

Processing and Thermal Properties of Molecularly Oriented Polymers

By

Erik Skow

B. S., Mechanical Engineering (2000)
United States Coast Guard Academy

Submitted to the Department of Mechanical Engineering
in partial fulfillment of the requirements for the degrees of

Master of Science in Mechanical Engineering

and


Master of Science in Naval Architecture and Marine Engineering


at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

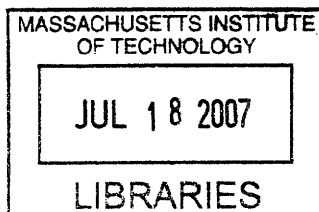
June 2007

© 2007 Massachusetts Institute of Technology
All rights reserved

Signature of Author  _____
Department Of Mechanical Engineering
May 8, 2007

Certified by  _____
Gang Chen
Warren and Townley Rohsenow Professor of Mechanical Engineering
Thesis Supervisor

Approved by _____
Professor Lallit Anand
Chairman, Department Committee on Graduate Students



ARCHIVES

Processing and Thermal Properties of Molecularly Oriented Polymers

By
Erik Skow

Submitted to the Department of Mechanical Engineering
on May 8, 2007 in partial fulfillment of the requirements for the
degrees of Master of Science in Mechanical Engineering and
Master of Science in Naval Architecture and Marine Engineering

Abstract

High molecular weight polymers that are linear in molecular construction can be oriented such that some of their physical properties in the oriented direction are enhanced. For over 50 years polymer orientation and processing has been extensively studied to improve the mechanical properties of polymers. In more recent history the anisotropic thermal properties of oriented polymers have been studied. This thesis investigates the thermal properties of Ultra High Molecular Weight Polyethylene (UHMW-PE) and explores applications for the same. This thesis details an effective means of aligning the molecules in bulk polyethylene sheets through stretching in the gel state. Tests have shown that bulk UHMW-PE can be stretched 50-80 times in xylene. The thermal conductivity of bulk UHMW-PE is 0.3 W/mK, while that of a sample stretched 20-25 times is over 4.5 W/mK.

Thesis Supervisor: Gang Chen

Title: Warren and Townley Rohsenow Professor of Mechanical Engineering

Acknowledgements

I would like to thank Professor Gang Chen for his guidance and support. I would also like to thank everyone in the Nanoengineering Group for all of their assistance. The opportunity to work with and receive the assistance from such a highly motivated and innovative group of people has been invaluable to me. I would most like to thank my wife, Gillian and daughter Irene for being so supportive of me on a daily basis.

Table Of Contents

Abstract.....	3
Acknowledgements.....	4
Table Of Contents.....	5
Table Of Figures.....	6
1 Introduction.....	7
1.1 Polymers Defined.....	7
1.2 Polyethylene.....	10
1.3 Thermal Conductivity of Polyethylene.....	12
2 Ocean Applications.....	15
3 Investigation of Orientation Techniques.....	18
3.1 Mechanical stretching.....	18
3.2 Thermodynamics of Solutions.....	18
3.3 Gel Forming and Stretching.....	19
3.4 Flow Induced Orientation.....	21
3.5 Electrospinning.....	23
4 Experimental Methods and Technique.....	25
4.1 Creating a gel from a piece of polyethylene sheet.....	25
4.2 Uniform Gel Creation and Manipulation.....	26
4.3 Initial stretching machine.....	27
4.4 Second generation stretching machine.....	29
4.5 Progression of experiments and samples produced.....	30
5 Sample Tests and Thermal Conductivity Estimation.....	34
5.1 Stretch ratio estimation.....	34
5.2 IR microscope images.....	39
5.3 FTIR Spectroscopy.....	43
5.4 Angstrom method.....	47
5.5 Xylene Evaporation from Samples.....	51
6 Discussion.....	53
6.1 Advantages of Bulk Gel Stretching Process.....	53
6.2 Drawbacks of Bulk Gel Stretching Process.....	54
6.3 Applications of Oriented UHMW-PE Sheet.....	54
6.4 Future Work.....	55
7 Conclusions.....	57
Appendix.....	58
References.....	61

Table Of Figures

Figure 1.1 Graphical representation of molecular weight	9
Figure 1.2 Diagram of polymer structure	10
Figure 1.3 Graph of UHMW-PE thermal conductivity as a function of draw ratio from C. L. Choy (a) is the oriented direction (b) is the non oriented directions. ¹³	14
Figure 3.1 Diagram of a Poiseuille flow apparatus for producing an oriented UHMW-PE fiber. ²²	21
Figure 3.2 Diagram of a Couette flow apparatus for producing an oriented UHMW-PE fiber. ²²	22
Figure 3.3 Diagram of a typical electrospinning set up	23
Figure 4.1 First Generation stretching machine.....	28
Figure 4.2 Set up for yield strength calculation (experiment performed with the sample immersed in Xylene).....	29
Figure 4.3 Second generation drawing machine with a sample of UHMW-PE that has been stretched.....	30
Figure 4.4 Five stretched UHMW-PE samples.....	33
Figure 5.1 Side view diagram of one shaft of the second generation drawing machine ..	34
Figure 5.2 Top view of sample held by the stage of the IR microscope.....	40
Figure 5.3 Side view of sample and stage for the IR microscope.....	40
Figure 5.4 IR microscope image of an un-stretched sample, 2.1 mm thick.	41
Figure 5.5 IR microscope image of a stretched sample, 0.2 mm thick, stretch ratio of 20-25. The rectangle superimposed on the image is 106 pixels high by 170 pixels wide.	41
Figure 5.6 IR microscope image of a stretched sample, 0.2 mm thick, stretch ratio of 20-25. The left side of the sample was compressed, the right side was not.....	42
Figure 5.7 IR microscope image of a stretched sample, 0.2 mm thick, stretch ratio of 20-25. This is the same image as Figure 5-7 shifted to the right.	43
Figure 5.8 FTIR transmission spectrum.....	45
Figure 5.9 FTIR Absorbance spectrum.....	46
Figure 5.10 Drawing of the angstrom method set up.....	48
Figure 5.11 Temperature output from the two thermocouples on the sample.	50
Figure 5.12 Angstrom method results for thermal conductivity as a function of temperature	50
Figure 5.13 Graph of xylene evaporation as a function of time	52
Figure 6.1 An example of a manufacturing process to orient UHMW-PE sheets.....	53

1 Introduction

For the last century the use of polymers in engineered products has increased dramatically. Not only have thousands of polymers been discovered, existing polymers have been modified to improve their physical properties and increase their usefulness.¹ Polymers are used widely due to their resistance to corrosion, ease of molding, and electrical insulating properties. Nearly all electrically insulating polymers have very low thermal conductivity. However, there are many applications where high thermal conductivity, low electrical conductivity polymers would be useful for heat removal. Some commercial ventures mix high thermal conductivity materials with polymers in order to address this need. Another means of producing polymers with higher thermal conductivity is through the processing of linear polymers such as polyethylene or polytetrafluoroethylene (Teflon®). The purpose of this thesis is to explore means of improving the thermal conductivity of polymers through processing, measuring their thermal properties, and examining their potential uses.

1.1 *Polymers Defined*

Monomers are molecules that have the ability to bond to like molecules. Polymers are molecules made up of bonded monomers. Because they are composed of multiple monomers, polymers can be made up of hundreds or even millions of atoms. In order to determine the size of the molecules that one is dealing with, the concepts of number average molecular weight and weight average molecular weight are useful.

Number average molecular weight (\overline{M}_n) is determined by simply adding up all the atomic weights (M) of a polymer and then dividing by the number of atoms (N).

$$\overline{M}_n = \frac{\sum M_i N_i}{\sum N_i} \quad (1.1)$$

This is a simple concept but in practice it is not the most useful definition. The physical properties of the polymer will be dominated by the larger atoms which contain the vast majority of the total mass of the polymer. However, if a large percentage of the molecules in a given polymer have very low molecular weight, the number average molecular weight will be smaller than that of the significant molecules.

Weight average molecular weight (\overline{M}_w) most accurately defines the size of the average larger molecules which dominate the mechanics of the polymer.

$$\overline{M}_w = \frac{\sum (M_i N_i) M_i}{\sum N_i M_i} \quad (1.2)$$

The graphical representation of \overline{M}_n and \overline{M}_w , shown in Figure 1.1, is helpful in understanding these concepts. A third useful definition combines the first two, that of Polydispersity:

$$\frac{\overline{M}_w}{\overline{M}_n} = \text{Polydispersity} \quad (1.3)$$

One can tell how many stray smaller molecules are present from the polydispersity. Since the weight average molecular weight is always larger than or equal to the number average molecular weight, polydispersity will have a value of one or greater. The higher the polydispersity the more stray molecules are present in the polymer.

Certain physical properties are a function of the number average molecular weight, but most are a function of the weight average molecular weight.²

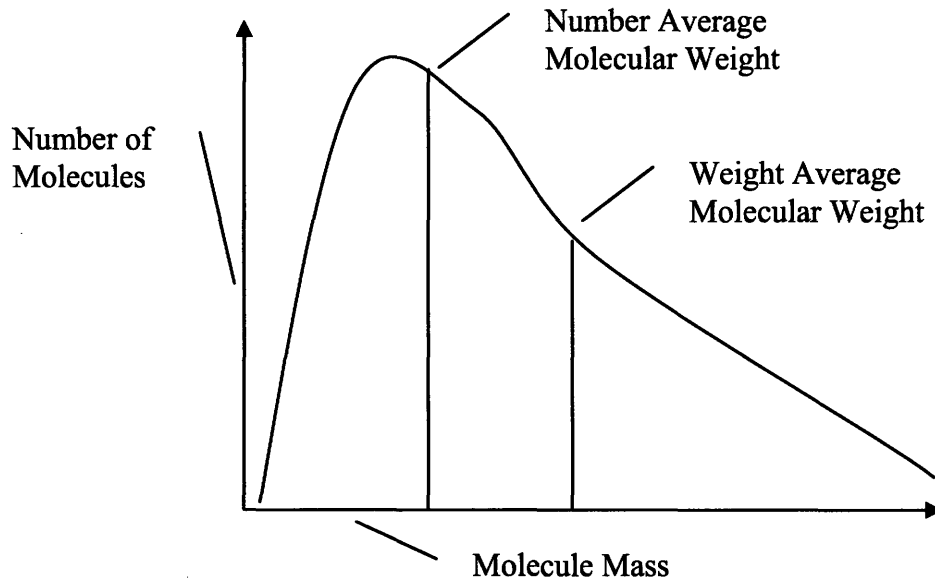


Figure 1.1 Graphical representation of molecular weight

Some polymers have molecular structures that are branched, while others are almost perfectly linear. A branched polymer molecule can have monomers bonded together at multiple angles, and each monomer may be bonded to multiple other monomers or only one. In a linear polymer every monomer (except the two at the extreme ends of the molecule) is bonded to exactly two adjacent monomers. Figure 1.2 illustrates the structural differences between linear and branched polymers.

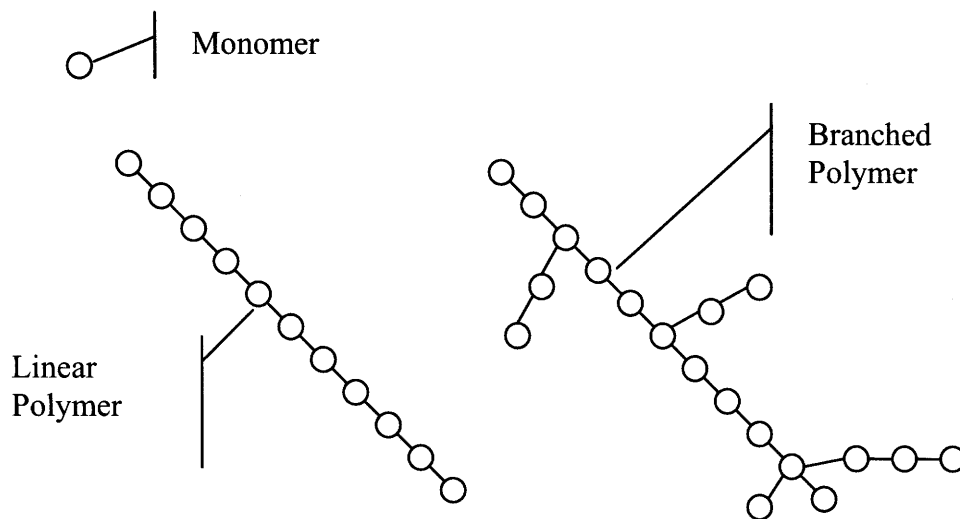
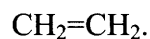


Figure 1.2 Diagram of polymer structure

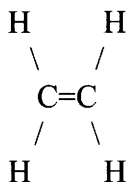
Large linear molecules, when oriented, provide polymers with strength. Kevlar is an extreme example of this. Kevlar molecules are made up of large monomers bonded in a linear configuration, which provide strength in tension of up to 200 Mpa or ten times that of steel. Kevlar is also a superior insulator, with a thermal conductivity of 0.0482 W/mK similar to that of fiberglass insulation.³

1.2 Polyethylene

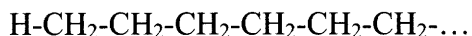
One of the most useful linear polymers due to its simple structure and wide range of molecular size characteristics is polyethylene. Polyethylene is a very common polymer made up exclusively of covalently bonded carbon and hydrogen atoms; however the linear backbone of the molecule is made up exclusively of carbon atoms. The monomer which makes up polyethylene is ethylene which has the chemical form



The molecular form of ethylene can also be written as:



It follows then that polyethylene has the chemical formula:



The polyethylene structure, a long chain of covalently bonded carbon atoms stabilized by hydrogen atoms, gives the polymer many valuable properties. Each individual polyethylene molecule is chemically balanced and therefore polyethylene reacts chemically with almost no other substance. Carbon has an atomic number of six, and therefore four vacancies in its outer electron shell. In polyethylene, these four vacancies are filled (covalently bonded) by two hydrogen atoms and two carbon atoms. This fills the valance of every atom in the molecule. Because there are no free electrons or holes in the polyethylene molecule, polyethylene does not conduct electricity or bond with other molecules. This also means that adjacent polyethylene molecules are not chemically bonded to one another. The molecules in polyethylene are slightly polar, because the electrons are not equally shared between the covalently bonded carbon and hydrogen atoms.⁴ The surface of many materials will bond with oxygen (oxidize) at ambient temperatures, but this is not the case with polyethylene. Polyethylene does not oxidize below 50 degrees Celsius.⁴

Polyethylene is a thermoplastic which allows its physical shape to be manipulated. A thermoplastic is made up of linear molecules which are joined with secondary bonds, such as van der Waals forces, rather than the stronger chemical bonds

which hold the molecules together. By using heat and pressure the secondary bonds can be broken and the molecules moved and aligned without changing any of the chemical or electrical properties. Thermoplastics can be heat-softened, melted and molded repeatedly which makes them very desirable as consumer goods.⁵

Polyethylene is made up of large or small molecules that can be branched or linear. These properties are determined during the polymerization process. Different polymerization processes are used to make low density polyethylene (LDPE) which is made up of small branched molecules, and linear low density polyethylene (LLDPE). Likewise other polymerization processes are used to produce high density polyethylene (HDPE) and Ultra High Molecular Weight Polyethylene (UHMW-PE). UHMW-PE is linear and typically has a \bar{M}_w of 3,000,000 to 6,000,000 although that is not a hard fast rule.⁶ Companies will sell polyethylene as UHMW-PE with \bar{M}_w of closer to 2,000,000.

1.3 Thermal Conductivity of Polyethylene

Polyethylene typically has low thermal conductivity, approximately the same as that of wood. However, if the polyethylene is linear and the molecules are aligned such that the carbon backbones are all oriented in the same direction, the thermal conductivity in the oriented direction will increase. Phonons can travel down the carbon backbone with small impediment or scattering. Additionally, the larger the \bar{M}_w of the molecules the greater the theoretical maximum thermal conductivity. The theoretical maximum thermal conductivity is achieved in conjunction with perfect molecular alignment of the

polyethylene molecules.⁷ The extension of the chains into more one-dimensional conductors can be thought of as increasing the phonon mean free path, by decreasing scattering, and therefore increasing the thermal conductivity in the direction of alignment.⁸

Consider a piece of UHMW-PE with a \overline{M}_w of 4,200,000 as an example, the relevant average molecules are made up of about 300,000 carbon atoms and 600,000 hydrogen atoms. A published atomic spacing between carbon atoms in linear polyethylene is 1.26 angstroms.⁶ If this example material were stretched out linearly in one direction the total length of the single molecule would be nearly 38 microns. Theoretically the thermal conductivity along the carbon backbone should approach that of a perfect crystal lattice (diamond) which has the highest thermal conductivity of any natural material known⁹. Since there are very few materials with high thermal conductivity and low electrical conductivity, this has the potential to be a very useful material. Unfortunately, UHMW-PE is made up of molecules which are tangled together like spaghetti. The method of orienting the molecules in UHMW-PE in order to improve the thermal conductivity was one focus of my research.

Prior work using fibers and films of stretched polyethylene have been conducted which show evidence of large gains in thermal conductivity.^{10,11} Groundbreaking work in this area has been done by C. L. Choy et al. Choy's group published that the thermal conductivity of UHMW-PE can be increased by two orders of magnitude when draw ratios of 100 or more are obtained. This means that UHMW-PE with an unstretched thermal conductivity of 0.3 W/mK can be stretched such that the thermal conductivity in the stretched direction is 30.0 W/mK or more. They also found that after stretching the

thermal conductivity in directions perpendicular to orientation slightly decreased (about .05 W/mK).^{12,13} Figure 1.3 shows the results of the thin film stretching done by C.L. Choy.

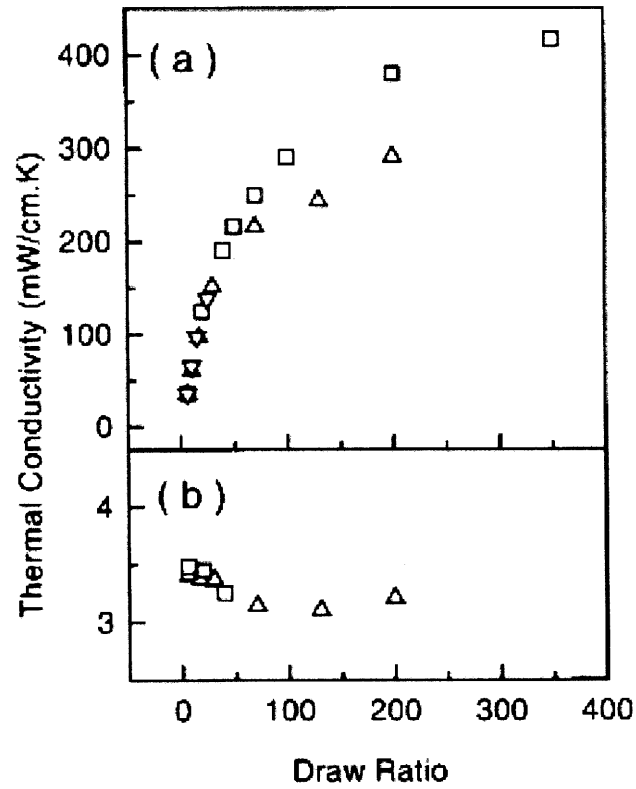


Figure 1.3 Graph of UHMW-PE thermal conductivity as a function of draw ratio from C. L. Choy (a) is the oriented direction (b) is the non oriented directions.¹³

2 Ocean Applications

Polyethylene is used in a wide variety of applications from milk jugs to power line insulation, but it is particularly useful in highly corrosive environments such as the marine environment. As mentioned before, polyethylene is chemically inert and for this reason many solvents and corrosive liquids are stored in polyethylene. Saltwater in the marine environment causes rapid oxidation of most metals and therefore exposed metal must be protected by coatings and sacrificial metal (such as zinc) or complex and expensive cathodic protection systems. Oriented polyethylene has a higher strength to weight ratio than most metals and wood currently used in marine applications. In addition polyethylene does not absorb liquid like materials such as wood.

Metal and wood are much more difficult to shape and join than polyethylene which can be manufactured to nearly any shape without seams. This means that components in the marine environment made out of polyethylene will be more streamlined and require less maintenance to keep clean. Also welding metals into complex shapes such as bulbous bows or sonar domes is very time consuming and therefore costly. For military applications, polyethylene is also non-reflective, meaning components made of polyethylene are invisible to radar.⁵ Recent work has been done to adhere HDPE to steel as a protective coating far superior to the paints currently in use.¹⁴ The heat exchangers in marine systems require frequent maintenance and repair due to corrosion, and marine growth. Using polyethylene would eliminate galvanic corrosion. Marine growth is also less of a problem with polyethylene than many other current marine materials due to the difficulty that marine growth has in adhering to it.

Polyethylene is not superior to metals and wood in all respects. Polyethylene can break down or lose strength by melting or being exposed to solar radiation. Polyethylene has a fairly low melting point, about 110 to 140 degrees Celsius depending on the molecular weight (LDPE melts at a lower temperature than HDPE). This is typically not a problem in the marine environment apart from engines. When exposed to the sun's radiation polyethylene will oxidize over time, however, adding pigmentation to the polyethylene can mitigate this problem. Studies have shown that polyethylene will retain its strength after being exposed to sunlight if it is effectively coated with materials such as iron oxide or carbon black. These coatings will increase the useful life of polyethylene exposed to direct sunlight from 3-6 months to 30-40 years, which is the typical lifespan of ocean going vessels.¹⁵

Currently there are many companies constructing small saltwater boats out of polyethylene, including kayaks, fishing boats, and tenders. One company, Ocean Kayak, used to build kayaks out of fiberglass but has shifted to polyethylene because it has higher impact resistance and can be formed with sharper corners.¹⁶

Another current use of polyethylene in the marine environment is for marine pipelines. Pipelines are subjected to many harsh forces as well as corrosion at sea. Makai Ocean Engineering Inc. has built marine pipelines that have withstood the elements for over 12 years.¹⁷ These pipelines are up to 63" in diameter and 2 miles long. They are currently used for ocean thermal energy conversion in the tropics and to provide cooling water in a variety of locations.

DSM Deneema is testing their oriented polymer fibers for use as nets in offshore fish farming operations.¹⁸ These nets are currently being used in a very large commercial fish farming operation in the Canadian Maritimes.¹⁹

Polyethylene has the potential to be used more widely to protect engines and electronics from the corrosive marine environment. A major problem in using polyethylene in these applications is its inability to remove the waste heat produced by these components. By significantly increasing the thermal conductivity of polyethylene, more of the metal components of electronics and engines could be shielded from the salt air by polyethylene, thereby increasing their lifespan and reducing the man-hours required to maintain them.

The use of polyethylene in the marine environment has been steadily expanding since ethylene was first polymerized. Development of polyethylene with high thermal conductivity would serve to further reduce the costs and dangers to people who live and work in marine industries.

3 Investigation of Orientation Techniques

3.1 Mechanical stretching

The first and most obvious method of orienting polyethylene molecules is to use a mechanical pulling device to physically stretch the polymer. In order for the polymer to stretch, the secondary bonds between molecules must break. The molecules will become more aligned the more stretching occurs. Because polyethylene is a thermoplastic, heat can be applied to reduce the force required to stretch. However, when heat is applied the risk of oxidation must be considered.

Josef Miler wrote a thesis that investigated stretching polyethylene mechanically from its solid state.²⁰ Polyethylene was heated to temperatures just below the melting point and then large forces were used to achieve a stretch ratio up to 10. All of the samples parted under the strain either before reaching a stretch ratio of 10 or at approximately 10 times its initial length. In published research on the subject, one cannot find instances of anyone exceeding a stretch ratio of 10 using this technique. In order to obtain greater stretch ratios and thus more unidirectional molecular alignment, polyethylene must be dissolved into a solution, or worked with past its melting point.

3.2 Thermodynamics of Solutions

A thorough explanation of solution thermodynamics can be found in the Textbook of Polymer Science by Fred Billmeyer, although such information is widely published.^{4,6}

In order for a polymer such as polyethylene to dissolve in a solvent, the free energy of mixing (G) must be negative. The governing equation is:

$$\Delta G = \Delta H - T\Delta S \quad (3.1)$$

where H is enthalpy, T is temperature and S is entropy. G is also known as the Gibbs free energy.

In order to minimize the change in enthalpy, the solution should be dilute (much more solvent than the material you wish to dissolve) and the solvent should be chosen such that its solubility parameter is as close as possible to the material one wishes to dissolve. Solubility parameters are a function of the molecular weight, density, and the molar-attraction constant. Values for solubility parameters are widely published.^{4,6}

The change in entropy is a function of the solvent and material being dissolved. In the case of polymers, this value is small due to the disparity in molecular size.⁶ The addition of heat will always help allow or increase solubility, as shown by the equation and common experience.

3.3 Gel Forming and Stretching

The first realization that polyethylene could be oriented using dilute solutions occurred when researchers stirring dilute polyethylene solutions discovered fibers precipitating onto their stirring rods. A.J. Pennings was the first to publish these findings in 1966.²¹ This led others to investigate the production of fibers of aligned polyethylene and the properties of such fibers. Researchers quickly recognized that stretching polyethylene would improve the material strength in the direction of stretch.²² The alignment of polyethylene molecules increases the ultimate strength in the oriented

direction as well as the thermal conductivity. This is due to the fact that the chemical bonds which hold individual molecules together are far stronger than the intermolecular van der Waals forces that hold the molecules to one another. The success in improving the strength of polyethylene fibers led to commercialization of the technology in the mid 1980s.

Gel Spinning is the process by which Spectra® and Dyneema® fibers are manufactured. This process contains three main steps. First the UHMW-PE is transformed into a gel. Second the fiber is pulled, extruded or otherwise spun from the solution and some of the solvent is allowed to evaporate. Finally the fiber is stretched to many times its initial length while the remaining solvent is removed. The maximum draw ratio is a function of the solution concentration and the molecular weight of the polyethylene. In general lower concentrations lead to greater draw ratios because there are fewer molecular chain entanglements. However, at a certain point the concentration is too low for there to be sufficient chain overlap and the fiber will break. This threshold concentration is lower for polyethylene with larger weight average molecular weight.²³

Spectra® fibers are used to form ropes, and body armor which is 10 times the strength of steel by weight, even stronger than Kevlar®.²³ Dyneema fibers are up to 15 times the strength of steel. The companies that own the patents for the UHMW-PE production process continue to improve their manufacturing process and the quality of their fibers to this day. There is no mention of these UHMW-PE fibers being used for heat transfer. Because this method of producing oriented polyethylene fibers is so well patented, further research into gel spinning has been the province of industry for the last 20 years.

3.4 Flow Induced Orientation

Flow induced orientation was a common early method to orient polyethylene fibers. Fibers can be oriented in Poiseuille flow or Couette flow, while they are in solution or in a molten state.²² To maintain alignment in a solid state the fibers must be removed from the solution or cooled below the melting point while the alignment is taking place. To orient the molecules in Poiseuille flow, a seed crystal is drawn up a pipe, such that the hydrodynamic forces in the pipe align the polymer molecules parallel to the draw direction. As shown in Figure 3.1 the continuous fiber drawn from the pipe can then be wound on a spool.

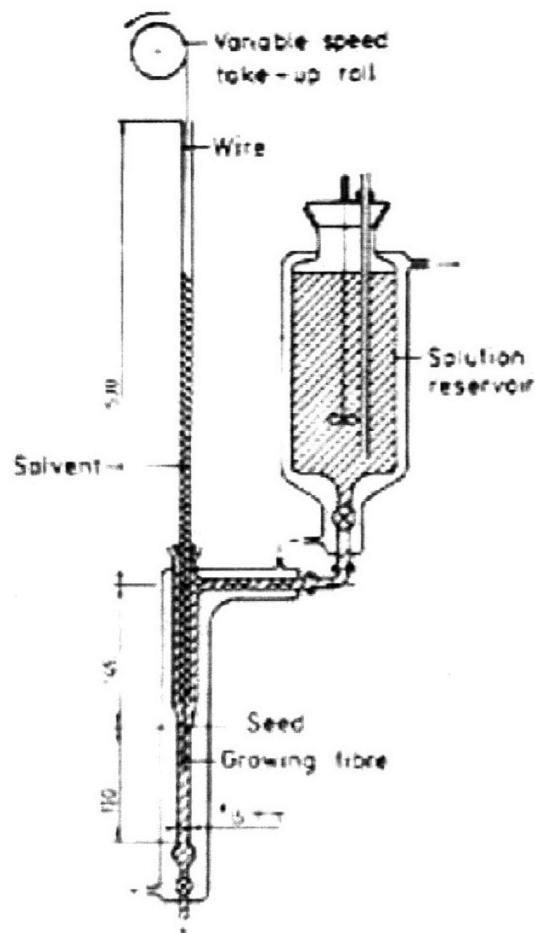


Figure 3.1 Diagram of a Poiseuille flow apparatus for producing an oriented UHMW-PE fiber.²²

In order to orient the molecules in a Couette flow a drum is rotated in a cylindrical bath of polymer solution as shown in Figure 3.2. There is more alignment and much faster growth of the fiber in the Couette flow than in Poiseuille flow, especially when the seed crystal comes into contact with the rotating drum.²²

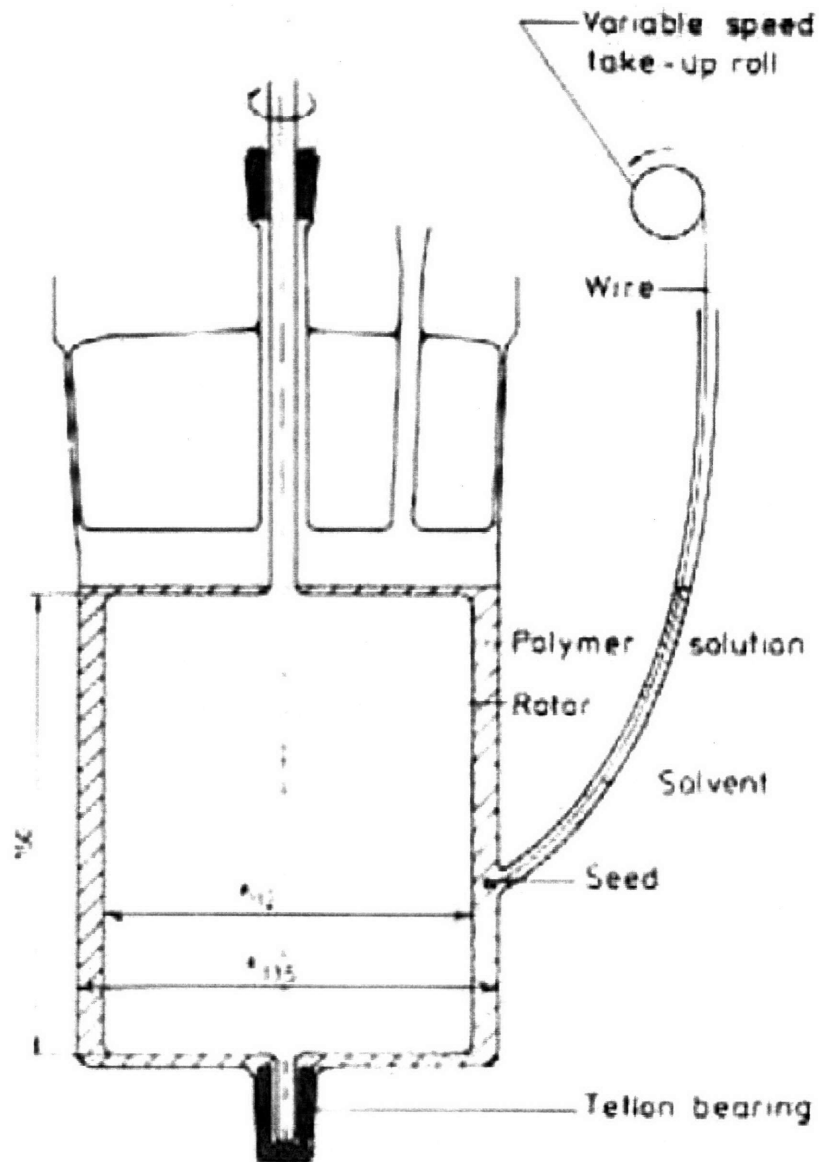


Figure 3.2 Diagram of a Couette flow apparatus for producing an oriented UHMW-PE fiber.²²

3.5 Electrospinning

Electrospinning is a process of using a strong electric field to draw a very fine stream of polymer solution or molten polymer from a syringe. A single thin stream that is drawn from the syringe then develops a bending instability and begins to whip around very wildly and quickly.²⁴ The fiber moves so fast that one visually sees a cone, called a Taylor cone. The physics of the electrospinning process is not completely understood, however, the Rutledge group at MIT has had some recent success predicting aspects of their electrospinning process with computer models.²⁵

The set up for this process is quite simple as shown in Figure 3.3. A strong electric field is created between two parallel metal plates. The positive plate is in contact with the metal syringe that contains the polymer. The fiber then is collected on a negatively charged electrode. The distance between the plates, the voltage level, and the flow rate from the syringe are variables which must be adjusted to start electrospinning and then to modify the thickness of the fiber.

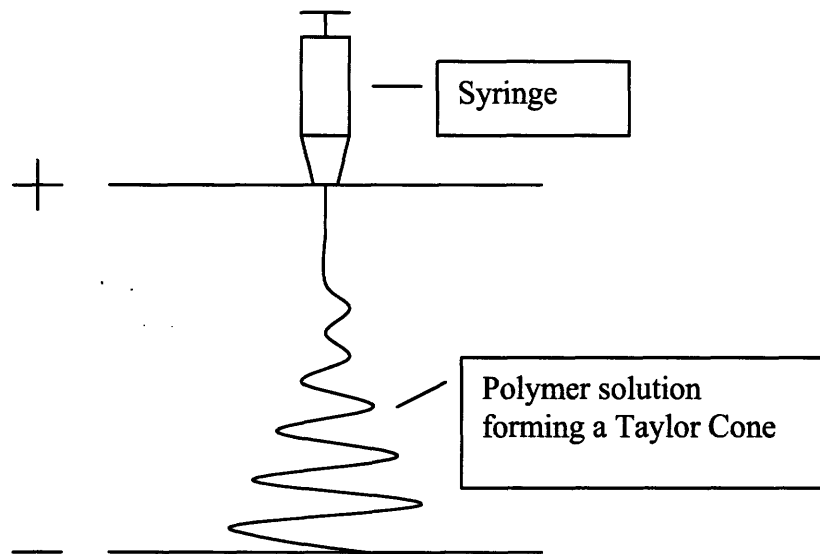


Figure 3.3 Diagram of a typical electrospinning set up

Electrospinning polyethylene has been accomplished in a melt process.²⁶ For UHMW-PE this would require temperatures of 150 degrees Celsius at a minimum. This type of process could also theoretically be used for tetrafluoroethylene (Teflon) above its melting point of approximately 500 degrees Celsius.

Because polyethylene does not dissolve in any solvent or other liquid at room temperature, electrospinning molten polyethylene would be much easier to accomplish than spinning a polyethylene-xylene solution. One of the drawbacks to this process is the amount of heat needed. Not only does the polyethylene need to be heated past its melting point, the process must take place in an environment which is hot enough that the polymer does not immediately solidify again after exiting the syringe, such as an oven.²⁷ Another drawback to electrospinning in general is that a very low flow rate through the syringe is needed for the process to work. This means that for industrial purposes the throughput would be quite low without massive parallel processing. There are some small scale commercial electrospinning operations for the production of filters, however, to date electrospinning has been primarily confined to the lab.

4 Experimental Methods and Technique

4.1 *Creating a gel from a piece of polyethylene sheet*

Xylene is an inexpensive solvent that can be used to dissolve polyethylene. Xylene was the solvent used for all experiments in this thesis due to its low cost and widespread use in the literature. Another solvent that could have been used in place of xylene is decahydronaphthalene (decalin) which was used by Choy et al and others. Decalin is not only more expensive it is more harmful to human health and more difficult to obtain. The main advantage of decalin is it has a boiling point of 187 degrees Celsius, while xylene boils at 137 degrees Celsius. The melting point of UHMW-PE is about 140 degrees Celsius, therefore, if decalin was used as a solvent the temperature could be increased to the melting point of UHMW-PE or beyond. It is unknown whether xylene is superior to decalin when stretching bulk polyethylene or vice versa.

Polyethylene does not dissolve in any solvent, including xylene, at room temperature. In fact xylene is commonly stored in bottles made of HDPE. In initial experiments 3mm cubes of UHMW-PE were placed into a bath of xylene, then the temperature of the mixture was slowly raised. Nothing occurred until the mixture reached a temperature of about 85 degrees C at which point the pieces of UHMW-PE began to stick to one another and to the glass beaker. Between 85 and 120 degrees C the pieces of polyethylene swelled approximately three times their initial size and they changed color from a slightly opaque white to completely clear. At 120 degrees C there was no visual evidence of the UHMW-PE in the xylene; unless upon stirring, a cube would crest the surface of the fluid. When the samples were removed from the fluid they

appeared to have the consistency of gelatin, however, they cooled quickly and begin to change color, size, and consistency. After the UHMW-PE cubes had cooled to room temperature and most of the xylene absorbed during the heating had evaporated, evidence of only a few changes could be observed. The cubes were slightly flared at the edges, meaning each surface of the cube was perceptibly concave. This can be attributed to the swelling since the xylene would diffuse into the edges sooner than the interior bulk. The only other change was a non-uniform white color. This coating was very thin and could be scraped away with a razor blade. It is possible that this seemingly foreign substance was due to surface oxidation, but it is most likely that parts of the outer layer of UHMW-PE develop numerous air pockets due to the rapid evaporation of xylene at the surface when it is removed from the xylene bath.

In this initial experiment I had expected that the polyethylene would form a uniform solution. The only reason that bulk UHMW-PE was used rather than an UHMW-PE powder was the fact that the bulk pieces were readily available. The fact that the bulk pieces swelled to form a gel rather than dissolving turned out to be a fortuitous accident.

4.2 Uniform Gel Creation and Manipulation

In order to form uniform solutions of polyethylene and xylene UHMW-PE powder was purchased from Alfa Aesar. First a mixture, composed of 1.5% UHMW-PE powder and 98.5% xylene by weight, was made. At 120 degrees Celsius this produced a very thick gel much like a thick batter or wet dough. This dough like gel was very sticky and would adhere to the end of a stirring rod well, but it was a bit too thick to pull a fiber

out of the solution this way. Next a solution that was 0.1% UHMW-PE by weight was produced. This solution was much more uniform. When a room temperature glass stirring rod was introduced into the solution and then quickly removed, polyethylene would adhere to the end of it. Rather than pulling out a small glob of the polyethylene, the wet fiber that was fixed on the end of the glass rod would be connected to the solution at the other end. Fibers being pulled from solution in this manner could reach a meter or more in length despite the fact that the total amount of UHMW-PE in the solution was less than a gram.

Fibers thus drawn out of solution could be placed over rollers and stretched. This type of process was pioneered in the mid 1970's to early 1980's by A.J. Pennings, I. M. Ward, P. J. Lemstra and others. As mentioned previously it was extensively patented in the mid 1980's and is the basis for the commercially marketed UHMW-PE fibers Spectra® and Dyneema®.

4.3 Initial stretching machine

The initial experiments with cubes of UHMW-PE in xylene at 120 degrees Celsius provided evidence that there was a potential for stretching polyethylene sheets in a gel like state. A small machine was created and built, shown in Figure 4.1, that could be immersed in a hot xylene bath and then used to stretch the UHMW-PE sheet after it had transitioned into the gel form.

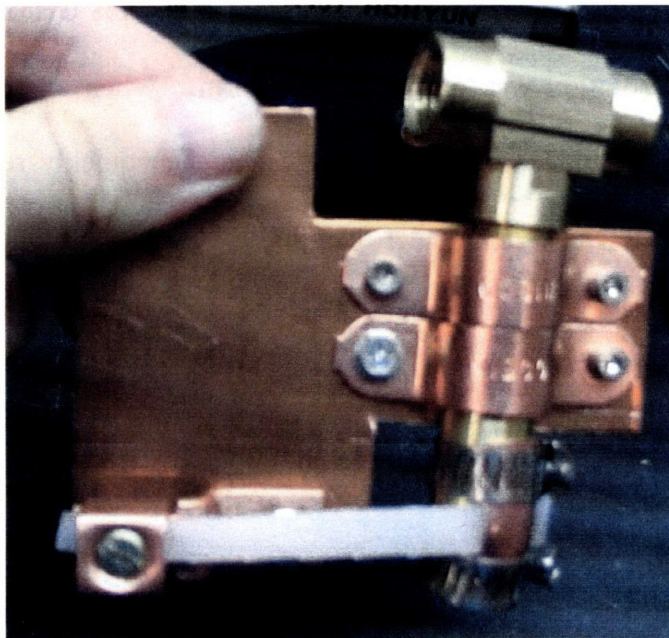


Figure 4.1 First Generation stretching machine

The machine was used successfully to stretch a section of bulk UHMW-PE sheet; however, the manner in which the polymer was attached to the machine caused the stretching to be non-uniform. Also the connections tended to tear the polymer causing it to part. This machine proved that this was an effective means of stretching UHMW-PE, but significant modifications needed to be made in order to produce uniform samples whose stretch ratio could be estimated.

The machine was used to estimate the yield strength of an UHMW-PE sheet in the gel state. Using the set up depicted in Figure 4.2 the yield strength was measured to be 0.35 ± 0.15 Mpa. This experiment was performed mainly to aid in the design of the next generation stretching machine; therefore, the high degree of uncertainty in the yield strength calculation was acceptable.

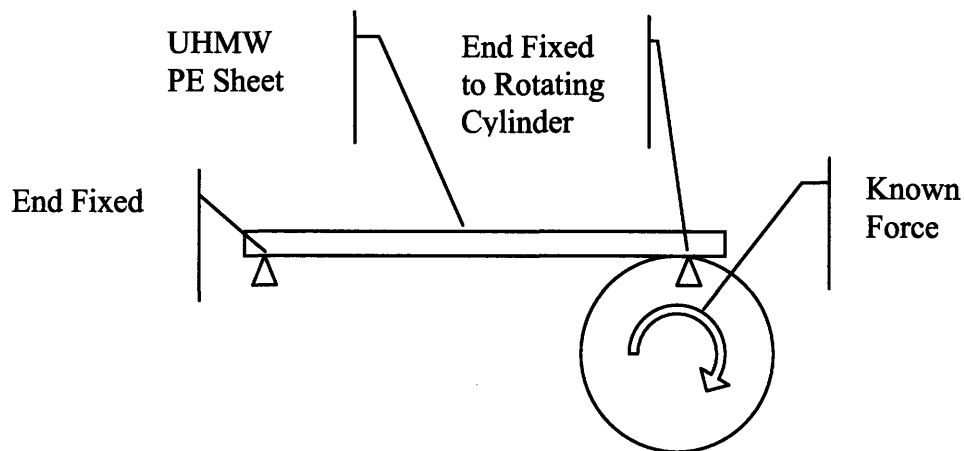


Figure 4.2 Set up for yield strength calculation (experiment performed with the sample immersed in Xylene).

4.4 Second generation stretching machine

The second generation stretching machine, shown in Figure 4.3, was built to overcome the major drawbacks of the first. Whereas the first machine had one rotating shaft, to stretch the UHMW-PE sample on only one side, the second machine has identical shafts on each side to better distribute the stress and to avoid the stress concentration that one fixed end creates. Ratchets and pawls were attached to each shaft to ensure that they did not unwind after the UHMW-PE sample had been stretched. The second generation machine was also built to handle larger samples. In order to ensure that the nuts did not loosen on the shafts, the shafts were constructed out of aluminum and the nuts were made of steel. Because aluminum expands more than steel with increasing temperature, the bolts do not become loose when the machine is heated to 120 degrees Celsius.

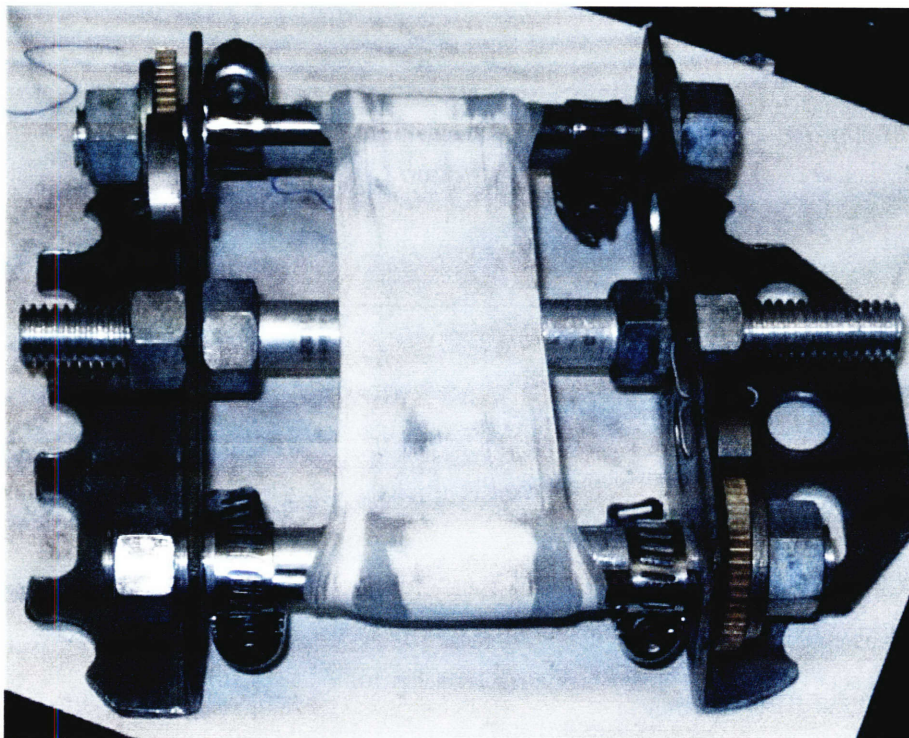


Figure 4.3 Second generation drawing machine with a sample of UHMW-PE that has been stretched.

The center shaft of the second generation machine, in Figure 4.3, was used to keep the steel angles a fixed distance apart. The samples were clamped to the front and rear shafts by thin pieces of steel attached using pipe clamps. The pawls were connected with cotter pins and remained engaged with the ratchets due to gravity. When the machine was immersed in xylene the shafts were rotated with wrenches.

4.5 Progression of experiments and samples produced

The procedure for using the second generation stretching machine was to cut a piece of UHMW-PE sheet to obtain a sample that was 2.5 cm wide and 8 cm long. After the sample was clamped to the shafts at both ends, the apparatus was placed in a glass dish, and xylene was added until the sample was well covered. Then the solution was heated to 120 degrees Celsius. A glass cover was placed over the dish in order to limit

xylene loss due to evaporation. Xylene has an evaporation rate ten times that of water, so leaving the heated solution uncovered for long periods was not feasible. The entire experiment was carried out under a chemical hood, due to the danger of breathing xylene vapors. Gloves made of Viton® were required, as xylene quickly penetrates most polymers. Once the solution reached the required temperature and the sample became a uniform gel, the cover was removed and wrenches were used to stretch the sample. Visually one could tell that the sample had become a uniform gel when it was completely clear.

Initially it was assumed that stretching the samples slowly would lead to the greatest possible stretch ratio. One concern was that stretching the samples quickly would cause the molecules to bind and break; more time would give them an opportunity to slide past one another. The first few samples produced this way were very thin, and it was difficult to keep them from breaking. Later an attempt was made to stretch a sample as quickly as possible; just to see what would happen (it was expected they would break even more quickly and easily). Using this rapid stretching technique one could stretch the sample far more before they parted. The reason for this may be that, as time passes the sample thins and relaxes in order to achieve a lower equilibrium energy state. This led to the conclusion that the stretching apparatus should be removed from the solution immediately after stretching was completed. Upon removal from the xylene the sample began to transform from a gel back to a solid immediately. The yield strength of the sample increased noticeably as the samples were stretched, to the point that it was difficult to stretch them by hand.

Experimentation has shown that the samples are quite vulnerable to tearing if a defect (cut) is present perpendicular to the stretching direction. It is quite likely that all of the samples that parted while being stretched, failed due to this mechanism, however, the size of the defect needed obviously decreases as the tension in the sample increases.

When the samples are removed from the xylene they are clear, but they turn white as they cool. This is most likely due to some combination of three factors: oxidation, crystallization, and air pockets left behind when the xylene evaporates from the samples. In order to mitigate these factors, C clamps were used to compress samples between two flat pieces of stainless steel immediately after removing them from the solution. This had the effect of squeezing xylene out of the samples, making the samples noticeably clearer in color, and more uniform in shape.

Shown in Figure 4.4 are five of the samples that were stretched. From left to right the stretch ratios are as follows: 10-15, 20-25, 10-15, 20-25, and 35-45. The three samples on the right were compressed between two flat pieces of steel immediately after they were removed from the xylene bath. The second sample from the left has a clear section at the top due to impacting it with a hammer. It is this second sample that was used most in the testing of thermal properties described in following sections.

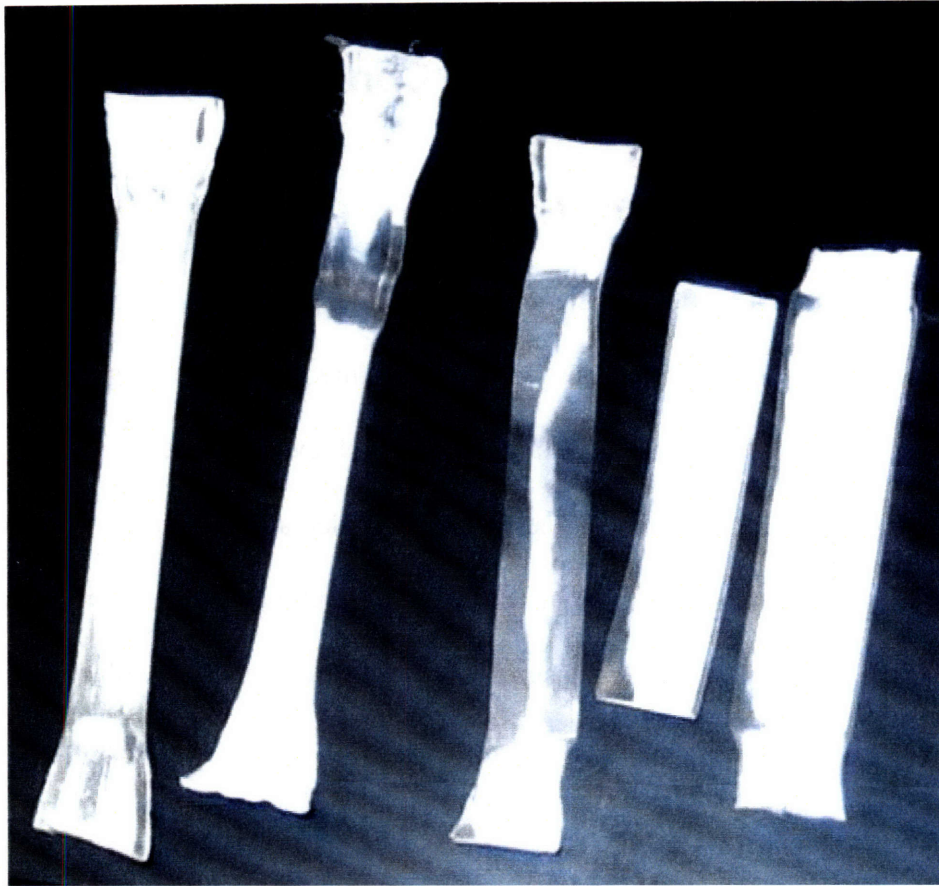


Figure 4.4 Five stretched UHMW-PE samples

5 Sample Tests and Thermal Conductivity Estimation

5.1 Stretch ratio estimation

In order to make a comparison between the stretching of bulk UHMW-PE described in this thesis and previous work, which involved stretching fibers and thin films, an accurate measurement of the stretch ratios achieved are needed. Three methods were used to estimate the stretch ratios: theoretical calculations based on the initial and final lengths of the samples, an estimate of the stretch ratio based on the initial and final cross sectional areas, and a direct measurement of the stretch ratios by placing pins in the sample prior to stretching and then measuring the distance the pins moved during stretching.

Figure 5.1 is provided to depict the relevant dimensions used for the theoretical calculations. Table 5.1 provides the relevant dimensions used for the theoretical calculations.

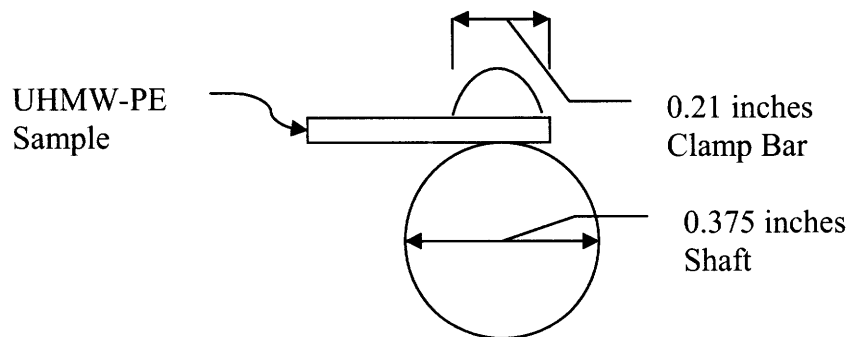


Figure 5.1 Side view diagram of one shaft of the second generation drawing machine

Table 5.1 Relevant dimensions of the second generation stretching machine

Shaft Diameter (Sd)	0.375	inches
Sample Thickness (St)	0.1	inches
Clamp Bar Diameter (Cd)	0.21	inches
Sample Length (Sl)	2.85	inches

Using the values in Table 5.1 the length that the sample is stretched after one revolution of each shaft (1rev) can be calculated as follows:

$$1rev = 2 \cdot Sd \cdot \pi + 4 \cdot St + Cd \cdot (\pi - 2) = 3.0inches \quad (5.1)$$

Assuming the Polyethylene slips freely on the metal, the first revolution of the shafts will produce a stretch ratio (λ) of:

$$\lambda = (1rev + Sl) / Sl = 2.05 \quad (5.2)$$

During subsequent revolutions one can assume there is no slip; due to the observation that the polyethylene adheres to itself when in the gel state. To derive an equation for the stretch ratio in the no slip case, begin with an example where the start length is 5 and the end length is 15. In the slip case the stretch ratio is 3. First consider discrete sticking: If the piece were stretched in ten separate one inch pulls (stretch from 5 to 6 inches, cut off one inch and repeat) the stretch ratio would be:

$$\left(\frac{6}{5}\right)^{10} = 6.192$$

In order to have a no slip condition the number of discrete stretches must be increased from ten to infinity. The following equations will be used for this calculation:

$$\lambda_s = X_f / X_i \quad (5.3)$$

$$\lambda_{NS} = \left(1 + \frac{\lambda_s}{x}\right)^x \quad (5.4)$$

where λ_s is the stretch ratio when the sample slips on the shaft or itself, λ_{NS} is the stretch ratio when the sample sticks to the shaft or itself, X_f is the final length of the sample, X_i is the initial length of the sample and x is a positive integer. Taking the limit as x approaches infinity and then taking the natural log of both sides yields the following:

$$\lim_{x \rightarrow \infty} (\ln \lambda_{NS}) = \lim_{x \rightarrow \infty} \left\{ x \cdot \ln \left(1 + \frac{\lambda_s}{x} \right) \right\} \quad (5.5)$$

Then if $x = \frac{1}{h}$ where h is a real number, L'Hôpital's rule can be applied to the limit.

$$\ln \lambda_{NS} = \lim_{h \rightarrow 0} \left\{ \frac{\ln(1 + \lambda_s h)}{h} \right\} = \lim_{h \rightarrow 0} \left\{ \frac{\lambda_s / (1 + \lambda_s h)}{1} \right\} = \lambda_s \quad (5.6)$$

The natural log can then be removed from the equation by using the base e .

$$\lambda_{NS} = e^{\lambda_s} \quad (5.7)$$

Using equation (5.7) the stretch ratios of my samples can be estimated making appropriate assumptions about when the sample is slipping and when it is sticking. As the sample is stretched past 1 revolution of each shaft, the sample begins to be wrapped upon itself and the perimeter increases. This is somewhat variable since the sample thickness continues to decrease as it is stretched, but a reasonable estimate for the increase in perimeter is 0.15 inches for the second layer, 0.1 for the third, 0.05 for the fourth, and 0.025 for the fifth. These estimates combined with the value for 1 revolution calculated in equation (5.1) leads to the data presented in Table 5.2. In the table 1rev is the increase in the sample length during the first revolution of both shafts, 2rev is the increase in sample length from the end of the 1st revolution until the end of the second revolution and so on.

Table 5.2 Sample length increase during a discrete revolution

1rev	3	inches
2rev	3.3	inches
3rev	3.5	inches
4rev	3.6	inches
5rev	3.65	inches

Using the assumption that the slip equation (5.3) should be used for the first revolution and the no slip equation (5.7) should be used final stretch ratios can be estimated for any amount of stretching. Some of these values are presented in Table 5.3 as λ : Theory1.

The assumption of no slip when the UHMW-PE is wrapped onto itself is not an accurate assumption, there is certainly some slip. Also the assumption that the sample slips perfectly on the bare aluminum shaft is not accurate.

The second method of estimating the stretch ratio is based entirely on the initial and final cross sectional areas of the samples. The density of the samples does not change significantly, if at all, after stretching (slightly buoyant in water) so this should be a reasonably accurate method of stretch ratio estimation. Some stretch ratio values obtained using this method (initial cross section divided by final cross section) are presented in Table 5.3 as λ : Cross section.

A third method of estimating the stretch ratio was to place metal pins in the sample, then compare the initial and final distance between the pins. First one pin was placed in the center of the sample. Since the sample is stretched from both ends, the center pin remains stationary throughout the experiment. The second pin was placed 0.2 inches from the center pin. Midway through the stretch the second pin had to be reset, and therefore measurements recorded. In order to calculate the stretch ratio equation

(5.3) was used substituting distance between pins for length of the sample. Since the pins had to be reset (two measurements), the stretch ratios of the first and second measurements were multiplied. The result of this test is presented in Table 5.3 as λ :Pins.

It is fairly obvious that these last two methods of stretch ratio determination are much more accurate than the initial theoretical calculations. For this reason a stretch ratio of 20-25 will hereafter be assumed for samples that have been stretched using 4 rotations on the second generation machine. Using the results of the last two tests the original stretching theory could be adjusted to match the more accurate data. A good fit is found if the sample is assumed to not stick at all for the first rotation (equation (5.3)) and then stick discretely every 4.7 inches of total stretching following equation (5.4). This new theoretical stretch ratio is presented in Table 5.3 as λ :Theory 2.

Table 5.3 UHMW-PE stretch ratios, based on the number of shaft rotations of the second generation stretching machine.

Shaft Rotations	λ :Theory 1	λ :Cross section	λ :Pins	λ :Theory 2
1	2.05			2.05
2	17.75			5.50
3	60.61	10		11.74
4	214.34	22	24	25.08
4.5	406.63	40		36.76
5	771.43			53.82

These calculations are mainly useful for comparing to previously published results. I cannot assume a direct comparison however, because my samples are thicker than the samples in prior studies by an order of magnitude.

5.2 IR microscope images

In order to ensure that the stretched samples did indeed have anisotropic thermal conductivity they were viewed under an IR microscope shown in Figures 5.2 and 5.3. The samples were clamped in a stage and exposed to a point source of heat. The source is a thin copper probe, wrapped in insulation. The stage is a piece of plastic with low thermal conductivity. The stage has a hole in the center, and there is a copper plate attached to the top of the stage. The copper plate both serves to secure the stage in place and act as a heat sink. In the thermal images one can see the circular edge of the copper plate is much cooler than the sample. The IR microscope used is the Infrascop 2, built by the Quantum Focus Instruments Corporation, which outputs thermal images directly to an attached computer.

Figure 5.2 is an overhead view of the experimental set up. Figure 5-3 shows a side view of the stage which has been lifted from the copper probe that serves as the point source. The plastic piece around the copper probe fits into the corresponding hole in the stage.

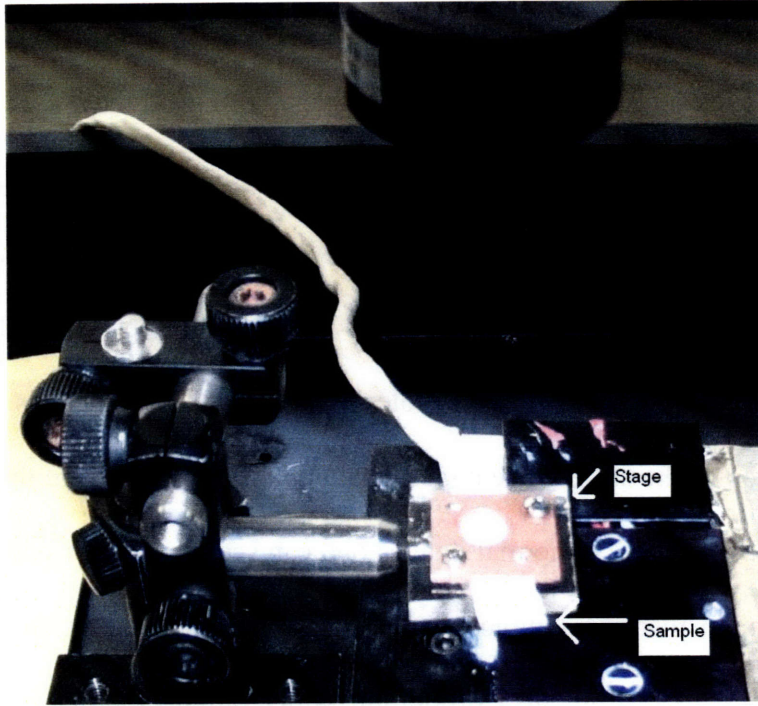


Figure 5.2 Top view of sample held by the stage of the IR microscope

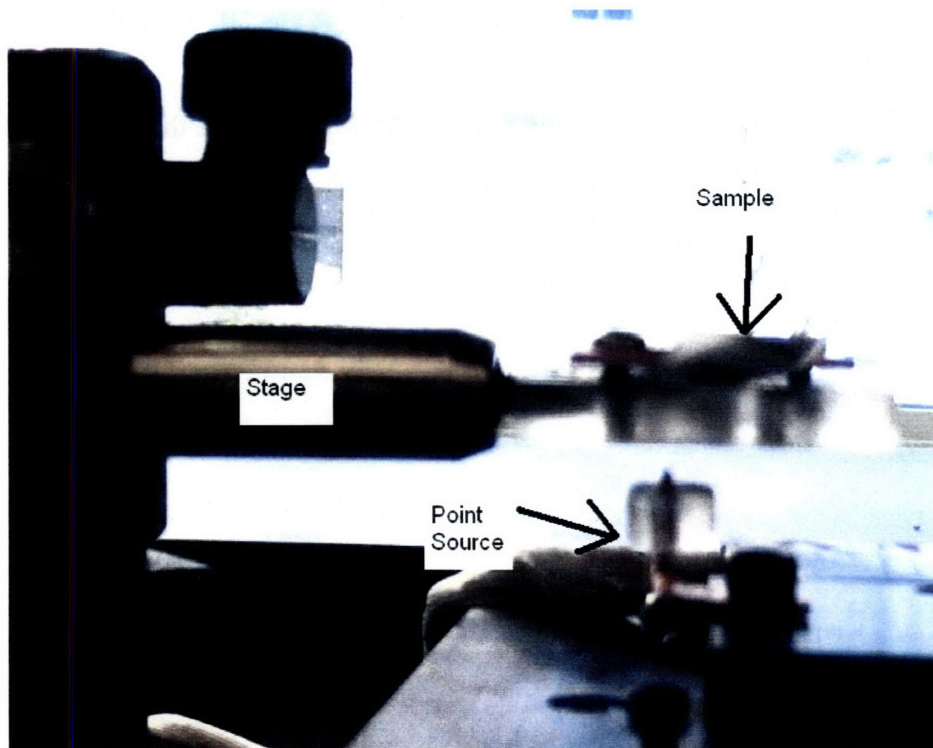


Figure 5.3 Side view of sample and stage for the IR microscope.

The temperature bar shown in Figures 5.5-5.8 show which colors illustrate more radiant heat than others. The thermal images taken are qualitative in nature only, the temperatures listed in temperature bar are not relevant. The color does accurately depict the temperature gradient across the sample, which is sufficient to prove if the heat transfer is anisotropic or not.

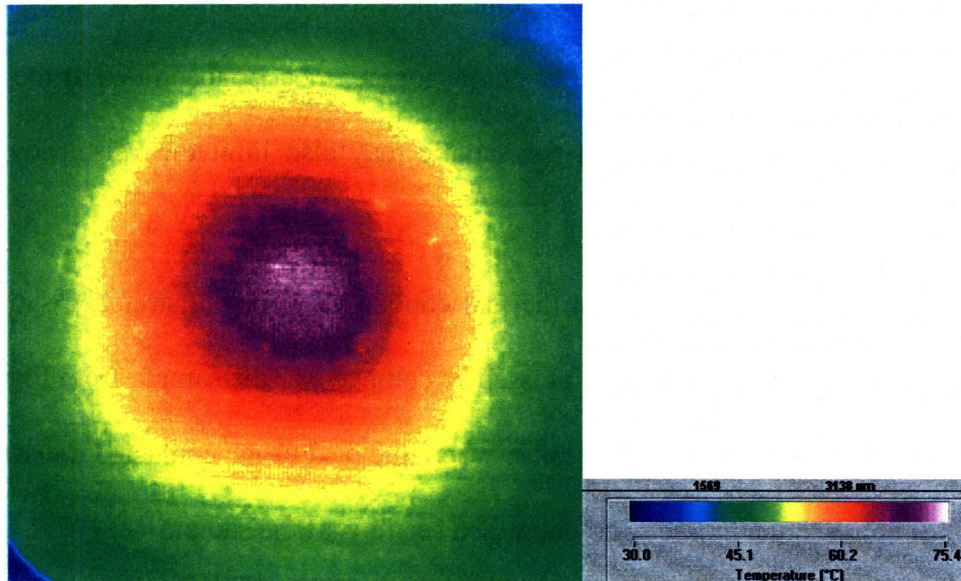


Figure 5.4 IR microscope image of an un-stretched sample, 2.1 mm thick.

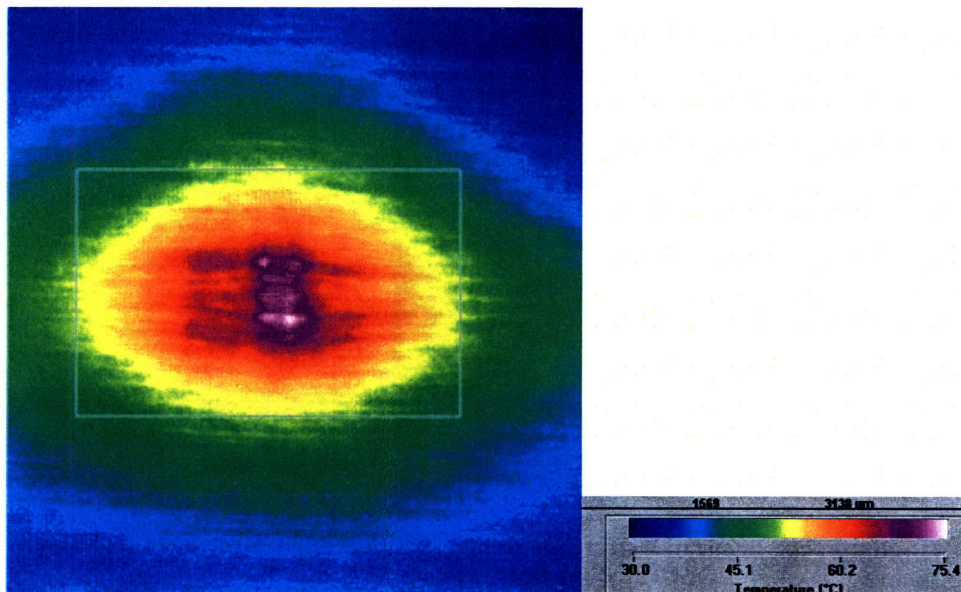


Figure 5.5 IR microscope image of a stretched sample, 0.2 mm thick, stretch ratio of 20-25. The rectangle superimposed on the image is 106 pixels high by 170 pixels wide.

It is not possible to infer the increase in thermal conductivity based on these images. Because the stretched sample exhibits anisotropic heat transfer one can conclude that molecular alignment has occurred to some extent. The anisotropy of the thermal image may have been even greater if the heat source were a perfect point source. Because there is an air gap between the point source and the sample it is likely that the heat source is more accurately a circular plume source, most concentrated at the center. Natural convection on the surface of the sample may also limit the anisotropy of the image.

In order to test the theory that thermal conductivity for the stretched samples is increased after the samples have been pressed or compacted, the sample from Figure 5-6 was pressed and a thermal image was taken where the heat probe contacted the sample at the interface between the pressed and unpressed sections of the sample.

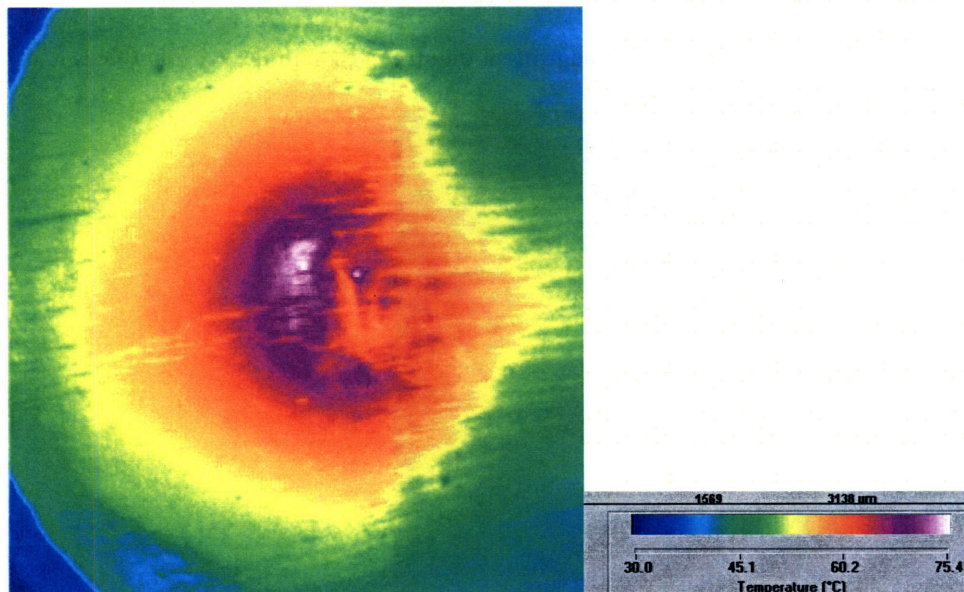


Figure 5.6 IR microscope image of a stretched sample, 0.2 mm thick, stretch ratio of 20-25. The left side of the sample was compressed, the right side was not.

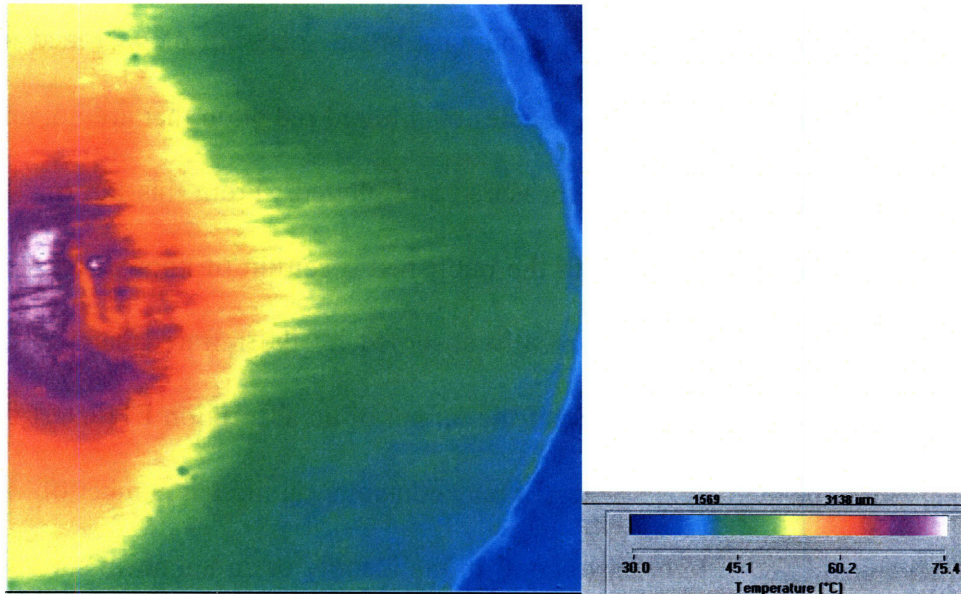


Figure 5.7 IR microscope image of a stretched sample, 0.2 mm thick, stretch ratio of 20-25. This is the same image as Figure 5-7 shifted to the right.

In Figures 5-7 and 5-8 the pressed section of the polyethylene sample is on the right. The Anisotropy of the unpressed side is evident as before in Figure 5-7, however, the pressed side appears to have much greater thermal conductivity and less anisotropy. It is possible for an oriented sample to become less oriented when it is heated to the melting point, but the act of pressing the oriented polymer should have no effect on orientation. These results led me to seek another method of determining the anisotropy of my samples

5.3 FTIR Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a method of determining the chemical composition of a sample as well as the molecular orientation. A 2007 PerkinElmer™ Spectrum GX FTIR system was available to examine the stretched samples.

FTIR spectroscopy involves sending a broad spectrum of polarized infrared radiation through a material. The frequencies of infrared radiation that are not absorbed by the material being tested are then measured and plotted. From this information one can compare a sample's spectrum with the published spectrum of known samples. For example, stretching N-H bonds is typically absorbed by the infrared band with wave numbers from 3400-3300 (cm^{-1}).²⁸ So if the output of an absorption FTIR test shows a peak in that band, the material being tested may contain a significant number of nitrogen-hydrogen chemical bonds. In order to confirm the identity of an unknown substance, all the peaks of the tested sample must be compared with a library of known spectrums, and even then, it may be difficult to find an exact match. Since I was only interested in comparisons between stretched and unstretched samples, the task was not this difficult. Analyzing spectra is something of an art, but it can provide useful information. This technology has been used since the 1940's but recent advances in computers has made FTIR spectroscopy much more accurate and faster than ever before.²⁹

It had been estimated that the test samples contained 3% more mass after becoming gels and then allowing time for all the xylene to evaporate. The details of this estimated mass increase are presented in section 5.5. FTIR testing could show if there was a chemical change which had occurred during stretching. If the samples had significantly oxidized there should be a distinct peak in the spectrum. Examining the spectrum in Figure 5.9, as well as many other spectrum of both my samples and one of Josef Miler's stretched samples I was unable to detect any significant spectrum changes. Significant oxidation should present itself in the spectrum as a new valley. There do

appear to be some new peaks in the stretched spectrum from 4000-5000 $1/\text{cm}$, this implies a loss of certain chemical bonds, or could be due to the molecular alignment.

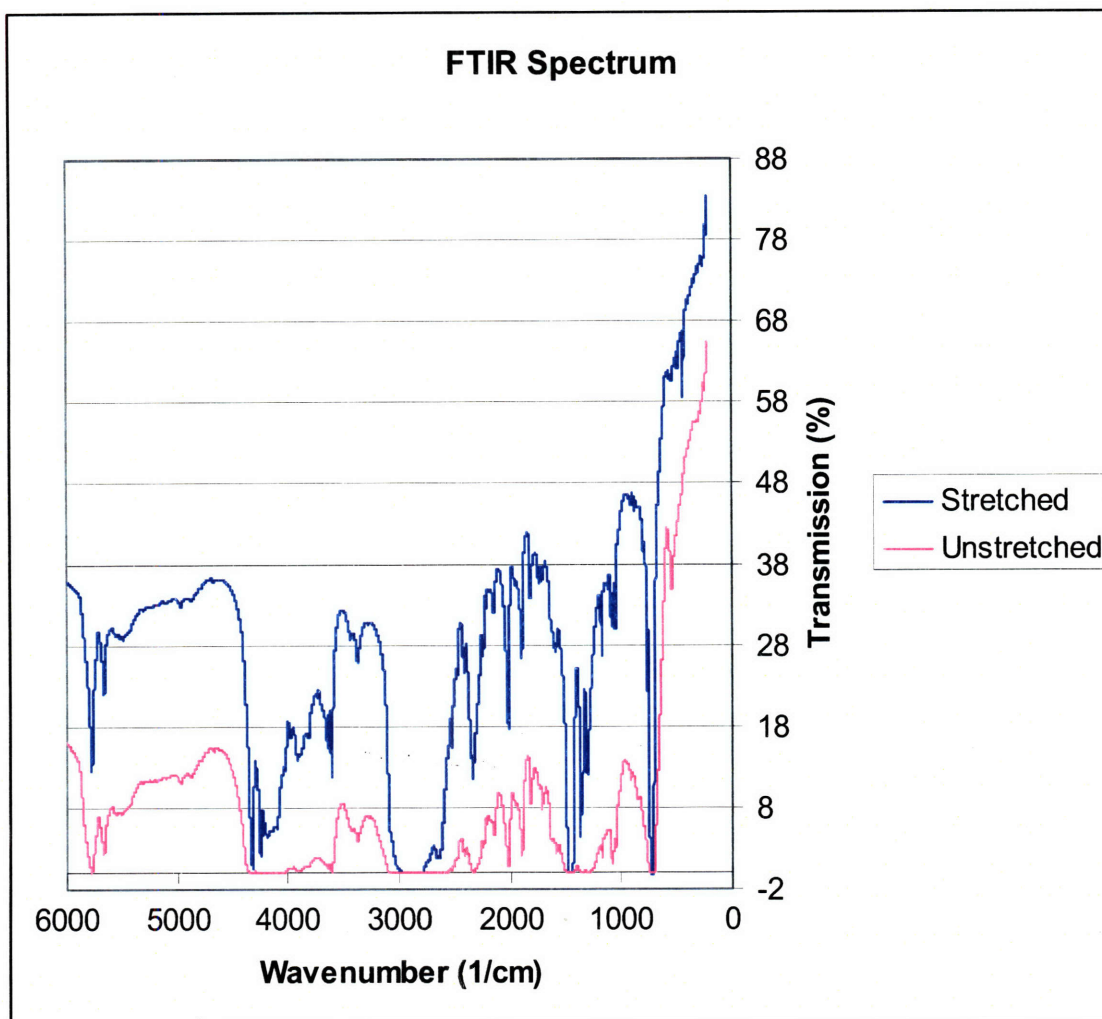


Figure 5.8 FTIR transmission spectrum

Another useful test was to determine molecular alignment based on a spectrum change when the sample was tested in two different orientations. First the sample was placed in the machine with the stretched direction pointing up, then for the second test it was rotated 90 degrees. The result of this test is shown in Figure 5.10. Because the FTIR sends polarized light through the sample, the change in absorption based on orientation of the sample must be due to the molecular orientation. This

phenomenon has been widely published.²⁹ The relevant information from this type of test is the ratio of the absorption, called the dichroic ratio.

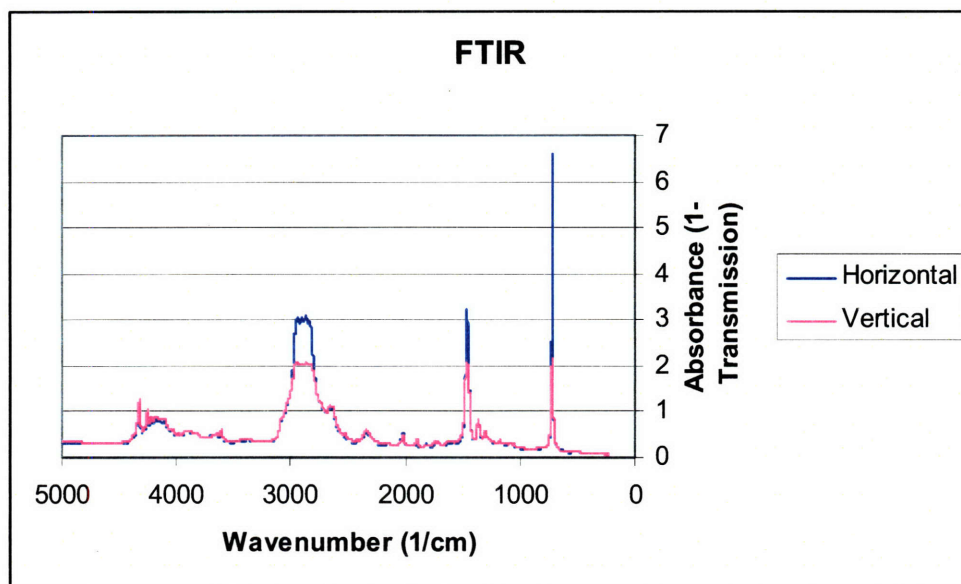


Figure 5.9 FTIR Absorbance spectrum

This test was done to prove that the sample is oriented, but it does not give quantitative information at this point because the orientation of the polarized input is unknown. However, since this test confirmed that the sample was anisotropic, I felt confident using it for further testing.

One key reference used was “Infrared Spectroscopy of High Polymers” by Zbinden. In the text there were FTIR absorbance vs. wave number graphs for stretched polyethylene similar to the graph obtained through testing. Zbinden also published dichroic ratios for a thin film of polyethylene stretched by a factor of ten that were the same order of magnitude as the ratios observed in Figure 5.10.³⁰

5.4 Angstrom method

In order to quantify the thermal conductivity along the sample the Angstrom method was used. The Angstrom method is a very old method of determining heat transfer that is not commonly used due to the complexity of the set up. It was the most practical method for me to use due to the small size of my sample and the fact that a program for running Angstrom method tests was already available in the lab.

The standard Angstrom method assumes one-dimensional heat flow and imposes the boundary conditions of semi-infinite sample length and a sinusoidal heat source. To obtain the modified Angstrom method equation the works of Angstrom, King, Starr, Sidles and Danielson were referenced.^{31,32}

$$k \frac{\partial^2 T}{\partial x^2} - h_r T = \rho c_p \frac{\partial T}{\partial t} \quad (5.6)$$

This is the equation for one-dimensional heat flow; where k is thermal conductivity, T is the temperature difference between sample and ambient, x is length, h_r is the equivalent radiation heat transfer coefficient, ρ is density, C_p is specific heat, and t is time. Next are the mathematical expressions for the boundary conditions mentioned above.

$$T(\infty, t) = 0 \quad (5.7)$$

T is a function of position and time

$$T(0, t) = T_1 \cos(\omega t) \quad (5.8)$$

Again, T is a function of position and time, ω is frequency.

The set up for this experiment is to have a heat source fixed to one end and then two thermocouples which are a known distance apart. The length of the sample must be much greater than the width and thickness for the one dimensional heat flow equation to

be valid. The sample must also be long enough that the boundary condition in equation (5.7) is satisfied. This experiment is carried out in a vacuum chamber in order to eliminate convection along the sample. This is a useful method of measuring thermal conductivity because as long as the rate of radiation and convection along the sample remain constant, radiation and convection rates do not affect the measurement. The amount of heat being put into the sample by the heater also does not affect the calculation and therefore does not need to be determined. A diagram of the experimental set up is as follows:

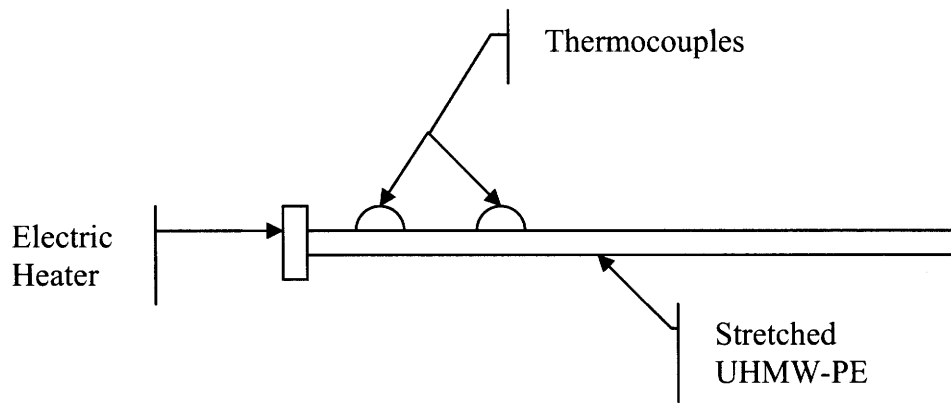


Figure 5.10 Drawing of the angstrom method set up

After solving the one-dimensional differential equation the modified Angstrom method equation is found to be:

$$k = \frac{Lv}{2 \ln q} \cdot (\rho c_p) \quad (5.9)$$

where L is the distance between thermocouples, v is the velocity of the sinusoidal temperature peak down the sample, and q is the amplitude decrement (or the ratio of the voltages from the two thermocouples.)

In this equation the values for L , v , and q can be easily calculated by a computer which records the data during the test. In order to ensure that the data being taken was not dependent on the heater power output or the frequency of the sinusoidal heat input, multiple tests were done at different frequencies and voltages. These results were then checked to ensure they were randomly distributed (ensuring heat magnitude and frequency independence). As they were randomly distributed the resulting data was averaged. Published values for density of UHMW-PE are in the range of 940-970 kg/m³. I measured the density of the unstretched UHMW-PE to be 950 ± 5 kg/m³. Specific heat is more difficult to quantify. Published values for the specific heat of oriented UHMW-PE are around 2000 J/kg K.³³ There is some uncertainty in this value because specific heat is a function of the polyethylene crystallinity and rises with temperature.³⁴

Figure 5-12 shows an example output from the thermocouples during one of the many tests of the sample. Figure 5-13 show the results of the calculated thermal conductivity of the sample. The decline in thermal conductivity in oriented UHMW-PE as a function of temperature above 300 Kelvin seems to agree with the results published by B. Nysten, P. Gonry and J. P. Issi.¹¹ However, their paper only showed results at temperatures up to 300 Kelvin, with thermal conductivity increasing as a function of temperature below 200 Kelvin, leveling off and then slightly decreasing just before reaching 300 Kelvin.

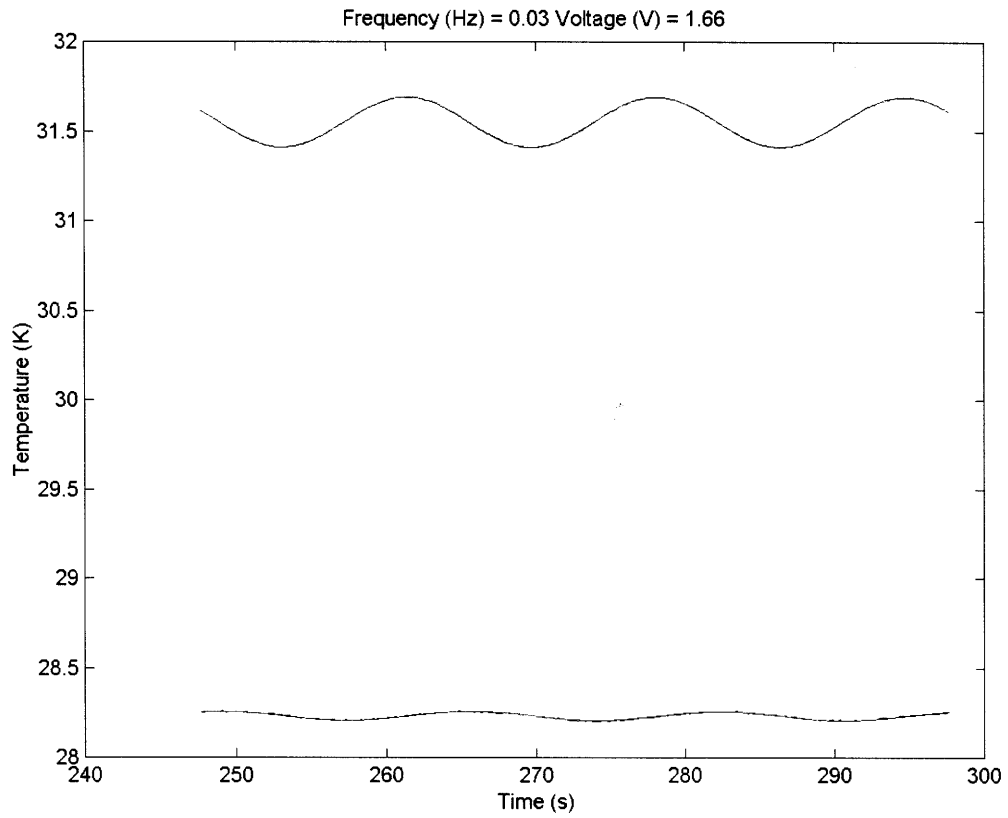


Figure 5.11 Temperature output from the two thermocouples on the sample.

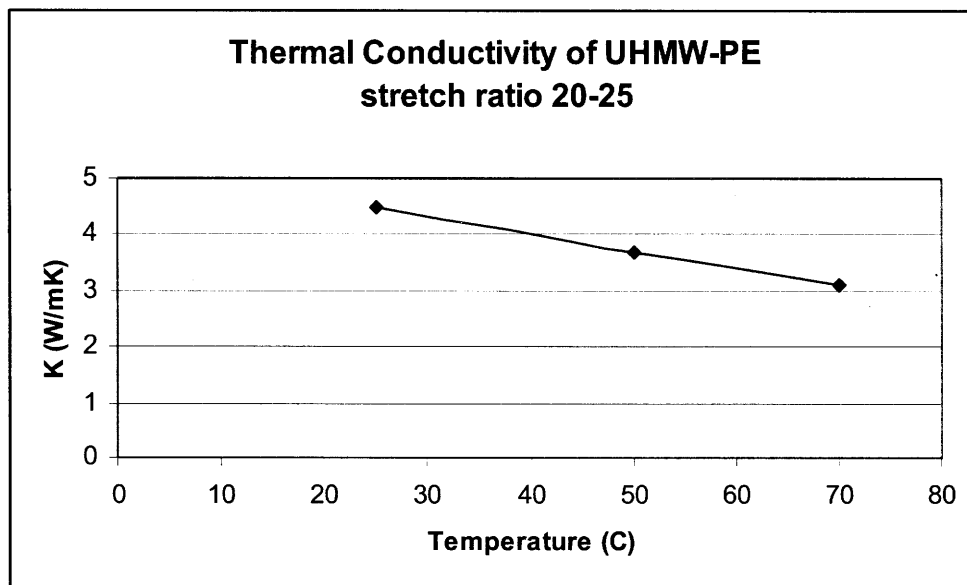


Figure 5.12 Angstrom method results for thermal conductivity as a function of temperature

5.5 Xylene Evaporation from Samples

One major component that has been referred to previously but not explained, is the time it takes for all the xylene to evaporate from the samples after they have been turned into a gel. In some initial experiments it was apparent that the samples would still off gas xylene vapor many days after they had been removed from the xylene bath. Also if the stretched samples were not kept under tension until the xylene had completely evaporated they would contract. This contraction is a function of the amount of xylene remaining in the sample and the stretch ratio. In order to quantify the time it takes for xylene to evaporate, an experiment was performed in which three samples were turned into the gel state, removed from the xylene bath, and then let to sit until the xylene had evaporated. To determine how much of the xylene remained the samples were weighed prior to being placed in the xylene bath and then at known times after removal from the xylene. The results of this test is shown in Figure 5.14.

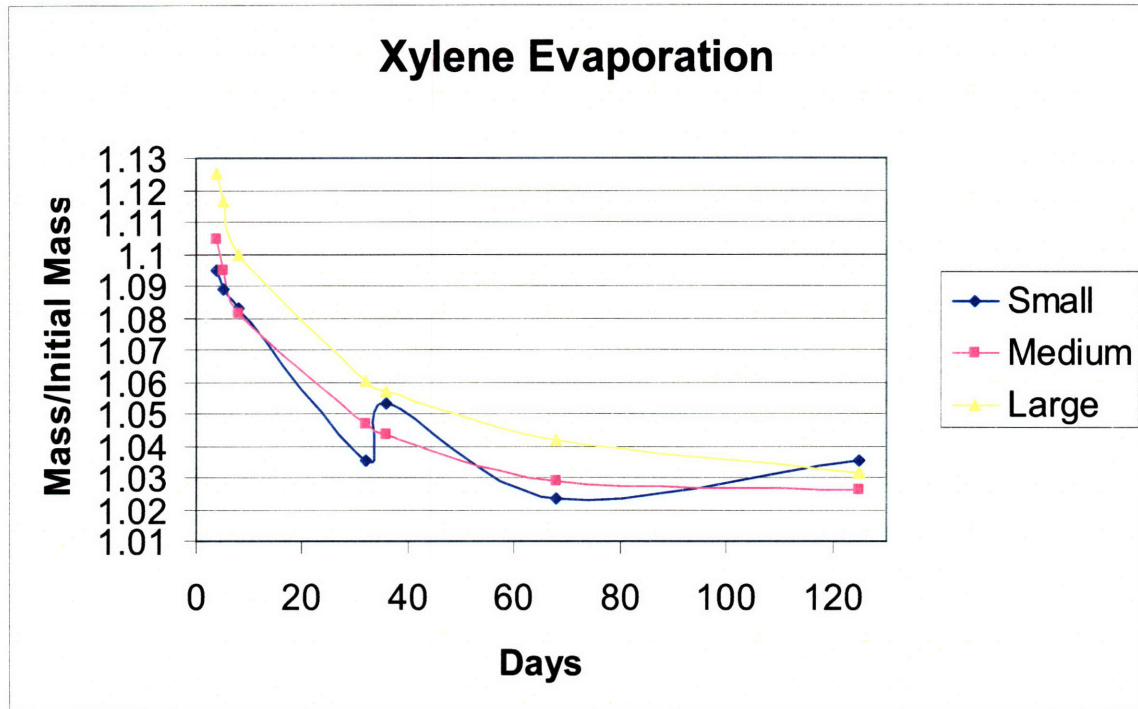


Figure 5.13 Graph of xylene evaporation as a function of time

In Figure 5-14 the small sample was 2.1 mm thick, the medium sample was 5 mm thick and the large sample was 10mm thick. Because the samples stretched by the second generation stretching machine were one tenth the thickness of the small sample they were allowed to dry for at least 10 days prior to being taken out of tension. These results show that the samples achieve a final mass that is approximately three percent larger than their initial mass. The specific cause of this mass increase is unknown.

6 Discussion

6.1 Advantages of Bulk Gel Stretching Process

There are a finite number of known methods to orient UHMW-PE. Gel spinning of fibers and tapes, electrospinning polymer melts, mechanically stretching heat softened UHMW-PE and the bulk gel stretching process described in this thesis. Each of these methods will produce UHMW-PE with thermal conductivity on the order of 5-40 W/mk, except the mechanically stretched heat softened method which has a stretch ratio limit of only 10. The bulk gel stretching process has the advantage of producing a thick sheet of oriented UHMW-PE as opposed to fiber or very thin tape which must then be layered or woven into a bulk material in order to transfer any significant amount of heat. A method of manufacturing oriented UHMW-PE sheet in bulk can be easily inferred from the description of the bulk gel stretching method and is shown in Figure 6.1.

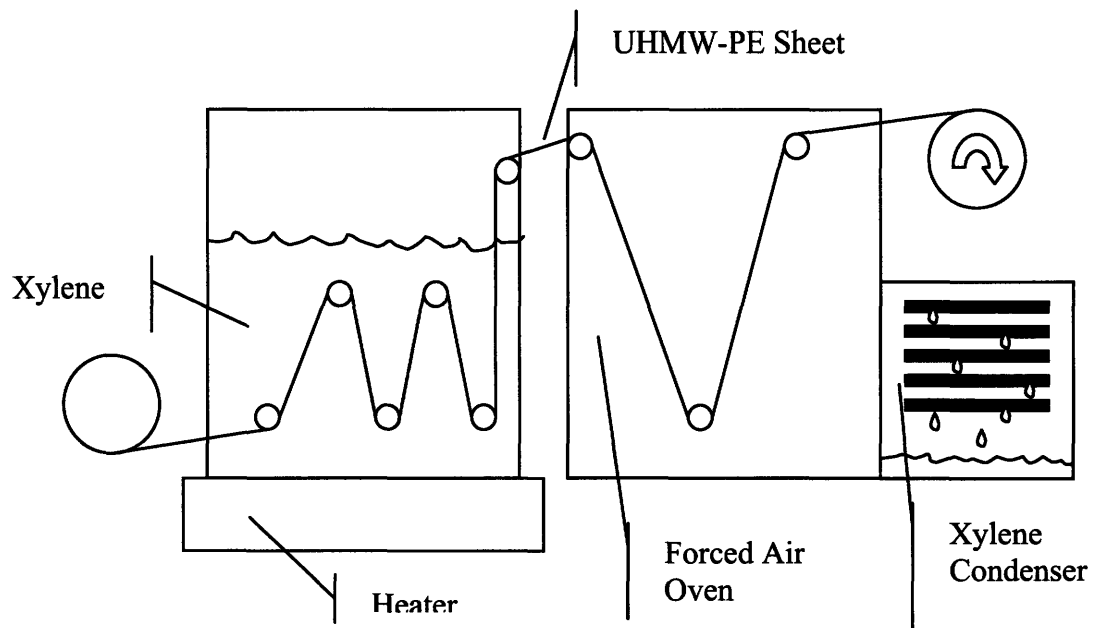


Figure 6.1 An example of a manufacturing process to orient UHMW-PE sheets

6.2 Drawbacks of Bulk Gel Stretching Process

The use of xylene in the bulk gel stretching process makes the process more expensive than traditional polymer manufacture. Xylene evaporates at ten times the rate of water and exposure is limited by OSHA to 100ppm. Because xylene will off gas from the completed material for some time after manufacturing is complete, a lot of care must be taken to keep the xylene container sealed, and the entire space where stretching and drying takes place well ventilated. Obviously the time it takes for the xylene to evaporate from the sample is also a major drawback, but further study may lead to a means of mitigating this problem. For example heating the sample in a nitrogen environment should accelerate drying without causing oxidation.

Another problem is that this oriented material cannot be put into an injection mold without destroying the alignment. Many companies have injection molding equipment and molds to make their plastic parts. If companies purchase plastic beads that have thermal conductivity increasing additives (such as from cool polymers®) then they can continue to use existing equipment. The change to a polymer stretched in xylene would require large capital expenditure for retooling and retraining.

6.3 Applications of Oriented UHMW-PE Sheet

Oriented polymers have not been produced in bulk for the purpose of heat transfer, but the applications for such material abounds. One useful application would be cases for hand held electronics devices, laptop computers, or other compact electronics

devices that require cases with the physical properties oriented UHMW-PE provides. These properties are: high thermal conductivity to prevent the electronics from overheating, electrically insulating to prevent electric shock or short circuiting, corrosion resistance for a long service life, and toughness to prevent damage if the device is dropped. Oriented UHMW-PE could be made into heat sinks for electronics in the form of thin parallel fins. Thin parallel fins of this type are commonly made of metal, but it is possible that fins made of oriented UHMW-PE could be less expensive and safer due to their electrically insulating property. The heat spreading fins for a baseboard heating element, or any other type of heat spreading fins attached to pipes could be made of oriented UHMW-PE. Assuming the elements could be made for the same price of steel elements, they would have superior corrosion resistance. A semiconductor chip package with superior heat transfer properties could be made from oriented UHMW polyethylene. Currently chip packaging has thermal conductivity of less than 20 W/mK.

Example drawings of these applications are included in the Appendix

6.4 Future Work

There are still several aspects of the bulk gel stretching process that need to be optimized prior to manufacture. The maximum draw ratio achieved using the bulk gel stretching process described in this thesis is approximately 50-80, but this might be improved if the sample were drawn in two stages, or drawn faster. The maximum achievable draw ratio may also be a function of the initial thickness of the sheet.

Thus far xylene to turn UHMW-PE sheet into a gel form. Decalin could be used so that temp is a variable in the stretching process. Also antioxidants could be added to the xylene solution in order to prevent oxidation of the samples. Oxidation could also be limited by running the experiment under nitrogen or argon gas.

The pump probe method or laser flash method could be used to better test the thermal conductivity of stretched samples. Even if the pump probe method of testing thermal conductivity were more laborious, it would be useful to compare the results with those obtained using the angstrom method.

The wide angle x-ray spectroscopy (WAXS) method of determining molecular alignment is more accurate than FTIR. The reason the FTIR was used is because it was readily available, while a WAXS set up was not. The FTIR measurements could also be greatly enhanced if the PerkinElmer FTIR attachment for determining polymer alignment were utilized.

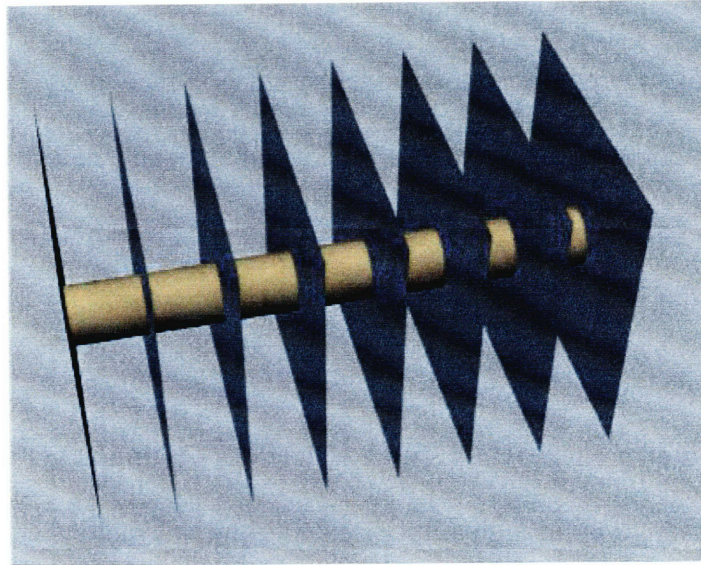
7 Conclusions

UHMW Polyethylene has numerous desirable properties as an engineering material such as strength, fracture toughness and chemical resistance. These properties are what make polyethylene the most widely used polymer today. Polyethylene has replaced or is currently replacing metals and wood in many industries, including the marine industry. Orienting the molecules of polyethylene dramatically increases the ultimate strength and thermal conductivity in the direction of orientation. As such this processing further increases the value of UHMW-PE as an engineering material.

The method of orienting bulk sheets of UHMW-PE in the gel state is original to this thesis. After searching through all prior patents and relevant papers on the subject of molecular orientation I have concluded that this is the only method known of orienting bulk UHMW-PE with stretch ratios above 10. This realization, and the validation of the bulk UHMW-PE sheet stretching method through testing with the Angstrom method, led to the discussions of commercial applications. I am hopeful that this work will lead to further research on the subject, and eventually a widely available new engineering material: oriented sheets of UHMW-PE.

Appendix

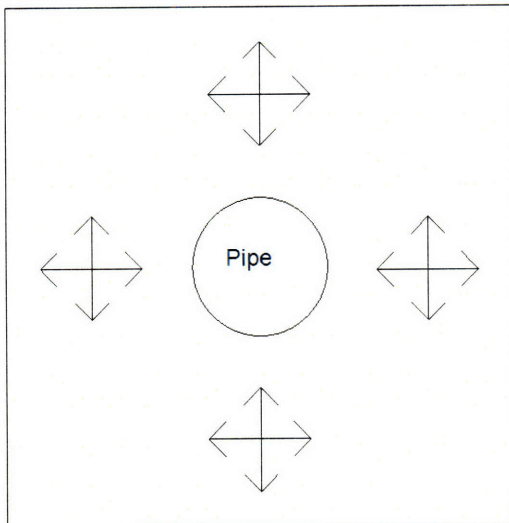
Drawings of Applications for Oriented UHMW-PE



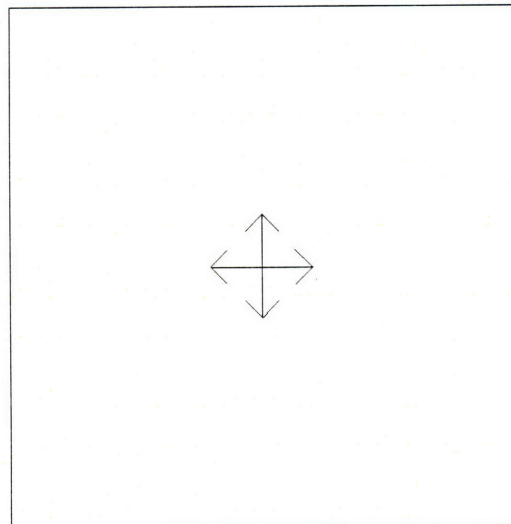
Heat Exchanger Composed of a pipe with multiple heat spreading plates

Detailed view of individual square heat spreading plate

Example 1



Example 2

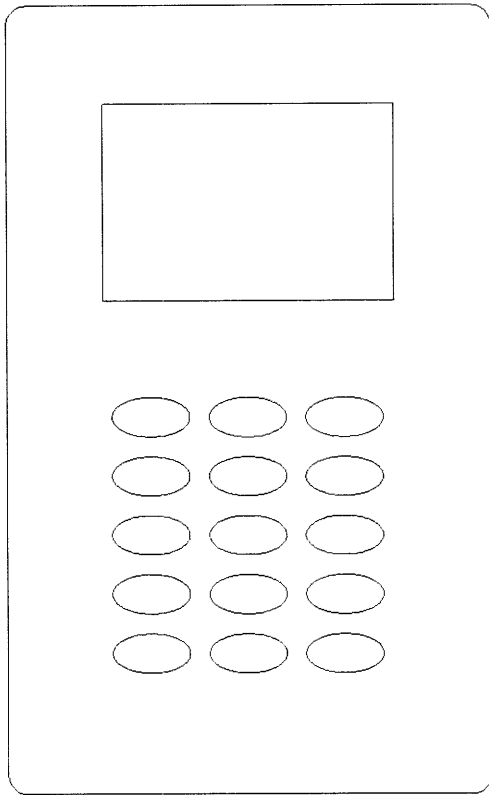


Arrows depict direction of molecular orientation

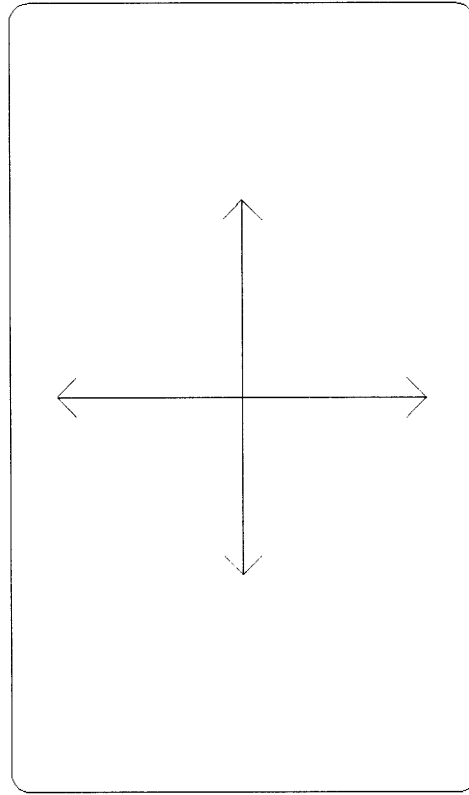


Side view of the plate. Each plate is made up of two oriented pieces of UHMW-PE sheet, laminated together. The orientation of molecules in the top sheet is rotated 90 degrees from that of the bottom sheet.

Personal Electronics Case



Front

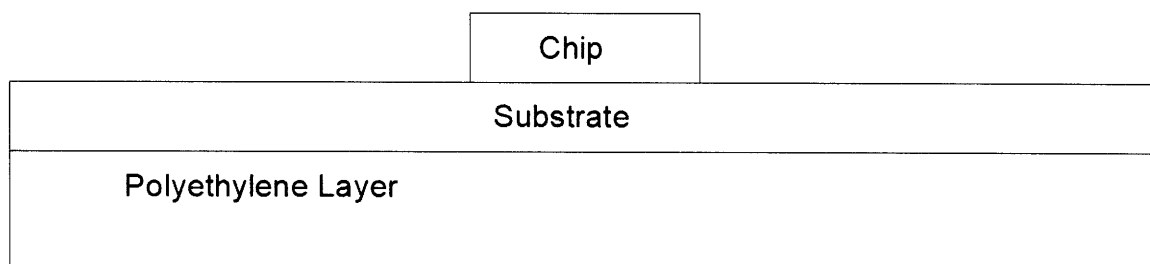
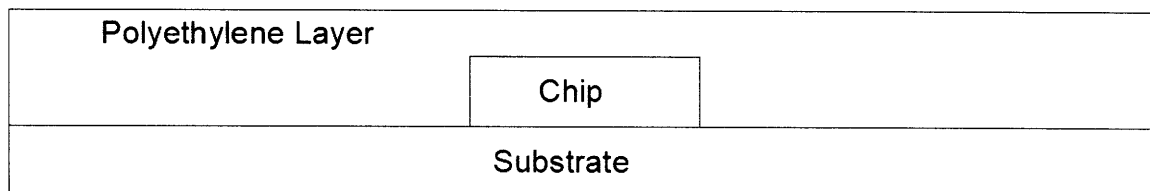


Back

Arrows depict direction of molecular orientation.

Each side of the electronics case is made up of two oriented pieces of UHMW-PE sheet, laminated together. The orientation of molecules in the top sheet is rotated 90 degrees from that of the bottom sheet.

Computer Chip Packaging



References

- ¹ Oswald T. A., Baur, E., Brinkmann, S., Oberbach, K. and Schmachtenberg, E., International Plastics Handbook, Munich: Hanser, pp. 1-2. (2006)
- ² Deanin, Rudolph D., Polymer Structure, Properties and Applications, Boston: Cahners Books, pp. 53-58. (1972)
- ³ Peters, S. T., Handbook of Composites (2nd edition), Springer – Verlag, pp. 202-212. (1998)
Online version available at:
<http://www.knovel.com/knovel2/Toc.jsp?BookID=359&VerticalID=0>
- ⁴ Brydson, J., Plastics Materials (7th Edition), Elsevier, pp. 77-79, 82-84, 100-103, 265, 224. (1999)
Online version available at:
<http://www.knovel.com/knovel2/Toc.jsp?BookID=440&VerticalID=0>
- ⁵ Schwartz, Mel M., Composite Materials (Volume 2), Prentice Hall, pp.9, 504. (1997)
- ⁶ Billmeyer, Fred W., Textbook of Polymer Science, New York: Wiley pp. 367 151-180, 503. (1984)
- ⁷ Choy, C. L., “Thermal Conductivity of Polymers,” Polymer, Vol. 18, pp. 984-1004. (1977)
- ⁸ Lepri, S., Livi, R. and Politi, A., “Thermal conduction in classical low-dimensional lattices,” Physics Reports, vol. 377, pp 1-80. (2003)
- ⁹ Chen, Gang, Nanoscale Energy Transport and Conversion, New York: Oxford University Press, p.10. (2005)
- ¹⁰ Rantala, J., “ A Measurement Method for the determination of the anisotropy ratio of thermal conductivity of plastic foils,” Review Of Scientific Instruments, Vol. 63, No. 11, pp. 5472-5474. (1992)
- ¹¹ Nysten, B., P. Gonry, and J. P. Issi, “Intra and Interchain Thermal Conduction in Polymers,” Synthetic Metals, Vol. 69, pp. 67-68. (1995)
- ¹² Choy, C. L., Yang, G.W. and Wong, Y.W., “Thermal Diffusivity of Polymer Films by Pulsed Photothermal Radiometry,” Journal of Polymer Science: Part B: Polymer Physics, Vol. 35, pp. 1621-1631. (1997)

- ¹³ Choy, C. L., Wong, Y.W., Yang, G. W., and Kanamoto, Tetsuo, “Elastic Modulus and Thermal Conductivity of Ultradrawn Polyethylene,” Journal of Polymer Science: Part B: Polymer Physics, Vol. 37, pp. 3359-3367. (1999)
- ¹⁴ Love, C. T., G. Xian and V. M. Karbhari, “Thermal, Mechanical, and Adhesive Properties of HDPE/ Reactive Ethylene Terpolymer Blends,” Journal of Applied Polymer Science, Vol. 104, pp. 331-338. (2007)
- ¹⁵ Davis, Anthony and Sims, David, Weathering of Polymers New York: Applied Science Publishers pp.200-205. (1983)
- ¹⁶ Ocean Kayak™ a brand of Johnson Outdoors Inc. (April 2007)
<http://www.oceankayak.com/innovation/history.html>
- ¹⁷ Makai Ocean Engineering Inc. (April 2007) <http://www.makai.com/p-pipelines.htm>
- ¹⁸ DSM Deneema Press Release DYNPR031E0207 “Offshore Fish Farming Trials New Cage With Dyneema®” (March 2007)
http://www.dsm.com/en_US/html/hpf/home_dyneema.htm
- ¹⁹ DSM Deneema Press Release DYNPR034E0107 “Leading Canadian Salmon Farmer Selects Nets With Dyneema®” (March 2007)
http://www.dsm.com/en_US/html/hpf/home_dyneema.htm
- ²⁰ Miler, Josef L. Methods for Increasing the Thermal Conductivity of Ultra-High Molecular Weight Polyethylene, Massachusetts Institute of Technology BS Thesis, (June 2006)
- ²¹ Ward, I M. “Preparation, Properties and structure of High-Modulus Polyolefines and Polyoxymethylene,” Strong Fibers. Ed. W. Watt and B. V. Perov, North-Holland: Elsevier, pp.705-740. (1985)
- ²² Van Dingenen, Jan L. J., “Gel-spun High-performance Polyethylene Fibres,” High-Performance Fibres, Ed. J.W.S. Hearle, Boston: CRC Press, pp.63,67. (2001)
- ²³ Honeywell International Inc. website (March 2007)
http://www.honeywell.com/sites/sm/afc/spectra_fiber.htm
- ²⁴ Li, Dan and Xia, Younan, “Electrospinning of Nanofibers: Reinventing the Wheel?,” Advanced Materials, Vol. 16, No. 14, pp. 1151-1170. (2004)
- ²⁵ Prof. Gregory C. Rutledge group web page (March 2007)
<http://web.mit.edu/rutledgegroup/>

- ²⁶ Larrondo, L and St. John Manley, R., "Electrostatic fiber spinning from polymer melts. I. Experimental Observations on Fiber Formation and Properties," Journal of Polymer Science: Polymer Physics Edition, Vol. 19, pp. 909-920. (1981)
- ²⁷ Yu, Jian H. interview with (grad student in Prof Rutledge group, MIT)
- ²⁸ Stuart, Barbara, Infrared Spectroscopy: Fundamentals and Applications, New York: Wiley, pp. 1-2, 46. (2004)
- ²⁹ Siesler, H. W., and Holland-Moritz, K., Infrared and Raman Spectroscopy of Polymers, New York: Dekker, p. 281. (1980)
- ³⁰ Zbinden, Rudolf, Infrared Spectroscopy of High Polymers, New York: Academic Press, pp. 90, 225. (1964)
- ³¹ King R. W., "A Method of Measuring Heat Conductivities" Physical Review Vol. 6, No. 6, pp. 437-445. (1915)
- ³² Sidles, P. H. and Danielson, G. C., "Thermal Diffusivity of Metals at high Temperature," Journal of Applied Physics, Vol. 25, No. 1, pp 58-66. (1954)
- ³³ Mergenthaler, D. B., Pietralla, M., Roy, S., and Kilian, H.G., "Thermal Conductivity in Ultraoriented Polyethylene," Macromolecules Vol. 25, pp. 3500-3502. (1992)
- ³⁴ Wunderlich, Bernhard, "Motion in Polyethylene. I. Temperature and Crystallinity Dependence of the Specific Heat," The Journal of Chemical Physics, Vol. 37, No. 6, pp. 1203-1207. (1962)