumulate elastic energy only by compression, thus by an increase in internal energy [11],

$$\dot{E} = \dot{U} \tag{2.10}$$

On the opposite side of the spectrum, we have rubbery solids which according to the Theory of Rubbery Elasticity (TRE) [19], where a decrease in conformational energy exclusively causes an accumulation of elastic energy. The significant decrease in conformational entropy is associated with the lower number of degrees of freedom of extended chains [11]:

$$\dot{E} = -T\dot{S} \tag{2.11}$$

As mentioned earlier, polymers are viscoelastic in nature, as are also either simple fluids with fading memory [6, 7] or cross-linked networks with temporary junctions [10].

The internal energy of a *viscoelastic* liquid is considered as a unique function of temperature (i.e. not a function of deformation). This is the *Theory of Purely Entropic Elasticity* (PEE) developed by Astarita and co-workers [1-3, 16],:

$$\hat{U} = \hat{U}(T) \tag{2.12}$$

The effect of this assumption is that the constant volume heat capacity per unit mass is also independent of deformation. Thus the usual definition of the constant volume heat capacity applies:

$$\hat{c}_v = \frac{d\hat{U}(T)}{dT} \tag{2.13}$$

This further simplifies the heat equation to become

$$\rho\hat{c}_v \frac{DT}{Dt} = -(\nabla . q) - p(\nabla . \mathrm{v}) + (\tau : \nabla \mathrm{v}) \tag{2.14}$$

For an incompressible fluid with PEE- (eqn. 2.5 and 2.12), the final heat equation is

$$\rho \hat{c}_v \frac{DT}{Dt} = -(\nabla . q) + (\tau : \nabla \mathrm{v}) \tag{2.15}$$

This provides an equation in terms of temperature, which is a measurable quantity. This equation is exactly the same as for a Newtonian fluid, and there is no explicit information related to the internal structure or conformation of the fluid, except only indirectly through the stress tensor [11].

2.3 Theoretical Deviations from Theory of Purely Entropic Elasticity

As has been proven by others, such as Ionescu *et al*. (2008) [11], Dressler *et al*. (1999) [8], and Dressler (2000) [9], the Theory of Purely Entropic Elasticity (PEE) has its limitations.

Ionescu *et al*. [11] examined the complete form of the temperature evolution equation if the assumption that the free energy is purely entropic in nature was not made. First, the consideration that internal energy of a fluid has a dependence on one or more internal structural variables aside from temperature is made. The most widely used quantity to describe the internal structure is the conformation tensor, C defined as

$$c \equiv \langle RR \rangle \tag{2.16}$$

Then the internal energy is taken as a function of temperature and an appropriate internal structural variable (conformation tensor):

$$\hat{U} = \hat{U}(T, c) \tag{2.17}$$

Next we define the heat capacity as

$$\hat{c}_v = \left.\frac{\partial \hat{U}}{\partial T}\right|_c \tag{2.18}$$

Then, the substantial time derivative of the internal energy becomes:

$$\frac{D\hat{U}}{Dt} = \hat{c}_v \frac{DT}{Dt} + \left.\frac{\partial U}{\partial c}\right|_T : \frac{Dc}{Dt} = \hat{c}_v \frac{DT}{Dt} + \left.\frac{\partial \hat{U}}{\partial c}\right|_T : \left(\frac{\partial c}{\partial t} + \mathrm{v}.\nabla c\right) \tag{2.19}$$

The complete form of the heat equation thus becomes

$$\rho \hat{c}_v \frac{DT}{Dt} + \rho \left.\frac{\partial \hat{U}}{\partial c}\right|_T : \left(\frac{\partial c}{\partial t} + \mathrm{v}.\nabla c\right) = -(\nabla . q) - p\,(\nabla.\mathrm{v}) + (\tau : \nabla \mathrm{v}) \tag{2.20}$$

An additional term appears in equation 2.20 that does not appear in 2.14. This term contains structural information missing in 2.14. However, by careful choice of flow conditions, this term could be phased out. If one is interested in steady state of a homogenous flow, then equation 2.20 takes the form of 2.14. However, for a non-steady state in homogenous flow, it has been demonstrated by Ionescu *at al.* [11], that this additional term is of equal importance to the frictional heating term.

2.4 Direction of Current Work

The main objective of the current work is to design the apparatus and put together the set up to further the research and increase the understanding of the limitations of PEE. Furthermore, a key new aspect of non-isothermal flows is herein considered: the effect of stationary or translating temperature probes. In other words, we design and set up apparatus and equipment to perform two sets of experiments, one in which the temperature probe is stationary in an Eulerian

sense (i.e., fixed in space), and another one in which the temperature probe is translated with the fluid at the local flow rate (Lagrangian description).

Once the design has been setup and all parts of it are functional, the design is such that the material is subjected to steady shear flow using the two temperature measurement methods just described.

Chapter 3

Methodology of Experiments

3.1 Materials

Hydroxypropyl cellulose (HPC) is used as the test polymer in the experiments. Figure 3.1 below shows the structure of HPC [14]. Major applications of HPC include paints, coatings, inks, cosmetics, papers, pharmaceuticals, and encapsulations [14]. Solutions were made by dissolving a certain weight percent of HPC in distilled water. The dissolution capacity of the polymer in water was one of the major reasons for its selection. Other materials such as polyethylene, polystyrene, etc., require expensive organic solvents that are typically toxic. HPC of molecular weights 100,000, 370,000, 1,000,000 g/mol were obtained from Sigma Aldrich [18]. Varying concentrations of solutions were made by dissolution in distilled water ranging from the most viscous at 10 wt. % 370,000 MW to the least viscous at 0.05 wt. % of 1,000,000 MW.

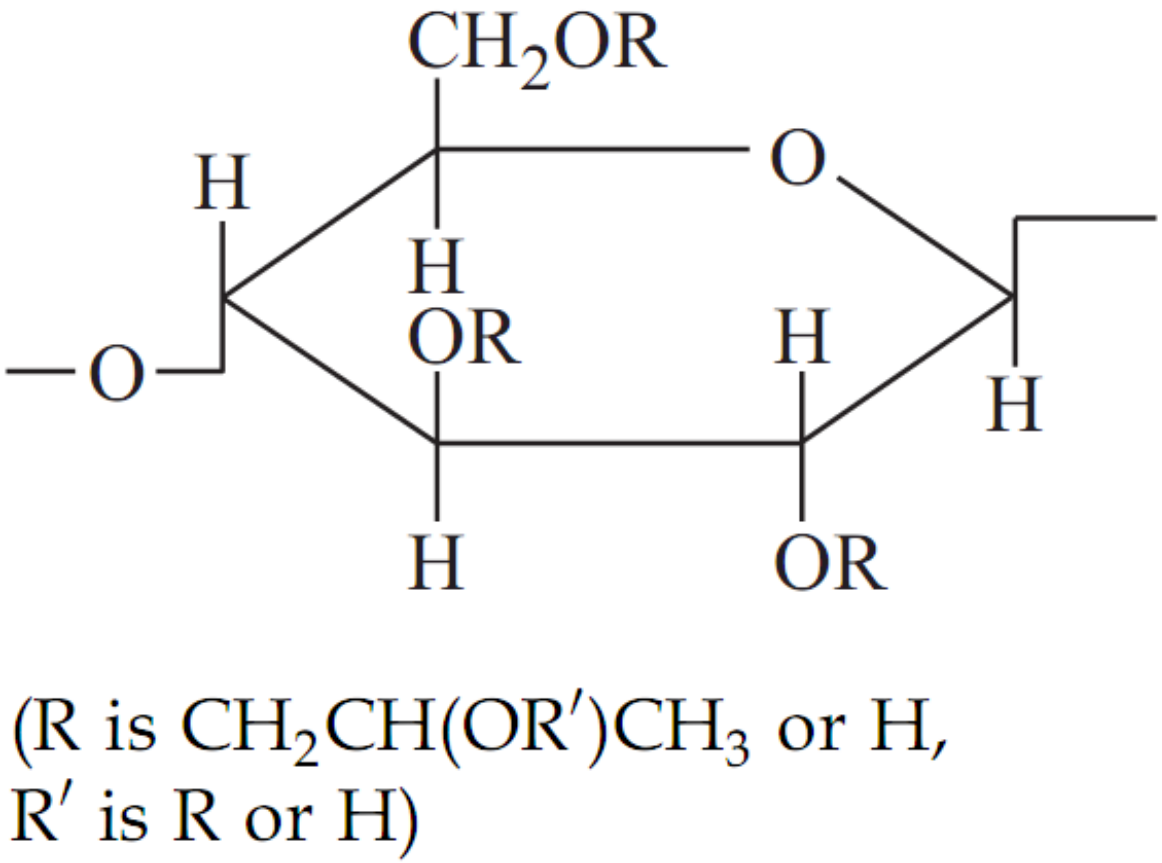


Figure 3.1 Structure of Hydroxypropyl Cellulose (HPC)

3.2 Rheological Measurements

Rheology is the science that studies the deformation and flow of materials in liquid, melt, or solid forms in terms of the material's elasticity and viscosity. This is accomplished by applying a precisely measured strain or strain rate to the sample to deform it, and accurately measuring the resulting stresses developed within the sample. The developed stresses are related to material properties through Hooke's and Newton's laws [12], as simple examples. Rheology is an important tool in polymer processing because it provides information related to the stresses that a polymer experiences during processes such as extrusion, fiber spinning, and film blowing.

Rheological behavior influences the mechanical behavior of the polymeric material. Two types of flow exist in a flowing polymeric material: shear flow and extensional flow. Measurements of shear/extensional viscosity and storage/loss moduli can contribute to understanding intermolecular interactions and their influence on the flow and mechanical properties in solutions and melts. In rheometric experimentation, the most commonly used flow is shear flow. Shear viscosity is the main measure of resistance to flow and therefore affects real processes, especially when there are changes in temperature and flow rates. The normal stresses quantify the elastic response of these so-called "viscoelastic fluids."

A rheometer is an instrument that measures both stresses and deformation history of a sample material for which the constitutive relation is likely to be unknown. A rheometer can also be used to determine material functions [12]. A strain-controlled rheometer with a cone-and-plate configuration was used herein for the rheological measurements, as well as strain-rate controlled configurations. A cone and plate (as opposed to a parallel plate) rheometer was

utilized because of its inherent accuracy at reproducing a homogenous shear field throughout the sample.

3.2.1 Advanced Rheometric Expansion System (ARES)

The Advanced Rheometric Expansion System (ARES) is a rheometer that is capable of subjecting a sample to either a dynamic or steady shear rate, and then measuring the resultant torque expended by the sample in response to the strain. Through this instrument, the rheological properties can be measured. Strain is applied by motor, and a transducer measures the resulting torque [13].

Cone-and-plate and parallel plate rheometers are both established methods used in characterizing polymers and determining their material functions. The primary advantage of cone-and-plate geometry is that the shear rate $\dot{\gamma}$ is approximately uniform within the fluid sample. Hence, unlike torsional flow between parallel disks, or pressure-driven flow in a capillary, the shear stress at a given shear rate, $\sigma(\dot{\gamma})$ is uniform throughout the sample, even for fluids displaying highly non-linear rheological behavior. In addition, the first normal stress difference $N_1(\dot{\gamma})$ can be obtained from a single axial force measurement. If the radial distribution of stress on the plate is measured, both $N_1(\dot{\gamma})$ and the second normal stress difference $N_2(\dot{\gamma})$ can be obtained [21].

Using UCMM mentioned in the previous chapter, the relaxation time is a key characteristic function that is involved in Eq. 2.3. The ARES rheometer can be used to provide accurate measurement of this very important material property. The relaxation time is

determined by measuring the loss (G'') and storage (G') moduli under small-amplitude oscillatory shear (SAOS). The loss modulus gives the viscous response to shear while the storage modulus gives the elastic response to shear. At low frequencies, when G'' is greater than G', the polymer fluid is said to be viscous. At high frequencies, when is G' greater than G'', the polymer fluid is said to display or exhibit elastic characteristics. The point at which they cross is called the "crossover point". The inverse frequency of oscillation ($1/\omega_{crossover}$) of the "crossover point" gives the characteristic relaxation time λ.

The measurement of the dynamic characteristic functions is performed using the dynamic frequency sweep with the ARES rheometer. This gives the G' and G'' values. It also provides the dynamic viscosity. Also performed is the steady-state shear-rate sweep to provide information about the shear and normal stresses. Stress relaxation tests were also conducted at various values of applied strain to examine the relaxation behavior of the samples. All measurements were performed at 25 ^{o}C.

Figure 3.2 shows the setup of the ARES rheometer with the data logging and analysis computer side by side. The computer has TA instrument software that controls the rheometers. In Figure 3.3 [11], a schematic of the cone and plate ARES rheometer is presented. The lower flat plate is connected to the motor while the force and torque sensors (transducer) are connected to the upper, conical plate. The plates are surrounded by a gas oven chamber. The temperature in the chamber is precisely controlled by passing air over two resistive heaters.



Figure 3.2 ARES rheometer with the data logging and analysis computer.

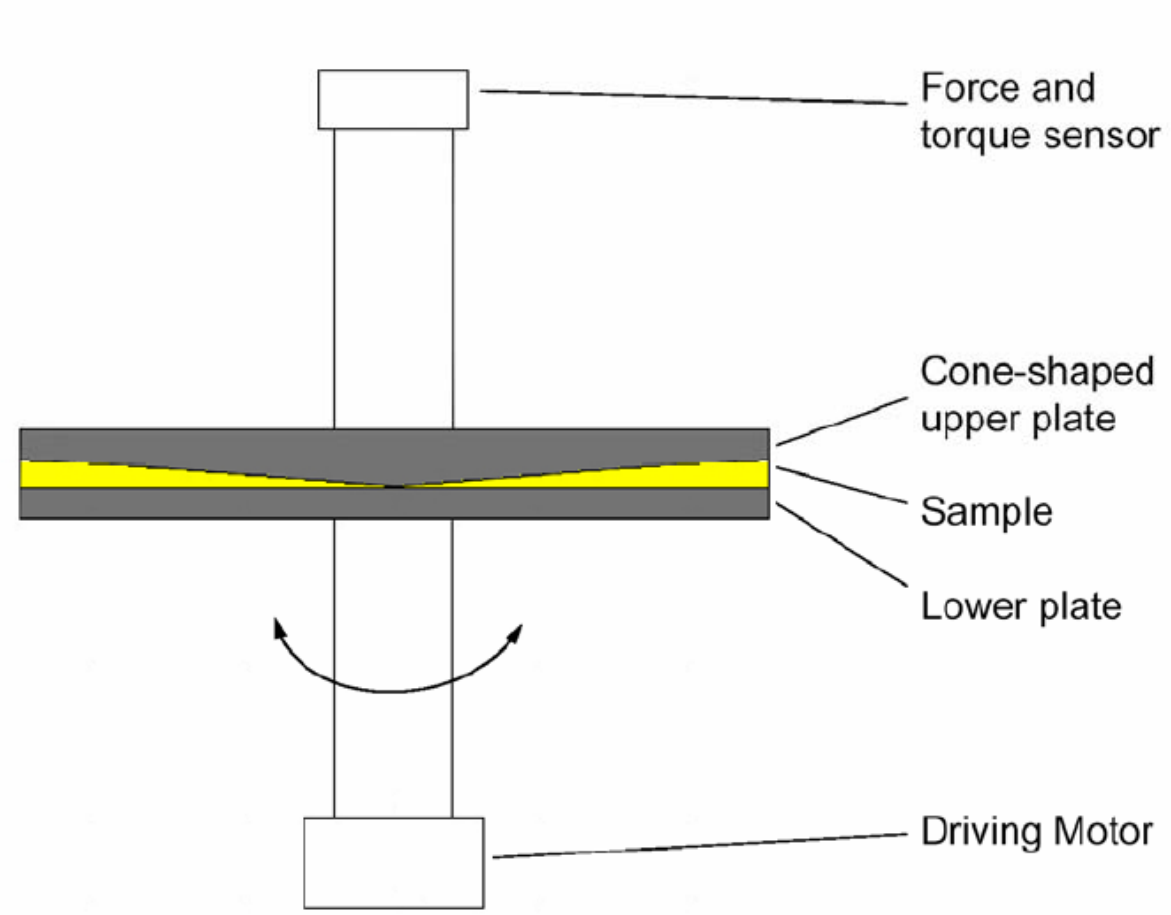


Figure 3.3 Schematic of cone and plate geometry on ARES rheometer.

The sample is loaded between the plates in such a way that there is a slightly concave outer free surface for best results. During testing, it is likely that the sample shrinks due to solvent loss, which is why best results are attained with a slight bulge- see Figure 3.4 [15]. Over-loading or under-loading of sample will produce incorrect torque readings, leading to inaccurate rheological measurements.

The frequency ranges applied to different samples in SAOS are varied from solution to solution. This is so because the concentration variations of different solutions imply different material relaxation times, and the frequencies required to observe the crossover point (if observed at all) will decrease as the concentration increases. Sometimes the relaxation times of some solutions are not going to be able to be captured with the ARES rheometer, because starting measurements from very low frequencies is not feasible. Also, the experiment duration can be quite long and the sample solvent evaporates at long times. To avoid this, the lowest frequency that will give a relatively close approximation of the crossover point is attained by trial and error, and the crossover point is extrapolated from the data, if necessary. Of course, one can also determine the relaxation time from stress relaxation experiments using ARES, as mentioned above.

3.3 Temperature Measurements

The concept underlying this research was to measure the temperature rise due to viscous heating and/or elastic deformation during shear flow. An experimental apparatus was designed and constructed to accomplish this plan. A Couette flow apparatus was designed to induce shear on the polymer solution. The apparatus also involved the use of a pulley

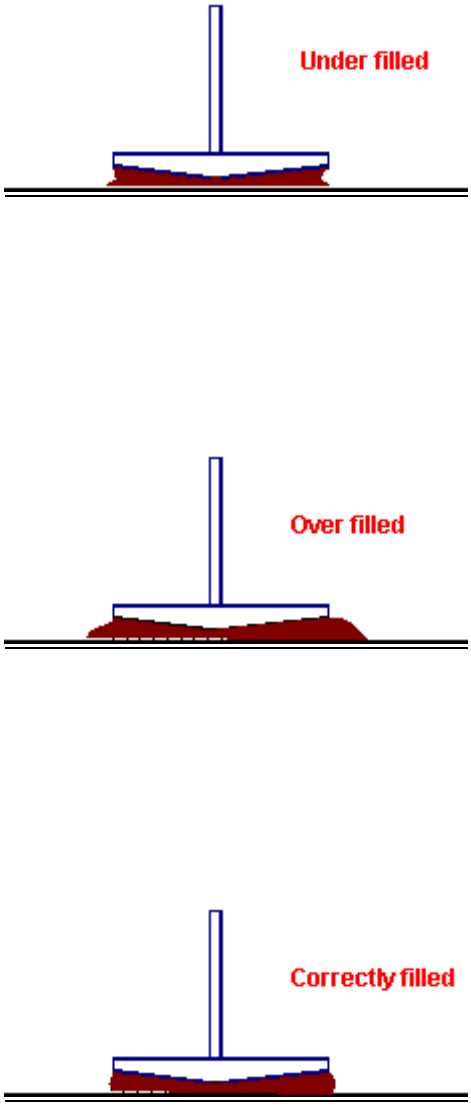


Figure 3.4 Proper loading of cone-plate geometry.

system and motor to drive the device. The temperature was measured using a thermocouple, which was placed both at the top of the rotating and stationary parts of the Couette flow apparatus. The descriptions of these apparatus and devices with accompanying schematics are given below. The hydroxypropyl cellulose (HPC) solution was placed in the space between the rotating and stationary cylinder. The thermocouple was run through a protective tubing to maintain the rigidity of the wires while performing the experiment. The initial temperature of the HPC was measured and the outer cylinder was rotated. The tip of the thermocouple (the active temperature measuring part) was exposed to the fluid and the temperatures were measured according to both the Eulerian and Lagrangian frameworks. Multiple temperature measurements were taken at different rotational rates. The rotation rates were varied and controlled using of a stepper motor.

3.3.1 Couette Flow Apparatus

The design of the Couette flow apparatus for the temperature measurements in the different configurations is presented in this section. A description of the design is presented, accompanied by pictures and a schematic of the apparatus with appropriate dimensions. Also described are the basics of the motor used to induce motion and the overall schematics and picture of the whole system.

3.3.1.1 Basic Design

The Couette flow device used for this thesis produces a shear flow by the rotation of the outer cylinder with the aid of a stepper motor. The inner cylinder is stationary throughout the whole process. Below are schematic and illustrations of the design of the Couette flow device

and set up (Fig. 3.5-3.8). The inner cylinder, outer cylinder and the housing are all made of aluminum.

The inner cylinder (stationary part) rests on the bottom of the housing. The outer cylinder (the rotating part) sits on a bearing in the housing (C) attached to the inner frame of the housing. The presence of a bearing reduces friction and maintains concentricity of the two cylinders. The bearing housing sits on a dynamic seal (B) to prevent the polymeric solution from leaking out of the gap between the two cylinders and damaging the bearing or equipment.

The inner radius of the outer cylinder is 5 inches. Three different inner cylinders (A) were machined to get three varying diameters of the gap between the two cylinders. The gap producing the shear flow between the two cylinders varies from 0.12 inches to 0.39 inches. The angle machined at the bottom of the outer cylinder is 1^{o} to reduce the friction between the outer cylinder and the base during rotation. This also avoids the thermal effect that occurs during friction to assure accurate data is being gathered. The outer diameter of the outer cylinder is 7 inches and the outer diameter of the housing is 9.5 inches. The housing base (B) is a square base of dimensions 10.5 x 10.5 inches.

The rotating cylinder rests on a bearing (Roller Bearing Company of America, KD065ARO) located at position (C) in the figure. The bearing has an inner diameter of 6.5 inches and a width of 0.5 inches. The dynamic seal (SKF Industries, 537301) rests on the housing base (B) at the position denoted by (D).

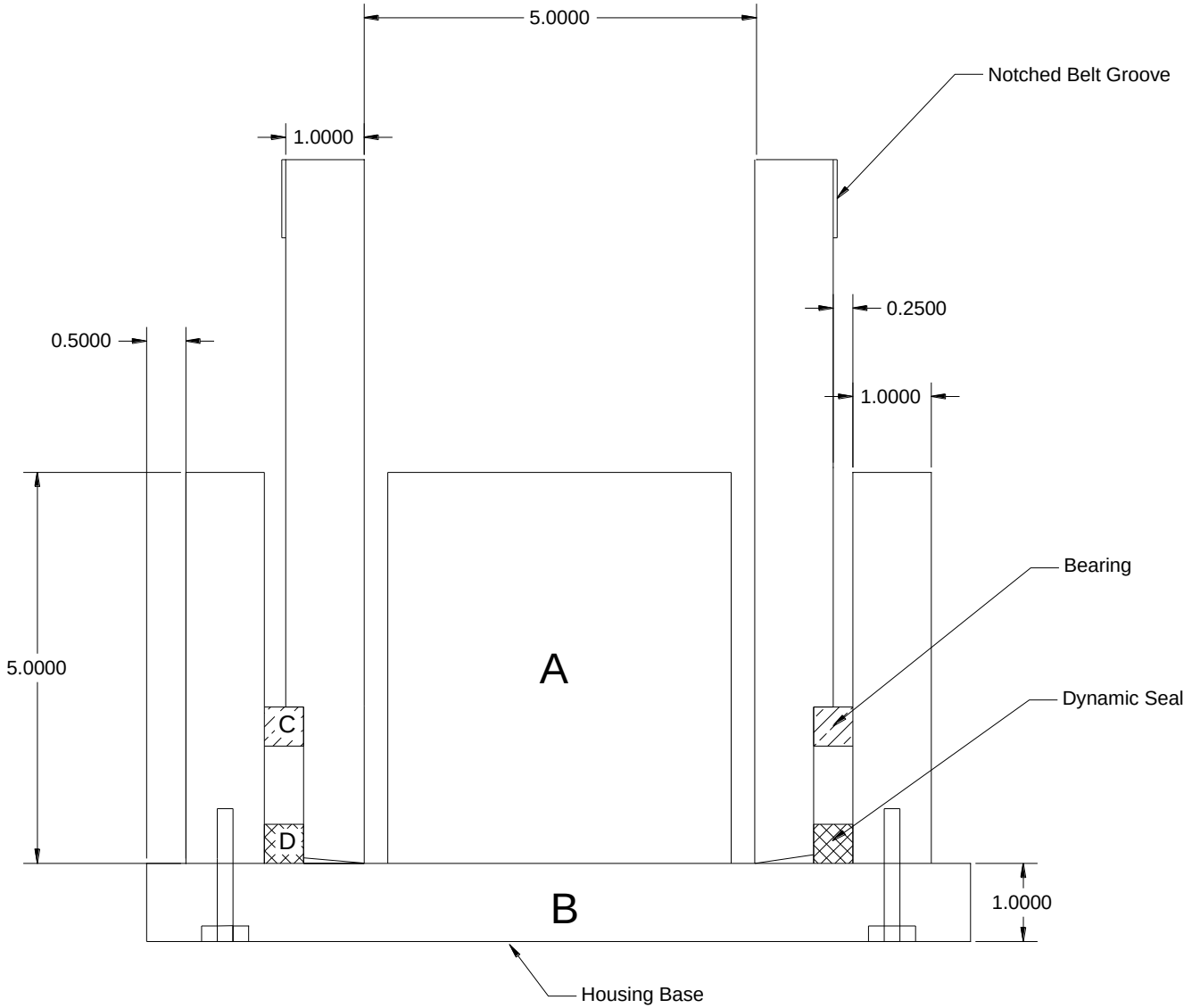


Figure 3.5 Schematic of the Couette apparatus.

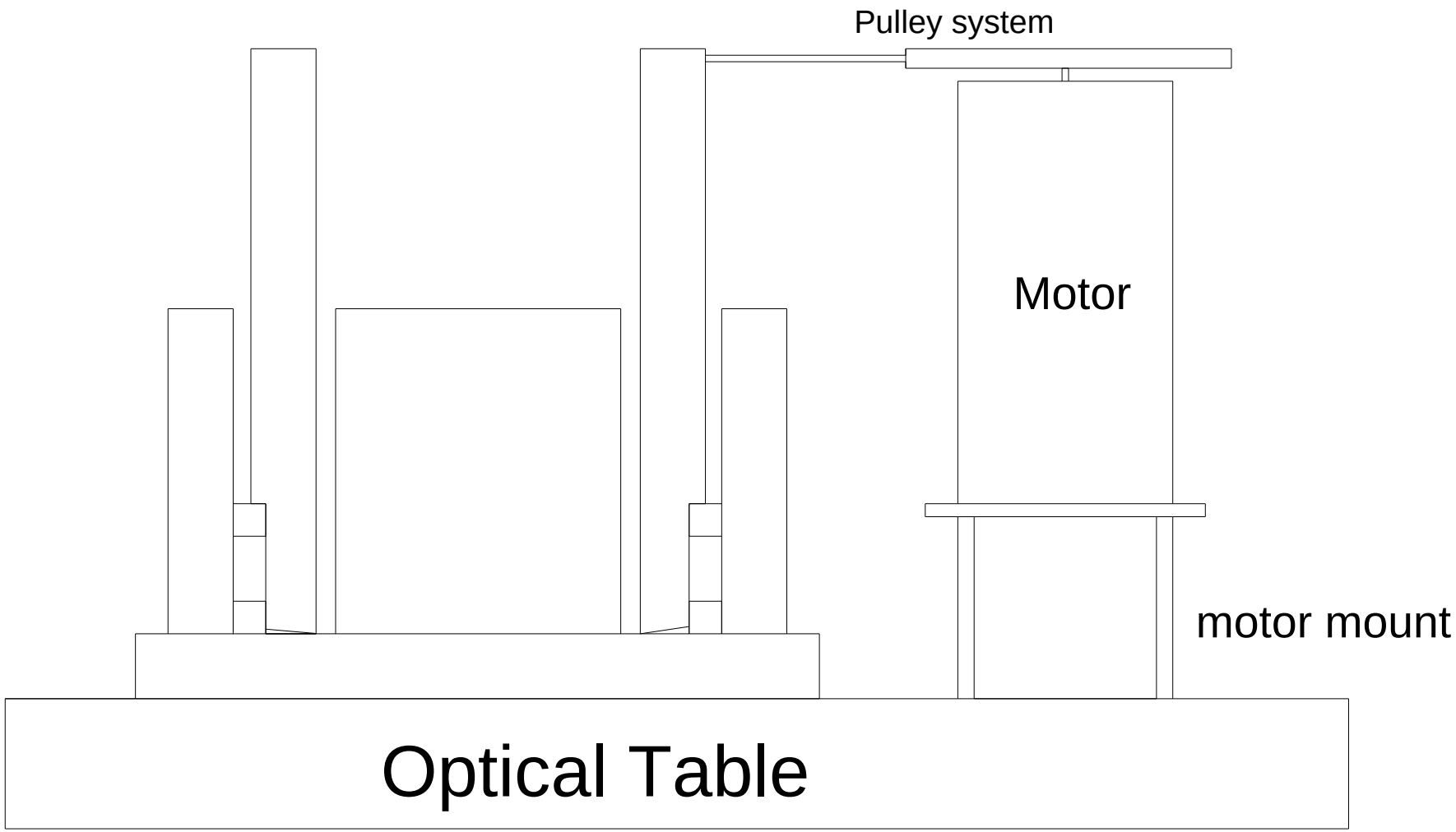


Figure 3.6 Schematic of the experimental set up.



Figure 3.7 Experimental set up on the optical table.

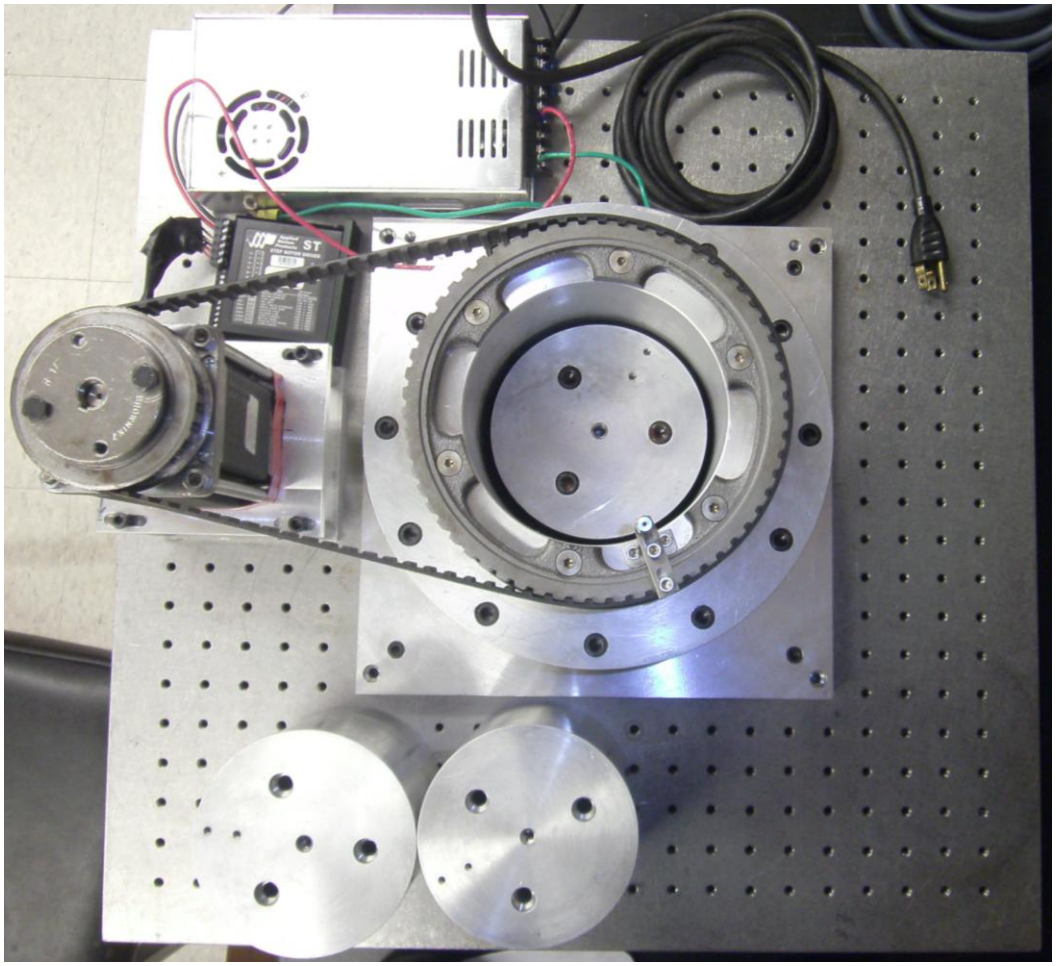


Figure 3.8 Top view of the experimental set up.

3.3.1.2 Stepper Motor

The motor is a NEMA 34 size motor (OMHT34-506) and has a 1260 oz-in holding torque. It was purchased from Omega Engineering. Additional parts, such as a step and direction drive controller that accepts serial commands from a computer (ST10-S) and a power supply (OMPS300A48, 48 VDC, 6.7A) for the drive/controller, were also purchased. The motor is controlled using Windows-based software. A command is sent from this software to the motor specifying different parameters such as the acceleration rate, deceleration rate, speed in r.p.s, start and stop commands. A pulley system is employed between the motor and the Couette flow apparatus. The movement of the pulley is aided by a notched belt, as shown in Figure 3.9 below.

3.3.1.3 Thermocouple

A thermocouple (TJ36-CPSS-020U-84-SMPW-M) with fitting, a data logger unit (OM-CP-TC4000) and a stainless steel shield (SS-116-6OPEN) were purchased from Omega Engineering. The thermocouple is a T-type (copper constantan) thermocouple with probe diameter of 0.02 inches, ungrounded junction type and 84 inches in length. The probe diameter is the property of the most significance because that signifies how fast the thermocouple can make readings. The smaller the probe diameter, the shorter the lag time between two separate measurements.

The data logger consists of a Windows software and 3.7 m (12') USB interface cable (OM-CP-IFC200) as shown in Figure 3.10 below.

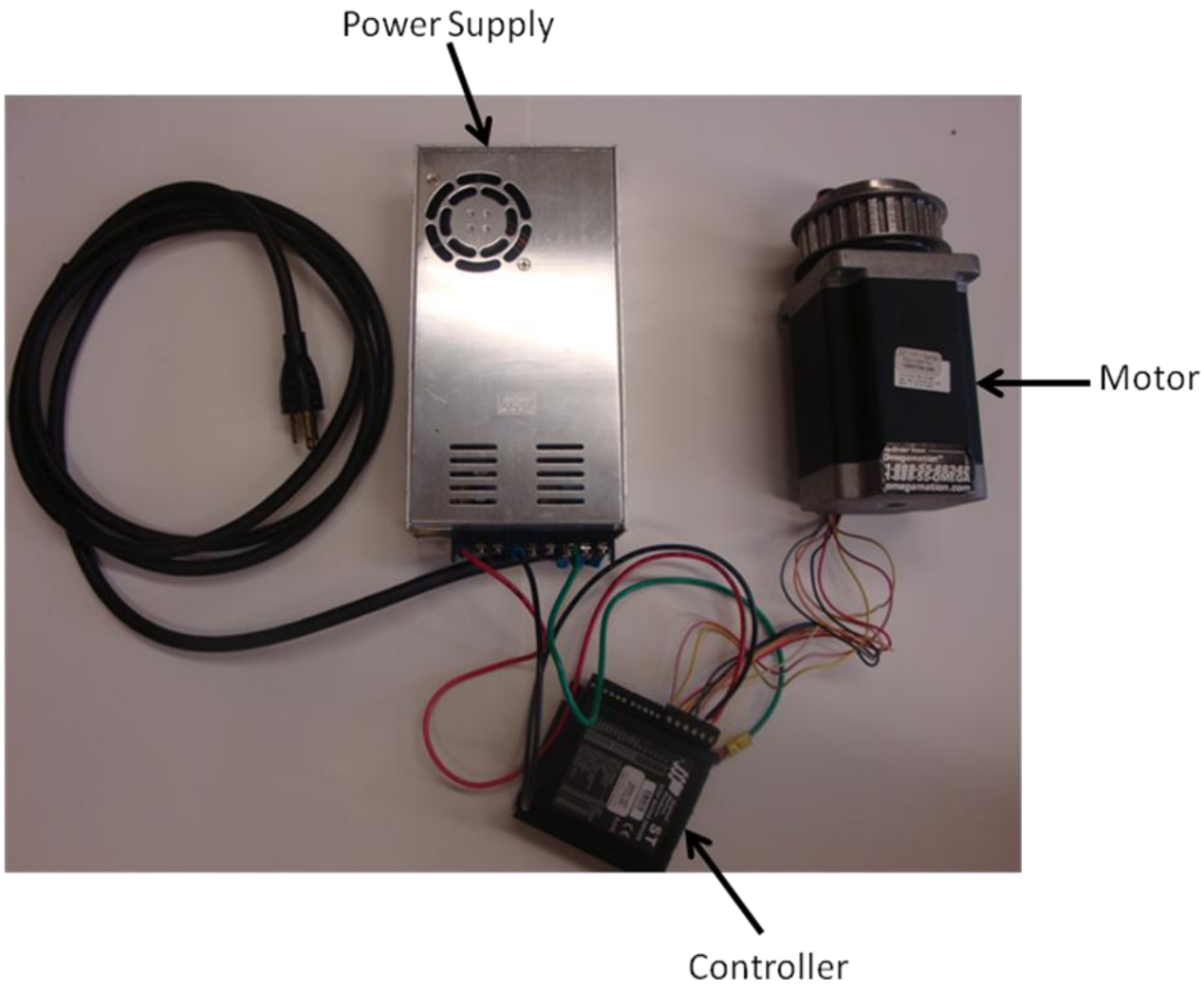


Figure 3.9 Stepper motor with the controller and power supply.

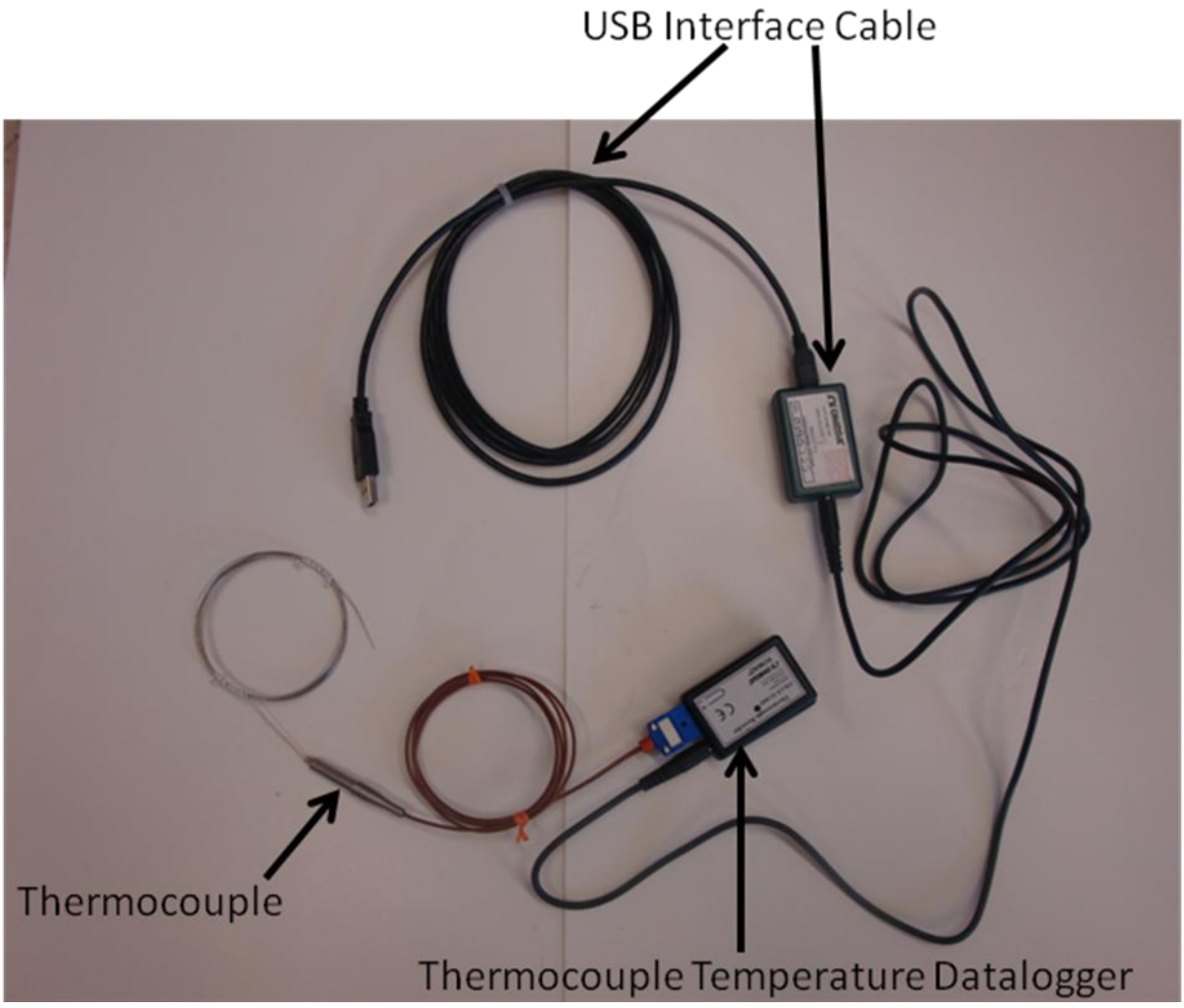


Figure 3.10 Thermocouple, data logger and connecting USB cable.

Chapter 4

Results

4.1 Rheology

To be able to properly study the non-isothermal effects of flow in polymeric fluids, the rheological characterization has to be performed as explained in Chapter 3 (Methodology of Experiments). Measurements were made to study the viscoelastic behaviors at steady (constant) and dynamic stresses. Results for the steady and dynamic stresses are presented in Figure 4.1 and 4.2 respectively for 1,000,000MW at 2%. Figure 4.1 displays the log-log plot of torque, first normal stress (N1), steady state viscosity (η), and stress (τ) vs. shear rate. Figure 4.2 provides the log-log plot of the dynamic viscosity (η^*), loss (G") and storage (G') moduli vs. frequency (ω). Steady-state shear-rate sweeps provide information about the shear and normal stresses. They also provide information about the steady state viscosity. The dynamic frequency sweep gives the G' and G'' values, which in turn provide information about the relaxation time. The inverse frequency of oscillation ($1/\omega_{crossover}$) of the "crossover point" gives the characteristic relaxation time λ. It also provides the dynamic viscosity. A regression was performed on the G' and G" lines to provide the crossover point presented in Figure 4.3. The relaxation time was calculated to be 1.78s. Regression calculation and details are provided in the appendix at the end of the chapter.

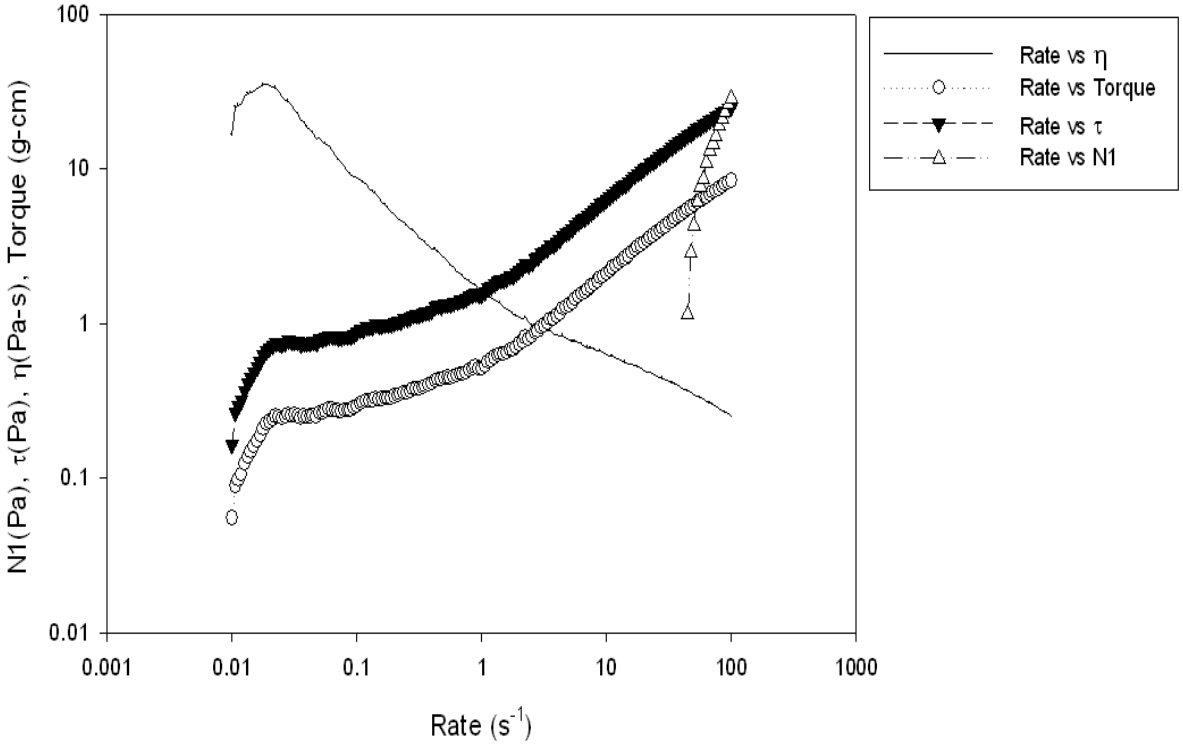


Figure 4.1 Steady state characterization.

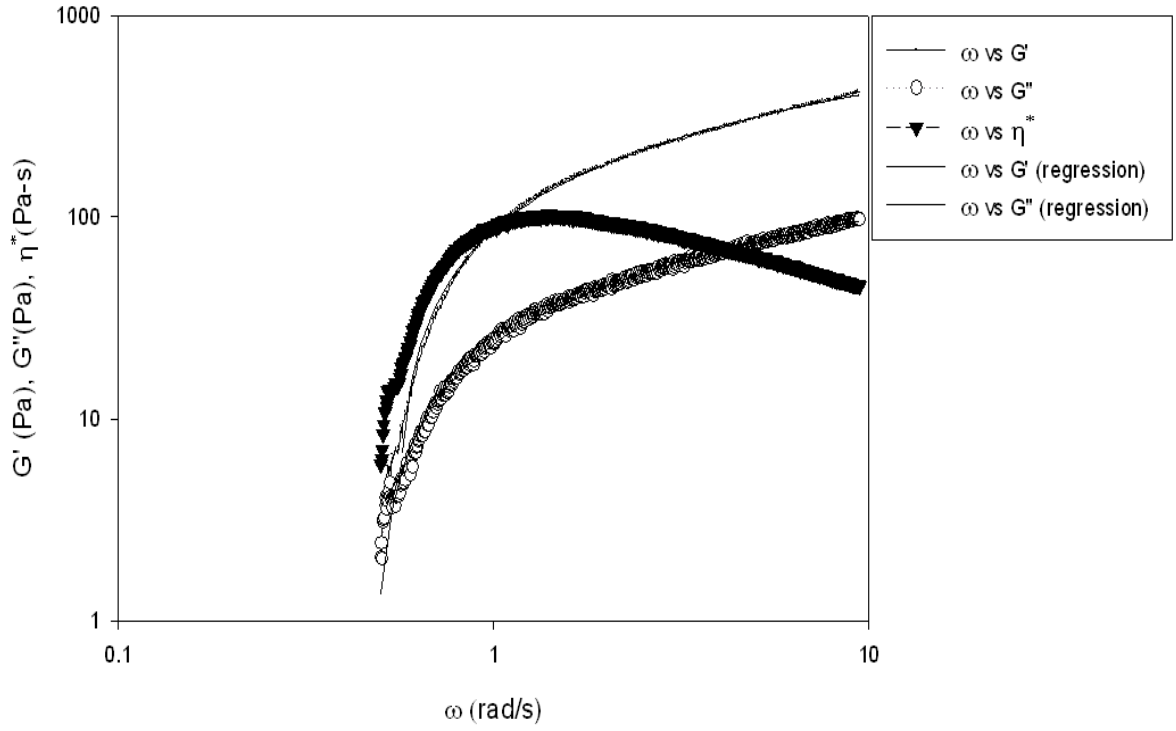


Figure 4.2 Dynamic state characterization.

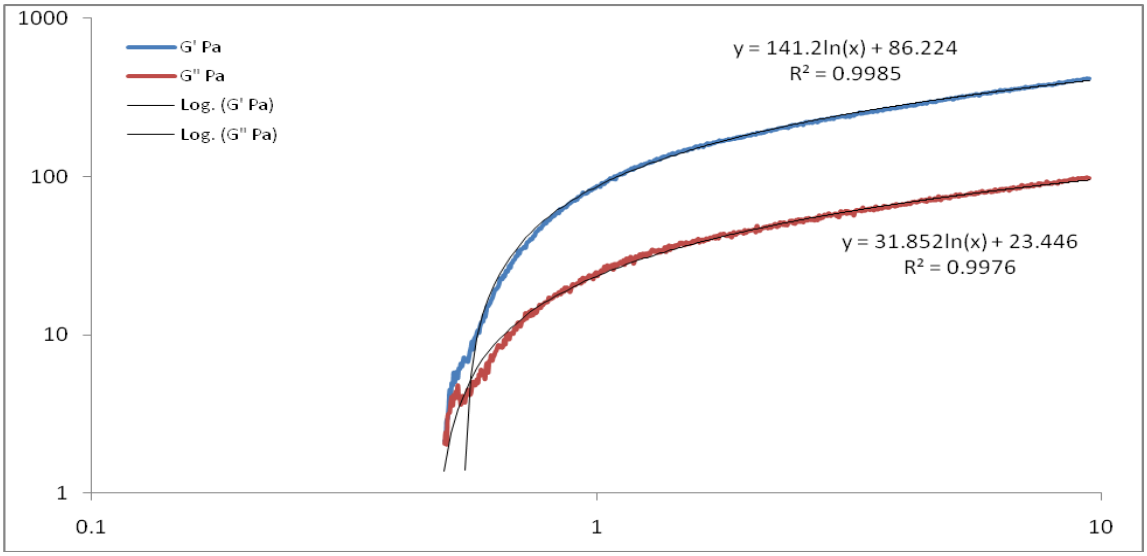


Figure 4.3 Regression analysis to provide G' G" crossover.

4.2 Temperature

Test of the Couette flow apparatus and other surrounding parts is the next step that has to be completed. Each individual part on its own was individually tested and worked excellently, but for the end result of the project to be achieved, they all have to work together in synchronization.

The first step was to check the set up in Figures 3.6 - 3.8, where the motor is connected to the Couette apparatus with the aid of a pulley system as shown in Figures 3.6 - 3.8. This step proved to be a success with the motor having enough torque to rotate the cylinder. The torque allows rotation of the cylinder up to 55 r.p.m. without any of the polymer solution in it. With varying levels on concentrations (see 3.1), the maximum speed that can be attained reduces as the viscosity of the solution increases. The necessary torque needed for the rotation of the device with the most viscous solution in it could not be achieved. Therefore a less viscous solution (5 wt. % 370,000 MW) was used to conduct the tests of the setup.

Once the motor was tested to work with the Couette apparatus, the next stage was to confirm that the thermocouple will work in the framework of the design. The first stage is putting the thermocouple into a stainless steel shield (to provide rigidity due to the thermocouple being thin). Once that was completed, it was placed into the Couette flow cell and held in place with the help of a stand as shown in Figure 3.8. The thermocouple was then connected to the data logger. The data logger was then connected to the computer with the aid of the USB cable as shown in Figure 3.10. The recording of temperature was then started. In this case, this was a measurement of polymer solution inside the Couette apparatus. The measurement is displayed below in Figure 4.4. The measurement was steady and within the tolerance value of $1^{o}F$ as specified by the Omega Engineering.

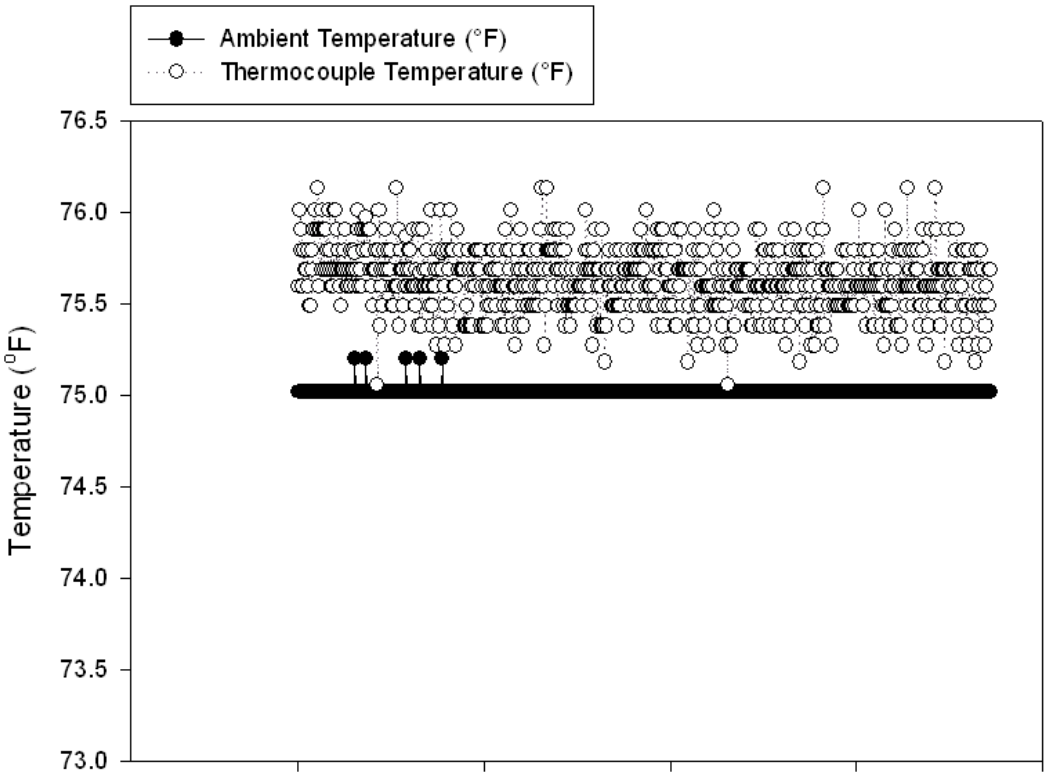


Figure 4.4 Temperature measurement with motor off.

The next stage was to test the thermocouple in the context of the design objective of trying to measuring the temperature of the polymer solution in which the outside cylinder of the Couette apparatus is being rotated by the motor. The motor was turned on and the rotation of the out cylinder commenced and the thermocouple readings was also started. The resulting temperature measurements are given below in Figure 4.5. Looking at the graph, it is evident that the measurement became far outside the tolerance level of 1^{o}F. According to Figure 4.5, we are measuring a temperature reading with a tolerance range of about 16^{o}F. So the question is why are we getting this kind of data? We then set out to find out the cause.

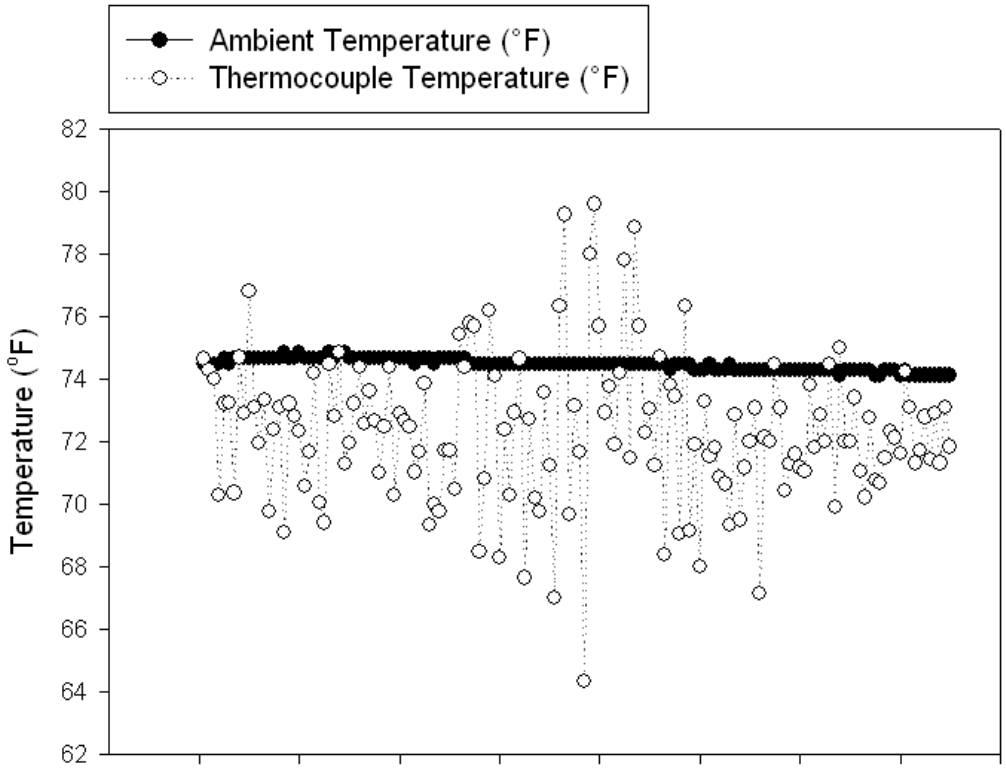


Figure 4.5 Temperature measurement with rotation of Couette flow cell.

The school of thought was that there has to be some kind of electromagnetic interference between the thermocouple and the motor. There was only one way to test this school of thought. We started the temperature measurement of the liquid with the motor turned off. After a couple of minutes measuring the temperature, we turn on the motor. At the point of turning on the motor, there is a noticeable change in the measurement and the thermocouple starts picking up electrical noise. This is shown in the Figure 4.5 below. As demonstrated in the graph, there is a stable measurement of the temperature of the polymer solution when the measurement is started. At the point the motor is turned on, electrical induced noise is observed in the measurements. After a few minutes, once the motor is turned off, we start getting stable and constant measurements of the solution temperature again. This confirms the school of thought of electromagnetic interference.

The next step was to try to figure out a way to separate the motor from interfering with the thermocouple. The constraint in this was that the motor had to be in close proximity to the Couette set up on the optical table (placed on the working bench) as shown in Figure 3.8. The methods tried included using a plastic tube shield (instead of the stainless steel), getting longer wires to connect from the power supply to the controller (as shown in Figure 3.9), wrapping all wires with electrical tape and placing electromagnetic obstructers (like aluminum foil and metal plates) between the motor and the Couette apparatus. None of these methods solved the interference problem that was observed in the process.

Contact was made with the manufacturers of the thermocouple to determine what was happening. The problem might possibly be solved using low band-pass filtering software to remove the noise from the signal. This will be pursued in future research.

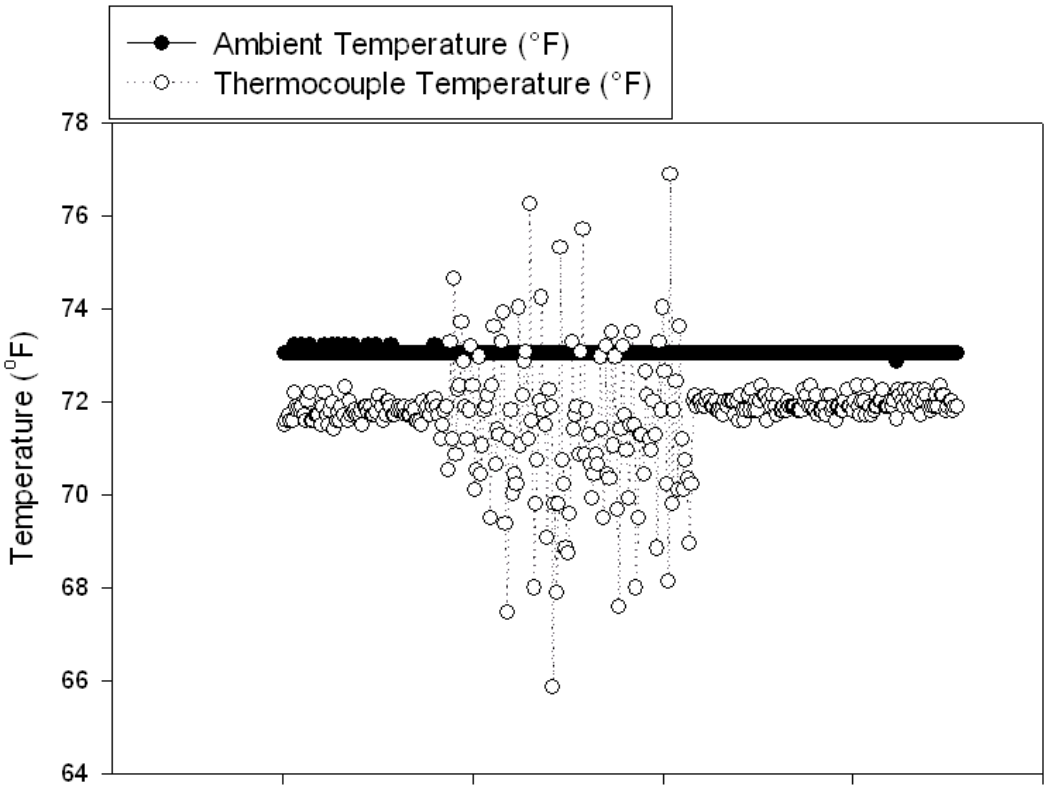


Figure 4.6 Temperature measurements to isolate source of electrical noise.

Chapter 5

Conclusion

5.1 Summary

The underlying theme of this thesis was to design the apparatus and setup all the corresponding components to study the non-isothermal flow of polymeric fluids. The research was divided into three parts. The first was to design of the Couette apparatus and the acquisition of the other components. The second was to understand the basic rheological properties of the polymer in use (hydroxypropyl cellulose). The third was to test the design and ensure that the set up was working as designed

The basic design objective was achieved although there are a few technical issues that need to be resolved moving forward. The Couette flow apparatus was designed and a maximum rotation of 55 r.p.m. was achieved with a 1260 oz-in holding torque motor. Rheological tests were conducted to obtain knowledge about the viscosity, torque, normal stress and, most importantly, the relaxation time of hydroxypropyl cellulose solutions, which was deduced and calculated to be 1.78s. Improvement of the setup is needed to attain the optimum level of operation and to completely achieve the overall goal of eventually being able to make temperature measurements in Eulerian and Lagrangian flows.

5.2 Future Direction

From the results in Chapter 4 and the summary above, future research should seek to understand more about the polymer rheology, improvement to the functionality and performance of the Couette apparatus, and the experimental set up in general.

As mentioned in the results, thermocouples are more susceptible to electrical noise so a method to reduce noise will be required. A Resistance Temperature Device (RTD) is another option to consider. They are less sensitive and more resistant to electrical noise than was the observation in the case of the thermocouples.

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APPENDIX

Appendix

G' Nonlinear Regression

Equation: Logarithm, 2 Parameter I
f = if(x>0, y0+a*ln(abs(x)), 0)

R	Rsqr	Adj Rsqr	Standard Error of Estimate
0.9992	0.9985	0.9985	4.721

	Coefficient	Std. Error	t	P
y0	86.2235	0.2529	340.8865	<0.0001
a	141.2022	0.2199	642.2601	<0.0001

Analysis of Variance:

	DF	SS	MS
Regression	2	33687113.5	16843556.75
Residual	637	14197.4747	22.288
Total	639	33701310.98	52740.7058

Corrected for the mean of the observations:

	DF	SS	MS	F	P
Regression	1	9193767.447	9193767.447	412497.9973	<0.0001
Residual	637	14197.4747	22.288		
Total	638	9207964.922	14432.5469		

Statistical Tests:

Normality Test (Shapiro-Wilk)
Failed (P = <0.0001)
W Statistic= 0.9616 Significance Level = 0.0500

Constant Variance Test
Failed (P = <0.0001)
Fit Equation Description:

```
[Variables]
x = col(1)
y = col(2)
reciprocal_y = 1/abs(y)
reciprocal_ysquare = 1/y^2
reciprocal_pred = 1/abs(f)
reciprocal_predsqr = 1/f^2
'Automatic Initial Parameter Estimate Functions
F(q) = ape(ln(abs(x)),y,1,0,1)
[Parameters]
y0 = F(0)[1] "Auto {{previous: 86.2235}}
a = F(0)[2] "Auto {{previous: 141.202}}
[Equation]
f = if(x>0, y0+a*ln(abs(x)), 0)
fit f to y
"fit f to y with weight reciprocal_pred
"fit f to y with weight reciprocal_predsqr
"fit f to y with weight reciprocal_y
"fit f to y with weight reciprocal_ysquare
[Constraints]
[Options]
tolerance=0.0000000001
stepsize=1
iterations=200

Number of Iterations Performed = 1
```

G" Nonlinear Regression

Equation: Logarithm, 2 Parameter I
f = if(x>0, y0+a*ln(abs(x)), 0)

R	Rsqr	Adj Rsqr	Standard Error of Estimate
0.9988	0.9976	0.9976	1.3374

	Coefficient	Std. Error	t	P
y0	23.446	0.0717	327.2181	<0.0001
a	31.8525	0.0623	511.4428	<0.0001

Analysis of Variance:

	DF	SS	MS
Regression	2	1949947.998	974973.999
Residual	637	1139.3104	1.7886
Total	639	1951087.309	3053.3448

Corrected for the mean of the observations:

	DF	SS	MS	F	P
Regression	1	467839.2715	467839.2715	261573.6904	<0.0001
Residual	637	1139.3104	1.7886		
Total	638	468978.5818	735.0761		

Statistical Tests:

Normality Test (Shapiro-Wilk)
Passed (P = 0.0516)
W Statistic= 0.9953 Significance Level = 0.0500

Constant Variance Test
Failed (P = <0.0001)

Fit Equation Description:

[Variables]
x = col(1)
y = col(3)
reciprocal_y = 1/abs(y)
reciprocal_ysquare = 1/y^2
reciprocal_pred = 1/abs(f)
reciprocal_predsqr = 1/f^2
'Automatic Initial Parameter Estimate Functions
F(q) = ape(ln(abs(x)),y,1,0,1)
[Parameters]
y0 = F(0)[1] "Auto {{previous: 23.446}}
a = F(0)[2] "Auto {{previous: 31.8525}}
[Equation]
f = if(x>0, y0+a*ln(abs(x)), 0)
fit f to y
"fit f to y with weight reciprocal_pred
"fit f to y with weight reciprocal_predsqr
"fit f to y with weight reciprocal_y
"fit f to y with weight reciprocal_ysquare
[Constraints]
[Options]
tolerance=0.0000000001
stepsize=1
iterations=200

Number of Iterations Performed = 1

VITA

Opeoluwa Oluwaseun Kolawole was born in Lagos, Nigeria on March 9, 1987. He attended high school at Adesoye College Offa, from which he graduated in 2003. From there, he attended the University of Tennessee as an undergraduate where he received a Bachelor of Science in Chemical Engineering. In August, 2008, he joined the graduate school at the University of Tennessee. In May 2011, after years of hard work and much struggle, he will receive his Master of Science degree in Chemical Engineering with a focus in thermodynamics of polymers.