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Effect of liquid rheology on jetting of polymer solutions

Long Han
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EFFECT OF LIQUID RHEOLOGY ON JETTING OF POLYMER SOLUTIONS

by

Long Han

**Dissertation submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
in
Chemical Engineering**

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**Morgantown, West Virginia
2005**

**Keywords: rheology, extensional viscosity, conjugated polymers, jetting, polystyrene,
DECALIN**

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ABSTRACT

EFFECT OF LIQUID RHEOLOGY ON JETTING OF POLYMER SOLUTIONS

by Long Han

Light Emitting Devices (LEDs) containing conjugated polymers are fabricated using ink-jet printing. A common problem in the processing of these materials is that the Newtonian viscosity of the polymer solution is not sufficient to describe the jetting performance, because the molecular weights and concentrations employed are such that the resulting solutions are elastic. These differences in fluid elasticity levels cannot be measured using traditional techniques like dynamic mechanical experiments or the first normal stress difference in shear, but they strongly impact the jetting behavior of the liquid. Here, a polystyrene-DECALIN system has been formulated, and the level of elasticity has been varied by varying the polymer concentration, molecular weight and molecular weight distribution. Although the shear viscosity of these solutions was as low as 3 mPa-s, elasticity levels (as quantified by the Trouton ratio) and differences in elasticity levels could be determined by making extensional viscosity measurements. The measurements themselves were made using a modified version of the extensional viscometer introduced by Agarwal and Gupta in 2002.

The jetting behavior of these liquids was examined with the help of two jetting set-ups, one located at the DuPont Experimental Station and the other that was locally-fabricated; both could supply a liquid drop on demand. It was found that a liquid with a high Trouton Ratio (higher molecular weight, higher concentration, use of a polydisperse polymer) was more likely to form a long tail and would be difficult to detach from the jet port; contrarily, a liquid with a low Trouton Ratio (a Newtonian liquid or one containing a low molecular weight polymer or a low concentration of monodisperse polymer) is more likely to form a short tail, give satellite drops and detach cleanly from the jet port. To obtain ideal jetting behavior, therefore, one needs a solution with a Trouton Ratio or fluid elasticity level that is high enough that satellite drops are not formed but is low enough that the drop separates easily and cleanly from the jet port.

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LIST OF SYMBOLS / NOMENCLATURE

Latin

A	Area (m^2)
A_0, A_1	Cross section area at different positions (m^2)
d	Diameter (m)
E	Rate of strain tensor (1/s)
d	Gap (m)
D	Diameter (m)
D_0	Initial diameter (m)
De	Deborah number (-)
F	Force (N)
F(G)	Gravity force (N)
F(I)	Inertia force (N)
F(ST)	Force due to surface tension (N)
g	Gravity constant (9.8 m/s^2)
Δh	"Altitude" difference (m)
I_1, I_2	Modified Bessel functions of the first kind (-)
k	Wave number (-)
l	Length (m)
L	Length (m)
L_1, L_2	Length (m)
L_0	Initial length (m)
m	Mass of liquid drop (kg), or consistency index (-)
n	Power law index (-)
n_{ref}	Refractive index of the film (-)
P	Pressure (Pa)
ΔP	Pressure difference (Pa)
P_0, P_1	Pressure drop (Pa)
$P_{11}-P_{22}$	Tensile stress (Pa)
Q	Volume flow rate (m^3/s)
Q_0, Q_1	Volume flow rate (m^3/s)
r	Radius (m)
r_0, r_1	Radius at different positions (m)
r_0	Jet radius (m)
R	Radius (m)
R_0	Initial radius (m)
Re	Reynolds number (-)
t	Time (s)
t_1, t_2	Drainage time with and without stretching (s)
T_1	Tensile stress (N/m^2)
u	Velocity field (m/s)
v	Velocity (m/s)
v_0, v_1	Velocity at different positions (m/s)
V	Volume (m^3), or Velocity (m/s)
W	Vorticity tensor (1/s)
We	Weber number (-)
x	Position (m)
x_0, x_1	Different positions (m)

Greek

$\dot{\epsilon}$	Extensional or stretching rate (1/s)
γ	Surface tension coefficient (mN/m)
$\dot{\gamma}$	Shear rate (1/s)
η	Fluid viscosity (Pa.s)
η_E	Extensional, or “tensile” viscosity (Pa.s)
η_{ext}	Extensional, or “tensile” viscosity (Pa.s)
λ	Wavelength of laser beam (m)
μ	viscosity (Pa.s)
θ	Angle between flow stream line and vertical line (-)
ρ	Density (kg/m ³)
σ	Coefficient of surface tension (mN/m)
σ_E	Extensional, or “tensile” stress (N/m ²)
σ_{11}, σ_{22}	Stress applied (N/m ²)
τ	Fluid characteristic relaxation time (s)

1 Introduction

1.1 Background for electroluminescence and light emitting polymers

When electrons and holes are electrically introduced into a luminescent semiconductor, they radiatively combine with each other to emit light. This phenomenon is called electroluminescence (EL). Inorganic semiconductors like GaAs and In-GaAs are used to build traditional EL devices. In 1962, the first GaAsP light-emitting diodes (LEDs) were released to market (Sheats et al., 1996). At about the same time, electroluminescence was observed in single crystal anthracene and in single crystal anthracene with approximately 0.1mol % tetracene (Pope et al., 1963). This was the first time that electroluminescence was examined using an organic material.

In the late 1970s, the first conjugated polymer, trans-polyacetylene – $(CH)_x$, was discovered (MacDiarmid et al., 1997). It could be *chemically* p-doped (partly oxidized) or n-doped (partly reduced) and at the same time its conductivity could be raised to surpass semiconductors and display similar properties as metals. This discovery resulted in the inventors, A.J. Heeger, A.G. MacDiarmid, and H. Shirakawa, getting the Nobel Prize in chemistry in 2000. Owing to their high conductivity, these conjugated polymers are sometimes called “synthetic metals”. It is not surprising that in both industry and academic areas, researchers have been attracted by the amazing electrochemical properties of conjugated polymers. Many potential technological applications have been brought forward, including electrochemical drug-delivery systems, rechargeable batteries, and light-emitting devices. The light-emitting devices are used in applications from low information content segmented displays like score logos in stadiums to full color video and graphics displays like flat screen liquid crystal displays. Table 1-1 illustrates some features and potential benefits of light emitting polymer (LEP) technology.

In 1987, Tang and Van Slyke at Eastman Kodak made an important breakthrough on electroluminescence. By using multilayers of sublimated organic molecules, they efficiently reduced the operating voltage of the organic EL devices and significantly raised the quantum efficiency. This discovery stimulated research around the world, especially in Japan and at the Kodak company in the US, to further increase the device lifetime and efficiency to meet commercial requirement. In 1990, Burroughes et al. at Cambridge University made another important discovery. By using a diode made from luminescent conjugated polymers, they observed EL successfully (Yang, 1997). Low weight, flexibility, ease of processing, and unique electrical and photonic semiconducting properties are among the most attractive features of these conjugated polymers.

Development of applications of organic electroluminescent devices (OLED's) has been very rapid since the appearance of research publications from Kodak and the Cambridge University group. Polymer EL devices with efficiencies up to 18 Lumens/Watt and lifetimes in excess of 10,000 hours have been made. Figure 1-1 shows the progress in LED efficiency. Lifetime is typically defined as the time for luminance to decay to 50% of its initial value (Sheat and Roitman, 1998) and efficiency is defined as the ratio of the output (luminous flux, unit:lumen) to the input (power, unit:W) in the LED system. The progress on increasing the efficiency of LEDs is illustrated in Figure 1-1, which includes the data for both *dye* sublimation OLED's (D-OLED's) as well as *polymer*-based OLED's (P-OLED's). There are two main manufacturing processes: dye sublimation was utilized to deposit the organic films on substrates by the Kodak group, while spin coating of conjugated polymer solutions onto the substrates was used by the Cambridge University group to construct their devices (Roitman, 1998). Although efficiency, drive voltage, and color selection had attained adequate levels for commercialization soon after the introduction of organic LEDs, device lifetimes were far from adequate; most applications require the device operating lifetime to be more than 20,000 hours. Significant research is being carried out to improve material lifetimes either by use of materials that are resistant to oxidation or through improved encapsulation.

Table 1-1 Features and potential benefits of LEP technology (CDT, 2001)

Features	Benefit
Processability	Flexible substrates possible Large area coating Simple construction Single substrate processing
Light Emitting/Optical	No Backlight No Color filter No polarizers High contrast No aperture loss 180 degree viewing angle
Patternable	Define complex light emission patterns simply Very high resolution potential Any pixel shape and size possible
Low Voltage	Battery driven devices DC drive <5V activation No high voltage
Formable Substrates	Innovative designs for end products Displays shaped to product Easy manufacturing integration Continuous coating for manufacture
Fast Switching Speed	Video display capability Unaffected by temperature

Lightweight	Portability Ultra thin materials Potential System-on-Glass structures
Solid State Devices	Ruggedness No open cell No vacuum
Thin Films	Allows use of polarisers to give high contrast Ultra thin construction Potential plastic substrates

Figure 1-1 Progress in LED efficiency (Roitman et al., 1998)

1.2 Conjugated polymers, working principle and fabrication of LED

Conjugated polymers are commonly known as “synthetic metals”. They are new class materials which not only retain the original advantages of conventional polymers, such as processability and mechanical properties, but also add some new amazing properties of electronic conductivity. In other words, these new materials possess the strong points of both conventional polymers and metals.

Conjugated polymers are made by the method of “doping”. The π bonds in the backbone of an organic polymer are partially oxidized (p-doping) or partially reduced (n-doping) during the “doping” process. This gives them a dramatic change of conduction properties; the doped polymers change from being insulators or semiconductors (small conductivity), in the range of 10^{-10} to 10^{-5} S/cm, to the metal-like conductors with a conductivity of 1 to 10^4 S/cm (MacDiarmid and Epstein, 1991). Many polymers have been used to synthesize the conjugated analogs, such as poly(phenylene vinylene), polythiophene, and poly (p-phenylene) (Yang, 1997). Figure 1-2 shows some of the typical conjugated polymers.

A typical polymer LED is often made by sandwiching a layer of one of the light emitting conjugated polymers between a pair of electrodes (Yang, 1997). The electrodes can be a pair of thin films or orthogonal strips (“wells”). One or both electrodes need to be transparent to let the light generated to pass through it for display. The anode and the cathode need to be biased positively with respect to each other. When electrons and holes are injected into the polymer, electron exchange reactions happen as they meet together during movement in the electric field. The result is an emissive excited state generated when the electrons and holes recombine. The emitted light passes through the transparent electrode to be seen by an observer. The total polymer film thickness is around 100-150 nm, and the voltage bias is between 2 and 20 V. The transparent electrode is usually chosen to be indium-tin oxide (ITO) as anode, though very thin Au film also works. The materials normally chosen as cathode are Ca, Mg, and Al or Al:Li alloys. To form the excitation

status, the work functions of the electrodes must correspond fairly closely to the energy levels of the polymer (refer to Figure 1-3).

Figure 1-2 Structures of some typical conjugated polymers (Yang, 1997)

A normal fabrication process begins with a routine cleaning procedure and followed by ultraviolet (UV) ozone treatment of the patterning ITO-coated glass substrates. The routine cleaning procedure involves substrate sonication in detergent followed by repeated rinsing in deionized water, acetone and isopropanol (Shi et al., 2000). Any contamination and tiny particles on the surface of the substrate are removed during the cleaning procedure. The polymer film is coated onto the ITO-coated glass substrate by one of several film formation methods, such as ink-jet printing and spin coating. Details related to these methods are

discussed in the following section. This procedure can be used to make a device for many applications, even to fabricate large-area display devices. Above the polymer film, the top metal cathode is deposited by standard deposition technique in an ultra-high-vacuum environment (Yang, 1997). Figure 1-3 shows a typical polymer light-emitting-diode (LED) configuration with ITO as anode, Ca as Cathode and MEH-PPV as the polymer interlayer.

Figure 1-3 Typical polymer light-emitting-diode (LED) configuration (Left) and the corresponding energy-band diagram (Right) (Yang, 1997)

1.3 Polymer film fabrication

There are many ways to form a conjugated polymer film onto a substrate even when controlling the polymer film thickness (100~150 nm) is very important. For liquid crystal display applications, polymer film thickness and thickness uniformity are two most important factors. Optimization of the film thickness can simultaneously maximize the transmittance and minimize the resistance (MacDiarmid et al., 1996; MacDiarmid and Epstein, 1997); in this way satisfactory devices can be obtained.

The film can be formed by evaporation after coating; coating techniques include spray coating, dip coating, spin coating, and the new method of ink-jet printing.

For evaporation, the substrate is covered by conjugated polymer solution; evaporation removes the solvent and forms a polymer film. During the spray coating process, fluid is atomized into tiny droplets and propelled onto the substrate. In dip coating, the entire substrate is immersed into the conjugated polymer solution, and then it is removed from solution under controlled speed. With all these methods, uniform film thickness cannot be obtained. Repeatability becomes a problem, which prevents use of these techniques for mass fabrication. It is often noticed that the luminescence spectra, both photoluminescence and electroluminescence, of polymer films are somewhat different when the film thickness varies (Shi et al., 2000). For use in flat screen liquid crystal display, it is necessary to optimize the thickness of the deposited polymer so as to simultaneously obtain the maximum transmittance and minimum resistance necessary for satisfactory devices (MacDiarmid et al., 1997).

Spin coating has been the most commonly used method to form polymer thin films. A typical process is as follows (refer to Figure 1-4): A small amount of conjugated polymer solution is dispensed onto the substrate. Then the substrate is forced to spin at high speed, which can be as high as several thousand rpm. Most of the solution is thrown off the substrate at the beginning of the rotation. Then the formed polymer film is further thinned by a combination of evaporation of solvent and convective outflow. Residual solvent can be removed by drying in an oven. By spin coating, a polymer film of uniform thickness can be formed. However, there are some disadvantages which cannot be avoided by this method. These disadvantages include the waste of most of the very expensive polymer solution and lack of flexibility in color selection (this technique is limited to a single polymer film, which can only emit one specific color). These disadvantages have limited its commercial application in polymer electronic devices.

Figure 1-4 Spin-coating process (Jenekhe, 1987)

To overcome the drawback of the method of spin coating, ink-jet printing (IJP) was invented for applications in polymer electronic devices, such as flat panel displays. IJP technology employs an ink-jet printer with ink of conjugated polymer solution to print polymer light-emitting diodes with high resolution. With this method, the process can be very efficient, and there is no wastage of expensive polymer solution and large areas can be coated (Yang and Bharathan, 1998). The polymer light-emitting logo fabrication process is a typical application of the IJP technology. The fabrication procedure is illustrated in Figure 1-5. First, glass/ITO substrates are subjected to a series of cleaning steps to remove any surface contaminants. Substrates are then baked at an elevated temperature for a period of time. By use of a commercial available ink-jet printer, the conducting polymer logo is printed into desired pattern above the precleaned substrate. The luminescent polymer layer and cathode layer (Ca) are then deposited onto the patterned substrate by use of spin-

coating. The finished devices are encapsulated by epoxying the active device area with a cover glass.

Figure 1-5 The polymer light-emitting logo fabrication process. (a) preparation of substrate; (b) printing of the conducting polymer into desired pattern; (c) deposition of the luminescent polymer and the cathode material (Yang and Bharathan, 1998).

For better understanding the advantage of this method, Table 1-2 gives some comparison between spin-coating and ink-jet printing technologies. The multicolor patterning capability enables one to use IJP technology to manufacture LED with the display of multicolor and patterned design.

Table 1-2 Comparison of spin-coating and ink-jet printing technologies (Yang and Bharathan, 1998)

Characteristics	Spin-coating	Ink-jet printing
Patterning capability	No patterning capability	Capable of patterning with micrometer resolution
Large device area capability	Sensitive to dust particles and substrate defects, and not suitable for large area processing	IJP is not sensitive to substrate defects, and it is a better technology for the fabrication of large area device
Efficiency of using material	More than 99% of the polymer solution is wasted	Only less than 2% of the material is wasted
Multi-color display fabrication capability	No multicolor patterning capability	Ideal for multicolor patterning

1.4 Rheological properties and jetting behavior of commercial polymer solutions

During the coating process, several important factors such as coating condition (nozzle geometry and jetting parameter setting for coating using ink-jet printing technique) and polymer solution properties play important roles in optimization of the device performance of the polymer LEDs.

Of all the factors, the effect of the rheological properties of commercial polymer solutions on jetting and coating uniformity is a major unknown at present. For these polymer solutions, there are some common properties. First of all, they are extremely

expensive liquids. Owing to this characteristic, ink-jet printing technology is the obvious choice for the coating process.

It is found that commercial liquids normally have a low shear viscosity of 3~5 cp, and constant viscosity over a large shear rate range, which is Newtonian liquid-like behavior. As for the dynamic response in shear, these liquids have very small storage modulus, which means they have low elasticity. Although commercial liquids all have these common shear and dynamic responses, their jetting behavior can show surprising differences. Thus, we need other methods to characterize fluid properties. To understand and explain these differences, extensional viscosity has become our method of choice and is the focus for studying these phenomena.

Next, let us get some basic understanding of the jetting behavior of these conjugated polymer liquids. The following Figure 1-6 contrasts the ideal with the undesirable behavior of the polymer liquid during the jetting process. The liquid drop leaves the jetting nozzle from the top of the figure and moves to the bottom. We can see that there is only one spherical drop and no satellites formed in the photo on the left, while several satellites are formed in the photo on the right. We can easily imagine that these satellites will adversely affect the quality of the coating, and diminish the performance of the polymer LED devices.

In summary, a spherical drop and no satellites (left photo of Figure 1-6) are ideal behavior; a non-spherical drop, tail-formation and satellite drops (right photo of Figure 1-6) are undesirable behavior. Liquid drop behavior is related to the fluid rheology.

Figure 1-6 Typical jetting behaviors of polymer liquids: ideal behavior (left photo); undesirable behavior (right photo).

1.5 Problems and objectives

According to the previous introduction, two main problems need to be solved. The first problem is how to characterize the conjugated polymer fluids having the same shearing properties but different jetting performances. The proposed method has to take into account the unique issue related to low viscosities and availability of small quantities (high cost) of polymer liquids; this problem makes any measurement more difficult. The second problem is to identify fluid rheology and process conditions that result in desirable jetting behavior.

The objective of our research is to define a procedure to characterize fluid rheology and use this to optimize the jetting stability such that there is no tailing/satellite drops formation. Noted that tailing means that liquid drops are still connected to the nozzle by a string after jetting and satellite drops are the undesirable additional drops formed (besides the main drop) during the jetting. It is also desired to have uniform and accurate thickness of the deposited polymer film.

To fulfill this objective, we have used our newly modified extensional viscometer to measure the extensional viscosity of polymer liquids to characterize their properties, and to observe and study how the polymer liquid rheological properties affect their jetting behavior.

2 Literature Review

2.1 Film coating and laser interferometry

Spin coating, a technique of coating of thin film onto substrates, has been developed for many years. This technique is used to deposit a thin uniform film onto a substrate for various applications, including those involving paint, varnish and asphalt (Borkar et al., 1994). Some current applications include (i) coating of monitor screens and optical devices, (ii) deposition of magnetic dispersions on aluminum substrates for the production of magnetic memory devices, (iii) depositing of photoresist films for microlithography, and (iv) spin-on glass for interlevel dielectric planarization (Peurrung and Graves, 1993).

Let us use the spin-coating process (refer to Figure 1-4) as a typical coating process and see what happens during the process. Normally silicon wafers or some other material are used as the substrate. Each wafer undergoes a series of cleaning processes as a clean wafer surface is necessary for defect-free films and good adhesion between substrate and film. When preparing the polymer solution, some amount of adhesion promoter is usually added. The adhesion promoter prevents retraction of the polymer film after spinning, but it adds only negligible thickness to the final film (Borkar et al., 1994).

After polymer solution and substrate have been prepared, the spin coating process can begin. First, a small amount of the polymer solution is dispensed onto the center of the stationary substrate, or on one rotating at a low speed. Next, the spinner is accelerated to the final process speed (2000~6000 rpm) in very short time (0.5~1.5s). Most of the solution is thrown off the substrate almost instantly. The spinner keeps rotating at the final process speed for some time (one minute is a normal value). During this period, the polymer film further thins due to the combined effects of convective outflow and solvent evaporation. With the loss of the solvent inside the solution, the viscosity of solution can greatly increase and this will hold back the flow along the radial direction of the substrate disk. Solvent will keep evaporating until the disk stops rotating.

Subsequent to the spinning step, a common procedure is followed to further remove the remaining solvent. The coated disk is placed inside an oven with substrate kept horizontally. The temperature is usually about 80~85°C inside the oven. The solution is placed there for about 15 minutes in a nitrogen atmosphere before removing it from there to get the final film. This step is normally referred as “soft baking” (Borkar et al., 1994).

During the coating process, uneven film surfaces have been a normal problem. It is reported that during the spin-coating process, the initial uneven film surface does flatten and flow becomes asymptotically uniform along the radius for Newtonian liquids; however for non-Newtonian liquids with complex rheological properties (or liquid of Bingham type), no constant thickness film can be formed along the radius (Alekseev et al., 2001). This is a consequence of fluid elasticity, which can make significant changes to the fluid velocity profile from the Newtonian, affecting the film thickness uniformity. Moreover, the fluid can be lifted from the surface of the substrate by increased lifting force by normal stress (Jenekhe, 1983). This problem leads to many defects. For example, an uneven surface for interlevel dielectric films may lead to line width variation in the interconnects deposited on top of it. Note that a planar surface helps in preventing depth of focus and registration problems in wafer alignment during lithography (Manske and Graves, 1990). Therefore, controlling film thickness and uniformity in the order of a micron are most important issues during the coating process.

Spin coating also leads to tremendous changes in the properties of the polymer solutions. Mass transfer and transient fluid flow that occur lead to drastic changes of fluid viscosity and solvent-solute diffusivity during the process. Moreover, surface tension and surface tension gradients have also been the driving force of the mass flow and transport. It is very common that some “skin” forms at the surface of the film due to the rapid loss of the solvent near the surface (Manske and Graves, 1990).

The final film thickness is affected by many factors. These factors can be divided into two categories. One group of factors is related to the processing conditions. The other group of factors is related to the fluid properties.

These operation conditions include the nozzle dispense height, volume of liquid dispensed, acceleration of spinning disk, spinning speed, spin time and nozzle dispense offset from substrate center (Krishna et al., 1998); these conditions can be adjusted to find the optimum situation.

The other group of factors is related to the fluid properties. The final film thickness has been related to the following parameters: Polymer concentration in solution, fluid viscosity related to the rheology of polymer solution, solvent mass transfer (mass transfer rate inside the solution and evaporation rate), surface and interfacial phenomena and heat transfer and the interplay of these effects (Jenekhe, 1987). It is reported that many photoresist materials have suppressed the problem caused by surface tension effects with the addition of surface leveling agents. It seems that all the experimental facts are related to one or another aspect of the rheological properties of the polymer solution. For example, by changing the rheological properties of the polymer solution, the solvent evaporation effects can be changed (Jenekhe, 1983).

Many different types of mathematical models have been constructed to describe the spin coating process. It is necessary to compare the calculation results with the film thickness profile. Profilometry has been the common method to determine the dry film thickness after “soft baking”. Stylus profilometer was used to measure the film thickness. Before making a measurement, a reference point was chosen by using a sharp blade to scratch off a corner of dry film which is near to the measuring point (Borkar et al., 1994).

But it is not satisfactory to compare only the final film thickness to the model prediction. From the standpoint of understanding the physics of the coating process, the evolution of the film topography needs to be examined. This is also useful for the

systematic verification of proposed mathematical models. Due to its dependence on physical contact, the profilometry method is not suitable for measuring wet films. Due to its distinctive advantage, laser interferometry is a convenient technique for measuring real-time film thickness profile with minimal disturbance to the film..

Laser interferometry is a technique that uses a single wavelength and a single angle of incidence at fixed polarization. But the changes in film reflectivity are used to detect the film thickness change instead of the actual film thickness. Thus, the real-time film thickness profile can only be obtained by combining the results with the final film thickness. Then in reverse time direction, a film thickness profile at the earlier time can be inferred from that at the later time. A typical procedure is as follows, as shown in Figure 2-1. When a monochromatic laser beam falls on a transparent film on a reflective substrate, part of the light is reflected from the film surface, while another part of light passes through the film and reflects from the substrate (Peurrung and Graves, 1991). Then the two parts of light recombine together and interfere with each other, forming fringes which correspond to film thickness contour (refer to Figure 2-2).

Figure 2-1 Schematic of laser interferometry during spin-coating procedure
(Perrung and Graves, 1991)

Figure 2-2 Interferometric picture of a contour diagram (Peurrung and Graves, 1993)

The left picture in Figure 2-2 shows an actual photo taken during the process, while the fringes show the contour diagram of the film thickness profile. The picture on right is a sketch of the fringes. The liquid flow is from left to right. The laser wavelength is 514.5 nm and the refractive index is 1.64; the spacing between contours is 0.157 μm .

Each interference fringe stands for a certain film thickness. The distance between two adjacent dark fringes corresponds to the change in “altitude” of corresponding position of the film thickness. The “altitude” difference can be calculated by following equation,

$$\Delta h = \frac{\lambda}{2n_{ref}} \quad (2-1)$$

where λ is the wavelength of laser beam and n_{ref} is the refractive index of the film (Peurrung and Graves, 1993). Note there are two limitations of this technology. If the interfering beams have to travel a long distance, the interferometer can be disturbed since

the air current will disturb the two beams differently. Another limitation is about the refractive index. As the film refractive index and thickness are inseparable, one must find a way to relate these two variables.

To get a better understanding of the laser interferometer, let take a look at the Michelson interferometer --- the classical instrument employing the division of amplitude. The division of amplitude is usually brought about by simple reflection. When light falls on to a thin film, part of the amplitude of the incident wave is reflected at the film surface of the top side and the remainder continues until it meets the second face where a similar fraction is reflected; these two fractions being coherent and having traveled different lengths interfere with each other (Tolansky, 1973).

Michelson interferometer is so important that it has been widely used in many different fields of optics and physics. Figure 2-3 is the schematic of Michelson interferometer. The first form of this instrument was described by Michelson in 1881. It consists of a half-silvered mirror (beam splitter), which divides a beam into two parts of equal intensity, one transmitted, the other reflected. Light from source S is incident at 45° on the front of the beam splitter A. The amplitude of the beam is divided into two equal parts, one half goes to M1, the other half to M2. The beams reflect from M1 and M2 and return to A. From A the two beams recombine and go to the observer at B, where fringes are seen. The traveled path difference between the two beams is given by $2(AM_1 - AM_2)$.

Figure 2-3 Schematic of Michelson interferometer (Tolansky, 1973)

2.2 Break-up of liquid jets

When a liquid is ejected continuously from a nozzle or orifice into air or another fluid with which it is immiscible, the liquid jet tends to break down into a stream of droplets (Middleman, 1965). For Newtonian jets, evenly spaced droplets and interspersed satellite droplets are formed when the liquids are forced out of the capillary. This phenomenon is due to the well-known Rayleigh-Tomotika instability. However, for even a very dilute polymer solution, a stable jet or “beads-on-a-string” structure is formed and it can maintain itself for a relative long time (Anna and McKinley, 2001).

In recent times, the capillary jet has been utilized in many practical applications such as ink jet printing, heat transfer by liquid droplet radiators (LDR), particle sorting, pelletizing, dispersing liquids, spinning of synthetic fibers, fuel injection, hydraulic mining, machining, etc. Of these applications, ink jet printing and particle sorting have the most significance

for our purpose. Here, it is necessary to have a series of drops with the same size and shape (Chaudhary and Maxworthy, 1980c).

An example in the field of material processing is the formation of small spheres. This can be done by jet breakup due to surface tension. The practical operation is to melt the solid first, and then put it inside a container with a perforated bottom. After this, the liquid flows out of the holes and breaks up into droplets, which solidify as they fall. Lead shot has been made in this way for centuries; fertilizer in various forms is also made by this method. The main concern during the operation is to make droplets of uniform size (Rutland and Jameson, 1970).

It is well known that ‘anti-misting’ polymeric additives can be used to suppress the phenomenon of liquid jet breakup that is driven by surface tension. This fact is very useful in controlling droplet size during jet break up in such situations as firefighting or spraying liquids from the air (Renardy, 1995). We have all known that disintegration of liquid fuel into mists can lead to a serious fire hazard. This disintegration can be suppressed by adding polymer additives into liquid fuel.

The study of liquid jets has a very long history. The earliest research related to this topic was probably begun by Savart’s experiments and Plateau’s observation (Lafrance, 1975). They discovered that when a liquid jet breaks up into a series of drops, it is not always one drop per wavelength. On the contrary, very often some smaller intermediate drops appear, especially at long wavelengths (Rutland and Jameson, 1970). Their observation led Plateau to attribute capillary instability to the presence of surface tension.

The decisive breakthrough was brought by Lord Rayleigh more than a century ago. He developed a mathematical model for the breakup of liquid jets (Lafrance, 1975). Theoretically, he studied the capillary instability of liquid jets for inviscid and very viscous jets when the influence of the surrounding fluid was neglected. By means of a first-order perturbation calculation, he showed that the capillary jet is stable for all non-axisymmetric

disturbances, and that the jet stability for axisymmetric disturbances depends on whether the wavelength is longer than the circumference of the jet or not. He also showed that the unstable waves grow exponentially as $\exp(qt)$, and he gave the dispersion relation as follows (Chaudhary and Redekorp, 1980a)

$$q^2 = \frac{\sigma}{\rho r_0^3} \frac{I_1(k)}{I_2(k)} k(1 - k^2) \quad (2-2)$$

where σ is the coefficient of surface tension, ρ is the density, r_0 is the jet radius, I_1 and I_2 are modified Bessel functions of the first kind and k is the wave number. The maximum value is taken at wave number k equal to 0.698. This indicates that the disturbance of this wave number would grow very fast and finally dominate the character of the breakup. Rayleigh inferred that the breakup would happen when the amplitude of the disturbance grows to the size of the jet radius. Therefore, a good mathematical framework for jet breakup was established (Lafrance, 1975).

Many experiments about the breakup of a liquid jet have shown that Rayleigh's uniform drop model is inadequate. In fact, the main drop is observed to be interspersed with smaller satellite drops. Therefore, Rayleigh's theory has proved to be inappropriate as it cannot predict the appearance of satellites. This encouraged researchers to calculate higher-order terms in the disturbance series in addition to the first-order model. In a perturbation analysis of the capillary instability of an inviscid liquid jet, it has been proved that the higher order (nonlinear) terms are responsible for the presence of satellite drops (Lafrance, 1975). Since the 1990s, numerical methods have been introduced to solve the behavior of liquid jets. Bousfield and co-workers successfully used the finite element method to simulate the transient evolution of a viscoelastic jet forming a bead-on-a string structure. An asymptotic analysis also has been used for a system with non-linear evolution equation to model the dynamics of a viscous fluid jet under the action of capillary force,

and numerical simulation has been used to describe the behavior of the jet (Anna and McKinley, 2001).

As might be anticipated, considerable research has been focused on the behavior of jets of Newtonian liquids. However, for many years, research on the behavior of viscoelastic jets has proceeded at a much slower pace due to the complexity of the viscoelastic fluid properties. Linear stability analysis has shown that an axisymmetric wave disturbance grows faster on a liquid jet of a viscoelastic fluid than on a Newtonian liquid jet with same shear viscosity, and this conclusion is independent of the form of the constitutive equation chosen (Renardy, 1995; Goldin et al., 1969). Experiments with low elasticity fluid jets have confirmed this prediction. However, non-linear phenomena dominate the behavior of the jet when fluid elasticity is more pronounced. For highly elastic fluid jets, they become stabilized and form a bead-in-a-string configuration instead of breaking up. Figure 2-4 gives typical appearances of Newtonian, non-Newtonian inelastic and viscoelastic jets.

There has been considerable progress in understanding the behavior of Newtonian jets. Numerical simulation can describe the jet evolution process until the moment near to the final breakup by using the classical Rayleigh linear theory. For the flow evolution of non-Newtonian jets, however, the situation is much more complicated. In addition to the effect of capillary force, viscoelastic properties, introduced by polymer addition, significantly change the breakup dynamics (Chang et al., 1999). To account for this, during a transient, extensional flow, there must be a reliable constitutive equation to describe the extra stresses. The additional rheological properties make the exhaustive numerical analysis almost impossible even with the use of modern computers. However, a linear stability analysis still can be done in the early stage of the breakup of viscoelastic jets since the viscoelastic effect can be triggered only when the polymers are significantly stretched by the flow. At a later stage, the polymers are stretched considerably at the stagnant points and the evolution dynamics are mainly depended on the viscoelasticity.

Figure 2-4 Typical appearances of Newtonian, non-Newtonian inelastic and viscoelastic jets, solvent is distilled water if not mentioned (Goldin et al., 1969). (a) 75% Glycerin-water, (b) Ethylene glycol, (c) 0.1% Carbopol, (d) 0.05% Separan, (e) 0.25% Separan, (f) 0.25% Polyox, (g) 0.25% CMC.

Experiments have shown that an order of magnitude delay happens during the breakup. In some cases, the viscoelastic jets may not even break during the entire experiment. Instead of forming satellites as in the case of a Newtonian jet, a unique filament-bead structure is observed. If the viscoelastic jet does breakup, the filament breaks at the neck and join to the beads. This bead-filament configuration has been predicted by numerical simulation (Chang et al., 1999). During the necking and breakup procedure of the viscoelastic jet, elastic tensile stresses resist the pinching caused by capillary action.

Extensional or normal stresses grow in the elastic fluid, and polymer chains are stretched along the axial direction near the breakup region (Anna and McKinley, 2001). Because the breakup of a jet is a predominantly extensional flow, extensional flow of viscoelastic fluids plays a very important role during the evolution process of jet breakup. This tells us that the extensional viscosity would be an important factor for controlling the jetting behavior of viscoelastic fluids. Recent studies also attribute these differences of jet breakup mechanism to the high extensional viscosity of polymer solutions arising from strong resistance of polymer molecules to extensional flow (Christanti and Walker, 2001). Experiments show that a fluid jet with low extensional viscosity has similar or even shorter break up length than the jet of a Newtonian liquid, while the fluid jet with high extensional viscosity has a longer break up length. Note that sometimes this high extensional viscosity also suppresses the appearance of satellite drops. The break up length is defined as the distance from the capillary exit point to the jet break up point. The break up length can be further divided into three parts: the distance over which the jet shows no visible disturbance, the distance within which an axisymmetric disturbance is developing, and the final distance over which a beads-on-string structure is formed.

Polymer molecular weight and concentration are two important parameters for determining the extensional viscosity of the polymer solution (viscoelastic fluid), further influencing the jet break up behavior. Increasing polymer molecular weight leads to longer break up lengths and less satellite drops (Christanti and Walker, 2001). For some intermediate polymer molecular weights, the number of satellite drops decreases although the break up length does not increase. High molecular weight polymer solutions are found to suppress the formation of satellite drops but can lead to the appearance of very small drops instead. Increasing the polymer concentration in the dilute to semi-dilute region increases the break up length and the numbers of very small drops.

Figure 2-5 shows pictures captured at the point where the jet begins to disintegrate into drops for the solutions with increasing molecular weight but similar shear viscosity, static surface tension, or density. In Figure 2-5 (a), the 50% glycerol forms the expected main

drop and satellite drops. We can see from Figure 2-5 (b) that the break up process is retarded by the adding of PEO polymer. In Figure 2-5 (c), the filaments connecting the drops appear to be thinner. With the polymer of largest molecular weight, Figure 2-5 (d) shows that the 0.05% 1000k PEO completely suppresses the formation of satellite drops.

Figure 2-5 Final break up mechanism of (a) 50% glycerol, (b) 0.3% 100k PEO, (c) 0.1% 300k PEO, and (d) 0.05% 1000k PEO. Each image is 5.120mm x 3.840mm (Christanti and Walker, 2001).

For Newtonian fluids, the jet breakup situation is decided by the interplay amongst surface tension (σ), fluid viscosity (η), and density (ρ) (Christanti and Walker, 2001). These factors can be combined and described by the Reynolds number (Re) and the Weber number (We), they are defined as follows,

$$Re = \frac{\text{inertial stress}}{\text{viscous stress}} = \frac{\rho v d}{\eta} \quad (2-3)$$

$$We = \frac{\text{inertial stress}}{\text{interfacial stress}} = \frac{\rho v^2 d}{\sigma} \quad (2-4)$$

where d is the jet diameter, and v is the jet velocity.

For viscoelastic fluids, the jet breakup mechanism is also affected by the fluid characteristic relaxation time (τ). The Deborah number (De) can be used to describe it and is given by

$$De = \tau \dot{\epsilon} \quad (2-5)$$

where $\dot{\epsilon}$ is the extensional rate. When $De \rightarrow 0$, the fluid behaves like a Newtonian fluid; while the fluid acts like a pure elastic material when $De \rightarrow \infty$.

We can find from the above description that the surface tension is also an important factor during the jetting process. Middleman (1965) pointed out in his study of stability of viscoelastic jets that low surface tension and larger viscosity tend to enhance jet stability. Clarke (1969) pointed out the relation between surface tension and liquid jet radius. At the region of the jet well away from the capillary orifice, increasing surface tension leads to increasing of the radius of the jets no matter what condition is imposed at the orifice providing that the volume flux of liquid in the jet remains the same. Vrentas (1982) found that for the low to moderately high Reynolds number range, surface tension has a significant effect on the jet shape for sufficiently low Weber number.

When a liquid jet flows out of a capillary, under the influence of some axial disturbance, it may break up into several equally spaced drops. Small satellite drops may appear between these main drops. This is undesirable since we can rarely find any application that says that satellite drops are favorable. Therefore, we need to understand the mechanism of forming satellite drops in order to suppress the appearance of satellite drops by controlling the jetting conditions or fluid properties.

Figure 2-6 is a typical schematic of experiment apparatus for studying jetting behavior (Vassallo and Ashgriz, 1991). The test fluid is pumped from a pressurized tank to a tube which is connected to a nozzle. The fluid is forced out of the nozzle by some disturbance. The behavior of the jet is observed by a high speed video camera, which is illuminated by and synchronized to a strobe light.

From Rayleigh's linear theory to nonlinear theories, researchers continue to explain the jetting behavior. It has been shown that linear theory cannot predict the formation of satellite drops at all. Nonlinear theories always predict the appearance of satellite drops. In addition, these nonlinear theories always predict that satellite drops separate from the two ends of the main drop at the same time. But these predictions are not really consistent with what people get from the experiments (Pimbley and Lee, 1977).

Figure 2-6 Schematic of jetting experimental apparatus (Vassallo and Ashgriz, 1991)

Pimbley and Lee (1977) studied the formation of satellite drops and their relation with the main drops. They found that satellite drops can separate from the front side of the droplet first, the rear side of the droplet first, or separate from both ends of the droplet simultaneously. They define the satellite interaction time as the time between the break-offs of the two ends of a satellite; this allows a momentum transfer between the satellite drop and main drop. These break-offs change the momentum of the satellite and lead the satellite to merge with the main drop. The satellite separates first from the rear side of the main drop and this results in forward merging; when the satellite separates first from the front side of the main drop, there is rear merging. Figure 2-7 is a picture taken during the experiment, showing the typical ways of satellite formation and merging (Chaudhary and Maxworthy, 1980c).

Pimbley and Lee (1977) took a nonlinear analysis through second order of the drop formation problem using a spatial instability analysis to study satellite formation and behavior. They believed that the amplitude of the perturbation and the wavelength-to-diameter ratio of this perturbation are the two most important parameters that control satellite drop formation. They found that a very small perturbation amplitude results in rear merging. At a higher amplitude both ends of the droplets separate simultaneously. When this amplitude increases further, forward-merging occurs and the satellite interaction time also increases. They also sum up the effect of the wavelength-to-diameter ratio into Figure 2-8. The x-axis, or λ/d is the ratio of wavelength to jet diameter. Wavelength is defined as the distances between two drops and is obtained by measuring the distances between the first ten drops after drop separation. The y-axis, or t_b , is the breakup time. Infinity condition, or infinite satellite condition occurs when the satellite moves with the same velocity as the main drops and no merging occurs. In Figure 2-8, the upper solid curve is the infinity condition which divides the rear-merging zone at the upper position and the forward-merging zone at the lower position. Below the lower solid curve, there is no satellite formation. The best range for depressing satellite drops was determined to be 5 to 7 for ratio of wavelength to diameter.

Figure 2-7 Typical ways of satellite formation and merging (Chaudhary and Maxworthy, 1980): (a) forward separation and rear merging; (b) rear separation, (c) forward merging

Vassallo and Ashgriz (1991) investigated the effect of disturbance amplitude and frequency on the breakup of a liquid jet. According to the ratio of disturbance wavelength (λ) and undisturbed jet diameter (d), or λ/d , they divided the jet breakup into four regions. Region I is the random breakup region, $\lambda/d < 3$. Random drop is formed in this region, where it is predicted by Rayleigh linear theory which states that the disturbance will grow only when disturbance wavelength is larger than the circumference of the jet, or πd . Region II is the short wavelength Rayleigh breakup region, $3 < \lambda/d < 5.5$. This region is characterized by immediate merging satellite, or reflexive satellite formation, which is a new kind of

satellite merging and will be introduced in the following paragraph. Region III is the medium wavelength Rayleigh breakup region, $5.5 < \lambda/d < 11$. Constant formation of satellite drops in this region is affected by the amplitude of the disturbance. Region IV is the long wavelength Rayleigh breakup region, $\lambda/d > 11$. Periodic drops are formed in this region due to the long wavelength disturbance.

Figure 2-8 “Map” of the satellite condition (Pimbley and Lee, 1977)

In region II, a new type of satellite merge, reflexive satellite merging, happens. For $3 < \lambda/d < 5.5$, a satellite formed after jet breakup tends to rear merge. Nevertheless, at particular jet diameters and Weber number, the satellite cannot merge with the main drop

due to the oscillation of the main drop. Instead of merging, the satellite is bounced off from the main drop. If the velocity of satellite is large enough, the satellite will front merge with the next main drop. If not, the satellite will successfully remerge with that main drop. Since this type of merger is due to the reflexive action of the internal flow, it is defined as reflexive satellite merging. This type of merging is usually observed for small amplitude disturbances.

It needs to be noted that the flow is continuous for the jetting situation introduced in this section; however, the flow is periodic for the jetting situation in inkjet printing, which is the focus of our study on jetting. Although differences exist for these two situations, they share some behavior, such as jet break-up and forming of satellites. In addition, it seems the same factors (for example, polymer molecular weight) which affect the jetting behavior in jet break-up should also play important roles in inkjet printing.

2.3 Previous work on extensional viscometry of polymer solutions

1) Introduction

The viscosity of polymer solutions under extensional flow can be several orders of magnitude higher than the corresponding value in simple shearing flow. Polymer solutions with high molecular weight and flexible chains, when present even in only minute quantities, are the reason for this tremendous difference between extensional viscosity and shear viscosity. In shear flow, molecular alignment with the flow stream will minimize the resistance to flow. On the other hand, in extensional flow, this alignment maximizes the resistance to flow. This gives us some insight about the flow mechanism difference between shear flow and extensional flows. Extensional flows exist and impact many processes, such as jet stability, flow through porous media and turbulent drag reduction. To model the flow behavior in these important processes, such as fiber spinning, high speed coating, and oil spill removal, the knowledge about extensional flow behavior is essential due to its important role played during the process (Fuller & Cathey, 1991).

Flow fields can be categorized in terms of the relative amount of extension and rotation component (Fuller & Cathey, 1991). In general, a velocity field, $u(r)$, can be expanded at a position, R , as

$$u(r) = u(R) + \nabla u \bullet (r - R) + \frac{1}{2}(r - R) \bullet (\nabla \nabla u) \bullet (r - R) + \dots \quad (2-6)$$

The uniform flow term, $u(R)$, will not affect the microstructure of the fluid. Only the velocity gradient term, ∇u , according to the scale of a constituent macromolecule, normally needs to be considered. For the purposes of flow field classification, this term is divided into symmetric and antisymmetric parts according to,

$$\nabla u = \frac{1}{2}(\nabla u + \nabla u^+) = E + W \quad (2-7)$$

The rate of strain tensor, E , characterizes deformations (including the extensional component) and the vorticity tensor, W , produces rigid body rotations (rotation component).

A simple shear flow has a velocity gradient

$$\nabla u = \dot{\gamma} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \frac{\dot{\gamma}}{2} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \frac{\dot{\gamma}}{2} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (2-8)$$

and therefore has an equal amount of extension and vorticity.

According to the standard nomenclature introduced by the Society of Rheology, the terms “tensile viscosity”, “elongational viscosity” or “uniaxial extensional viscosity” (Petrie, 1999) are defined as follows. When a material is subjected to homogeneous simple extension, i.e. to a flow which is spatially uniform, with constant rate of strain, $\dot{\varepsilon}$, in the x_1 direction and $-\frac{1}{2}\dot{\varepsilon}$ in every direction perpendicular to the x_1 axis; the ratio of “net tensile stress”, $\sigma_E \equiv \sigma_{11} - \sigma_{22}$, to rate of strain is monitored as a function of time. And the “tensile viscosity” is defined as

$$\eta_E(\dot{\varepsilon}) = \lim_{t \rightarrow \infty} \left[\frac{\sigma_E(t, \dot{\varepsilon})}{\dot{\varepsilon}} \right] = \frac{\sigma_{11} - \sigma_{22}}{\dot{\varepsilon}} \quad (2-9)$$

There are three different forms of extension: these are uniaxial (e.g. fiber pulling), biaxial (e.g. balloon inflation) and planar (e.g. cylinder inflation). The latter two forms are less demanding on any polymeric microstructure (Barnes, 1989). People normally refer to “uniaxial extensional viscosity” when they talk about “extensional viscosity”. η_T sometime is used in honor of Trouton, and the extensional viscosity may be called Trouton viscosity. For a Newtonian liquid, the extensional viscosity is given by Trouton's rule to be simply three times the shear viscosity.

For the situation with significant surface tension, “net tensile stress” can be expressed as the following equation to correct for the effect of surface tension.

$$\sigma_E = \frac{\text{Applied force}}{\text{Area}} - \frac{\text{Coefficient of surface tension}}{\text{Radius}} \quad (2-10)$$

Note that the equation $\sigma_E \equiv \sigma_{11} - \sigma_{22}$ is only valid for incompressible fluids.

In rheometry, it is desirable to consider flows with simple histories of the rate of strain tensor. With simple shear flow, rotational flow devices (Couette and cone-and-plate geometries, for example) are capable of creating flows where molecules travel in closed streamlines with uniform histories of deformation. Extensional flows, however, cannot be created with closed streamlines and experiments are inherently transient in nature.

We need to distinguish extensional viscosity measurement under two different situations. In the first case, steady spatially homogeneous extensional flow is attained (to a reasonable approximation), this gives the extensional viscosity function directly. In the second case, only transient flow is attained during measurement; this gives a stress growth function or transient extensional viscosity (Petrie, 1999). To understand intuitively about fluid deformation and flow, the true extensional viscosity is an important property we want to measure accurately and reliably. However, transient extensional viscosity is also an important property when we deal with geometrically complicated unsteady flows. In practice it is normally more meaningful to report extensional viscosities not only as a function of the velocity gradient, but also as a function of the average total strain produced by the measurement. High viscosity materials such as polymer melts can be handled with testing equipment that is similar in many ways to tensile instruments used for solids. Low viscosity polymer solutions are very difficult to study in extension and the field is still under development for this class of materials.

In the past, extensional flow measurement for a polymer solution has been full of contradictions (Petrie, 1999). Many devices have been developed for the measurements. These devices are classified as either “flow-through” devices or “stagnation-point” devices. Flow-through geometries would include the fiber spinning experiment, the tubeless siphon, and contraction flows. Stagnation point flows are generated by a variety of instruments including the four roll mill and opposed nozzles. However, most experimental techniques

cannot reproduce uniform uniaxial elongation. Furthermore, although a filament stretching technique, which is often used to make measurement on polymer melts, can be used to measure the extensional viscosity of a polymer solution at constant stretch rate, it cannot deal with polymer solutions of low viscosity.

Among these techniques, the following techniques are introduced briefly:

filament stretching,

fiber spinning,

opposing nozzles,

tubeless siphon,

four roll mill,

converging channels, and

the triple jet.

Each of these techniques has its advantages and drawbacks.

2) Filament stretching technique

The filament stretching technique has been very successful in measuring the extensional properties of polymer melts. The high elasticity and viscosity of polymer melts help them to keep uniform shape during the stretching. However, the low viscosity of polymer solutions makes them more susceptible to gravity and more difficult to keep a uniform shape using this technique (Spiegelberg, Ables, and McKinley, 1996). Due to the

no-slip boundary condition, which exists at a liquid-solid interface, shear forces normally accompany extensional forces during the measurement. Therefore, an “apparent” extensional viscosity, rather than a “true” extensional viscosity, is measured. The most successful measurements of the true transient extensional viscosity have been performed by Sridhar and co-workers (Gupta and Sridhar, 1998). They used two identical plates to hold the fluid sample. With the top plate kept still, the bottom plate was moved downward at a known rate or by a constant force. Figure 2-9 shows the sequence pictures of the stretching of a constant viscosity, ideal elastic liquid. It is shown that the filament diameter remains almost the same over 95% filament length along the axial direction except for the two ends.

Figure 2-9 Sequence of photos showing the stretching of a filament of a solution of 0.185% PIB in a solvent of kerosene and polybutene (Gupta and Sridhar, 1998).

The set-up for filament stretching technique was later developed to working at various situations. It can be used to work at vertical (Gupta and Sridhar, 1998; Spiegeberg et al.,

1996; McKinley, 2000; Stelter et al., 1999; Stelter et al., 2000; Verhoef et al., 1999; Nieuwkoop et al., 1996; Liang and Mackley, 1994; Sridhar et al., 1991; Matta and Tytus, 1990), horizontal configuration (Gupta and Sridhar, 1998; Tirtaatmadja and Sridhar, 1993; Oliver, 1990) and under situation of microgravity (Berg et al., 1994; Berg et al., 1992).

For a slender fluid filament, the middle point or the point far from the end plate has essentially one dimension at velocity field that is extensional in character (McKinley, 2000). Two geometries have proved optimal to measure extensional response.

First geometry is to utilize one endplate with exponential movement in order to create constant stretching rate rather than constant tensile force. The changing axial tensile force is measured at the endplate, and the filament diameter in the middle of the filament length is obtained by using an optical device. These data are then used to compute the transient extensional viscosity.

In the second geometry, an extensional step strain of order unity is applied to the filament; then the filament evolves under the influence of capillary pressure alone. A large extensional strain can be attained. The midpoint of the filament gradually necks down and finally breaks up. The only measured parameter is the diameter change of the midpoint of the filament as a function of time.

Figure 2-10 shows a typical setup for vertical filament stretching (Stelter et al., 2000). The setup includes an optical measurement unit, a fixed bottom plate, and an upper plate, whose motion can be accurately controlled by an electrical coil. The optical measurement unit is comprised of a laser diode, an optical slit orifice, and a photoreceiver. This unit allows for the measurement of filament diameter as a function of time by evaluating the intensity of scattered light on the detector. The procedure of measurement is as follows: a droplet is placed between the two plates. Then the upper plate is suddenly pulled up until it reaches a preset position. This will produce a fluid filament with constant length which is

subjected to the self-thinning due to capillary pressure. This setup is a typical example of the second geometry introduced above.

Figure 2-10 Experimental setup for vertical filament stretching (Stelter et al., 1999)

Figure 2-11 shows the filament thread thinning process for a 1000 ppm Praestil 2540 solution (Stelter et al., 2000). The “necking” process of the diameter of the fluid filament can be divided into two stages. In the first stage, polymer molecular chains are stretched by the extensional flow and the second stage is a quasi-Newtonian one, where full stretching has already been reached, resulting in a very high and constant extensional viscosity. The thread shape is expected to be cylindrical to avoid strong shear flow effects. Figure 2-11 shows a symmetrical filament, which means it fits the above situation. In addition, the gravity effect plays no role in the self-thinning process due to symmetry of the thread. Table 2-1 shows that the tested dilute polymer solution has a relatively large Trouton Ratio. Note that the Trouton Ratio is the ratio of the extensional viscosity to the shear viscosity.

To get a pure uniaxial extension of a liquid sample at a constant stretching rate, the liquid sample must remain cylindrical at all times during the stretching. The length of the liquid filament has to increase exponentially with time as

$$L(t) = L_0 \exp\left(\dot{\epsilon} t\right) \quad (2-11)$$

Figure 2-11 Thread thinning process of a 1000 ppm Praestol 2540 solution

where $\dot{\varepsilon}$ is the stretching rate and $L(t)$ is the instant length and L_0 the initial length of liquid filament (Berg et al., 1994). At the same time, conservation of mass requires, that the radius of the fluid cylinder decreases exponentially with time as

$$R(t) = R_0 \exp\left(-\dot{\varepsilon} t / 2\right) \quad (2-12)$$

where $R(t)$ is the instant radius of the fluid cylinder.

Table 2-1 Comparison between shear and extensional viscosities for all polymer solutions with concentrations of 1000 ppm (Stelter et al., 2000)

Fluid	Behavior	Shear rate (1/s)	Shear viscosity (Pa·s)	Extensional viscosity (Pa·s)	Trouton Ratio
CMC-g-PAM	Vicoelastic	1	0.013	12.6	969
GG-g-PAM	Newtonian like	1	0.002	4.5	2250
Praestol 2500	Vicoelastic	1	0.023	17.5	761
Praestol 2540	Vicoelastic	1	0.7	70.7	101

In order to make an accurate measurement of the extensional viscosity of polymer solutions, a pure extensional flow with a constant stretching rate and a zero stress history is necessary. Most researchers have neglected the effect of gravity in their experiment analysis. However, the constant endplate diameter leads to significant “necking” of the fluid column at the initial phase of the elongation. As a result, “the elongation is not purely uniaxial and the extension rate is inhomogeneous” (Berg et al., 1994). Actually this is a situation which cannot be accessed under terrestrial conditions; Berg et al. (1992, 1994) carried out the experiments in the drop-tower facility which provides microgravity conditions of about 10^{-5} g for 4.7s to overcome above depicted limitation.

Their experimental method is to stretch the liquid sample from a state of rest at different stretching rates. As the liquid is held between two adjustable plates by surface tension, the apparatus is operated under microgravity in the Bremen drop tower. The whole experimental setup is installed inside a drop-capsule. After 4.7s free fall and weightlessness, the capsule reaches the end of the drop tube. Figure 2-12 shows a sketch of the basic experiment setup. The fluid filament is stretched in the vertical direction. The lower plate device is mounted on a linear drive which is driven by a micro stepping motor. The exponential functions for length and radius control are calculated and transmitted by a central controlling processor. The upper plate device is at rest and attached to a micro balance system, which can measure forces up to 1 N with an accuracy of 0.001 N. The output of the micro balance system is recorded on the same central controlling system. A technical sketch of the plate devices is shown in Figure 2-13. Figure 2-14 shows a photo of the entire apparatus. Different aqueous solutions of an acrylamide co-polymer were tested using this device.

The apparatus works under microgravity and realizes a nearly pure uniaxial extensional flow field. The fluid samples are stretched from a state of rest. The whole fluid sample is subjected to the extensional flow field. The effect of necking has been avoided by using variable plate diameters. Due to the short stretching time of 2.5 s, the Hencky strain is

limited to $\varepsilon = 1.4$. This measurement technique offers exactly defined boundary conditions at constant extension rates.

Figure 2-12 Basic experimental setup (Berg et al., 1994)

Figure 2-13 Technical sketch of the stempel device for adjustable filament diameter (Berg et al., 1994)

The filament stretching device can also work in horizontal configuration. Tirtaatmadja and Sridhar (1993) designed the horizontal filament stretching setup. Its schematic diagram is shown in Figure 2-15 (Gupta and Sridhar, 1998). This device consists of two linear drive units (L) which are mounted on a shaft (S). This shaft is coupled with a servomotor (M). An arbitrary waveform generator (AWG) is used to control the motor speed and hence the horizontal speed of the linear drive units. A force transducer (T) is attached to the drive unit at left side of rheometer, while a fixture is attached to the other unit. Two identical Teflon disks (D) are used to hold fluid sample. One disk is attached to the arm of the force transducer, while another disk is attached to the fixture. An optical diameter-measuring device (Z) is used to measure the diameter of the filament diameter. When a beam of light passes the filament and is received by the receiver, then the amount of light can be measured and then transformed to the filament diameter. The voltage signals from the force transducer and diameter-measuring device can be sent to a PC for further analysis through an analog-digital converter (ADC) card.

During the experiment, both discs move apart simultaneously with the help of the servomotor. Then the information about filament diameter and driving force is sent to a computer to record.

The instantaneous length of filament must increase with time as described by equation 2-13.

$$L(t) = L_0 \exp\left(\dot{\epsilon} t\right) \quad (2-13)$$

where L_0 is the initial length of the filament. And the filament diameter, D , should decrease according to the equation 2-14,

Figure 2-14 Photo of the entire apparatus (Berg et al., 1994)

Figure 2-15 Schematic diagram of the filament stretching rheometer (Tirtaatmadja and Sridhar, 1993)

$$D(t) = D_0 \exp\left(-\frac{\dot{\varepsilon}t}{2}\right) \quad (2-14)$$

where D_0 is the initial value of filament diameter. It is easy to show that, in the absence of the fluid inertia, the net tensile stress can be described by the following equation 2-15 (Gupta and Sridhar, 1998),

$$\sigma_E = \frac{4F}{\pi D^2} - \frac{2\gamma}{D} - \frac{\rho g L}{2} \quad (2-15)$$

where σ_E is the net tensile stress, F is the measured force, γ is the surface tension coefficient, and ρ is the density of the fluid. Last term of equation 2-15 is the effect of gravity, and it is only used when dealing with the vertical stretching. Next, the extensional viscosity can be easily obtained.

3) Fiber spinning technique

In the fiber spinning technique, the liquid jet emerging from a nozzle or a capillary is stretched by a suction device or a take-up wheel (Gupta and Sridhar, 1998). The tensile stress is measured to get the apparent extensional viscosity. The fiber spinning technique with a suction device can be used to measure the extensional response of very dilute, low elasticity polymer solutions.

Chan et al. (1988) refined the previous design using a suction device and measured the pressure drop to get the extensional stress. A slender liquid filament was stretched by the suction device, this results in the spinning of the fiber. The schematic diagram of their extensional viscometer is shown in Figure 2-16.

Figure 2-16 Schematic diagram of the extensional viscometer (Chan et al., 1988)

Polymer solution is pumped into a jacketed cylindrical tank C and leaves through the capillary E; the volumetric flow rate is kept constant with the help of a pump. If the liquid were Newtonian and had a viscosity μ , the pressure drop versus flow rate relation across capillary E would be

$$Q_0 = \frac{\pi d^4}{128 \mu L} [P_0 + \rho g L] \quad (2-16)$$

where P_0 is the pressure at the capillary inlet, d is the capillary diameter and L is the capillary length.

The liquid jet leaving capillary E can be stretched by sucking the liquid into another capillary G; average axial liquid velocity increases progressively in the air gap between capillaries E and G. Fluid stretching results in the application of a tensile stress T_1 at the exit of capillary E. As a consequence, the pressure drop versus flow rate relation across E becomes

$$Q_1 = \frac{\pi d^4}{128 \mu L} [P_1 + T_1 + \rho g L] \quad (2-17)$$

where P_1 is now the pressure at the inlet to E. Since at steady state, Q_0 , equals Q_1 , it must be true that (Sridhar and Gupta, 1985)

$$T_1 = P_0 - P_1 \quad (2-18)$$

It can easily be shown that $(P_0 - P_1)$ equals the reduction in air pressure above the liquid in tank C (Chan et al., 1988). This change in pressure is measured using a manometer H.

Even though Eqs. (2-16) – (2-18) have been shown to be valid for Newtonian liquids, Eq. (2-18) holds for non-Newtonian liquid also if the arguments are repeated using the power-law model to represent the fluid rheology. Thus, it is a straightforward matter to measure the tensile stress in the liquid at the exit of the capillary E. Multiplying this stress by the cross-sectioned area of the filament at the capillary exit gives the stretching force $F(0)$ shown in Figure 2-17. A knowledge of $F(0)$ then allows us to calculate $F(1)$, the tensile force in the stretching liquid, at any other axial position X , by means of a force balance (see Figure 2-17):

$$\rho \int_{CV} V(x) (V \cdot d\tilde{A}) = \sum F \quad (2-19)$$

If we neglect air drag, the above equation becomes

$$F(1) = F(0) + F(I) - F(ST) - F(G) \quad (2-20)$$

where $F(1)$ is the desired force at X_1 and

$$F(0) = (P_0 - P_1) * \text{cross sectioned area at } X_0$$

$$F(ST) = \pi\gamma(D_1 \cos \theta_1 - D_0 \cos \theta_0), \text{ the surface tension force}$$

$$F(I) = \rho \left(\int_{A_1} V^2 dA - \int_{A_0} V^2 dA \right), \text{ the force due to inertia}$$

$$F(G) = \rho g \int_{X_0}^{X_1} \pi r^2(\xi) d\xi, \text{ the gravity force}$$

The ratio of the force $F(1)$ to the cross-sectioned area at X_1 gives the viscoelastic stress in the axial direction $\sigma_{11}(X_1)$. A radial force balance at X_1 gives the radial stress σ_{22} in the fluid, and the difference between σ_{11} and σ_{22} can be shown to be (Chan et al., 1988)

$$\sigma_{11} - \sigma_{22} = \sigma_{11} + \gamma / R \quad (2-21)$$

where R is the filament radius at any location.

Figure 2-17 Control volume used for the integral linear momentum balance

Finally, the extensional viscosity η_E is defined as

$$\eta_E = \frac{\sigma_{11} - \sigma_{22}}{du/dx} \quad (2-22)$$

in which du/dx is the stretch rate obtained by differentiating the axial liquid velocity with respect to the axial distance. For a constant volumetric flow rate Q , and assuming no radial variation in the velocity, the local velocity and stretch rate $\dot{\epsilon}$ are given by

$$u = Q / (\pi R^2) \quad (2 - 23)$$

and

$$\dot{\varepsilon} = -2Q(dR/dx)/(\pi R^3) \quad (2 - 24)$$

The polymer that the authors have used is Separan AP 273 (an anionic polyacrylamide), which is dissolved into distilled water. The range of stretch rates could be changed in the range of 100-1000 s⁻¹ by varying the flow rate Q and by altering the distance between the upper and lower capillaries. The corresponding tensile stresses were very large, and these gave apparent extensional viscosities of the order of 20 Pa•s.

4) Opposing nozzles technique

Low-viscosity fluids are of fundamental importance for a variety of phenomena including turbulent drag reduction, jet stability and anti-misting. In addition to fiber-spinning technique, opposing nozzles rheometer can also be used to measure extensional viscosity of low viscosity fluids (Fuller et al., 1987).

The schematic diagram of opposing nozzles rheometer is shown in Figure 2-18. Two opposing nozzles have been attached to tubes and immersed in the test fluid. One tube is fixed, the other is mounted on a knife edge and is free to swing under the influence of a torque that arises from the fluid force between the nozzles. The fluid between two nozzles is sucked into the opposing nozzles, the fluid movement leads to an approximation of a uniaxial extensional flow in the region between the nozzles. Uniaxial compressive flow can be approximated by blowing the fluid out of the nozzles. Tensile stresses will induce a force which tends to bring two nozzles together. One thing needed to be mentioned is that the nozzles remain motionless during the measurement. The flow rates were measured by

simply measuring the rate at which fluid accumulated in a graduated cylinder. If we define this flow rate as Q , the effective stretching rate is

$$\dot{\varepsilon} = \frac{(Q/2)}{A(d/2)} \quad (2-25)$$

where A is the area of the nozzle openings and d is the gap between the two nozzles.

Figure 2-18 Schematic diagram of the opposed nozzle rheometer: N-opposing nozzles; S-fixture defining nozzle separation; K-knife edge fulcrum; T-flexible tubing; Q-tubing exiting to pump; TS-translation stage; F-force transducer; L_1 , L_2 -level arms. (Fuller et al., 1987)

Then the extensional viscosity can be obtained by,

$$\bar{\eta} = F(L_1 / L_2)d / Q \quad (2-26)$$

L_1 and L_2 are the moment arms shown in Figure 2-18. The force F is measured at the transducer, and it is actually the tensile stress. Equation 2-26 is obtained under the assumption that the tensile stresses are distributed uniformly across the area of the nozzle openings. Thus, the extensional viscosity obtained above is an “average” amount. Perfect agreement cannot be expected between measurements and predictions even for fluids whose flow behavior is known.

5) Tubeless siphon technique

The fiber spinning technique, mentioned before, has a very similar analysis method to that of the tubeless siphon technique (or Fano flow). The normal stresses are estimated from momentum balances, force measurements, or pressure measurements. The stretching rate range obtained by tubeless siphon often complements those obtained by fiber spinning (Matthys, 1988).

A schematic of the apparatus is shown in Figure 2-19. The fluid sample inside the beaker is aspirated in a tube which is above the surface of the pool and connected to a chamber under vacuum. The tube is first dipped in the fluid to start the siphon, then moved upward vertically to form a stable siphon. The height of tube above the surface of pool depends on the flow rate imposed by the vacuum condition and polymer solution properties. The tensile stress can be measured at the tube end. The optical equipment (laser and high-speed camera) can obtain the flow situation and finally get flow field information after analysis. Figure 2-20 gives a photo of the Fano extensional flow liquid column.

Figure 2-19 Schematic of the tubeless siphon set-up (Matthys, 1988)

Figure 2-20 Photo of Fano extensional flow liquid column (Peng and Landel, 1976)

6) Other techniques

Other techniques like four roll mill (Pope and Keller, 1977; Fuller and Leal, 1980), triple jet (Oliver and Bragg, 1974) and converging channels (James and Saringer, 1982) can also be used to measure extensional response of polymer solutions. Since no recent research developments have been reported for these techniques, details about these techniques are not discussed here.

7) Stretch rate for different techniques

The major limitation of most uniaxial extensometers is their inability to make measurement at a stretch rate of industrial processing magnitude. For example, the technique of filament stretching is the one which has received the most attention. The highest stretch rate is less than 10 s^{-1} . Figure 2-21 gives a typical result for the growth of tensile stress during the constant stretch rate extension of a constant-viscosity, ideal elastic liquid at a variety of stretch rates. While these results are useful in demonstrating the large resistance that polymer solutions offer to an extensional deformation, techniques are needed to stretch polymeric fluids at stretch rate of the order of 100 s^{-1} . The stretch rate which happens during the ink-jet printing even exceeds 1000 s^{-1} . One advantage of fiber spinning technique is that high stretch rates can be obtained by this technique. The stretch rate in fiber spinning can reach above 1000 s^{-1} . This is one of the reasons why the fiber spinning technique is used in our research to study the extensional behavior of fluids used in the application of ink-jet printing.

Figure 2-21 Tensile stress growth data for the constant-viscosity, elastic liquid (a solution of 0.185% PIB in a solvent of kerosene and polybetene, Tirtaatmadja and Sridhar, 1993)

3 Initial Liquid Characterization

3.1 Experimental plan

Mineral oils and DECALIN were chosen as Newtonian liquids for comparison with polymer solutions and calibration of the new extensional viscometer. The system of polystyrene in DECALIN was chosen for detailed examination. Polymer solutions with shear viscosities in the range of 3 to 10 cp were prepared by varying the polymer solution concentration, polystyrene molecular weight and molecular weight distribution. The reasons for choosing these liquids are explained in pertinent text. The whole experimental process was divided into three phases.

The first phase involved characterization of polymer solutions. Several groups of polymer solutions with similar shear viscosities were prepared. Their shear viscosities were decided by varying polystyrene concentration, molecular weight and molecular weight distribution. The surface tension values for these polymer solutions were also measured for using in the calculation of extensional viscosity.

The next phase involved measurement of the extensional viscosities for these liquids. First, extensional viscosities of Newtonian liquids were measured. As extensional viscosities of Newtonian liquids are three times of their shear viscosity according to Trouton's law, these measured extensional viscosities were used to calibrate the newly designed extensional viscometer by comparing them with theoretical values. This calibration method was effective in overcoming problems which existed in the course of experiments and analysis of results. After trial and error, the design of the viscometer was changed and the reservoir capacity of the viscometer was decreased from 200 ml to 50 ml to accommodate the practical requirement of limited availability of commercial liquids. These changes enabled this viscometer to measure extensional viscosity for solutions with shear viscosity as low as 3cp. At last, extensional viscosities of those polymer solutions

were measured. It should be noted that this is the first time that the extensional viscosity for solutions with shear viscosity as low as 3cp was obtained.

In the third phase, jetting experiments were carried out to test jetting behavior of those liquids whose rheological properties had been investigated. First, some liquids were tested on jetting equipment which is located at the DuPont Experimental Station. Along with jetting results for some liquids, knowledge about the jetting equipment and the jetting process was gained during this period. According to previous jetting experience, a similar jetting set-up was built in our laboratory in West Virginia University. Jetting behavior of various liquids was tested by this new set-up. Several effects were investigated by comparing jetting behavior of different test fluids. Existence of relations between jetting behavior and rheological properties, especially extensional viscosities, were confirmed.

3.2 Materials used

Liquids used as Newtonian liquids are listed in Table 3-1.

Table 3-1 Newtonian liquids used

Chemical	Cat. No.	Manufacturer	Address	Other Info
DECALIN	30490	Fluka	Industriestrasse 25, CH-9471 Buchs SG, Switzerland	Full name: Decahydronaphthalene
CANNON Oil	22288556	Cannon Instrument Company	P.O. Box 16 – State College, PA 16804, USA	S60, 100cp at 25°C
Same	22288555	Same	Same as above	S20, 30 cp at 25°C
Same	22288553	Same	Same as above	S6, 7.6 cp at 25°C
Same	22288554	Same	Same as above	S3, 3.3 cp at 25°C

As for Newtonian fluids, several mineral oils which were used as viscosity standards with different viscosities were used to calibrate the extensional viscometer. DECALIN and other mineral oils were also used to compare jetting behavior with polymer solutions.

Chemicals used for preparing polymer solutions are listed in Table 3-2.

Table 3-2 Chemicals used for preparing polymer solutions

Chemical	Cat. No.	Manufacturer	Address	Other Info
DECALIN	30490	Fluka	Industriestrasse 25, CH-9471 Buchs SG, Switzerland	Full name: Decahydronaphthalene
CL1		Available in our laboratory		Commercial liquid 1
CL2		Available in our laboratory		Commercial liquid 2
Polystyrene		Available in our laboratory		polydisperse, MW of 200~300,000
Polystyrene	400	Scientific Polymer	6265 Dean Pkwy, Ontario, NY 14519, USA	polydisperse, MW of 45,000
Polystyrene	P3625-S	Polymer Source	124 Avro Street, Dorval (Montreal), Quebec H9P 2X8, Canada	monodisperse, MW of 45,000
Polystyrene	P3578-S	Same	Same as above	monodisperse, MW of 140,000
Polystyrene	P628-S	Same	Same as above	monodisperse, MW of 300,000
Polystyrene	A11170	Alfa Aesar	26 Parkridge Road, Ward Hill, MA 01835, USA	polydisperse, MW of 100,000
Polystyrene	8099	Monomer- Polymer & Dajac Labs	1675 Bustleton Pike, Feasterville, PA 19053, USA	polydisperse, MW of 140,000
Polystyrene	7646	Same	Same as above	polydisperse, MW of 300,000
Polystyrene		Pressure Chemical Co.	Pittsburgh, PA	monodisperse, MW of 900,000

As for polymer solutions, most of them were prepared by dissolving polystyrene in DECALIN. Polystyrene is an obvious choice when one wants to choose a polymer which is available with different molecular weights and molecular weight distributions. As for the solvent for polystyrene, DECALIN was chosen due to its several good properties. This is discussed in the following chapter “Extensional Viscosity for polymer solutions”. All solutions which were prepared by using different polystyrenes and DECALIN were tested for their rheological properties and jetting behavior. Two commercial liquids were also used to test their rheological properties and jetting behavior. Details about these commercial liquids were not available to us.

To prepare solutions of polystyrene in DECALIN, magnetic stirrers were used to keep stirring the mixture of polystyrene solid particles and DECALIN liquid. This stirring process took about 24 to 48 hours for all polystyrene particles to be dissolved into DECALIN. Monodisperse polystyrenes are usually available as powder or small particles. These took much less stirring time to entirely dissolve into DECALIN as compared to the polydisperse polystyrenes.

3.3 Surface tension measurement

Surface tension values for all the liquid samples used in experiments were measured at the DuPont Experimental Station (Wilmington, DE) by Mr. Alan S. Green.

The equipment used for measurement was a Drop Shape Analyzer (Kruss GmbH, Hamburg, Germany, Model: DSA-10, Serial #: 99060). Software program was DSA Version 1.00.17.0, Copyright, 1996-1998). The photo for this equipment is shown in Figure 3-1. The surface tension value γ is calculated by the following equation,

$$\gamma = \frac{mg}{2\pi r \psi \left(\frac{r}{v^{1/3}} \right)} \quad (3-1)$$

Where m is the mass of the liquid drop, r is the radius of the needle, v is the volume of the liquid drop, and ψ is a function expression..

The method to decide the surface tension is described as follows:

A drop of fluid is suspended from the tip of a 0.56mm needle. Fluid is added to the point where the drop is about to separate from the needle (max. volume). A digital picture is recorded and an analysis is run using the software to determine the surface tension of the fluid. Final results are calculated by using Eq. (3-1).

Figure 3-1 Photo of Drop Shape Analyzer DSA-10

It is shown from the result that all the tested liquids have similar surface tension values. These values range from 27 to 31 mN/m. Detailed values for each liquid are shown in the appropriate section of the chapters that follows.

3.4 Shear viscosity measurement

All the measurements for shear viscosity have been done on a rotational viscometer, Carri-Med CSL 100. The measurement principle of this viscometer is that one controls the stress applied to the material, and measures the strain response of the material. Figure 3-2 is a photograph of the rotational viscometer used for this work.

Figure 3-2 Photograph image of the Carri-Med CSL100 Rheometer

Parallel plate fixtures were used during the shear viscosity measurement for all polymer solutions and Newtonian liquids. The plate temperature was kept at 25°C, which is same as the experiment temperature for testing extensional behavior, during the process. The gap between the two parallel plates was set to a small value of 200 μm . This was decided by the nature of low shear viscosity and surface tension of these liquids. During the measurement, these liquids could not completely fill the gap between two plates if the gap exceeded 300 μm . Therefore, a gap of 200 μm was chosen for the shear viscosity test.

It was found that all the polymer solutions had a shear response which is similar to the Newtonian liquid. In other words, their shear viscosity remained constant while varying the shear rate. Figure 3-3 shows typical results for a solution of 2% polystyrene in DECALIN; this is similar to the shear response behavior of the DECALIN itself. Shear viscosity values for each liquid are shown in the appropriate section of the following chapters.

Figure 3-3 Typical shear result of 2% polystyrene in DECALIN as compared with DECALIN

After the extensional stretching, the shear response was again measured on the polymer solutions, but no obvious difference has found upon comparing with the data before the stretching. This means that there was no reduction in molecular weight on stretching.

4 Extensional Viscosity for Newtonian Liquids

4.1 Experiment objective

An innovative extensional viscometer (Gupta and Agarwal, 2003) was used to make extensional viscosity measurement. To become familiar with this new viscometer, verify the feasibility of it and calibrate it to make some further improvement, measurements were done on Newtonian liquids at first. The goal was to measure extensional viscosity for mineral oils of various viscosities (1.016, 0.562 and 0.291 poise), and to use the results as a guide to make further modifications on the design to get a better outcome. As viscosity standards, mineral oils have wide range of viscosity values. This is convenient for us to choose test liquids which can satisfy our test needs. Above three mineral oils have been tested in the order of decreasing viscosities. In this way, tests were designed in the order of increasing difficulty.

4.2 Measurement principle

Refer to the viscometer in Figure 4-1. Let the fluid within the reservoir flow out through a capillary under the influence of gravity. The drainage time of liquid can be recorded when the liquid level passes through two levels marked on the reservoir. Next, by applying vacuum suction underneath the exit of the capillary, the drainage time decreases by the combination effects of gravity and stretching stress.

By applying the Hagen-Poiseuille Equation (Bird, Stewart and Lightfoot, 1960),

$$\frac{V}{t} = \frac{\pi r^4}{8\eta l} [P + \rho g l] \quad (4-0)$$

to the situations without and with vacuum, the following equation can be obtained for the Newtonian liquid,

Figure 4-1 Schematic diagram of 200 ml viscometer

$$P_{11} - P_{22} = \frac{8\eta l V}{\pi r^4} \left[\frac{1}{t_2} - \frac{1}{t_1} \right] \quad (4-1)$$

where P_{11} - P_{22} or σ_{ext} is the tensile stress at the exit of the capillary, η is the shear viscosity of liquid, l is the capillary length, (all capillaries used in extensional experiments have the same value of 5 cm), V is the reservoir capacity between upper and lower mark (here is 200 ml), r is the inner radius of the upper capillary, t_1 is the drainage time without stretching and t_2 is the drainage time with stretching. Next, by analyzing the filament

profile at the exit of upper capillary, stretching rate $\dot{\varepsilon}$ can be obtained by differentiating the axial liquid velocity, v , with respect to the axial distance, x ,

$$\dot{\varepsilon} = \frac{dv}{dx} \quad (4-2)$$

For a constant volumetric flow rate and assuming no radial variation in the velocity, the local velocity and stretch rate $\dot{\varepsilon}$ are given by

$$v = \frac{V}{t_2} \frac{1}{\pi r^2} \quad (4-3)$$

and

$$\dot{\varepsilon} = (-2) \frac{V}{t_2} \frac{dr/dx}{\pi r^3} \quad (4-4)$$

where dr/dx can be obtained by analyzing the liquid filament profile.

Then the apparent extensional viscosity at the exit of upper capillary can be obtained by the following equation,

$$\eta_{ext} = \frac{P_{11} - P_{22}}{\dot{\varepsilon}} \quad (4-5)$$

Figure 2-17 Control volume for force balance calculation

Knowing the flow situation at the exit of the upper capillary, the tensile stress at the lower position can be obtained by applying a force balance for the control volume between the exit of upper capillary and lower position. The control volume for the force balance calculation is illustrated in Figure 2-17, which is also shown here for convenience. Inertia force $F(I)$, surface tension $F(ST)$, and gravity force $F(g)$ are to be considered in the force balance.

$$P_{11} - P_{22} = \frac{A_0}{A_1} [P_{11} - P_{22}]_0 + \gamma \left(\frac{1}{r_1} - \frac{A_0}{A_1 r_0} \right) + \frac{F(I) + F(ST) - F(g)}{A_1} \quad (4-6)$$

where subscription 0 denotes the value at the exit of upper capillary or the upper position, 1 denotes the value at the lower position. A is the cross section area of the filament at specific position. Similarly, r is the radius of the filament. And γ is surface tension of fluid. Expressions for the forces are as follows,

$$F(I) = \rho \left(\frac{V}{t_2} \right) \left(v_1 - \frac{4}{3} v_0 \right) \quad (4-7)$$

$$F(ST) = 2\pi\gamma [r_0 \cos(\theta_0) - r_1 \cos(\theta_1)] \quad (4-8)$$

$$\theta = -\tan^{-1} \left[dr/dx \Big|_{x=x} \right] \quad (4-9)$$

$$F(g) = \rho g \pi [(r_0 + r_1)/2]^2 (x_1 - x_0) \quad (4-10)$$

where ρ is the density of the fluid, x is the position along the filament profile, and v is velocity of fluid at specific position; here we assume velocity profile is parabolic at the exit of upper capillary while it is flat along the filament profile. It needs to be noted that Eqn. (4-7) only applies to the situation when subscription 0 denotes for the exit of upper capillary. In that position, the velocity profile has been assumed to be parabolic.

In the same way, the stretching rate at new position can be acquired by analyzing the filament profile at that spot. Then reapplying Eqn. (4-5), the apparent extensional viscosity at this position can be calculated. It need noted that when subscription 0 denotes for the position below the exit of upper capillary, Eqn. (4-7) should be replaced by Eqn. (4-11) considering the flat velocity profile for such position.

$$F(I) = \rho \left(\frac{V}{t_2} \right) (v_1 - v_0) \quad (4-11)$$

Following the similar procedure, the apparent extensional viscosities at different positions along the filament between upper and lower capillary can be calculated.

By summing up the results, apparent extensional viscosity profile along the filament can be plotted against the stretching rate.

4.3 Newtonian liquids used

Experiments were done at 25 (± 0.01) °C using mineral oils (MO) obtained from the Cannon Instrument Company of State College, PA. Three different mineral oils were used for measurement, and these had a shear viscosity of 1.016, 0.562, 0.291 poise, respectively. They had the same surface tension value, which is 28.5 mN/m. Their densities were 0.8627, 0.8606 and 0.8595 g/ml.

4.4 Experimental apparatus and procedure

The capacity of the extensional viscometer used with Newtonian liquids was 200ml. A CCD camera fitted with a zoom lens was used with this viscometer. This CCD camera is used to take the image of the stretching liquid profile between the upper and lower capillaries. The schematic of the apparatus is shown in Figure 4-1, note that the CCD camera fitted with a zoom lens is not shown in Figure 4-1. The viscometer is made of glass and consists of two connected glass bulbs forming a liquid reservoir; two lines were marked at the top and bottom of the lower bulb. The capacity of viscometer is the liquid volume between the upper mark and the lower mark for the liquid reservoir. A water bath around the viscometer helped maintain the temperature of liquid inside the reservoir at 25°C, a Fisher Scientific Isotemp circulator was used to keep a constant temperature in the water bath. The liquid inside the reservoir drains from a thin wall stainless capillary which is attached at the bottom of viscometer.

Different inner diameter stainless steel capillaries of 5 cm length were chosen for making measurements on the mineral oil with different shear viscosity. The principle for choosing the upper capillary is based on the following consideration: for larger diameter, the liquid will drain out from the reservoir quickly and lead to a shorter drainage time and drainage time difference for situations with and without fluid stretching; for smaller

diameter, the liquid tends to drip when it exits from the upper capillary. To obtain reliable and accurate results, we need to have a drainage time as long as possible (by decreasing the capillary diameter) but avoid dripping phenomenon. Also, diameter for lower capillary should be equal to or smaller than upper capillary. By trial and error, a set of capillaries was chosen for measuring the fluids with different shear viscosity. Table 4-1 lists the inner diameter of different capillaries for measuring different fluids.

Table 4-1 Capillary ID (inner diameter) for different fluids

	1.016 poise MO	0.562 poise MO	0.291 poise MO
Upper Capillary ID (mm)	2.692	2.159	1.829
Lower Capillary ID (mm)	2.413	1.829	1.600

Figure 4-2 Image when obstruction (smaller capillary) is placed under the upper capillary for non-stretching situation

After selecting the proper capillaries, the fluid was filled into the reservoir, and allowed to rest for several hours until its temperature reached 25 ± 0.01 °C for a while. Then the fluid was allowed to flow freely through the capillary out of the reservoir. An obstruction was

put under the upper capillary to avoid fluid stretching when flow occurs due to gravity alone. Figure 4-2 is the photo taken during the situation without stretching. The drainage time is measured for the fluid draining between the upper mark and the lower mark.

Figure 4-3 Upper photo is taken during the stretching, lower photo is the 5X magnification of the upper photo, which is used for analysis

The liquid was refilled into the reservoir again and allowed to reach thermal equilibrium. To cause stretching, another capillary which is connected to vacuum was put under the upper capillary. The liquid emerging from the upper capillary is sucked into the

lower capillary and stretched in the air gap between the capillaries. The drainage time is recorded again. During the stretching, the image of the stretched liquid profile between the upper and lower capillary is taken by a CCD camera fitted with a zoom lens. Figure 4-3 gives a typical image when stretching is applied to the liquid.

Many measurements were done to get reliable data, and the error in the measurement came from the difficulty of keeping temperature constant at $25 \pm 0.01^\circ\text{C}$. In addition, since a part of the viscometer (lower glass tube connected to the reservoir, refer to Figure 4-1) was exposed to the air, the accuracy of measurement was affected by the room temperature. To minimize this effect, a thick polyester fiber “jacket” was used to cover the outside of the glass tube, and a heating fan was used to blow warm air to the tube to keep the nearby air temperature around 25°C . This problem was later overcome with a new design for this viscometer. Details are given in the next chapter.

4.5 Results and discussion

For each Newtonian fluid, identical results were obtained for the extensional viscosity under three different conditions of measurement (different gap between two capillaries), and the measurement results were also close to the expected value (shear viscosity multiply by Trouton ratio of 3 for Newtonian liquids). Table 4-2 lists the drainage time under the situation of with and without stretching. The measurement error for each drainage time is within ± 0.15 s.

According to the method described in the “measurement principle” section, the apparent extensional viscosities were calculated as a function of stretching rates. Next, calculation details are explained using the second data set of 1.016 poise mineral oil as example.

Table 4-2 Drainage time for different fluids under the situation with and without stretching

Fluids Time	1.016 poise mineral oil			0.562 poise mineral oil			0.291 poise mineral oil		
Drainage time (s)	1	2	3	1	2	3	1	2	3
With stretching	369.07	367.34	367.64	504.14	500.11	505.13	481.40	483.30	483.52
Without stretching	372.87	372.44	372.87	514.95	514.32	514.95	492.96	492.96	493.39

From Table 4-2, it can be seen that drainage time without stretching, or t_1 , is 372.44 s, and drainage time with stretching, or t_2 , is 367.34 s. Shear viscosity of liquid, η , is 1.016 poise. Capillary length, l , is 5 cm and reservoir capacity between upper and lower mark, V , is 200 ml. After analysis of photo taken during stretching (which is similar to Figure 4-3), the filament radius at the exit of upper capillary, r , is obtained to be 0.150 cm. By applying Eqn. (4-1), the tensile stress at the exit of upper capillary, P_{11} - P_{22} , or σ_{ext} , can be calculated as follows,

$$P_{11} - P_{22} = \frac{8\eta l V}{\pi r^4} \left[\frac{1}{t_2} - \frac{1}{t_1} \right] = \frac{(8)(1.016)(5)(200)}{\pi(0.150)^4} \left[\frac{1}{367.34} - \frac{1}{372.44} \right] = 189.49 \text{ dyne} / \text{cm}^2$$

And the stretching rate at the exit of upper capillary can be calculated as follows,

$$\dot{\varepsilon} = (-2) \frac{V}{t_2} \frac{dr/dx}{\pi r^3} = (-2) \frac{200}{367.34} \frac{-0.61}{\pi(0.150)^3} = 62.71 \text{ 1/s}$$

where dr/dx is calculated from the liquid filament profile as -0.61 at the position of the exit of upper capillary. Therefore, the apparent extensional viscosity at the exit of upper capillary can be calculated as,

$$\eta_{ext} = \frac{P_{11} - P_{22}}{\dot{\epsilon}} = \frac{189.49}{62.71} \approx 3.02 \text{ poise}$$

The position at the exit of upper capillary is set for $x=0$; next the apparent extensional viscosity at $x=0.0174$ cm is calculated as follows (here all values at $x=0$ are denoted by subscript of 0 and all values at $x=0.0174$ cm are denoted by subscript of 1). According to observed liquid filament profile and drainage time, the following values at position 0 and position 1 are listed in Table 4-3.

Table 4-3 Values obtained at position 0 and 1 for 1.016 poise mineral oil

Position	Distance, x , cm	Radius, r , cm	Cross section area, A , cm ²	dr/dx	θ	Velocity, v , cm/s
0	0	0.150	0.0710	-0.6144	0.551	7.670
1	0.0174	0.138	0.0596	-0.6046	0.544	9.129

$$F(I) = \rho \left(\frac{V}{t_2} \right) (v_1 - \frac{4}{3} v_0) = 0.8627 \left(\frac{200}{367.34} \right) (9.129 - \frac{4}{3} 7.670) = -0.516 \text{ dyne}$$

$$\begin{aligned} F(ST) &= 2\pi\gamma[r_0 \cos(\theta_0) - r_1 \cos(\theta_1)] \\ &= 2\pi(28.5)[0.150 \cos(0.551) - 0.138 \cos(0.544)] \\ &= 1.819 \text{ dyne} \end{aligned}$$

$$\begin{aligned} F(g) &= \rho g \pi [(r_0 + r_1)/2]^2 (x_1 - x_0) \\ &= 0.8627(981)\pi [(0.150 + 0.138)/2]^2 (0.0174 - 0) \\ &= 0.960 \text{ dyne} \end{aligned}$$

$$\begin{aligned}
P_{11} - P_{22} &= \frac{A_0}{A_1} [P_{11} - P_{22}]_0 + \gamma \left(\frac{1}{r_1} - \frac{A_0}{A_1 r_0} \right) + \frac{F(I) + F(ST) - F(g)}{A_1} \\
&= \frac{0.0710}{0.0596} 189.49 + 28.5 \left(\frac{1}{0.138} - \frac{0.0710}{0.0596 * 0.150} \right) + \frac{-0.516 + 1.819 - 0.960}{0.0596} \\
&= 212.46 \text{ dyne / cm}^2
\end{aligned}$$

$$\dot{\varepsilon} = (-2) \frac{V}{t_2} \frac{dr/dx}{\pi r^3} = (-2) \frac{200}{367.34} \frac{-0.6046}{\pi (0.138)^3} = 80.11 \text{ 1/s}$$

Therefore, apparent extensional viscosity for the position of $x=0.0174$ cm can be calculated as,

$$\eta_{ext} = \frac{P_{11} - P_{22}}{\dot{\varepsilon}} = \frac{212.46}{80.11} \approx 2.65 \text{ poise}$$

For next lower position, it can set as position 1, while position 0 can be set as the position where $x=0.0174$ cm. Following the above procedure, apparent extensional viscosity at this new position can be obtained. However, when one is calculating the apparent extensional viscosities at all the lower positions, Eqn. (4-11) should be used to calculate inertial force instead of Eqn. (4-7) which is used for above calculation process.

Following above calculation procedure, a series of curves for apparent extensional viscosities against stretching rates for all liquids can be obtained.

Apparent extensional viscosities against stretching rates for 1.016, 0.562, 0.291 poise mineral oil are presented in Figure 4-4, 4-5, 4-6, respectively. It need to be noted that the expected theoretical values of extensional viscosity for each liquid are horizontal lines in each Figure.

Figure 4-4 Extensional viscosity vs. stretching rate results for 1 poise mineral oil

Figure 4-5 Extensional viscosity vs. stretching rate results for 0.562 poise mineral oil

Figure 4-6 Extensional viscosity vs. stretching rate results for 0.2913 poise mineral oil

Figures 4-4, 4-5, 4-6 show that the apparent extensional viscosity of the liquid exiting from the upper capillary is close to three times the shear viscosity of the Newtonian liquid. By obtaining the correct extensional viscosity even for the Newtonian liquid of shear viscosity as low as 0.2913 Poise, the effectiveness and accuracy of the instrument was proved.

Note that the stretch rate increases as one moves from the upper to the lower capillaries, and the deviation from the expected results at high stretching rate is the result of the neglect of momentum transfer from the air to the fluid in the data analysis; this momentum transfer becomes increasingly important at large axial distance and needs to be taken into account, but there is no simple way to do this.

5 Extensional Viscosity of Polymer Solutions

5.1 Experiment objective

After Newtonian liquids were successfully characterized, the extensional viscosities of the various polymer solutions were measured using the newly designed extensional viscometer. For the purpose of this research, we wanted to use this viscometer to evaluate extensional viscosities of polymer solutions, which include the polystyrene-DECALIN system and commercial polymer solutions. There are two reasons which can explain why the polystyrene-DECALIN system is the ideal system to use. First, solutions made by this system have similar properties to commercial liquids. They have similar shear viscosity, density and surface tension. This made polystyrene-DECALIN system a good substitute for the commercial liquids. One can first test solutions which are made from polystyrene and DECALIN instead of the very expensive commercial liquids when one is fine-tuning this viscometer. Secondly, different polystyrenes can be used to test their effects on extensional behavior. For this purpose, polystyrenes with different molecular weight and different molecular weight distribution were chosen.

For this phase of experiments, it was also necessary to further improve the design of this viscometer. It has been mentioned in the chapter entitled “Extensional viscosities of Newtonian liquids” that the accuracy of measurement was affected by variations in the room temperature because a part of viscometer was not immersed in the water bath. Although measures were taken to minimize the effect of the room temperature, the best way to solve this problem was to redesign this viscometer. In addition, another issue arose from the nature of commercial liquids. They are very expensive liquids (around \$1000 for 1 liter). For our 200 ml viscometer design, it took about 250 ml test liquid for one measurement, and the test liquid could not be reused as it had been “stretched” during the test. This is not what we want to see for our test. It is a practical matter for us to decrease the need of the amount of liquid for each test. Therefore, it is worthwhile that the capacity

of the viscometer be decreased dramatically although this does increase the difficulty in making measurements.

We also want to compare the extensional behavior of polymer solutions of different concentrations, or polymer solutions which have same viscosity, but with different molecular weights or different molecular weight distributions. Two commercial liquids were also evaluated for their extensional viscosity.

5.2 Measurement principle

For Non-Newtonian liquids, if their behavior follows the power law, the volumetric flow rate Q can be expressed as Eqn. (5-1) (Chhabra and Richardson, 1999) if we consider gravity-driven liquid flows through a capillary of radius r and length l ,

$$Q = \pi \left[\frac{n}{3n+1} \right] \left[\frac{\Delta P}{2ml} \right]^{\frac{1}{n}} r^{\frac{(3n+1)}{n}} \quad (5-1)$$

where m is the consistency index, n is the power law index and ΔP is the pressure difference between the two ends of the capillary, including effect of gravity.

For the procedure described in Chapter 4, the above equation can be changed into the following two equations to calculate the tensile stress,

$$\frac{V}{t_1} = \frac{\pi m}{3n+1} \left(\frac{\rho g l + P_0}{2ml} \right)^{\frac{1}{n}} r^{\frac{(3n+1)}{n}} \quad (5-2)$$

$$\frac{V}{t_2} = \frac{\pi m}{3n+1} \left(\frac{\rho g l + P_0 + \sigma_{ext}}{2ml} \right)^{\frac{1}{n}} r^{\frac{(3n+1)}{n}} \quad (5-3)$$

For a Newtonian liquid, the value of n is 1 and m is shear viscosity of liquid or η . By substituting the value of n and m , Eqn. (5-2) and (5-3) can be simplified into (4-1).

For the polymer solutions used here, they all have Newtonian liquid like behavior under an imposed shear stress (refer to Figure 3-2) due to their low polymer concentrations. Therefore, data analysis is the same as it was for the Newtonian liquids described in section 4.2.

5.3 Polymer solutions

Two categories of solutions were prepared for measurement. One category of solution is polystyrene dissolved in DECALIN; another category of solution is commercially obtained.

Several considerations were applied to the process of finding a proper solvent for polystyrene. Solutions which have similar properties with commercial liquids need to be prepared. Among these properties, requirement of a shear viscosity of 3~5 cp is the most important one. To be suitable for the experiment needs, the solvent shear viscosity had to be several centipoises; to avoid environmental concerns, the solvent should be not volatile (i.e. it must have low vapor pressure); For theoretical reasons, the surface tension of solvent should be low; To maintain a safe work area, the solvent should be non-toxic.

After reviewing the literature and handbooks, DECALIN (cis+trans, obtained from Fluka) was chosen as it fits all the key requirements. Table 5-1 lists the relevant data for DECALIN.

A large number of polymer solutions of polystyrene and DECALIN system have been tested for extensional viscosity. According to their applications, these polymer solutions can be divided into two groups. The solutions in group one are mainly for testing this new

viscometer, and they were also evaluated for their jetting behavior in the jetting equipment located at the DuPont Experimental Station (Wilmington, DE). The solutions in group two were used mainly for comparing their extensional and jetting behaviors and obtaining the qualitative relation between their extensional and jetting behaviors. Next these solutions will be introduced by their groups.

Table 5-1 Property data for DECALIN at 25°C

DECALIN	Formula	Viscosity (cp)	Vapor Pressure (kPa)	Surface Tension (dyne/cm)	Density (g/cm ³)
Cis	C ₁₀ H ₁₈	3.042	0.10	-	-
Trans	C ₁₀ H ₁₈	1.948	0.16	-	-
Cis+Trans	C ₁₀ H ₁₈	2.281 ¹	~0.10	27.6 ²	0.881
Water	H ₂ O	0.89	3.169	72	1.0

¹: the shear viscosity is obtained by measuring the DECALIN (cis+trans) with a capillary viscometer.

²: the surface tension value is for the solution of 2% (wt.) polystyrene in DECALIN, this value is found from the literature (Polymer Letters, Vol. 2, pp. 51-53, 1964).

Four different solutions of polystyrene in DECALIN were prepared. The reason to use this system is that we can easily vary the shear viscosity by varying polymer concentration, polymer molecular weight and polydispersity. Three different polystyrenes have been used as solute. They are polydisperse polystyrenes having a weight-average molecular weight of 100,000 and 255,000, and monodisperse polystyrene of molecular weight of 900,000. These three different polystyrenes were dissolved in DECALIN at the same concentration of 2 wt% to study the effect of molecular weight. Another 0.5 wt% of polystyrene of

molecular weight of 100,000 in DECALIN was prepared to study the influence of polymer concentration and to compare the rheological properties with commercial polymer solutions which have similar shear viscosity.

It took about two days for polystyrene grains to dissolve entirely into DECALIN. Once the polystyrene grains are put into DECALIN, the solution needs to be stirred continuously. A magnetic stirrer was used for this purpose. Depending on whether polystyrene grains have been entirely dissolved into DECALIN or not, stirring time differs in accordance with the shape of polystyrene grains. Normally, monodisperse polystyrenes are available in the form of powder or crumb, which greatly shortens the required stirring time to slightly more than one day. While polydisperse polystyrenes are normally available in the shape of pellets, it took much longer time to dissolve all polystyrene particles. Sometimes it took more than two days to complete the process of dissolution.

In group one, two commercial polymer solutions available to the DuPont company were also used for measurement. As we are not allowed to release the details about these solutions, they were only recognized as commercial liquid one (CL1) and commercial liquid two (CL2). The basic properties of all solutions in group one are listed in Table 5-2. This Table lists the density, surface tension and rheological properties of six polymer solutions examined. It is seen that density values of all liquids are comparable. Similarly, there is little difference amongst the surface tension values. The shear viscosity of each of the fluids is constant and independent of shear rate, and CL1 and CL2 have essentially the same shear viscosity.

Table 5-2 Basic properties of polymer solutions in group one

Polymer Solution	Density (ml/gm)	Surface Tension (mN/m)	Shear Viscosity (cp)
0.5% PS (polydisperse, Mw= 100,000) in DECALIN	0.883	27.43	2.76
2% PS (polydisperse, Mw= 100,000) in DECALIN	0.885	29.73	4.5
2% PS (monodisperse, Mw= 900,000) in DECALIN	0.890	29.71	9.8
2% PS (polydisperse, Mw=255,000) in DECALIN	0.887	29.48	4.75
Commercial liquid 1 (CL1)	0.9454	30.08	3.2
Commercial liquid (CL2)	0.9634	30.41	3.1

There are eight polymer solutions which have been prepared for group two. All of them consisted of polystyrene and DECALIN. One objective of this measurement was to compare polymer solutions which have same shear viscosity of 5 cp but different molecular weight and molecular weight distribution. Based on this consideration, six different polystyrenes were chosen. These polystyrenes had three different molecular weights of 45,000, 140,000 and 300,000. One polydisperse and one monodisperse polystyrene were chosen for each molecular weight listed above. Two other polymer solutions of approximately 3 cp were prepared mainly for comparing the jetting behavior with Newtonian liquid of DECALIN. The basic properties of solutions in group two are listed in Table 5-3.

Table 5-3 Basic properties of polymer solutions in group two

Polymer Solution	Density (ml/gm)	Surface Tension (mN/m)	Shear Viscosity (cp)
4% PS (monodisperse, Mw= 45,000) in DECALIN	0.887	29.5	5
5% PS (polydisperse, Mw= 45,000) in DECALIN	0.891	29.5	5
3% PS (monodisperse, Mw= 140,000) in DECALIN	0.887	29.5	5
2% PS (polydisperse, Mw= 140,000) in DECALIN	0.886	29.5	5
2% PS (monodisperse, Mw= 300,000) in DECALIN	0.888	29.5	5
2% PS (polydisperse, Mw= 300,000) in DECALIN	0.893	29.5	5
1.5% PS (polydisperse, Mw= 45,000) in DECALIN	0.883	29.5	2.8
2.5% PS (polydisperse, Mw= 45,000) in DECALIN	0.883	29.5	3.3

Considering the fact that all polymer solutions of group one have a similar surface tension value, the surface tension value for polymer solutions in group two was assumed to be the same value of 29.5 mN/m. We can see from Table 5-3 that the first six polymer solutions all have same shear viscosity of 5 cp. The polystyrene concentration was chosen by trial and error so as that each solution had the same shear viscosity. As for the last two polymer solutions, especially the solution of 2.5% polystyrene (polydisperse, MW=45,000) in DECALIN, its purpose was to compare the extensional behavior with other

concentration solutions (1.5% and 5%). The more important thing is that we can get ideal jetting behavior at this concentration. This jetting behavior will be introduced in detail in following Chapters.

5.4 Experimental apparatus and procedure

In light of the experimental error caused by temperature non-equilibrium and requirement of the nature of commercial liquids, two new viscometers were made for measuring properties of polymer solution and commercial liquids. These two viscometers had reservoir volumes of 100 ml and 50 ml. The reason that two new viscometers were made instead of one with 50 ml capacity was to make gradual improvements. Testing of 100 ml viscometer gave information on what significant changes happened in addition to the decrease of viscometer capacity, and this indicated the possibility to further decrease the viscometer size. If this change is successful, very expensive samples can be saved without compromising the accuracy of the test result. Another change made in designing the two new viscometers was that the “jacket” covered the entire viscometer (the lower glass tube is not covered for the viscometer of 200 ml used in measuring properties of the Newtonian liquid), so the water bath between the outside of viscometer and “jacket” could maintain the desired temperature inside the viscometer. Figure 5-1 is the schematic diagram of the new viscometers; the inside viscometer was made of glass, and the outside “jacket” was made of transparent plexiglass which allows for visual observation during the experiment.

A solution of 2% polystyrene (polydisperse, MW=100,000) in DECALIN was used as the candidate solution tested on all three viscometers of 200 ml, 100 ml and 50 ml capacities. Effectiveness of the new viscometer can be judged by comparing results obtained from the viscometer with 200ml capacity. Much effort was used to make good measurements but with decreasing reservoir capacity from 200 through 100 to 50 ml. A smaller reservoir means decreased drainage time and drainage time difference and increased difficulty for manipulating the experiment. But it is worth to do this considering that one is dealing with very expensive solutions. The effectiveness of the new viscometer

was demonstrated by using the test solution (2% polystyrene (polydisperse, MW=100,000) in DECALIN). Finally, the extensional viscosities for all polymer solutions were measured successfully using the reservoir whose capacity can be as small as 50 ml. The experimental procedure is same as that employed with the Newtonian liquid although more accuracy is required during the experiment, and the experiment lasts for a shorter time period.

Figure 5-1 Schematic diagram of 100 & 50 ml viscometer

Figure 5-2 is a photograph of the viscometer (including the CCD camera, which is used to take the image of the stretching liquid profile between the upper and lower capillaries) when measuring group one polymer solutions.

Figure 5-2 Photo of viscometer and CCD camera

One fact that needs to be noted is that liquid does not fill up the entire cross section of the lower capillary during the stretching process, and a sheath of air is drawn into the vacuum flask along with the liquid. This phenomenon is shown very clearly in Figure 4-3 and 5-1. In these experiments, the gap between the upper and lower capillaries was of the same order of magnitude as the capillary diameter. By varying this gap, stretching rate can be changed.

The capillary sizes used in the measurement of group one polymer solutions are listed in Table 5-4.

Table 5-4 Capillary ID (inner diameter) for polymer solutions of group one

Polymer solution	Upper Capillary ID (mm)	Lower Capillary ID (mm)
0.5% PS (polydisperse, Mw= 100,000) in DECALIN	1.067	0.889
2% PS (polydisperse, Mw= 100,000) in DECALIN	1.270	1.067
2% PS (monodisperse, Mw= 900,000) in DECALIN	1.397	1.270
2% PS (polydisperse, Mw=255,000) in DECALIN	1.270	1.067
Commercial liquid (CL1)	1.067	0.889
Commercial liquid (CL2)	1.067	0.889

Polymer solutions in group two were characterized in similar viscometer setup as those in group one. As the setup for polymer solutions of group two was rebuilt, and the photo of viscometer has more details of the measurement setup, it is shown here in Figure 5-3.

This new viscometer setup was housed inside a fume hood. The CCD camera fitted with a zoom lens was connected to a computer, which is not shown in Figure 5-3, to display the captured photo of the stretched filament profile. The conical flask is connected to vacuum by a plastic tube. The mouth of the conical flask is fitted with a silicone rubber stopper. The lower capillary is put through the stopper to draw the liquid leaving from the upper capillary during the measurement. The part located at left bottom of Figure 5-3 is a flow meter, which can control the circulation in the water bath. The plate behind the viscometer is a “U” tube manometer filled with mercury. This manometer was used to monitor the vacuum during the stretching process.

Figure 5-3 Photo of viscometer setup for polymer solution of group two

The upper capillary and lower capillary sizes used for polymer solutions in group two are listed in Table 5-5.

Table 5-5 Capillary ID (inner diameter) for polymer solutions of group two

Polymer Solution	Upper Capillary ID (mm)	Lower Capillary ID (mm)
4% PS (monodisperse, Mw= 45,000) in DECALIN	1.270	1.067
5% PS (polydisperse, Mw= 45,000) in DECALIN	1.270	1.067
3% PS (monodisperse, Mw= 140,000) in DECALIN	1.270	1.067
2% PS (polydisperse, Mw= 140,000) in DECALIN	1.270	1.067
2% PS (monodisperse, Mw= 300,000) in DECALIN	1.270	1.067
2% PS (polydisperse, Mw= 300,000) in DECALIN	1.270	1.067
1.5% PS (polydisperse, Mw= 45,000) in DECALIN	1.067	0.889
2.5% PS (polydisperse, Mw= 45,000) in DECALIN	1.067	0.889

5.5 Results and discussion

To make the transition from 200 ml viscometer to 50 ml viscometer, a large number of experiments were conducted. These focused on 2 wt% polystyrene (polydisperse, MW=100,000) in DECALIN. After obtaining satisfactory results for the above solution, the measurement then proceeded to all other polymer solutions on the 50 ml viscometer. Table 5-6 shows typical drainage times with and without stretching for polymer solutions in group one. The measurement error for each drainage time is within ± 0.15 s. All data were measured using the 50 ml viscometer.

Table 5-6 Drainage times for polymer solutions in group one under the situation with and without stretching

Polymer solution	Drainage time (s)	
	With stretching	Without stretching
0.5% PS (polydisperse, Mw= 100,000) in DECALIN	166.37	169.92
2% PS (polydisperse, Mw= 100,000) in DECALIN	152.67	155.73
2% PS (monodisperse, Mw= 900,000) in DECALIN	166.34	169.94
2% PS (polydisperse, Mw=255,000) in DECALIN	139.5	143.07
Commercial liquid (CL1)	168.59	172.19
Commercial liquid (CL2)	173.35	180.87

Table 5-7 shows drainage times for situations with and without stretching for polymer solutions in group two. The measurement error for each drainage time is within ± 0.15 s. All data were measured using the 50 ml viscometer.

The apparent extensional viscosities at the exit of the upper capillary and the corresponding Trouton Ratios (ratio of extensional viscosity to shear viscosity of one solution) for polymer solutions in group one and group two are listed in Tables 5-8 and 5-9, respectively. The extensional viscosities listed in Table 5-8 and Table 5-9 are all at the same location – exit of the upper capillary, and under these conditions polymer molecules are not likely to be particularly stretched out and aligned with the flow field. The measurement errors for apparent extensional viscosities of polymer solutions in group one and two are within $\pm 8\%$. We can see from the results that the ratio of extensional viscosity to shear viscosity is no larger than 15. This ratio is larger than the Trouton ratio of 3 for the Newtonian liquid but much less than the ratio of 10^4 observed with high molecular weight polymer solutions (Gupta and Sridhar, 1998).

Although the apparent extensional viscosity at the exit of the upper capillary is accurate, the calculated extensional viscosities below the exit of the upper capillary and along the axial direction have increasing errors. These errors reach maximum when one calculates the extensional viscosity at the upper tip of the lower capillary. As we have discussed earlier, the stretching rate increases as one moves from the upper to the lower capillaries, and the deviation from the expected results at high stretch rate is the result of the neglect of momentum transfer from the air to the fluid in the data analysis; this momentum transfer becomes increasingly important at the place near the upper tip of the lower capillary and needs to be taken into account, but there is no simple way to do this. One can understand this when one realizes that the distance between upper and lower capillary is only 0.6 mm and stretching rate can be as high as 4000 1/s for the solution of CL2. To solve this problem, a flow simulation around the liquid filament is needed in the future. Once this problem is solved, accurate apparent extensional viscosities can be calculated along the axial direction of liquid filament as a function of increasing stretch rate.

Table 5-7 Drainage time for polymer solutions in group two under the situation with and without stretching

Polymer solutions	Drainage time (s)	
	With stretch	Without stretch
4% PS (monodisperse, Mw=45,000) in DECALIN	135.27	138.41
5% PS (polydisperse, Mw=45,000) in DECALIN	122.01	126.3
3% PS (monodisperse, Mw=140,000) in DECALIN	150.8	154.86
2% PS (polydisperse, Mw=140,000) in DECALIN	139.45	145.27
2% PS (monodisperse, Mw=300,000) in DECALIN	145.71	154.31
2% PS (polydisperse, Mw=300,000) in DECALIN	139.05	148.51
1.5% PS (polydisperse, Mw=45,000) in DECALIN	167.36	168.44
2.5% PS (polydisperse, Mw=45,000) in DECALIN	182.91	184.69

It is pretty straightforward to calculate the extensional viscosity at the position of the exit of upper capillary. As these polymer solutions behave like a Newtonian liquid in their shear response, the process for calculating extensional viscosity is the same as the process described in the previous chapter for a Newtonian liquid. Next, the calculation process is shown for a solution in group two – 2% polystyrene (polydisperse, MW=140,000) in DECALIN.

From Table5-7, it can be found that the drainage time without stretching, or t_1 , is 145.27 s, and drainage time with stretching, or t_2 , is 139.45 s. Also, the shear viscosity of the liquid, η , is 0.05 poise, the capillary length, l , is 5 cm and reservoir capacity between upper and lower mark, V , is 50 ml. After analysis of the photo taken during stretching (which is similar with Figure 4-3), the filament radius at the exit of the upper capillary, r , is obtained as 0.0585 cm. By applying Eqn. (4-1), the tensile stress at the exit of upper capillary, P_{11} - P_{22} , or σ_{ext} , can be calculated as follows,

$$P_{11} - P_{22} = \frac{8\eta l V}{\pi r^4} \left[\frac{1}{t_2} - \frac{1}{t_1} \right] = \frac{(8)(0.05)(5)(50)}{\pi(0.0585)^4} \left[\frac{1}{139.45} - \frac{1}{145.27} \right] = 854.05 \text{ dyne/cm}^2$$

And the stretching rate at the exit of upper capillary can be calculated as follows,

$$\dot{\varepsilon} = (-2) \frac{V}{t_2} \frac{dr/dx}{\pi r^3} = (-2) \frac{50}{139.45} \frac{-1.21}{\pi(0.0585)^3} = 1511.48 \text{ 1/s}$$

where dr/dx is calculated from the liquid filament profile as -1.21 at the position of the exit of upper capillary. Therefore, apparent extensional viscosity at the exit of upper capillary can be calculated as,

$$\eta_{ext} = \frac{P_{11} - P_{22}}{\dot{\epsilon}} = \frac{854.05}{1511.48} \approx 0.565 \text{ poise}$$

Extensional viscosities for solutions in group one and two can be calculated by following the same procedure. Results are shown in Tables 5-8 and 5-9.

Table 5-8 Extensional results for polymer solutions in group one

Polymer solutions	Visc. (cp)		Trouton Ratio
	Shear	Exten.	
0.5% PS (polydisperse, Mw= 100,000) in DECALIN	2.76	9.78	3.54
2% PS (polydisperse, Mw= 100,000) in DECALIN	4.5	17.57	3.9
2% PS (monodisperse, Mw= 900,000) in DECALIN	9.8	46.29	4.72
2% PS (polydisperse, Mw=255,000) in DECALIN	4.75	22.95	4.83
Commercial liquid 1 (CL1)	3.2	13.43	4.2
Commercial liquid 2 (CL2)	3.1	35.02	11.3

Effect of polymer concentration

A polymer solution which has a higher polymer concentration should have a larger Trouton Ratio. It is obvious that a polymer solution with a higher concentration of polymer has more polymer molecules contributing to the extensional resistance. This increased extensional resistance leads to larger extensional viscosity and Trouton ratio. Polymer solutions in group one and two confirmed this fact. In group one, Trouton ratios for solutions of 0.5% and 2% polystyrene (polydisperse, Mw= 100,000) in DECALIN are 3.54

and 3.90. For polymer solutions in group two, Trouton Ratio increases from 4.02 to 5.00 when the concentration of polystyrene (polydisperse, $M_w=45,000$) in DECALIN changes from 1.5% to 2.5%

Table 5-9 Extensional results for polymer solutions in group two

Solution Name	Visc. (cp)		Trouton Ratio
	shear	Exten.	
4% PS (monodisperse, $M_w=45,000$) in DECALIN	5	29.2	5.84
5% PS (polydisperse, $M_w=45,000$) in DECALIN	5	37.2	7.45
3% PS (monodisperse, $M_w=140,000$) in DECALIN	5	42.4	8.47
2% PS (polydisperse, $M_w=140,000$) in DECALIN	5	56.5	11.30
2% PS (monodisperse, $M_w=300,000$) in DECALIN	5	66.3	13.26
2% PS (polydisperse, $M_w=300,000$) in DECALIN	5	74.9	15.00
1.5% PS (polydisperse, $M_w=45,000$) in DECALIN	2.8	11.3	4.02
2.5% PS (polydisperse, $M_w=45,000$) in DECALIN	3.3	16.5	5.00

Effect of polymer molecular weight

Extensional viscosity measurement results for polymer solutions in group one and made up of 2 wt % polystyrene in DECALIN with different molecular weight are shown in Table 5-8. A solution of 2 wt% polystyrene (monodisperse, 900,000) in DECALIN has the largest value of 46.29cp at the exit of upper capillary while the value for polystyrene (polydisperse, 255,000) and polystyrene (polydisperse, 100,000) solutions are 22.95cp and 17.57cp. Thus we may conclude from the results that the polymer solution with higher molecular weight has higher extensional viscosity as long as the other conditions are same. It needs to be noticed that Trouton Ratios did not follow the same rule with extensional viscosities. In group one, polymer solution with polystyrene (polydisperse, $M_w=255,000$) has a slightly larger Trouton Ratio of 4.83, while polymer solution with polystyrene

(monodisperse, $M_w=900,000$) has a slightly smaller Trouton Ratio of 4.72. One possible explanation is that although each molecule of polystyrene of molecular weight of 900,000 contributes more to the extensional resistance than that of polystyrene of molecular weight of 255,000, the higher molecular weight solution has much fewer molecular numbers than when they have same polystyrene weight percentage. Therefore, this trade-off leads to a slightly larger Trouton Ratio for the solution with polystyrene of molecular weight of 255,000.

The effect of molecular weight is pretty obvious for polymer solutions in group two. For these six polymer solutions with shear viscosity of 5 cp, all solutions with polystyrene of higher molecular weight have larger extensional viscosity and Trouton Ratio whether for monodisperse or polydisperse polystyrene. For example, solution of 2% PS (monodisperse, $M_w=300,000$) in DECALIN has an extensional viscosity of 66.3 cp and Trouton Ratio of 13.26. This extensional viscosity of 66.3 cp is larger than 42.4cp and 56.5 cp which correspond to extensional viscosities of solutions of 3% PS (monodisperse, $M_w=140,000$) in DECALIN and 2% PS (polydisperse, $M_w=140,000$) in DECALIN, respectively. This Trouton Ratio of 13.26 is larger than 8.47 and 11.30 which correspond to Trouton Ratios of solutions of 3% PS (monodisperse, $M_w=140,000$) in DECALIN and 2% PS (polydisperse, $M_w=140,000$) in DECALIN, respectively.

In one word, higher molecular weight leads to larger extensional viscosity for solutions with same polymer weight percentage; higher molecular weight leads to larger extensional viscosity and Trouton Ratio for solutions with same shear viscosity.

Effect of polymer molecular weight distribution

We can find the conclusion for the effect of polymer molecular weight distribution from extensional flow results for polymer solutions in group two. Three pairs of polymer

solutions have been used for comparison. Each pair of polymer solutions has the same shear viscosity of 5 cp but different molecular weight (45,000, 140,000, or 300,000) and different molecular weight distribution (monodisperse and polydisperse). It is found that all solutions with polydisperse polystyrene have larger extensional viscosities and Trouton Ratios when all other conditions are kept the same. For example, the solution of 2% PS (polydisperse, $M_w=140,000$) in DECALIN has an extensional viscosity of 56.5 cp and Trouton Ratio of 11.3, which are larger than the extensional viscosity of 42.4 cp and Trouton Ratio of 8.47 for the solution of 3% PS (monodisperse, $M_w=140,000$) in DECALIN.

All in all, the polymer solution with polydisperse polymer has larger extensional viscosity and Trouton Ratio than the one with monodisperse polymer when they have same shear viscosity and same molecular weight.

Results for polystyrene and commercial polymer solutions

In group one, three polymer solutions with similar shear viscosity of about 3cp have been prepared for measuring extensional response. The three polymer solutions are 0.5 wt% polystyrene (polydisperse, 100,000) in DECALIN, commercial liquid 1 and commercial liquid 2.

The measurement results show that commercial liquid 2 has much larger extensional viscosity and Trouton Ratio (35.02 cp and 11.30) compared to other two solutions. Commercial liquid 1 has slightly higher values (13.43 cp and 4.20) than polystyrene solution (9.78 cp and 3.54).

6 Preliminary Investigation of the Jetting Behavior of Various Liquids

6.1 Experiment objective

This part of the experiment was conducted at the DuPont Experimental Station, Wilmington, DE where ink-jetting equipment was available. The objective of the research there was to test the jetting behavior of several liquids which included non-commercial and commercial liquids, non-Newtonian and Newtonian liquids. After testing there, it was expected to gain some insight into two things. First, we wanted to gain some initial knowledge of liquid jetting behavior. This knowledge would be used to design experiments for further investigation on our own jetting set-up which was projected to be built in our lab at WVU after the visit to the DuPont Experimental Station. It is obvious that the second thing is to learn how to design and assemble such jetting equipment for our future use. It needs to be noted that the jetting situations for our project, whether the jetting equipment at DuPont's Experimental Station or in our lab in WVU, were not the same as the situation introduced in chapter 2.2 of "break-up of liquid jets", where the flow is continuous. Our jetting was not continuous although jetting was carried out at fairly high frequency. Other phenomena such as partial or full retraction of liquid back into the nozzle can also occur here.

6.2 Test liquids

Liquids which were tested on the jetting equipment at DuPont included all the "group one" solutions from the last chapter entitled "Extensional viscosity of polymer solutions" for measuring extensional viscosity and three more Newtonian fluids. Therefore, a total of nine liquids were tested at DuPont. Actually, another commercial suspension (two-phase, solid particle and water) was also tested, but we were unsuccessful in jetting it. It seemed that the jet nozzle was always clogged with solid particles.

All nine liquids were successfully jetted. Besides the six polymer solutions introduced in last chapter, three Newtonian liquids were also used to make comparison with polymer solutions. These three Newtonian liquids were DECALIN, mineral oil with shear viscosity of 3.4 cp and mineral oil with shear viscosity of 5.1 cp (50 wt% 3 cp mineral oil and 50 wt% 7 cp mineral oil). Of the three Newtonian liquids, DECALIN and 3 cp mineral oil have similar shear viscosity as compared to the two commercial liquids and the solution of 0.5% polystyrene (polydisperse, 100,000) in DECALIN. The 5.1 cp mineral oil had similar viscosity to the solutions of 2% polystyrene in DECALIN.

Table 6-1 lists rheological properties for each of the nine liquids employed in group one. Note that extensional viscosities of the Newtonian liquids used in Table 6-1 are theoretical values rather than experimentally determined values, while those of the polymer solutions are the values at the exit of the upper capillary. It needs to be noted that extensional viscosities were measured for some Newtonian liquids during liquid characterization phase and the anticipated theoretical values were obtained.

6.3 Jetting equipment and testing procedure

A jetting equipment which was located at the DuPont Experimental Station was used for initial investigation of liquid jetting behavior. Photos of this jetting equipment are shown in Figure 6-1. It includes the following parts:

- 1). Jet head 64 DD2
- 2). Strobe delay card, which is controlled by software
- 3). Computer Translator box, which is used to give orders to jet head
- 4). Procedure control software: MODU_VSI BASICAL

Table 6-1 Rheological properties of liquids for preliminary jetting test

Solution Name	Shear Viscosity (cp)	Extensional Viscosity (cp)	Trouton Ratio
DECALIN	2.5	7.5	3
0.5% PS (polydisperse, Mw= 100,000) in DECALIN	2.76	9.78	3.54
2% PS (polydisperse, Mw= 100,000) in DECALIN	4.5	17.57	3.9
2% PS (monodisperse, Mw= 900,000) in DECALIN	9.8	46.29	4.72
2% PS (polydisperse, Mw=255,000) in DECALIN	4.75	22.95	4.83
3.4 cp Mineral oil	3.4	10.2	3
3 cp Mineral oil +7 cp Mineral oil (1/1)	5.1	15.3	3
Commercial Liquid 1 (CL1)	3.2	13.43	4.2
Commercial Liquid 2 (CL2)	3.1	35.02	11.3

5). A driver board connected to the computer motherboard

6). CCD video camera module N50 (Edmund Scientific, Barrington, NJ.)

7). X, Y, Z control for the jet head

8). X, Y, Z control for the CCD camera

9). Jet head holder

Figure 6-1 a, b, c, Different views of the jetting equipment in DuPont

10). Two LEDs from Radioshack

11). Holder for LED mirror

12). Power module for LED (+30 V DC/ +15V DC), Sola Solids, Cat. No.: 84-05-150, Input: 115V AC, Output: 5V DC, 500 mA

13). Software to get image: Image Acquisition (Ink drop acquisition & tracing), written by Robert V. Canning Jr., E.I. du Pont de Nemours & Company, Inc., 2002

Jetting experiments were conducted at room temperature at the DuPont Experimental Station using a 64 DD2 jet head. The jetting area was covered by transparent plastic cover which is vented at the top. The schematic diagram of the DuPont jetting set-up is shown in Figure 6-2.

Figure 6-2 Schematic diagram of DuPont jetting set-up

During the experiment, all parameters used to control the jetting are set up at the computer (located at lower left corner of Figure 6-1 a) which has a strobe delay card and a translator box inside. Drop frequency was 200 Hz, and a voltage ranging from 35v to 90v was used. A screen shot of the software control interface on that computer is shown in Figure 6-3. After all the parameters were defined, a command signal was sent to the Jet-Head Assembly. This signal controls the voltages which are applied to the tiny reservoir inside the Jet-Head. This voltage is directly related to the reservoir capacity. A change in voltage results in a change in the reservoir capacity, which results in a change of the jetted drop velocity. The sequence of drop images was recorded with the help of a strobe light and a video camera. These drop images are then transferred from the CCD camera to the connected computer which stores these images. It should be noted that as the applied voltage increased, a drop was ejected with increasing force, but it left a liquid filament in its wake at the nozzle exit; this filament could either retract back into the nozzle or break up, yielding the main drop and some satellite drops. The possibility that liquid can retract, either completely or partially, into the nozzle is a major difference between the experimental situation considered here and the flow of a liquid continuously out of a nozzle and described in the literature review chapter. In the case of the monodisperse polystyrene solution of molecular weight of 900,000, there was no jetting at all – only a filament formed, and it retracted back into the nozzle (refer to Figure 6-13). We also noted that the jetting behavior was unstable even at the same voltage (say 80v and 88v) for the polydisperse polystyrene solution of molecular weight of 255,000. Under this situation, the liquid either broke from the jet nozzle and formed the main drop and satellite or retracted back into the nozzle (refer to Figure 6-12).

Figure 6-3 Screenshot of software control interface for jet head

6.4 Results and discussion

Results of the jetting experiments for the five liquids which have a shear viscosity between 2.5 cp and 3.4 cp are listed in Table 6-2 as a function of applied voltage. Results for the other four liquids are given in Table 6-3. In each case, the drops are more or less spherical, but there are differences in the drop velocities. The presence or absence of any satellite drops is noted in Table 6-2 and 6-3. These tables list the diameter ratio (vertical diameter to horizontal diameter) and velocity of main drop and satellite at each voltage used for each solution. The data for diameter ratio was calculated from the observed pictures by zooming into each picture. The data for drop velocity was calculated from a series of images which were normally taken at a time delay of 150, 250, 350 and 450 μs at each voltage for each solution. The typical images for each liquid are shown in Figures 6-4 to 6-13. Next, effects of each factor on liquid jetting behavior are discussed according to the jetting results.

Effect of voltage

It is obvious that the fluid inside the jet head will receive more power to be pushed off from the jet port by applying high voltage. There are two effects on jetting when applying a high voltage (refer Table 6-2).

First, at high voltage, the liquid velocity is larger than that at low voltage. For example, the main drop velocity changed from 0.439 m/s at 55V to 1.115 m/s at 60V for CL1.

Second, at high voltage, more liquid will be ejected from the jet port. This leads to a longer tail and the possibility of forming satellites increases. For example, there was no satellite at 45V but one satellite at 55V for 3.4 cp mineral oil.

Table 6-2 Jetting results for liquid with ~3cp shear viscosity

Voltage (V)	Drop Type	Solution Name	DECALIN	3.4 cp Mineral oil	0.5% PS (100,000) in DECALIN	CL1	CL2
45	Main drop	V. Dia. (mm)	0.073	0.053	0.058		0.079
		Dia. Rat. (V/H)	1.042	1.000	0.952		1.125
		Velo. (m/s)	0.594	0.314	0.647		5.203
	First Satellite	V. Dia. (mm)	-				0.079
		Dia. Rat. (V/H)	-				0.964
		Velo. (m/s)	-				3.710
50	Main drop	V. Dia. (mm)					0.070
		Dia. Rat. (V/H)					1.000
		Velo. (m/s)					5.233
	First Satellite	V. Dia. (mm)					0.076
		Dia. Rat. (V/H)					1.000
		Velo. (m/s)					3.680
55	Main drop	V. Dia. (mm)	0.058	0.044	0.053	0.067	0.064
		Dia. Rat. (V/H)	0.909	0.882	1.059	1.150	1.048
		Velo. (m/s)	2.938	1.856	2.132	0.439	5.352
	First Satellite	V. Dia. (mm)	0.064	0.044	0.050		0.079
		Dia. Rat. (V/H)	0.957	0.882	0.895		0.964
		Velo. (m/s)	2.302	1.544	1.318		3.650
60	Main drop	V. Dia. (mm)	0.061			0.070	0.067
		Dia. Rat. (V/H)	1.167			1.143	0.958
		Velo. (m/s)	4.854			1.115	5.379
	First Satellite	V. Dia. (mm)	0.076				0.073
		Dia. Rat. (V/H)	0.963				0.862
		Velo. (m/s)	2.662				3.654
Note			45v: no sate. 55v above: satellite.	45v: no sate. 55v: satellite.	45v: no sate. 55v: satellite.	No satellite	Long tail, satellite for all voltage

Table 6-3 Jetting results for liquids of group one with 5cp shear viscosity

Voltage (V)	Drop Type	Solution Name	3cp+7cp Mineral Oil (1/1)	2% PS in DECALIN (poly 100,000)	2% PS in DECALIN (Poly 255,000)	2% PS in DECALIN (Poly 255,000), high volt.	2% PS in DECALIN (Poly 255,000), high volt
60	Main drop	V. Dia. (mm)	0.051	0.056	0.053		
		Dia. Rat. (V/H)	0.874	1.000	0.973		
		Velo. (m/s)	1.504	1.684	-0.614		
	First Satellite	V. Dia. (mm)		0.032			
		Dia. Rat. (V/H)		1.101			
		Velo. (m/s)	2.049	1.553			
65	Main drop	V. Dia. (mm)	0.044	0.053	0.051		
		Dia. Rat. (V/H)	0.881	0.856	0.946		
		Velo. (m/s)	1.440	2.051	-0.569		
	First Satellite	V. Dia. (mm)	0.031	0.040			
		Dia. Rat. (V/H)	0.874	1.080			
		Velo. (m/s)	1.650	1.399			
70	Main drop	V. Dia. (mm)	0.041		0.057		
		Dia. Rat. (V/H)	0.902		0.975		
		Velo. (m/s)	2.394		0.264		
	First Satellite	V. Dia. (mm)	0.041	0.048			
		Dia. Rat. (V/H)	0.902	0.970			
		Velo. (m/s)	1.919	0.791			
80	Main drop	V. Dia. (mm)				0.050	0.053
		Dia. Rat. (V/H)				1.031	1.029
		Velo. (m/s)				0.329	-1.883
	First Satellite	V. Dia. (mm)				0.045	
		Dia. Rat. (V/H)				1.144	
		Velo. (m/s)					
88	Main drop	V. Dia. (mm)				0.034	0.076
		Dia. Rat. (V/H)				0.920	1.405
		Velo. (m/s)				3.580	-1.163
	First Satellite	V. Dia. (mm)					
		Dia. Rat. (V/H)					
		Velo. (m/s)					
Note:			Satellites are present at each voltage. Velocity increases with increasing voltage.	All have satellites, and velocity & tail length increase with increasing voltage	Tail lengths increase with volt. Increase, for 60&65v, main drop retracts to port.	At high voltage, very long tail forms, and due to the MW polydisperse, some variation happens. For (Mono 900,000) solu., thick tail just moves out the port then retracts back to port even at high voltage.	

Figure 6-4 Jetting image for DECALIN

Figure 6-5 Jetting image for 3.4 cp Mineral Oil

Figure 6-6 Jetting image for 0.5% polystyrene (polydisperse, 100,000) in DECALIN

Figure 6-7 Jetting image for CL1

Figure 6-8 Jetting image for CL2

Figure 6-9 Jetting image for 3.4 cp +7.7 cp (1/1) Mineral Oil

Figure 6-10 Jetting image for 2% polystyrene (polydisperse, 100,000) in DECALIN

Figure 6-11 Jetting image for 2% polystyrene (polydisperse, 255,000) in DECALIN

Figure 6-12 Jetting image for 2% polystyrene (polydisperse, 255,000) in DECALIN (continue)

Figure 6-13 Jetting image for 2% polystyrene (monodisperse, 900,000) in DECALIN

Voltage (v)
Time delay (μ s)

80

89

58 for 80v/52 for 89v

63

67

Chance to form satellites

For a Newtonian liquid, it is pretty obvious that a satellite is more likely to be formed at high voltage; but for a polymer solution, whether the satellite can be formed or not depends on the properties of the solution itself (refer to Table 6-3). For example, 3.4 cp mineral oil has no satellite at 45V but has a satellite at 55V.

For viscoelastic fluids, a solution with a higher molecular weight yields fewer satellite drops. This is again obvious from the results. For example, at 60, 65 and 70V, 2% polystyrene (polydisperse, 255,000) in DECALIN shows no satellites while 2% polystyrene (polydisperse, 100,000) in DECALIN has satellite drops (refer to Table 6-3, Figure 6-10 and 6-11). This finding is the same as the experimental results of Christanti and Walker (2001) although they were dealing with continuous jetting. In both situations, satellite drop formation should be suppressed on increasing the resistance to jet break up.

Diameter ratio (vertical diameter/horizontal diameter) of main drop

It seems that there is NO regular trend for the diameter ratio of the main drop whether you consider the changes on comparing different voltages or different solution types (Newtonian /viscoelastic fluid). However, for the main drop shape, the deviation from a sphere is not uncommon. For example, the diameter ratio of 3.4 cp mineral oil at 55V is only 0.882 (refer to Table 6-2).

But when you combine both diameter ratio and vertical diameter to consider, at the same voltage, the shape of the main drop of the polymer solution is more like to be spherical compared to the Newtonian liquid. For example, at 60V, the diameter ratios for 3cp+7cp mineral oil, 2% polystyrene (polydisperse 100,000) in DECALIN and 2% polystyrene (polydisperse 255,000) in DECALIN are 0.874, 1.000 and 0.973, respectively (refer to Table 6-3).

In a jetting situation, it seems that solution type (Newtonian or viscoelastic) is the most important factor to affect the main drop shape among all the factors, which include main drop velocity, and diameter.

Role of fluid velocity

The main drop must have a high enough velocity to get out of the confines of the port. And at high velocity, more liquid is likely to get out of the nozzle, but this increases the chance to form a satellite. For example, there is no satellite when the main drop velocity is 0.647 m/s at 45V for 0.5% polystyrene (polydisperse 100,000) in DECALIN, but satellite exists when the main drop velocity increases to 2.132 m/s at 55V for the same solution (refer to Table 6-2 and Figure 6-6).

It seems that the velocity of main drop is decided by voltage, solution properties and jet nozzle configuration.

Effect of molecular weight

The effect of molecular weight is quite clear when you compare solutions having different molecular weight of 2% polystyrene in DECALIN. When the polymer molecular weight increases, and this corresponds to an increase of extensional viscosity, a tail is more likely to form, the tail tends to be thicker, and the main drop velocity decreases (refer to Figure 6-9). For example, at 65V, the main drop velocity for PS (100,000) solution is 2.051m/s, while for PS (200-300,000), it is – 0.569 m/s. Further, for PS (900,000), the liquid cannot even get out of the port (refer to Table 6-4).

Solutions with a higher molecular weight yield less satellite drops. This has been noted when discussing the “chance to form satellite”. Increasing polymer molecular weight also leads to longer break up lengths. Here the break up length is defined as the distance from the capillary exit point to the jet break up point. This is obvious when you compare jetting

behavior for 2% polystyrene (polydisperse) in DECALIN with molecular weight of 100,000 and 255,000 at the voltage of 65V (refer to Figure 6-10 and 6-11). This observation is also consistent with the conclusion of Christanti and Walker (2001). It needs to be noted that their jetting is in continuous condition which is not same as the periodic jetting situation here.

As we know, a high molecular weight solution has a larger extensional viscosity, or larger Trouton Ratio. This means that liquid jet for high molecular weight solution is harder to extend and break due to higher extensional resistance. Therefore, a high molecular weight solution tends to have thicker string, longer break up length and less satellite drops.

Effect of fluid type (Newtonian vs. Non-Newtonian)

The most obvious difference between Newtonian and Non-Newtonian solution is the shape of the tail. A Newtonian fluid is more likely to form a short tail and is easy to break from the port to form satellites. But for a Non-Newtonian solution, one is more likely to observe a longer tail, and the thickness of the tail depends on the molecular weight of the polymer (refer to Figures 6-4 to 6-13). It is not difficult to infer that the polymer inside the Non-Newtonian liquids prevents the liquid jet from detaching from the jet port or breaking into satellite drops.

Undesirable behavior vs. Desirable behavior

The jetting behavior for two commercial liquids shows undesirable and desirable conditions. CL1 which has a low Trouton Ratio of 4.2 has no satellite (refer to Figure 6-7). Actually, it shows an ideal behavior at a voltage of 55V or 60V— single drop and no satellites. However, at the same voltage, CL2 which has a much higher Trouton Ratio of 11.3 forms a very long tail, and finally breaks into many satellites, and a small tail retracts back into the jet port — a typical undesirable behavior (refer to Figure 6-8).

To sum up, a liquid with high Trouton Ratio is more likely to form a longer tail, be hard to detach from the jet port, and lead to less satellite drops; while a liquid with low Trouton Ratio is more likely to form a short tail, form satellites and detach cleanly from the jet port.

7 Investigation of the Jetting Behavior of Various Liquids

7.1 Experiment objective

This part of the experimental work was conducted in our laboratory at WVU. A new set of ink-jetting equipment for producing a single drop or a series of drops was assembled here. This equipment was similar in design to the one used at the DuPont Experimental Station. Two issues were expected to be clarified. First, we wanted to study in detail how liquid elasticity affects liquid jetting behavior. Some insight on the liquid jetting behavior had been gained from the preliminary jetting experiments. Liquid elasticity levels were measured using our newly designed extensional viscometer. Experiments were now designed to investigate how the jetting behavior changes when liquids which have same shear viscosity have different molecular weight, molecular weight distribution or liquid type. Secondly, we want to define the proper elasticity level which leads to ideal jetting behavior.

7.2 Test liquids

Liquids which were tested on the WVU jetting equipment included all the “group two” solutions from the chapter entitled “Extensional viscosity of polymer solutions” for measuring extensional viscosity and two Newtonian fluids, namely DECALIN and 3cp Mineral oil + 7cp Mineral oil (1/1). Therefore, a total of ten liquids were tested on the jetting equipment in WVU.

These liquids were chosen to compare the jetting behavior for (1) solutions with same shear viscosity but different molecular weight and different molecular weight distribution; (2) liquids with jetting behavior from undesirable to desirable by increasing solution concentration. Their rheological properties are listed in Table 7-1. Here, DECALIN is used to compare with solutions of 1.5% and 2.5% Polystyrene (polydisperse, $M_w=45,000$) in DECALIN.

Table 7-1 Rheological properties of liquids for jetting test in WVU

Solution Name	Visc. (cp)		Trouton
	Shear	Exten.	Ratio
3 cp Mineral oil +7 cp Mineral oil (1/1)	5	15	3
4% PS (monodisperse, Mw=45,000) in DECALIN	5	29.2	5.84
5% PS (polydisperse, Mw=45,000) in DECALIN	5	37.2	7.45
3% PS (monodisperse, Mw=140,000) in DECALIN	5	42.4	8.47
2% PS (polydisperse, Mw=140,000) in DECALIN	5	56.5	11.30
2% PS (monodisperse, Mw=300,000) in DECALIN	5	66.3	13.26
2% PS (polydisperse, Mw=300,000) in DECALIN	5	74.9	15.00
DECALIN	2.5	7.5	3
1.5% PS (polydisperse, Mw=45,000) in DECALIN	2.8	11.3	4.02
2.5% PS (polydisperse, Mw=45,000) in DECALIN	3.3	16.5	5.00

7.3 Jetting equipment and testing procedure

To observe “ink-jetting” behavior of these liquids, a jetting equipment which can supply a liquid drop on demand was put together in our own laboratory in WVU. All the experiments were conducted at a room temperature of about 23°C. The schematic diagram of the experimental set-up is shown in Figure 7-1. Photographs of the experimental set-up are shown in Figures 7-2 and 7-3. Figure 7-2 includes the main components of this jetting equipment; an enlarged photo located at the upper right corner of this photo gives the detail about the area around the jet nozzle, which includes the jet nozzle, strobe light and microscope lens. All components for this jetting set-up are included in the photo in Figure 7-3. This setup is composed mainly of two portions: a jetting system and an optical system. The jetting system is made up of a MJ-AB jetting device, a JetDrive III controller and a small strobe light. All of these were acquired from Microfab Inc. The orifice size for this jetting device is 60 μm . It needs to be noted that the jetting setup in WVU only contains a

Figure 7-1 Schematic diagram of the jetting equipment in WVU

Figure 7-2 Photograph of the main components of the jetting equipment in WVU

Figure 7-3 Overview of the jetting equipment in WVU

single nozzle, whereas the DuPont setup used a Jet head containing 64 nozzles. A computer was connected to JetDrive III, and it controlled the process. Jetting parameters were set, and a command signal was sent to the jetting device; illumination was provided by a strobe light which was also computer controlled. A 3-axes position controller was used to adjust the position of the strobe light to obtain clear pictures. The optical system included a Stemi 2000-C stereo microscope (made by Carl Zeiss) and a CCD camera which was attached to the microscope and connected to a computer to record the observed image. A magnification of 100x was used to acquire pictures of jetting drops. In order not to inhale the DECALIN vapor, experiments were carried out inside a fume hood. During experimentation, a transparent plastic cover was used to cover the jetting set-up to avoid air flow disturbance inside the hood. To begin an experiment, the reservoir inside the jetting device was filled with the test fluid, and it provided proper back-pressure. After proper parameters were set by the software (a continuous jetting mode and a jetting frequency of 1000 Hz were employed), continuous signals were sent to the jetting device and the strobe light through the controller. The jetting frequency of 1000 Hz means that each jetting period lasts 1/1000 second or 1000 μ s. Continuous drops were ejected from the jetting device, and the strobe light fired at the set delay time (between 50 μ s to 450 μ s) after each drop was jetted. For example, the strobe light will fire at the moment of 50 μ s and last about 2 μ s for each jetting period. If one wants to observe the jetting behavior at a delay time of 50 μ s. Similarly, the strobe light may be set to fire at other specific delay times. A CCD camera was used to capture pictures. It takes images at a speed of 24 frames per second. In other words, it takes the CCD camera 1/24 second to capture one image. It is clear that about 42 (or 1000/24) jetting periods happen within the period of 1/24 second. We assume that these drops, which were jetted at different jetting periods, have the same behavior at the same delay time after each jet event. This assumption was confirmed by the clear (instead of fuzzy) image taken during experiments. The image of a single drop at any specific moment actually contains many drop images, although it appears as if we are looking at the motion of only one drop. In this way, multiple drops give the CCD camera enough light to capture a bright drop image. It is obvious that a brighter image can be taken when one increases the

jetting frequency. Drop images at different moments (between 50 μ s to 450 μ s, interval of 50 μ s) and different applied voltage (from 50v to 120v) can be taken by adjusting the strobe delay. In this manner, a series of images can be taken for jetting drops.

7.4 Results and discussion

A series of images was taken for each test liquid. Some typical images for each liquid are shown in Figures 7-4 to 7-13. Each Figure lists the images for the liquid in different time delays and voltages. Time delays are same for each Figure. They range from 100 μ s to 400 μ s with an interval of 100 μ s. However, the applied voltages are not same for each figure (liquid). The applied voltages range from 50v to 120v. The voltages chosen for each liquid depend on (1) whether that liquid can be jetted at that voltage and (2) convenience to compare results with other liquids which have similar properties. Figures 7-4 to 7-13 are discussed here.

Figure 7-4 shows the jetting images for DECALIN. Three voltages, 50v, 55v, and 60v, were applied. DECALIN shows the typical jetting behavior for a Newtonian liquid. At a time delay of 100 μ s, the liquid tail lengths jetted from the nozzle increase with increasing voltages. At a time delay of 200 μ s, part of the tails breaks into drops. However, part of the tail is still connected with the nozzle. At a time delay of 300 μ s, the tails have disappeared. Several drops form under the nozzle for each of the three voltages. It seems that the drop size at higher voltage is larger when compared to that at lower voltage. This maybe due to larger amount of liquid dispensed from the nozzle at the higher voltage. At a time delay of 400 μ s, more drops travel out of the field of view with increasing voltage. This can be explained by the higher momentum of liquid drops at high voltages.

Figure 7-5 shows the jetting images for 1.5% polystyrene (polydisperse, 45,000) in DECALIN. Three voltages, 50v, 55v, and 60v, were again applied. At a time delay of 100

Figure 7-4 Jetting images for DECALIN

Figure 7-5 Jetting images for 1.5% polystyrene (polydisperse, 45,000) in DECALIN

Figure 7-6 Jetting images for 2.5% polystyrene (polydisperse, 45,000) in DECALIN

Figure 7-7 Jetting images for 3 cp Mineral oil +7 cp Mineral oil (1/1)

Figure 7-8 Jetting images for 5% polystyrene (polydisperse, 45,000) in DECALIN

Figure 7-9 Jetting images for 4% polystyrene (monodisperse, 45,000) in DECALIN

Figure 7-10 Jetting images for 2% polystyrene (polydisperse, 140,000) in DECALIN

Figure 7-11 Jetting images for 3% polystyrene (monodisperse, 140,000) in DECALIN

Figure 7-12 Jetting images for 2% polystyrene (polydisperse, 300,000) in DECALIN

Figure 7-13 Jetting images for 2% polystyrene (monodisperse, 300,000) in DECALIN

μs , it is obvious that the liquid at 60v has the longest tail. At a time delay of 200 μs , a large portion of the tails breaks into drops. However, there still exists some liquid drop connecting to the nozzle by the liquid string. At a time delay of 300 μs , all liquid drops have already detached from the jet nozzle. Several drops form for each voltage. This is still undesirable behavior.

Figure 7-6 shows the jetting images for 2.5% polystyrene (polydisperse, 45,000) in DECALIN. Three voltages, 50v, 55v, and 60v, were still applied to compare with the previous two liquids. Similar behavior happens at the time delay of 100 μs , but the liquid tail is thicker than that for DECALIN or 1.5% liquids. At a time delay of 200 μs , a critical change happens. Only one liquid drop appears at a voltage of 50v, and a very short tail forms around the nozzle. However, a longer tail forms at the voltage of 55v and 60v. In addition, the tails at these two voltages appear to break soon. At a time delay of 300 μs , only one liquid drop formed at the voltage of 50v. The short tail that formed at the time delay of 200 μs disappears. It seems that the liquid tail retract back into the nozzle. It needs to be noted that this is ideal behavior in jetting. At least two drops formed at the voltage of 55v and 60v. This is undesirable behavior.

Figures 7-7 to 7-13 are the jetting images for seven liquids with the same shear viscosity of 5cp. These liquids include one Newtonian liquid (Mineral oil) and six solutions of polystyrene in DECALIN. These six solutions were prepared by varying the polystyrene concentration, molecular weight and molecular weight distribution. Their jetting behavior is discussed here.

Figure 7-7 shows the jetting images for 3cp mineral oil+ 7cp mineral oil (1/1). Three voltages, 80v, 100v, and 120v, were applied. It should be noted that mineral oils are Newtonian liquids. At the time delay of 100 μs , long tails formed. The tail length increases with increasing voltage. At a time delay of 200 μs , individual strings and drops formed for each voltage. At a time delay of 300 μs , these strings break into drops. At a time delay of

400 μ s, most drops disappear from the view field except that one drop at the voltage of 80v still exists at the bottom of the view field. Note that the larger shear viscosity and higher voltage (compare to voltages shown in Figures 7-4 to 7-6) are the reasons for the existence of individual strings and high momentum.

Figure 7-8 shows the jetting images for 5% polystyrene (polydisperse, 45,000) in DECALIN. Three voltages, 80v, 100v, and 120v, were still applied. At a time delay of 100 μ s, a thick tail formed at all three voltages. The liquid tails at the voltage of 100v are longer than those at the voltage of 80v. However, the liquid tail is shorter at the voltage of 120v. This maybe due to the nature of polydisperse polymer solutions. Polymer which has a distribution of chain lengths existed in such solutions. The jetting tail at the voltage of 120v maybe the results of polymer of longer chain length. Such long chains will prevent the liquid tail from detaching from the jet nozzle. At a time delay of 200 μ s, either individual drops or a long string formed. At a time delay of 300 μ s, all the strings either broke into drops or disappeared from the screen.

Figure 7-9 shows the jetting images for 4% polystyrene (monodisperse, 45,000) in DECALIN. Three voltages, 80v, 100v, and 120v, were still applied here to compare the jetting behaviors with other 5cp liquids. At a time delay of 100 μ s, a long, thick tail formed for each voltage. Tail length increases with increasing voltage. At a time delay of 200 μ s, strings, drops, and tails formed for each voltage. At a time delay of 300 μ s, all tails had already detached from the jet nozzle. Several liquid drops formed for each voltage.

Figure 7-10 shows the jetting images for 2% polystyrene (polydisperse, 140,000) in DECALIN. Two voltages, 100v, and 120v, were applied since liquid could not be jetted at the voltage of 80v. It seems that the increased elasticity prevents the liquid from jetting at the lower voltage. At a time delay of 100 μ s, a long, thick tail formed at the voltages of 100v and 120v. The tail at the voltage of 120v appears longer. At a time delay of 200 μ s, the tails appear even longer. There is still no detachment from the nozzle yet. At a time

delay of 300 μ s, tails still did not break from the nozzle. Therefore, very long tails formed for both voltages. The lower end of the tail at the voltage of 120v has already moved out the view field. At a time delay of 400 μ s, surprisingly the tail still did not break from the port. The tail at the voltage of 100v appears like a liquid drop connected by a long string.

Figure 7-11 shows the jetting images for 3% polystyrene (monodisperse, 140,000) in DECALIN. Three voltages, 80v, 100v, and 120v, were applied here. At a time delay of 100 μ s, a long, thick tail formed for each voltage. At a time delay of 200 μ s, tails, drops and strings exist for each voltage. At a time delay of 300 μ s, most tails and strings break into drops. However, a short tail with a large drop at the tip exists at the voltage of 120v.

Figure 7-12 shows the jetting images for 2% polystyrene (polydisperse, 300,000) in DECALIN. Two voltages, 100v, and 120v, were applied. Liquid cannot be jetted at the voltage of 80v. At a time delay of 100 μ s, a thick tail formed at both voltages. At a time delay of 200 μ s, a still longer tail formed at the voltage of 100v. It needs to be noted that a liquid drop is formed and is still connected to the tip of the tail. A shorter tail and one drop formed at the voltage of 120v. At a time delay of 300 μ s, the tail is still stretching and is even longer at the voltage of 100v. That shorter tail becomes longer at the voltage of 120v. At a time delay of 400 μ s, a very long tail formed at the voltage of 100v; the lower end of that tail falls even below the view field.

Figure 7-13 shows the jetting images for 2% polystyrene (monodisperse, 300,000) in DECALIN. Two voltages, 100v, and 120v, were applied. Liquid cannot be jetted at the voltage of 80v. At a time delay of 100 μ s, a short, thick tail formed for each voltage. At a time delay of 200 μ s, interesting tails formed for each voltage. Two large drops formed at each end of the tails. At a time delay of 300 μ s, a very thin tail connected by a large drop at the lower end appears at the voltage of 100v. However, at the voltage of 120v, two drops are connected by a very thin string. The upper liquid drop is connected to the nozzle by a very short tail. At a time delay of 400 μ s, an individual liquid drop forms by breaking of

the long thick tail at the voltage of 100v. For the situation of 120v, the lower drop already breaks from the upper drop. The upper drop is still connected to the nozzle by a longer tail.

Effects which influence the liquid jetting behavior are discussed here.

Effect of voltage

The results obtained at WVU were identical to those obtained at the DuPont Experimental Station. Using a higher voltage means that more momentum was transferred to the liquid. This leads to two effects.

First, the additional momentum brought by the use of high voltage enables the liquid to move faster. For example, at a voltage of 120v, the liquid tail for 2% polystyrene (polydisperse, 140,000) in DECALIN is longer than that at the voltage of 100v (refer to Figure 7-10). But this is not always true when the situation described next happens.

Secondly, higher voltage provides more momentum which can dispense a larger amount of liquid out of the nozzle. For this case, a higher voltage may not lead to a higher liquid velocity. Furthermore, larger the amount of liquid which is dispensed from the nozzle, greater may be the number of satellites formed. For example, for 3% polystyrene (monodisperse, 140,000) in DECALIN, it is obvious that more satellites are formed at a voltage of 120v when compared to the satellites at a voltage of 80v (refer to Figure 7-11).

To sum up, higher voltage gives liquid more momentum. This higher momentum may lead to higher liquid travel velocity or larger volume of dispensed liquid or to more satellites formed.

Effect of molecular weight

Of all the test fluids, 6 polymer solutions have a shear viscosity of 5cp. These solutions have the same shear viscosity but different molecular weights. A solution with a larger molecular weight has a larger extensional viscosity and Trouton Ratio. It can be found from an examination of Figure 7-9 for the voltage of 100v that, at the beginning of the jetting process, a low molecular weight solution, 4% polystyrene (monodisperse, $M_w=45,000$) in DECALIN, forms thinner, longer string, while a high molecular weight solution, 2% polystyrene (monodisperse, $M_w=300,000$) in DECALIN, forms thicker, shorter strings at the same voltage of 100v (refer to Figure 7-13); Eventually, the low molecular weight solution breaks into many drops, while the high molecular weight solution extends into very long strings (tail).

This verifies the results that were obtained for the experiments carried out at the DuPont Experimental Station. A high molecular weight solution has a larger extensional viscosity, or larger Trouton Ratio. This means that a liquid jet formed from a high molecular weight solution is harder to extend due to the higher extensional resistance. Therefore, a high molecular weight solution tends to form a thicker, shorter tail and is harder to break into drops.

Effect of molecular weight distribution (polydisperse vs. monodisperse)

We can see from Figures 7-10 and 7-11 that two polymer solutions with the same shear viscosity of 5cp and the same molecular weight of 140,000 but different molecular weight distributions (polydisperse vs. monodisperse) at the voltage of 100v show obvious differences in jetting behavior. Owing to its higher elasticity (Trouton Ratio), a polydisperse polymer solution tends to form a long tail that is harder to break into drops as compared to the monodisperse solution with the same molecular weight. Still the fluid elasticity plays its role in the liquid jetting behavior.

Effect of fluid type (Newtonian vs. Non-Newtonian)

A Newtonian fluid is more likely to form a short tail and is easy to break from the port to form satellites. For a non-Newtonian solution, one is more likely to observe a longer and thicker tail which is harder to separate from the port. For example, at the voltage of 80v, a liquid tail for 5cp mineral oil detached from the port at the delay time of 200 μ s (refer to Figure 7-7) while the tail for the solution of 5% polystyrene (polydisperse, $M_w=45,000$) was still connected with the port (refer to Figure 7-8). It is obvious that the higher elasticity of a polymer solution prevents it from separating from the port. This result agrees with what was obtained from the preliminary jetting experiments.

Undesirable behavior vs. Desirable behavior

Figures 7-4, 7-5 and 7-6 show three liquids of shear viscosity of 3 cp. When we compare the jetting behavior for the three 3cp liquids at the voltage of 50v, the Newtonian liquid, DECALIN, is easy to detach from the jet port, and forms several satellites. With increasing polystyrene (polydisperse, 45,000) concentration, a shorter, thicker tail is formed; the number of satellite drops decreases. When the polystyrene concentration increases to 2.5%, only one drop is formed. This is the ideal behavior.

It seems that ideal jetting behavior is related to a proper elasticity level which is high enough to prevent the appearance of satellites and low enough to allow the liquid to separate from the jet port.

To sum up, a liquid with high Trouton Ratio (higher molecular weight, higher concentration, polydisperse polymer) is more likely to form a longer tail, be hard to detach from the jet port; while a liquid with low Trouton Ratio (like Newtonian liquid, low molecular weight, low concentration, monodisperse polymer) is more likely to form short tail, give satellites but detach cleanly from the jet port.

8 Conclusion and Recommendations

8.1 Conclusions

A polystyrene-DECALIN system has been used to test extensional and jetting behavior by varying the polymer concentration, molecular weight and molecular weight distribution.

An extensional viscometer was redesigned from its previous version (Gupta and Agarwal, 2003). The working capacity of this viscometer was reduced to satisfy the nature of the very expensive liquid. This viscometer was calibrated by using several Newtonian liquids. The results prove the effectiveness and accuracy of this instrument.

Different polymer solutions, some of which have a shear viscosity as low as 3 cp, were tested for their extensional behavior on this viscometer to compare different effects. Results show that 1) extensional viscosity and Trouton Ratio increase with increasing the polymer concentration; 2) at same weight concentration, a solution with higher molecular weight has larger extensional viscosity; 3) at same shear viscosity, solution with higher molecular weight has the larger extensional viscosity and Trouton Ratio; 4) the polymer solution with polydisperse polymer has larger extensional viscosity and Trouton Ratio than the one with monodisperse polymer when they have same shear viscosity and same molecular weight.

All liquids which have been tested for their extensional behavior and several Newtonian liquids have been tested for the jetting behavior. The jetting behavior for these liquids was examined tested on two jetting set-ups, one at DuPont and one that was self-built. These two set-ups yielded the same conclusions on jetting behavior. It is shown that a higher driven voltage leads to a larger liquid drop velocity; the velocity of the main drop is decided by voltage, solution properties and other minor factors. A solution with high molecular weight polymer tends to form a thicker, shorter tail and is harder to break into drops. Owing to its higher elasticity (Trouton Ratio), a polydisperse polymer solution tends to form a long tail that is harder to break into drops as compared to the monodisperse

solution with the same molecular weight and shear viscosity. Newtonian liquids are more likely to form short tail and be easy to break from the port to form satellites. But for a Non-Newtonian solution, one is more likely to observe a longer tail, and the thickness of the tail depends on the molecular weight of polymer. In general, an ideal jetting behavior is defined as a spherical drop and no satellites. It seems that ideal jetting behavior is related to a proper elasticity level which is high enough to prevent the appearance of satellites and low enough to allow the liquid to separate from the jet port.

To sum up the jetting behavior, a liquid with high Trouton Ratio (higher molecular weight, higher concentration, polydisperse polymer) is more likely to form a longer tail, and be hard to detach from the jet port; while a liquid with low Trouton Ratio (like Newtonian liquid, low molecular weight, low concentration, monodisperse polymer) is more likely to form a short tail, give satellite drops and detach cleanly from the jet port.

A polymer solution having a Trouton ratio close to 3 can be easily detached from the jet port but tends to form satellite drops. By contrast, a solution with a larger Trouton Ratio forms a long tail that is difficult to separate from the jet port. A solution with a Trouton Ratio which is located in between these two situations results in the formation of uniformly-sized spherical drops that are connected to the jet port by a short tail that retracts into the nozzle upon drop separation.

8.2 Recommendations

The extensional results shown here are only for the location at the exit of the upper capillary. For the section of liquid filament between the upper and lower capillary, the stretching rate increases greatly down the filament axis. Although the apparent extensional viscosity at the exit of upper capillary is accurate, the calculated extensional viscosities below the exit of the upper capillary and along the axial direction have increasing errors. These errors are the result of the neglect of momentum transfer from the air to the fluid in the data analysis. This momentum transfer needs to be taken into account, but there is no simple way to do this. To solve this problem, a flow simulation around the liquid filament

is needed in the future. Once this problem is solved, the accurate apparent extensional viscosities can be calculated along the axial direction of liquid filament with the increasing stretch rate.

To optimize the jetting process, it would be helpful if one can monitor the change of film thickness above the substrate during the process of coating and drying to get a better understanding of the coating process and to propose a proper model to describe how the polymer film thickness changes with time. A laser interferometry technique can be built to fulfill this objective. The following schematic diagram (Figure 8-1) is the proposed experimental set-up of the interferometer to be used to monitor film thickness.

Figure 8-1 Proposed schematic diagram of the laser interferometer

A He-Ne laser can be used as light source. The film is formed right after the liquid drop leaving the nozzle falls onto the surface of the substrate. This process can be used to simulate the ink-jet printing process. Different types of substrate can be used for observation. The surfaces of substrates should include stripes, trenches and small wells. Solutions should be observed for film drying behavior onto each surface. Film thickness changes should be recorded for each solution on each substrate.

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10 Appendix: ICR2004 conference paper

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Effect of Liquid Rheology on Jetting of Polymer Solutions

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ABSTRACT

Light Emitting Devices (LEDs) containing conjugated polymers are fabricated using ink-jet printing. A common problem in the processing of these materials is that the Newtonian viscosity of the polymer solution is not sufficient to describe the jetting performance because the molecular weights and concentrations employed are such that the resulting solutions are elastic. These differences in fluid elasticity levels cannot be measured using traditional techniques like dynamic mechanical experiments or the first normal stress difference in shear, but strongly impact the jetting behavior of the liquid. In the present work, a variety of polystyrene solutions having a shear viscosity of about 5 mPa-s, were examined for their jetting behavior using a locally-fabricated apparatus that can supply a liquid drop on demand. The ease of separation of the liquid from the jet head, the extent of formation of a liquid tail, and the presence or absence of satellite drops varied with the level of fluid elasticity in a systematic manner. We believe that this is the first quantitative report which provides such design information.

INTRODUCTION

In 1962, the first GaAsP light emitting diodes were released to market [1]. At about the same time, electroluminescence was observed in single crystal anthracene and in single crystal anthracene with approximately 0.1mol% tetracene [2], making it the first time that electroluminescence was examined using an organic material. In the late 1970s, the first conjugated polymer, trans-polyacetylene-(CH)_x, was discovered [3], and this discovery resulted in the inventors, A.J. Heeger, A.G. MacDiarmid, and H. Shirakawa, getting the Nobel Prize in chemistry in 2000. Among the many technological applications of these materials are light emitting devices (LEDs). These are used both in low information content segmented displays like score logos in stadiums and in full color video and graphics displays like flat screen liquid crystal displays. A typical polymer LED is made by sandwiching a layer of light emitting conjugated polymers between a pair of electrodes. The polymer film can be deposited by spray coating, dip coating, spin coating or ink-jet printing (IJP). Of these, the most efficient method is ink-jet printing (IJP). IJP technology employs an ink-jet printer with ink of conjugated polymer solution to print polymer light-emitting diodes with high resolution. With

this method, there is no wastage of expensive polymer solution, and large areas can be coated [4]. However, fluid rheological properties influence jetting behavior and coating uniformity. Note that commercial liquids normally have a low and constant shear viscosity of 3~5 mPa-s and low elasticity. Although these elasticity levels are very difficult to measure, our previous work [5] has unambiguously demonstrated that drop formation can show surprising differences that can be related to differences in fluid elasticity; we believe that the best technique for the determination of fluid elasticity is extensional viscosity. We had found that a Trouton ratio slightly larger than 3 was needed to give proper drop formation. In the present work, we further verify our conclusions by examining the jetting behavior of a series of polystyrene solutions having a constant shear viscosity but varying elasticity. These results are compared and contrasted with similar results on a Newtonian oil of the same shear viscosity.

EXPERIMENTAL

Polystyrene of three different molecular weights (45,000, 140,000 and 300,000) and different molecular weight distributions was chosen for this research. Six polymer solutions were prepared by

dissolving the polymer in DECALIN. By varying the concentration, each solution could be formulated with a shear viscosity of 5 mPa-s. A mineral oil of the same viscosity acted as a Newtonian standard for comparison.

Figure 1 Schematic diagram and picture of the extensional viscometer

The extensional viscosities of these fluids were determined with the help of the extensional viscometer introduced by Agarwal and Gupta [6] (Figure 1) and modified to work with small quantities of fluids. The viscometer consists of two connected glass bulbs forming a liquid reservoir. The liquid inside the reservoir drains through a thin-wall stainless-steel capillary which is attached to the bottom of the viscometer. The drainage time is measured for the fluid draining between the upper mark and lower mark made above and below the lower bulb. One refills liquid into the reservoir and then lets it drain again, except that now the liquid stream is stretched by sucking the liquid into a lower capillary that is connected to a vacuum flask. The drainage time is recorded again, and it is less than before due to the presence of a tensile stress.

To observe “ink-jetting” behavior of these polymer solutions, jetting equipment which can supply a liquid drop on demand was used; it was put together in our own laboratory, and all the experiments were conducted at room temperature. A photograph of the experimental set-up is shown in Figure 2. This setup is composed mainly of two parts: a jetting system and an optical system. The jetting system is made up of a MJ-AB jetting device, a JetDrive III controller and a small strobe light. All of these were acquired from Microfab Inc. The orifice size for this jetting device is 60 μm . A computer was connected to JetDrive III, and it controlled the process. Jetting parameters were set, and a command signal was sent to the

jetting device; illumination was provided by a strobe light which was also computer controlled. The optical system included a Stemi 2000-C stereo microscope (made by Carl Zeiss) and a CCD camera which was attached to the microscope and connected to a computer to record the observed image. A magnification of 100x was used to acquire pictures of jetting drops. In order not to inhale the decalin, experiments were carried out inside a fume hood. During experimentation, a transparent plastic cover was used to cover the jetting set-up to avoid air flow disturbance inside the hood. To begin an experiment, the reservoir inside the jetting device was filled with the test fluid, and it provided proper back-pressure. After proper parameters were set by the software (a jetting frequency of 1000 Hz was employed), continuous signals were sent to the jetting device and the strobe light through the controller. Continuous drops were ejected from the jetting device, and the strobe light fired at the set delay time (between 50 μs to 450 μs) after each drop was jetted. Pictures of multiple drops, which appear at the same moment after jetting, were taken by the CCD camera. We assume that these drops have the same behavior at the same moment after jetting. The picture we took at a specific moment actually contains many drops although it appears as if we are looking at the motion of only one drop. In this way, multiple drops give the CCD camera enough light to capture a clear drop image. Drop images at different moments (between 50 μs to 450 μs , interval of 50 μs) and different applied voltage (80v, 100v and 120v) can be taken by adjusting the strobe delay. In this manner, a series of pictures can be taken for jetting drops.

Figure 2 Jetting equipment overview (two computers not included here)

RESULTS AND DISCUSSION

Drainage time data can be used to compute the fluid extensional viscosity and Trouton ratio as described in [6]. Our results showed that larger the molecular weight and more polydisperse the polymer, the larger the extensional viscosity and Trouton ratio. Measured values of the Trouton ratio are given in the captions of Figures 3-5.

Figure 3 Typical jetting behavior from previous work, images taken at 45v and 350 μ s: Left, ideal behavior, 0.5% polystyrene (poly-disperse, MW 100,000) in DECALIN (2.8 mPa-s) with Trouton ratio of 4; Right, undesirable behavior, 3.4 mPa-s mineral oil

Figure 4 Images taken at 100v and 200 μ s for polystyrene (MW 140,000) in DECALIN: Left, 3% mono-disperse with Trouton ratio of 8.47; Right, 2% poly-disperse with Trouton ratio of 11.3

Figure 5 Images taken at 80v and 200 μ s: Left, mineral oil; Right, 5% polystyrene (poly-disperse, MW 45,000) in DECALIN with Trouton ratio of 7.45

As shown in Figure 3, good jetting behavior involves no satellite, no tail and spherical drops that cleanly detach from the jet port.

A series of pictures at an interval of 50 μ s were taken for each polymer solution at the moment of jetting. Figure 4 shows that owing to its higher elasticity, a polydisperse polymer solution tends

to form a long tail that is harder to break into drops as compared to the monodisperse solution with the same molecular weight. On comparing the Newtonian liquid with a low molecular weight polymer solution, it is easy to see from Figure 5 that while the Newtonian liquid is easier to detach from the jet port it forms satellite drops. It seems that ideal jetting behavior is related to a proper elasticity level which is high enough to prevent the appearance of satellites and low enough to allow the liquid to separate from the jet port.

SUMMARY

A polymer solution having a Trouton ratio close to 3 can be easily detached from the jet port but tends to form satellite drops. By contrast, a solution with a large Trouton ratio forms a long tail that is difficult to separate from the jet port. A solution with a Trouton ratio which is located in between these two situations results in the formation of uniformly-sized spherical drops that are connected to the jet port by a short tail that retracts into the nozzle upon drop separation.

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