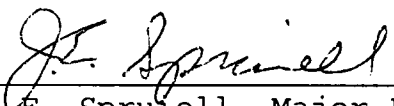
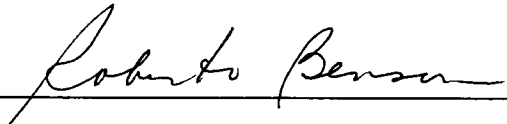


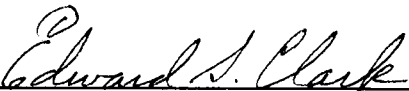
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**PROCESSING AND CHARACTERIZATION OF
POLY(ESTER-AMIDE) MONOFILAMENTS**

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Deepak D. Agrawal
December 1993

*To my Brother
Bhushan Gupta*

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ABSTRACT

The introduction of synthetic polymers has added a new dimension to the biomedical applications of fibers. Current biomedical applications of fibers include sutures, surgical implants, prosthetic devices, artificial ligaments, synthetic blood vessels, and controlled drug release. The 3M company has recently developed a new class of bioabsorbable polymers, known as the "poly(ester-amide)s", for potential application as surgical sutures. It is the purpose of the present research to conduct experimental and analytical studies on the processing of these materials into fibers for use as surgical sutures.

The values of amorphous and crystalline densities were determined for the PEA-10,2 polymer. These values were then used to calculate the crystallinity in the PEA-10,2 fibers and films by measuring their density. The effect of moisture plasticization on the T_g of PEA-6,2 polymer was studied using the dynamic mechanical analysis, and the DSC.

Melt spinning studies were performed on polymers PEA-10,2 and PEA-6,2. The melt spun fibers were drawn under several different drawing conditions, studying the effect of individual processing variables on the structure and properties of these fibers. It was found that the two stage drawing technique gave the best results, with the first stage drawing performed in-line.

It was noticed that the molecular weight of these polymers dropped significantly during the processing, and had an adverse effect on the properties of the fiber. It was concluded after further analysis that this drop was mainly due to the long residence times at high temperatures during the processing. In an effort to improve the molecular weight retention, extrusion of this polymer was tried using the Maxwell extruder. The new extrusion technique and an improvement in the high temperature thermal stability of polymer together gave significantly better results. The suitability of gel spinning technique for the processing of PEA fibers was also considered and the very preliminary results are presented.

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Chapter 1

INTRODUCTION

A fiber can be defined as a flexible, macroscopically homogeneous body whose length is at least one hundred times its diameter. Fibers are classified according to the origin as naturally occurring fibers or synthetic fibers. Natural fibers are those derived directly from the animal, vegetable, and mineral kingdoms, and are generally of finite length, with an exception of silk. Synthetic fibers are organic or inorganic materials that have been processed into the form of a fiber, and include man-made or naturally occurring organic polymers. The synthetic fiber can be categorized as either staple (short length) or continuous filament (very long length). The continuous filaments are then further categorized as monofilaments and multifilaments, and so on. The fibers based on synthetic organic polymers have revolutionized the textile industry since their initial commercialization in 1940s. The most widely used synthetic polymer fibers are based on: polyamides, polyesters, acrylics, polyolefins, polyurethanes, and certain vinyl derivatives (1).

Fibers have been used for many years in medical applications such as dressings, sanitary pads, tapes, and operating room apparel. Applications of fibers include sutures, surgical implants, prosthetic devices, and medical

equipment. Speciality fibers are also used for separations and purification such as kidney dialysis, and they will play important roles in emerging biotechnological applications such as substrates for large cell culture(2).

Fibers possess certain advantages applicable to biomedical uses. The surface-to-volume ratio is very large, which is important in surface dominated applications such as separations. They can also be processed into knitted, woven, or hollow structures that provide the varying degrees of porosity and strength needed in biomedical applications such as synthetic blood vessels, artificial ligaments, and controlled drug release. Both natural and synthetic fibers are used in the biomedical field. Natural fibers such as silk and catgut (collagen) have been used by physicians for many years. However, the introduction of synthetic polymers has significantly increased the use of fibers in biomedical applications (3). Polyester and nylon fibers are used in a large number of medical applications, and newer materials like carbon fibers are also being evaluated, particularly for use in applications requiring high strength and improved tissue compatibility.

One of the oldest and most important biomedical uses for engineering fibers is surgical sutures. A suture, by definition, is a strand of material, natural or synthetic, used to ligate blood vessels and to approximate tissue

together (3). Suture materials are required to keep wounds together until they hold sufficiently well by themselves. They provide artificial fiber support until the natural fiber (collagen) is synthesized and woven into a strong scar.

Increasing applications have led to the rapid growth and development of the fiber industry. This has brought about the need for a deeper understanding of the physical phenomena involved in the technological processes. Fibers can be manufactured on the basis of purely empirical knowledge, but optimization of existing technological processes as well as development of entirely novel processes is necessary for meeting the needs in a specific application, together with the growing quality requirements. For this reason, the leading fiber manufacturing companies and many academic institutions have extensive research programs concerned with fundamentals of fiber formation: mechanics, heat transfer, and structure formation during fiber spinning and drawing. It has been postulated that invention of new materials as well as modification of natural polymers cannot be achieved without a good background of synthetic chemistry. The development of technical know-how for fiber production is generally accompanied by, or, in many cases, preceded by more fundamental chemical studies.

The life sciences research laboratories at 3M have developed a promising class of bioabsorbable polymers with potential biomedical applications (5). These polymers, the poly(ester-amides) (PEA), are synthesized from a highly water soluble amidediol and a diacid under carefully controlled conditions to yield PEA-x,y resins. Preliminary studies by the fiber research group here at The University of Tennessee have shown that the PEA 6,2 and PEA 10,2 resins can be melt spun and drawn into monofilaments suitable for absorbable sutures (5-7).

It is the purpose of the present research to conduct experimental and analytical studies on the processing of these materials into fibers for use as surgical sutures. Experimental studies will include a detailed evaluation of the effect of processing variables on the final fiber properties, and the modification of the melt spinning and drawing techniques to achieve the most desirable properties in the fiber. Analytical studies will include the effect of orientation, molecular weight, and crystallinity of the fiber on its tensile properties. A method to measure the percent crystallinity in these fiber samples will also be developed. An effort will be made to determine the glass transition temperatures of these polymers, together with a study of the effect of moisture pick-up on the glass transition temperature.

Chapter 2

BACKGROUND

2.1 BIOMEDICAL MATERIALS

Materials that can be used in biological environments, and can remain in such environments for prolonged periods of time in order to perform a specific function, are called biomedical materials or *biomaterials*. In general, a biomedical material must possess properties that will enable it to perform a desired function at a specific location in the body. Examples of such materials include metals, polymers, ceramics, glasses, reprocessed biological tissues, and combinations of one or more of these, that are referred to as *composite materials* (8). As a result of collaborative efforts of material scientists, engineers, and surgeons, the horizon for use of biomedical materials in artificial tissues, and organs is expanding. The requirements of physical, chemical, and mechanical properties of the implant material vary with its intended function in the body. Polymeric materials have been found to exhibit good potential as biomedical materials as they can be tailor made according to the end use (9).

2.1.1 Biomedical Polymers:

The first medical applications of polymers made use of commercially available plastics, adapted as necessary.

Although the science of polymeric biomaterials is relatively new, use of these materials is becoming increasingly popular in virtually every aspect of medicine. Typical applications include tissue replacement, tissue augmentation, tissue support, drug delivery, special ion-exchange resins, vascular prostheses, and semipermeable membranes (10,11). Some of the important requirements of a polymeric biomaterial are given below (12):

- The polymer should have necessary chemical, physical, and mechanical properties for its proposed function.
- It should be free from all impurities such as residual catalysts, solvents, additives, etc., which may alter its performance.
- It should be fabricated into the desired implant without a change in its properties.
- It should not be adversely affected by the biological environment of the body.
- It should be biocompatible; i.e., it should not induce thrombus formation, inflammatory reaction, cell changes, tumor formation, immune response, etc..

On the basis of their behavior in living tissue, the polymeric biomaterials can be divided into three groups: biostable, biodegradable (absorbable or resorbable), and partially degradable. Biostable polymers are physiologically inert, cause only minimum response of the surrounding

tissues, and retain their properties for a very long time. The tissues often need only a temporary presence of a biomaterial. In such cases, biodegradable and partially biodegradable polymeric materials are better alternatives than biostable ones (13,14). Biodegradation and biological absorption of a material is the degradation induced by the vital activity of an organism (15). The use of term "bioabsorbable" is limited to those compounds which disappear from their initial implantation location with no physical degradation of the macromolecule; a definition which agrees well with the acceptance of the term "absorption" in physics. For example, this definition fits well with the slow dissolution of water-soluble implants in body fluids. Biomaterials that can degrade in such a way that the low molecular weight compounds formed during degradation can be eliminated from the body through natural pathways, are termed 'bioresorbable'. Accordingly, a bioabsorbable material can be called a *bioresorbable* material only if the dispersed macromolecules are excreted or metabolized (16).

Biodegradable polymeric and composite surgical materials retain their tissue supporting properties for given lengths of time (typically days, weeks, or months) and gradually they are degraded into tissue compatible components which are absorbed by living tissues and replaced by healing tissues (17). The biodegradable surgical

materials are the best alternative for the temporary internal fixation of many different kinds of tissue damage for the following reasons:

1. During the early stages of tissue healing, the biodegradable implant holds the healing tissue in place. With the passage of time, the implant decomposes gradually and the stresses are transferred to the healing tissue.
2. Biodegradable surgical devices do not require a removal operation, which is of substantial benefit, both economically and to the human being involved.

A variety of biomedical polymers have been introduced so far. Currently used polymers and their specific uses are given in Table 2.1 (18). It is commonly known that among the condensation polymers, aromatic polyesters and polyamides are non-biodegradable although aliphatic polyesters are susceptible to biological attack (19-21). As a class, the polyesters are by far the most commonly used synthetic bioerosible polymers (22,23). The family of aliphatic polyesters seems to be richer and most promising particularly because most of these materials break down to metabolites (16). Examples of rapidly degrading polyamides, by contrast, are rare. Nylon 6 and nylon 6,6 are generally considered to be non degradable, although partial degradation and loss of tensile strength have been reported

Table 2.1 Current biomedical applications of some polymers.

Polymer	Uses
Polyethylene	Orthopaedics, Cardiovascular devices.
Polypropylene	Sutures, Reconstruction Surgery.
Polyamides	Sutures, Wound dressing, Dentures.
Polyesters (biostable)	Orthopaedics, Tissue flaps.
Polyesters (absorbable)	Sutures, Drug delivery systems, Prostheses, Orthopaedics, Ligating clips.
Polytetrafluoroethylene	Cardiovascular devices, Sutures, Tissue flaps.
Polyacrylates	Contact lenses, Dentures, Orthopaedics, Tissue replacement, Macrocapules, Repair of brain lesions.
Polyurethanes	Prostheses, Wound dressings, Contraceptives, Liver support systems.

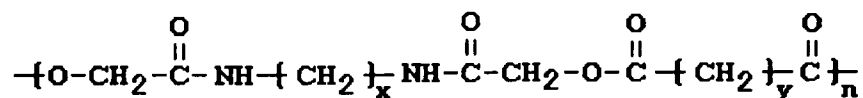
Source: J. Paul, Ph. D. Dissertation, I.I.T. Delhi, April 1991.

for both of these polymers when they were implanted in living organisms for long periods (24-27). Polyamides based on 4,4'-spirobibutyrolactone have recently been reported as biodegradable, and suitable for biomedical applications as absorbable sutures (28).

As an approach for obtaining further improvements in properties of synthetic absorbable polymers, the synthesis of polymers containing both amide and ester linkages was reported (29-40). In an attempt to unite the *ester* and *amide* functional groups in a single chemical molecule, different researchers have adopted different techniques. T. H. Barrows et al. (29-31) have reported the synthesis of poly(ester-amides) using *bis*-hydroxyacetamides; Shalaby and Jamiolkowski (32) have obtained poly(ester-amides) from *bis*-oxamidodiols and oxalic acid; Goodman et al. (33-36) have synthesized poly(amide-ester)s containing alternating residues of α -amino acids and α -hydroxy acids; and Y. Tokiwa et al. (37,38) have synthesized copolyamide-esters (CPAE) through amide-ester interchange reaction.

The idea behind designing poly(ester-amide) materials is to combine the absorbability of polyesters with the high performance of polyamides. by introducing hydrolytically unstable ester linkages into the polyamide structure (30). The polymers of interest in the present research are the poly(ester-amides) derived from reacting diamidediols with a

dicarboxylic acid or a bischloroformate (41). These polymers can be represented by the general formula

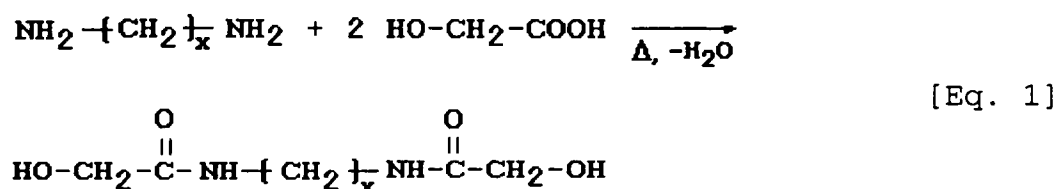


and are generally abbreviated as PEA-x,y*, where x is the number of methylene groups in diamine, and y is the number of diacid methylene groups.

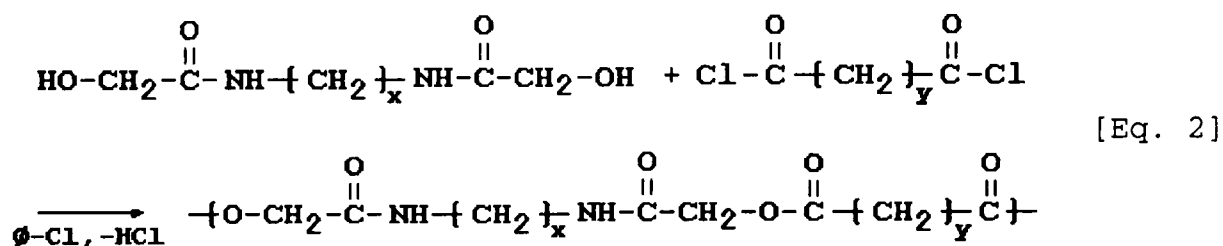
* The notations x and y have been sometimes used interchangeably (as in reference 42).

2.2 POLY(ESTER-AMIDES)

The synthesis of these polymers begins with the condensation of two moles of glycolic acid with one mole of linear, aliphatic diamine to form a diamidediol monomer (equation 1):



This diol with preformed amide linkages is then polyesterified, preferably with a diacid chloride under carefully controlled conditions in chlorobenzene to yield a regular, alternating copolymer (42):



This polymer structure offers considerable latitude of variation. For example, x and y can be varied independently or mixtures of different monomers with different values of x and y can be copolymerized in different ratios. Aromatic or heteroatomic substituents can also be present in the diamine or the diacid. While all these possibilities have been explored to some extent, simple variation of x and y has received the most attention (30).

The effect of diacid methylene chain length on polymer melting temperature is shown in Figure 2.1. The number of diamine methylene groups in this case was held constant at 12 (30). As seen from this figure, poly(ester-amides) with $y > 2$ have relatively low melting points ($T_m < 100^\circ\text{C}$) and produce low strength fibers which lose strength rapidly *in vivo*. Poly(ester-amides) with $y = 2$ and $x = 6, 8, 10$, or 12 are higher melting ($T_m \approx 165^\circ\text{C}$), and yield high strength fiber (30). Particular attention has been paid to polymers PEA-6,2 and PEA-10,2 for potential application as monofilament absorbable sutures.

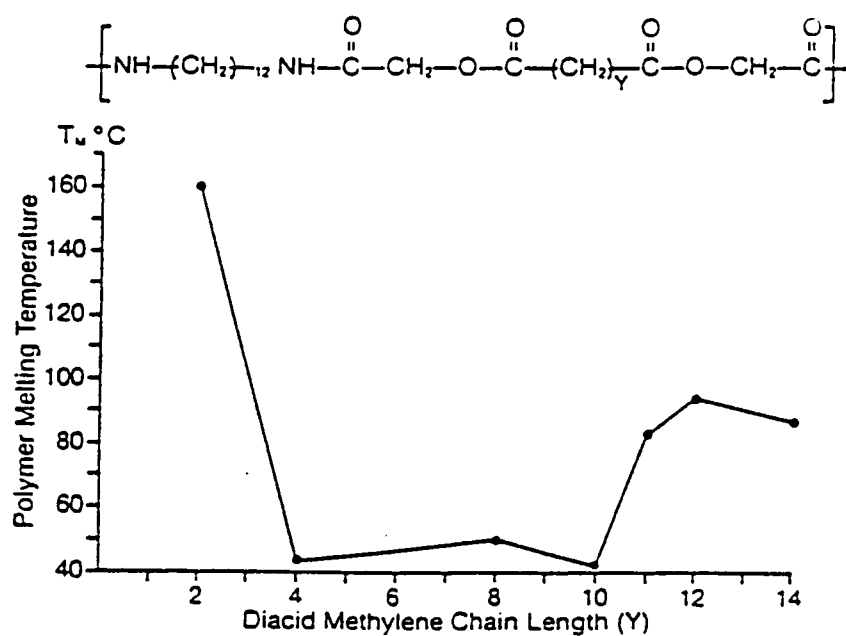


Figure 2.1 The effect of diacid methylene chain length on melting temperature of poly(ester-amide)s.

Source: T. H. Barrows, et al., "The design and synthesis of poly(ester-amide)s", private communication.

2.3 FIBER FORMATION PROCESSES

The manufacture of man-made fibers usually involves the following operations (43):

1. Preparation of fiber forming polymer;
2. Preparation of the spinning fluid;
3. Spinning, i.e., extrusion of the spinning fluid combined with solidification and deformation of the spinning line;
4. Drawing;
5. Heat treatment;
6. Textile processing (twisting, dyeing, oiling, etc.).

The first group involves purely chemical operations like monomer synthesis, polymerization, chemical modification of a natural polymer, etc.. The second group is comprised of typical unit processes of chemical engineering like melting, dissolving, mixing, deaeration, filtration, and such. In the third group, *spinning* refers to the overall process of polymer extrusion and fiber formation. The term 'spinning' has followed from the textile manufacturing operations where staple fibers are formed into continuous textile yarns by several consecutive attenuating and twisting steps. A yarn so formed from natural or synthetic staple fibers is a staple or spun yarn. In the *drawing* process, the spun fiber is elongated to several times its original length by the application of tensile force. The

main purpose of drawing is to increase the degree of molecular orientation and improve the mechanical properties of fibers, particularly the tensile strength. Drawing is performed either directly following the spinning operation, or in a separate operation starting with undrawn material previously collected on bobbins. *Heat treatment* is a process of thermal stabilization, sometimes combined with water or solvent treatment. The increase in molecular mobility accompanying the heat treatment or solvent treatment leads to the relaxation of internal stress, reduces the degree of fiber shrinkage, and brings the material structure closer to thermodynamic equilibrium (43). Group six includes methods applied equally to natural and man-made fibers and is a part of classical textile technology. In the present work, the emphasis is on groups two through five, i.e., on the manufacturing operations in synthetic fiber formation.

Synthetic fibers can be formed from polymers in a variety of ways, depending on the nature of the material. There are basically three types of fiber spinning processes; namely melt spinning, dry spinning, and wet spinning. The distinction between these techniques is primarily based on the process of solidification. Melt spinning involves extrusion of molten polymer into an appropriate medium (gas or liquid) where it solidifies by liberating heat. In dry spinning, a polymer solution is extruded into a heated chamber of gas where the solvent is removed and the fiber is

solidified. Wet spinning represents the extrusion of a polymer solution into a liquid chemical bath. The subsequent coagulation into solid fiber takes place by mass transfer (44). Other less common methods and variants of these basic processes include reaction spinning, dispersion spinning, emulsion spinning, dry-jet wet spinning, semi-melt spinning, fusion-melt spinning, centrifugal spinning, electrostatic spinning, gel spinning, and tack spinning. In each case, however, the fiber forming process (spinning) is similar. A polymer melt or solution is extruded through a small orifice (spinneret) which shapes it into the fiber form. Next, the material undergoes a phase transformation to the solid form after which it is wound up ("taken up") on a bobbin or spool. The processed or spun yarn can then pass through other operations so that it is brought to some final performance level.

2.3.1 Melt Spinning:

Melt spinning is by far the most commonly used process of fiber manufacture. High spinning velocities, the lack of auxiliary materials (solvents, precipitation agents, etc.) and simplicity of the spinning apparatus, make it the most convenient method of fiber manufacture. The primary limitation of the method is that the fiber forming material should be fusible and yield thermally stable, spinnable melts. Typical materials for melt spinning are

polycondensation polymers (polyamides, polyesters), linear polyolefins, and inorganic glasses.

A schematic of this process is shown in Figure 2.2. In melt spinning, the polymer can be fed through the hopper in powdered or chip form, and is most commonly melted with the aid of screw extruders. The molten polymer then flows to a metering gear pump, which delivers the polymer melt at a constant rate into the filter assembly. Filtration removes large solid or gel particles that might otherwise block spinneret holes, or, if passed through, occupy sufficient cross-sectional area in the filament to affect its processing or tensile properties.

After filtration, the molten polymer passes to the spinneret through a short distribution system. Spinnerets for continuous filament yarn production may have up to about 500 holes, most commonly 50 to 200, and those for tow may have several thousand. When spinning oxidation sensitive polymers, it is useful to continuously purge the polymer feed, and occasionally blanket a narrow zone immediately below the spinneret, with inert gas in order to prevent the degradation. Immediately below this region, cool, filtered air is blown across the thread line to encourage uniform cooling. Various arrangements have been described, where the air is directed from one side across the path of the filaments (cross flow quench) (45), inward (inflow quench)

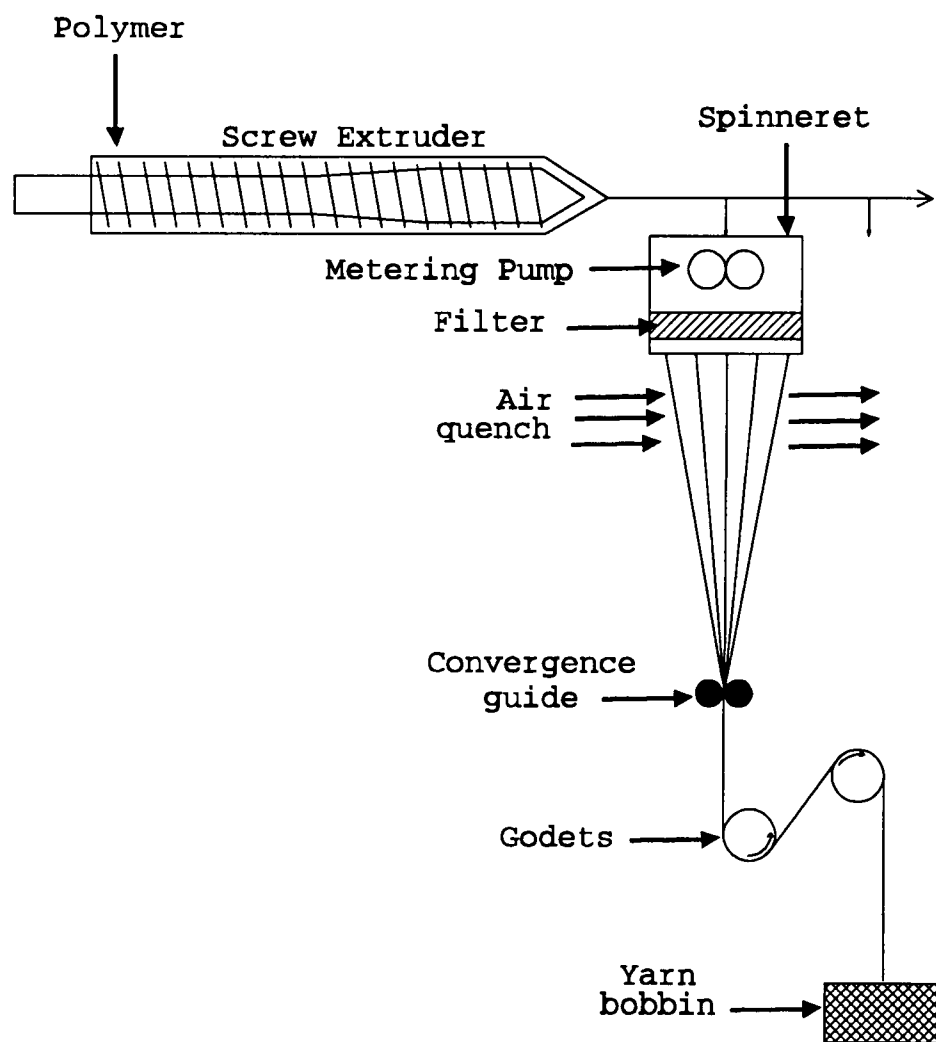


Figure 2.2 Schematic of a melt spinning equipment.

(46), or radially outward (outflow quench) (47). Thereafter the thread line is often protected from stray drafts by enclosing it in a protective chimney until close to the point where the filaments converge to form a yarn or tow. The take-up device mounted at a distance L from the spinneret gives the filament a constant velocity, V_L , related to the average diameter of the spun filament, d_L . Spinning velocities V_L , used in melt spinning range from 30-100 m/min for thick monofilaments in liquid baths, to several thousand meters per minute for obtaining thin filaments cooled in a gaseous medium. In this process, no mass is exchanged between the threadline and the surrounding medium.

The process can be characterized quantitatively in terms of several process variables. Three groups of such variables can be distinguished as shown in Figure 2.3. Primary variables are predetermined technical parameters, acting as boundary or initial conditions for the dynamic equations. These include material characteristics, conditions of extrusion, take-up, etc.. The rheological characteristics of the material govern the elongational flow of polymer along the spinline, and must be an important consideration in the melt spinning process (48-50).

Secondary variables are related to primary ones by the continuity equation , or similar relationships. Resulting

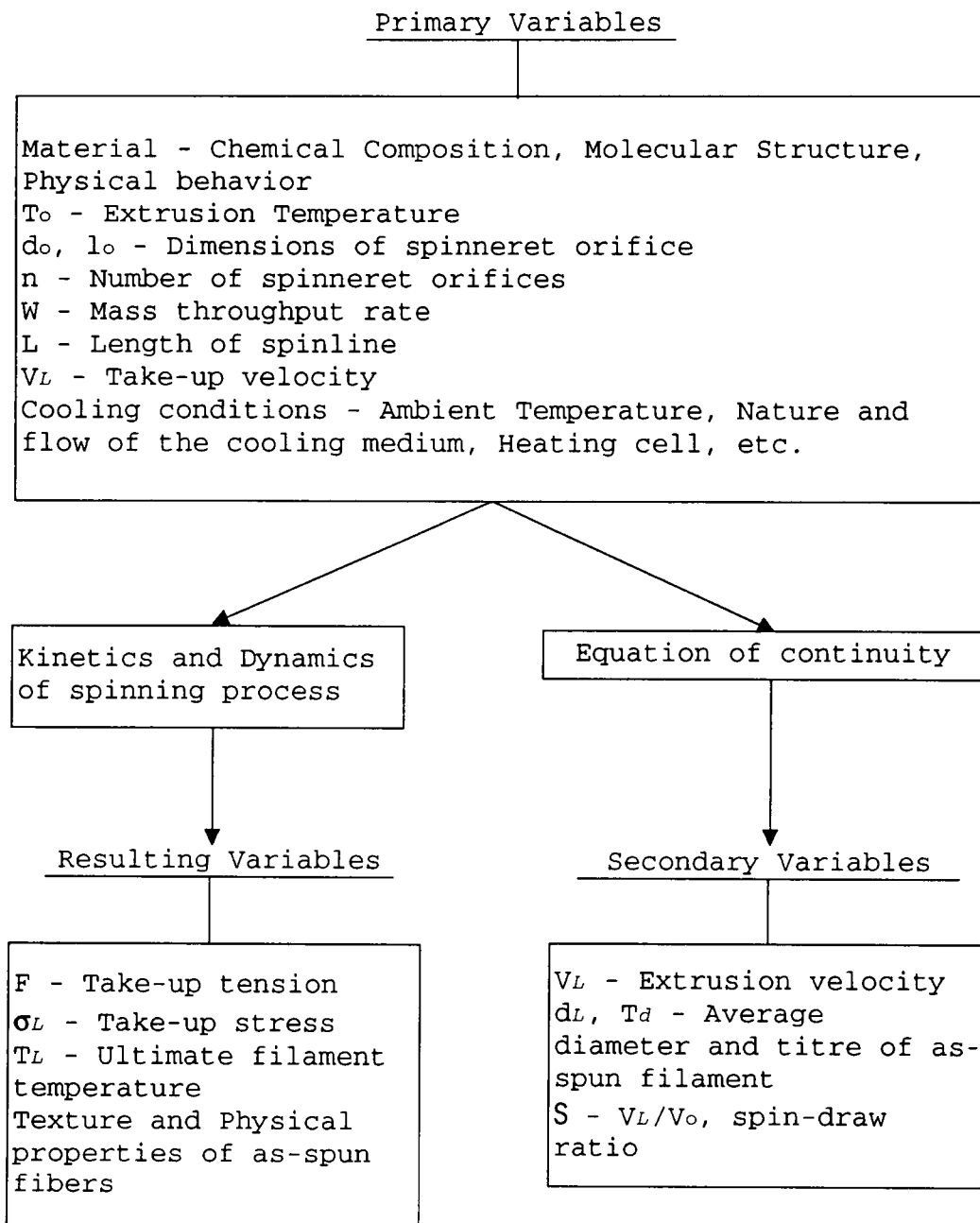


Figure 2.3 Principal process variables in melt spinning.

variables like texture of as-spun filaments are influenced by the primary variables and the kinetics of solidification, phase and structural transformation, etc.. One of the most significant aspects of the melt spinning process is the relationship between the processing variables and the properties of resulting fibers. The properties of fibers are determined by the morphology, orientation, and crystallinity, as well as the molecular structure of the polymer (51-57). Hence, the relationship of processing variables to the structure development is a key aspect to understanding the properties developed during fiber processing.

2.3.2 Drawing:

The as-spun fibers usually exhibit low tenacity, high irreversible (plastic) deformation, and low modulus. In most instances, the filaments obtained directly from melt spinning are not suitable for use in some application, until they have been subjected to one or more successive drawing operations.

Drawing is the hot or cold stretch and attenuation of synthetic filaments to achieve an irreversible extension, induce a molecular orientation with respect to the fiber axis, and develop a fine fibrillar structure. This type of structure is generally characterized by a high degree of crystallinity and by an orientation of both the crystallites

and the polymer chain segments in the non-crystalline domains.

Depending on the material to be drawn, the drawing operation is carried out at room temperature, in a hot air chamber, in contact with a hot surface, or in liquid baths which act as plasticizers and/or solidification agents (for wet-spun fibers). The assumed draw ratio R ,

$$R = V_R/V_F \quad <\text{Eq. 3}>$$

i.e., the ratio of drawing and feed velocities (equation 3) can be achieved in one or more steps with different drawing conditions. Drawing conditions and the structure and properties of resulting fibers strongly depend on the characteristics of the original, undrawn fiber. The drawability of a fiber also depends on its spinning speed; higher spinning speeds result in lower draw ratios. The draw ratio, in turn, affects tenacity and elongation. As draw ratio increases, tenacity increases, whereas elongation decreases. The maximum tenacity is customarily developed by drawing the filaments to the greatest extent consistent with good mechanical quality and freedom from breaks (58, 59). Therefore, in order to optimize any technical drawing process, one should know the relationships between the structure of undrawn material, drawing conditions, and the structure and properties of resulting (drawn) fibers.

2.3.3 Conditioning:

Mechanical treatment and solidification processes accompanying fiber spinning and drawing introduce some elements of instability into fiber structure and properties. Quenching of a polymer melt in melt spinning, destruction of the original crystal structure in cold drawing, etc. lead to thermodynamically unstable systems, which, given enough time, tend towards some equilibrium. The changes include fiber dimensions, crystallinity, micro porosity, relaxation of internal stresses, relaxation of molecular orientation, and the like (43).

Undrawn fibers, if not directly drawn after spinning, are subjected to conditioning for some time at room temperature. This conditioning is especially important for melt spun hydrophilic polymers like polyamides and polyurethanes, which should reach some equilibrium level of humidity and water induced structural changes.

2.3.4 Heat Treatment:

Heat treatment is normally the last operation of fiber formation. It is aimed at stabilization of fiber dimensions, reduction of residual shrinkage, reduction of elongation to break, stabilization of twist, and equilibration of crystalline structure (60). In some cases it is also used for chemical modification (e.g. cross linking) of fibers.

2.4 CHARACTERIZATION METHODS

As the polymers PEA-6,2 and PEA 10,2 are still in their developmental stage, the physical and thermal properties of these polymers are not fully known. Also, some of the basic information needed for characterization of the fibers processed from these materials is not readily available. This section is a brief description of the selection of characterization techniques for characterizing poly(ester-amide) fibers.

2.4.1 Crystallinity determination:

The degree of crystallinity is one of the most useful parameters in the characterization of semi-crystalline polymers. The determination of degree of crystallinity is usually based on the assumption that semi-crystalline polymer is a two phase system of crystalline and amorphous regions, with sharp delineation between the two phases. The most common methods for estimation of crystallinity are:

- By measurement of density, based on the fact that density or specific volume of the semicrystalline polymers varies between the limits of that of a perfectly crystalline and a perfectly non-crystalline sample,
- By infrared spectroscopy, as the IR spectra exhibit 'amorphous' and 'crystalline' absorption bands,

- By the nuclear magnetic resonance method. The NMR detects both relatively immobile or 'crystalline' chains and floppy or 'amorphous' chains,
- Crystallinity is also calculated from the heats of fusion routinely determined by the differential scanning calorimetry, and
- By X-ray diffraction. The X-ray diffraction patterns show both highly ordered and highly disordered regions of reasonable size (61-63).

However, the density, DSC, X-ray diffraction are the most widely used techniques to evaluate the crystallinity in a polymeric material. The determination of crystallinity using DSC needs the heat of fusion of the polymer crystal. As this value is not known, the DSC technique cannot be used to calculate the actual crystallinity in PEA polymers. However, it can be used to obtain the relative amounts of crystallinity in different samples. The PEA polymers also undergo some 'annealing' during heating on the DSC, and further complicate the analysis by this method. On the basis of available instrumentation and the suitability of each method, the X-ray and density methods were chosen for estimation of crystallinity in PEA fibers. There was also some difficulty in applying these methods to PEA fibers. It was observed that the PEA-10,2 specimens took a very long time to reach a stable equilibrium position in the density gradient column. The density of samples measured five hours

after dropping the samples into DGC was found to be very consistent, and was used in the calculations.

2.4.2 Orientation:

The orientation of macromolecules in fabricated polymers plays an important role in determining their performance, ranging from mechanical to optical characteristics. The three principal methods of measuring orientation in polymers are birefringence, dichroism, and X-ray (64-67).

Birefringence is a classical method to assess the state of molecular orientation in polymeric materials. This method has received considerable attention mainly because of the relative ease with which measurements can be made. The polarizing microscope offers the capability of highly accurate birefringence measurements on specimens down to a few micrometers in size (68). In many respects, fibers are ideal specimens for this technique, requiring very little or no preparation. For all these reasons, birefringence is chosen to assess the orientation in these fibers. As a large number of fibers were to be characterized, this technique appeared to be more attractive.

The wide angle X-ray diffraction (WAXD) technique can be used to obtain flat film X-ray patterns of different fiber specimens. These patterns range from something similar

to a powder pattern to a single crystal rotation pattern, depending on the orientation of crystallites in the fiber. The magnitude of the azimuthal spread of these reflections is indicative of the degree of crystallite orientation, and the breadth of the reflection is related to crystal size and imperfections (69). This technique was thus used for a qualitative analysis of the crystallinity and orientation in the PEA fibers and films.

2.4.3 Tensile Properties:

The mechanical characteristics of polymers can be determined by 'static' or 'dynamic' mechanical tests. *Static* tests are fairly simple to perform and reveal basic information like the modulus and strength of the material. The *dynamic* tests, however, are employed in the quantitative characterization of the viscoelastic behavior and for the determination of supramolecular structure of materials (70).

The data that can be obtained from the static tensile testing, i.e., the modulus of elasticity, the yield point, the elongation at break, and the ultimate strength, are at present sufficient for mechanical characterization of these fibers. Three types of tensile testing machines can be normally used for these tests as described in ASTM D 76 (71):

1. Constant rate of extension (CRE);

2. Constant rate of traverse (CRT); and
3. Constant rate of loading (force) (CRL).

In the CRE type machines, the rate of increase of specimen length is uniform with time; in CRT type machines, the pulling clamp moves at a uniform rate, and load is applied through the other clamp which moves appreciably to actuate a weighing mechanism, so that the rate of increase of load or elongation is dependent on the extension characteristics of the specimen; In CRL machines, the rate of increase of load being applied to the specimen is uniform with time after the first 3 s.

A few ASTM standard test methods recommended for testing of fibers in different forms are also listed in this standard. ASTM D 2256 was selected for tensile testing of PEA monofilaments, as it was found to be the most suitable. Any of the three types of tensile testing machines listed above can be used in this test method, and the CRE type tensile testing machine was used. This standard also describes the tensile testing and analysis in the "knot-pull" configuration. The knot-pull test is commonly used for testing of surgical sutures in addition to the straight-pull test, to study the behavior of suture while being tied with a "Surgeon's knot".

The birefringence and X-ray characterization techniques reveal the information on molecular structure of the fiber,

whereas the tensile testing measures the properties resulting from this structure. These three techniques together provide a good initial understanding of the structure-property relationships, and more specialized characterization methods can be used to obtain the information about the structure and properties of further interest.

Chapter 3

EXPERIMENTAL

The experimental techniques used for processing and characterization of PEA polymers are described in this chapter. The experimental techniques are discussed as a part of the experimental procedures, rather than a general description of the technique itself. Each technique is specifically discussed, as adopted to form a part of some particular experimental procedure.

3.1 FIBER PROCESSING

3.1.1 Melt Spinning:

Studies of fiber spinning from PEA polymers began with polymer PEA-10,2 in form of a powder which had been previously dried and sealed in containers. Preliminary results of extrusion from an Instron capillary rheometer showed that the material formed filaments easily. From these experiments, the extrusion temperature was established in the neighborhood of 180 °C.

The melt spinning of this polymer was carried out with the aid of a Fourné screw extruder with a 13 mm diameter screw. As the quantity of polymer was limited to a few pounds, the extruder was taken apart and cleaned thoroughly prior to this experiment. The extruder hopper was flushed

with dry nitrogen before filling the polymer in it, and purging was continued at a slow rate throughout the experiment. Initially it took a few trials to establish the right zone temperatures for extrusion of this polymer. The polymer melt was filtered through a screen pack before exiting through a single hole spinneret with a circular cross-section. The mass throughput rate of polymer was controlled by adjusting the speed of a *Zenith* gear pump between the screw and screen pack. The extrudate was drawn down with a godet immersed in iced-water, and wound up on bobbins with a *Leesona* winder. The godet was driven by a variable speed D.C. motor, connected to a infinitely variable speed controller. Fiber was wound around the godet at least four times to prevent any slippage. It was observed that the filament was tacky when it reached the draw-down device, and exhibited a tendency to stick to the godet. Passing the filament through cold water before it came in contact with the godet eliminated this problem.

Some difficulties were encountered in feeding the polymer powder into the extruder, and this also limited the mass throughput rates to a maximum of 6.5 g/min. The spinning conditions in this experiment are summarized in Table 3.1. Compaction of the polymer powder into granular form improved the feeding to some extent. The granular polymer with a lower initial IV was used in the next experiment, and the spinning conditions used in this

Table 3.1 Summary of experimental processing conditions
for melt spinning of polymer PEA-10,2, 1.2 IV.

Mass throughput rate	3 g/min to 6.5 g/min.
Spinneret	Circular cross section, single hole, diameter=1.5 mm.
Spinline length	3.5 m.
Cooling conditions	Ambient air cooling along the spinline with iced water quench at the take-up.
Zone Temperatures	1. 150 C.
	2. 170 C.
	3. 180 C.
	4. 185 C (extrusion temperature).

experiment for polymers PEA-10,2 and PEA-6,2 are listed in Table 3.2.

The feeding of polymer was further improved with the use of polymer pellets for extrusion. An additional band heater was placed directly below the spinneret to prevent the bottom face of the spinneret from cooling. The temperature of this heater was maintained equal to the fourth zone temperature on the extruder, with an independent temperature control unit attached to this heater.

In order to eliminate the need for water quench at the take-up, an air-cooling chimney was designed and successfully used in the following experiments. Figure 3.1 is an illustration of this device. The cooling is achieved by forced convection using well diffused inward radial flow of ambient air over a length of 1 m in the spinline. Monofilaments were also produced by melt spinning and inline drawing by setting up the draw bench at the bottom of the spinline, which functioned as a draw-down and take-up device. The first set of rollers on this draw bench were used for draw down, and the fiber was collected on a plastic spool after drawing. The spinning conditions used in these experiments are listed in Table 3.3.

In later experiments, extrusion of polymer was attempted using the CSI-MAX model CS 194 AV mixing extruder, referred to as the Maxwell extruder. The Maxwell extruder

Table 3.2 Summary of experimental processing conditions
for melt spinning of polymers PEA-10,2 with 1.0 IV,
PEA-10,2 with 0.73 IV, and PEA-6,2 with 1.0 IV.

Mass throughput rate	5 g/min for all polymers.
Spinneret	Circular cross section, single hole, diameter=2 mm for all polymers.
Spinline length	1. 3.65 m for PEA-10,2 1.0 IV.
	2. 2.45 m for PEA-10,2 0.73 IV and PEA-6,2 1.0 IV.
Cooling conditions	Ambient air cooling along the spinline with iced water quench at the take-up.
Zone Temperatures:	
PEA-10,2 1.0 IV	1. 158 C.
	2. 162.5 C.
	3. 167.5 C.
	4. 175 C (extrusion temperature).
PEA-10,2 0.73 IV	1. 150 C.
	2. 160 C.
	3. 167 C.
	4. 175 C (extrusion temperature).

Table 3.2 continued..

Zone Temperatures:	
PEA-6,2 1.0 IV	1. 150 C.
	2. 155 C.
	3. 167 C.
	4. 175 C (extrusion temperature).

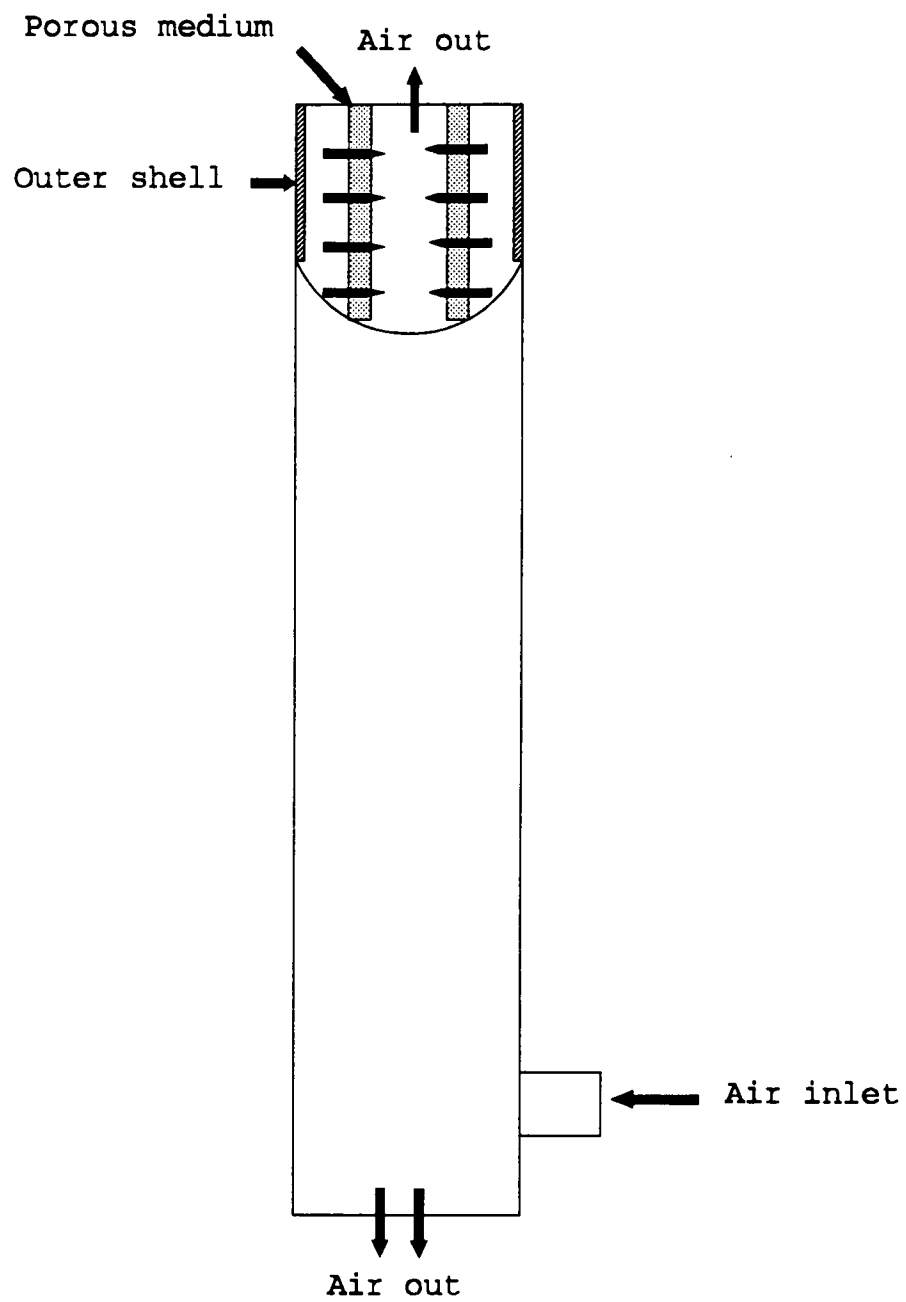


Figure 3.1 Illustration of the cooling chimney.

Table 3.3 Summary of experimental processing conditions
for melt spinning of polymer PEA-10,2 with 1.15 IV.

Mass throughput rate	5- 10 g/min.
Spinneret	Circular cross section, single hole, diameter=2.2 mm.
Spinline length	2 m.
Cooling conditions	1. Ambient air and iced water quench.
	2. Forced convection with radial flow of ambient air.
Zone Temperatures	1. 147 C.
	2. 153 C.
	3. 165 C
	4. 170 C (extrusion temperature).

operates on a very different principle as compared to the conventional screw extruders. The design of this extruder incorporates the advantages of drum type extruders and the elastic melt extruders (72-75). A cross-sectional view of this extruder is shown in Figure 3.2. The feed material is supplied to a cooled hopper from which it falls onto the hot surface of a cylindrical rotor. As the rotor turns, the feed material on its surface is dragged against the inclined surface of a stationary scroll. This produces a component of axial transport towards the outlet die. As the material is collected in the radial gap, it is compressed by the converging space between the scroll surface and the end of the case and by mechanical work input resulting from the rotor turning with respect to the case. When the material is sufficiently melted, it enters the axial gap, where it is rotationally sheared between the end of the rotor and the inside of the case. In addition to causing mixing and homogenization, this rotational shear induces a centripetal pumping effect as in the elastic melt extruder (75,76). This pumping transports the material radially inward and through the outlet die. The working of this extruder is dealt with in greater detail in Reference 77. Slight modifications in the hopper were made to maintain a constant purge of dry nitrogen during extrusion, and a vertical die adapter was made for fiber spinning.

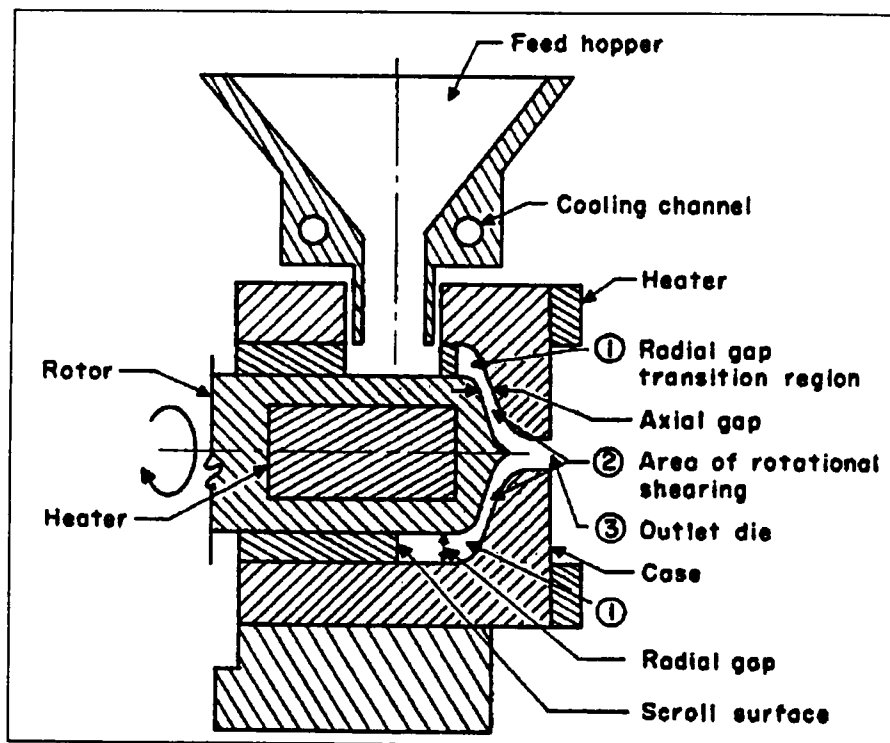


Figure 3.2 Cross-sectional view of the Maxwell extruder.

Source: Bryce Maxwell, *Plast. Eng.*, 40 (1974).

An entirely new melt spinning and drawing set-up was designed and fabricated for use with this extruder. This new set-up offers great flexibility to vary the processing conditions, and perform experiments using very small quantities of polymer. A picture of this set-up is shown in Figure 3.3. Polymers PEA-10,2 and PEA-6,2 were both spun using this set-up, and the extrusion conditions are listed in Table 3.4. During the spinning of polymer PEA-6,2, the filament remained tacky until it reached the draw-down device. Additional cooling of the thread line was achieved by placing a small blower directly below the godet, and by blowing cool ambient air vertically upwards along the spinline. This helped to some extent, and to overcome this problem completely, the filament was passed through a water bath before take-up.

Several fiber samples were collected in as-spun form, and with some in-line drawing under different experimental conditions. The spinning and drawing conditions for these fibers are listed in Table 3.5. This table also serves as a legend for identification of the fibers.

3.1.2 Drawing:

The fibers spun in earlier experiments using the *Fourne* extruder were then drawn on a two stage draw bench illustrated in Figure 3.4. This machine consists of three pairs of rollers, and the temperature and rotational speed

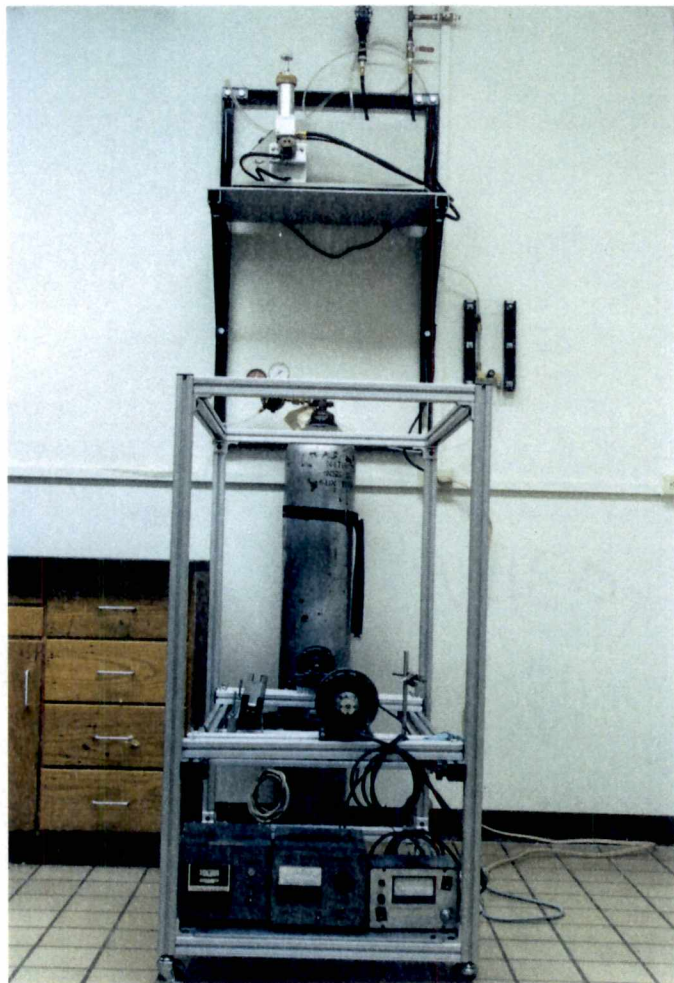


Figure 3.3 Picture of the melt spinning set-up with Maxwell extruder.

Table 3.4 Summary of experimental processing conditions for melt spinning of polymers PEA-10,2 with 1.15 IV, and PEA-6,2 with 1.18 IV using Maxwell extruder.

Mass throughput rate	2 g/min for all polymers.
Spinneret	Circular cross section, single hole, diameter=2.5 mm.
Spinline length	1.3 m.
Cooling conditions	1. Ambient air and iced water quench.
	2. Forced convection with radial flow of ambient air.
Zone Temperatures:	
PEA-10,2 1.15 IV	Rotor- 156 C, Rotor speed =30%,50%.
	Header - 176 C.
PEA-6,2 1.18 IV	Rotor- 155 C, Rotor speed=30%.
	Header - 168 C, 175 C.

Table 3.5 Legend for identification of fibers.

<u>READING THE FIBER ID</u>	
The fiber ID is in the format AB122-3.4H5, where:	
A = F or M. F stands for the fibers processed using the Fourne extruder, and M represents the fibers processed using Maxwell extruder.	
B = W, A, or I. W is used for fibers processed using water-quench at the take-up, A is used for fibers spun with air cooling, and I is used for the fibers spun with air cooling and in-line drawing.	
1 = 1 or 6. 1 is used for PEA-10,2 fibers, and 6 represents PEA-6,2 fibers.	
22 = ID number or serial number.	
3, 3.4 = Numbers representing drawing steps.	
H indicates heat setting.	
5 = A number representing heat setting steps.	

Table 3.5 continued..

Fiber ID	Description
FW101	As-spun with a drawdown ratio of 52.
FW101-1	FW101 drawn to 5X at 25 deg. C.
FW101-2	FW101 drawn to 3X at 50 deg. C.
FW101-3	FW101 drawn to 4X at 50 deg. C.
FW101-4	FW101 drawn to 5X at 50 deg. C.
FW101-5	FW101 drawn to 5X at 70 deg. C.
FW101-6	FW101 drawn to 4.5X at 90 deg. C.
FW102	As-spun with a drawdown ratio of 13.5.
FW102-1	FW102 drawn to 5.5X at 25 deg. C.
FW102-2	FW102 drawn to 5.5X at 50 deg. C.
FW102-3	FW102 drawn to 6X at 70 deg. C.
FW102-4	FW102 drawn to 5.5X at 90 deg. C.
FW103	As-spun with a drawdown ratio of 84.
FW103-1	FW103 drawn to 3.03X at 60 deg. C.
FW103-2	FW103 drawn to 3.45X at 60 deg. C.
FW103-3	FW103 drawn to 3.88X at 60 deg. C.
FA104	As-spun with a drawdown ratio of 19.
FA104-1	FA104 drawn to 3.24X at 60 deg. C.

Table 3.5 continued..

Fiber ID	Description
FA104-2	FA104 drawn to 4.71X at 60 deg. C.
FA104-3	FA104 drawn to 4.87X at 60 deg. C.
FA105	As-spun with a drawdown ratio of 33.5.
FA105-1	FA 105 drawn to 3.03X at 60 deg. C.
FA105-2	FA 105 drawn to 3.11X at 60 deg. C.
FA105-3	FA 105 drawn to 3.45X at 60 deg. C.
FA106	As-spun with a drawdown ratio of 53.
FA106-1	FA 106 drawn to 3.11X at 60 deg. C.
FA106-2	FA 106 drawn to 3.45X at 60 deg. C.
FA106-3	FA 106 drawn to 3.88X at 60 deg. C.
FI107	As-spun fiber with in-line drawing to 3.88X at room temperature, 25 deg. C.
FI108	As-spun fiber with in-line drawing to 4.6X at room temperature, 25 deg. C.
FI109	As-spun fiber with in-line drawing to 3.7X at room temperature, 25 deg. C.
FI109-1	FI109 redrawn to 1.27X at 60 deg. C.
FI109-2	FI109 redrawn to 1.78X at 60 deg. C.

Table 3.5 continued..

Fiber ID	Description
MI110	As-spun with in-line drawing to 3X at 50 deg. C.
MI110-1	MI110 redrawn to 1.76X at 65 deg. C.
MA111	As-spun fiber with a drawdown ratio of 45.
MA111-1	MA111 drawn to 3.19X at 65 deg. C.
MA111-2	MA111 drawn to 3.5X at 65 deg. C.
MA111-4	MA111 drawn to 7.13X at 65 deg. C.
MI112	As-spun with in-line drawing to 3X at 60 deg. C.
MI112-1	MI112 redrawn to 1.32X at 65 deg. C.
MI112-2	MI112 redrawn to 1.42X at 65 deg. C.
MI112-3	MI112 redrawn to 1.8X at 65 deg. C.
MA113	As-spun fiber with a drawdown ratio of 95.
MA113-1	MI113 drawn to 3.19X at 65 deg. C.
MI114	As-spun fiber with in-line drawing to 3.73X at room temperature, 25 deg. C. w/steel snubbing pin.
MI114-1	MI114 redrawn to 1.32X at 65 deg. C.
MI114-2	MI114 redrawn to 1.8X at 65 deg. C.

Table 3.5 continued..

Fiber ID	Description
MI115	As-spun fiber with in-line drawing to 3.8X at room temperature, 25 deg. C. w/steel snubbing pin.
MI115-1	MI115 redrawn to 1.32X at 65 deg. C.
MI115-2.1	MI115 redrawn to 1.22X at 65 deg. C.
MI115-2.1H1	MI115-2.1 heat-set at 100 deg. C.
MI116	As-spun fiber with in-line drawing to 3X at room temperature, 25 deg. C. w/Teflon snubbing pin.
MI116-1	MI116 redrawn to 1.83X at 65 deg. C.
MI116-2	MI116 redrawn to 2.53X at 65 deg. C.
MI116-3	MI116 redrawn to 2.8X at 65 deg. C.
MI116-2.1	MI116 redrawn to 1.22X at 65 deg. C.
MI116-2.1H1	MI116-2.1 heat-set at 100 deg. C.
MI116-2.2	MI116 redrawn to 2.33X at 65 deg. C.
MI116-2.2H1	MI116-2.2 heat-set at 100 deg. C.
MI116-2.2H2	MI116-2.2 heat-set at 105 deg. C.
MI116-2.3	MI116 redrawn to 2.58X at 65 deg. C.
MI116-2.3H1	MI116-2.3 heat-set at 100 deg. C.
MI116-2.3H2	MI116-2.3 heat-set at 105 deg. C.
MA117	As-spun fiber with a drawdown ratio of 138.

Table 3.5 continued..

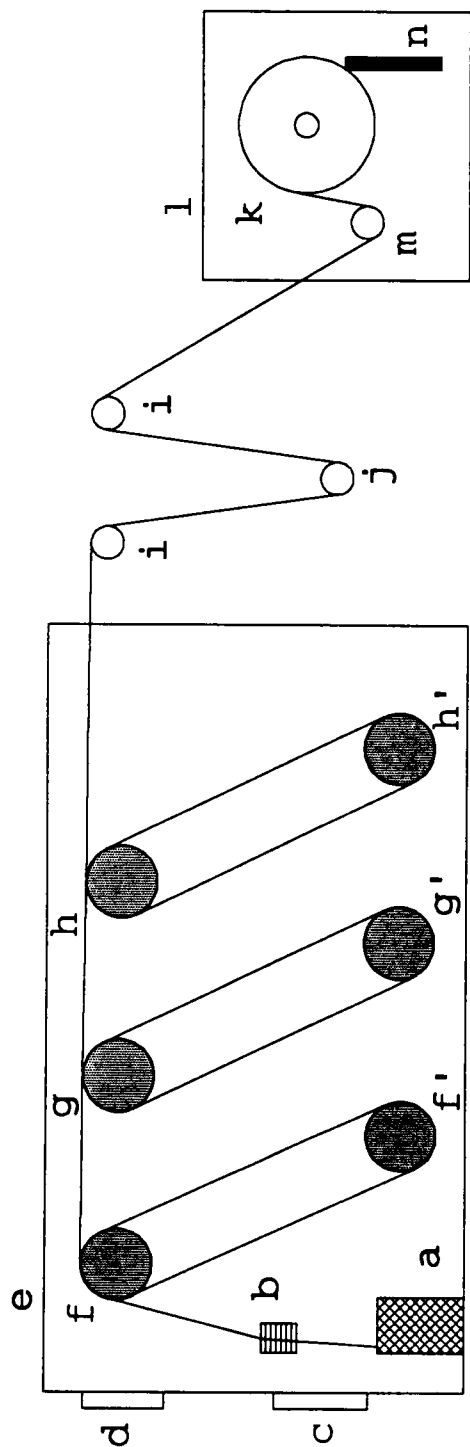
Fiber ID	Description
MA117-1	MA117 drawn to 3.19 X at 65 deg. C.
MI118	As-spun with in-line drawing to 2.2X at 65 deg. C without any snubbing pin.
MI118-1	MI118 redrawn to 1.32X at 65 deg. C.
MI118-2	MI118 redrawn to 1.8X at 65 deg. C.
MI118-3	MI118 redrawn to 2.53X at 65 deg. C.
MI118-4	MI118 redrawn to 2.8X at 65 deg. C.
MI118-5	MI118 redrawn to 3.2X at 65 deg. C.
MI118-6	MI118 redrawn to 3.82X at 65 deg. C.
MI118-6H1	MI118-6 heat-set at 100 deg. C.
MI118-7	MI118 redrawn to 5.15X at 65 deg. C.
MA119	As-spun fiber with a drawdown ratio of 22.
MA119-1	MA119 drawn to 3.19 X at 65 deg. C.
MA119-2	MA119 drawn to 4.44 X at 65 deg. C.
MA119-3	MA119 drawn to 5.15 X at 65 deg. C.
MA119R	MA119 drawn to 3X at room temperature, 25 deg. C.
MA119R1	MA119R redrawn to 1.22X at 65 deg. C.
MA119R2	MA119R redrawn to 1.65X at 65 deg. C.

Table 3.5 continued..

Fiber ID	Description
MA119W1	MA119 drawn to 3.19 X at room temperature, after immersing in water at 25 deg. C.. for two hours.
MA119W2	MA119 drawn to 4.44 X at room temperature, after immersing in water at 25 deg. C.. for two hours.
MA119S1	MA119 drawn to 4.44 X at room temperature, under a jet of steam focused on the feeding pulley.
MI120	As-spun fiber with in-line drawing to 3X at room temperature, 25 deg. C.
MI120-1	MI120 redrawn to 1.32X at 65 deg. C.
MI120-2	MI120 redrawn to 1.8X at 65 deg. C.
MI120-3	MI120 redrawn to 2.53X at 65 deg. C.
MI120-4	MI120 redrawn to 2.8X at 65 deg. C.
MI120-4H1	MI120-4 heat-set at 100 deg. C.
MI120-5	MI120 redrawn to 3.2X at 65 deg. C.
MA621	As-spun with a drawdown ratio of 10.9.
MW622-1	MW622 drawn during tensile testing to 5X.
MW622	As-spun with a drawdown ratio of 24.4.

Table 3.5 continued..

Fiber ID	Description
MA623	As-spun with a drawdown ratio of 23.3.
MA623-1	MA623 drawn to 2.4X at 60 deg. C.
MA623-2	MA623 drawn to 3X at 60 deg. C.
MA623-3	MA623 drawn to 3X at 80 deg. C.
MA623-4	MA623 drawn to 2.5X at 25 deg. C.
MW624	As-spun with a drawdown ratio of 23.3.
MW624-1	MA624 drawn to 2.5X at 60 deg. C.
MW624-2	MA624 drawn to 3X at 60 deg. C.
MW624-3	MA624 drawn to 3X at 80 deg. C.
MW624-4	MA624 drawn to 2.5X at 25 deg. C.
Fiber ID	Processing Conditions.
FW101 and FW102	Table 3.1.
FW103 to FW109	Table 3.3.
MI110 to MW624	Table 3.4



a-Fiber sample; b-Yarn guide and tensioner; c-Draw speed control; d-Draw temperature control; e-Drawing section; f-Feed roller or first roller (upper); f'-First roller (lower); g- Second roller (u); g'-Second roller (l); h-Third roller (u); h'-Third roller (l); i-Guide roll; j-Take-up arm; k-Drawn fiber on spool; l-Constant tension winder; m-Winding head; n- Brake lever.

Figure 3.4 Schematic of the two stage drawing machine.

of each pair can be controlled independently. The fiber is passed through the tensioner, which removes the slack in the feeding fiber, and maintains a small tension in fiber feeding onto the first set of rollers. It is then drawn between two sets of rollers, rotating at different velocities V_1 and V_2 , such that $V_1 < V_2$. These speeds can be adjusted to obtain the desired draw ratio V_1/V_2 . Similarly, the fiber can then be drawn between the next set of rollers for second stage drawing, or simply passed on to the take-up system, where the drawn fiber is collected on a plastic spool. The draw temperature can be set by adjusting the temperature of each set of rollers, variable in steps of 1 °F. In these experiments of single stage drawing, the first set of rollers was heated to the desired draw temperature, and the filament was wrapped around these rollers at least four times to ensure proper heating. Drawing of fibers was performed at different draw ratios and different draw temperatures to establish the right drawing conditions. After the right draw temperature was determined, fibers were drawn in the neighborhood of this temperature with small increments in draw ratio up to the maximum draw ratio.

With the information obtained from these initial drawing experiments, fibers spun using the *Maxwell* extruder were drawn using the smaller drawing system shown previously in Figure 3.3. As very short lengths of fibers were spun under each condition, it was necessary to draw the fibers at

very low speeds to have a control on the length of fiber being consumed in each drawing experiment. The feeding velocity of fiber on this apparatus was typically 2.4 m/min. This apparatus provided ease in varying the drawing conditions, however, it's control on draw ratio was not as good as on the bigger machine used in previous experiments.

Fibers were processed using predetermined *single stage*, *two stage*, and *three stage* drawing procedures. The desired draw ratio was achieved by adjusting the speed of feeding and drawing pulleys, driven by variable speed D.C. motors. The fiber was passed over a heater of 50 cm length to perform the drawing at elevated temperatures.

In single stage drawing, the as-spun fiber was drawn in one step at a fixed draw temperature of 65 °C. The fibers were drawn at increasing draw-ratios - up to the maximum attainable draw-ratio - after the formation of a stable 'neck' during drawing (draw-ratios exceeding 3X). A sample of as-spun fiber, MA119, was also drawn after keeping it immersed in water for two hours, to study the effect of moisture plasticization on its drawability. In order to study the combined effect of moisture plasticization and temperature, this fiber was also drawn with a jet of steam focused on the feeding pulley during drawing.

In the two stage drawing technique, the filaments were drawn in two steps, using different drawing conditions in

each step. The first stage drawing was performed either in-line or after winding the spun filaments, at various draw ratios and draw temperatures . Snubbing pins of Teflon and steel were used during in-line drawing to examine if their use would alter the fiber properties. This was followed by a second stage draw at 65 °C, with small increments in draw-ratio, reaching up to the maximum draw.

In three stage drawing, the third step was essentially heat setting of the drawn filaments, which was performed at 100 °C and 105 °C. A draw-ratio of 1.02X was maintained in this step, to keep the filament under tension.

3.2 CHARACTERIZATION

3.2.1 Tensile Testing:

After the initial few tests, the test method described in ASTM D2256 (78) was followed for the tensile testing of PEA fibers. The fibers were tested using a CRE type tensile testing machine. As suggested in this standard, the right cross head speed was determined to break the drawn fibers in 20 ± 3 seconds. This cross head speed was found to be in the vicinity of 100 mm/min for most of the fibers, and this speed was thus maintained constant. The same cross head speed was also maintained for testing as-spun fibers, which took longer time to break at this speed. Clamping pressure

at the grips was adjusted for each fiber sample to prevent any slippage or failure in the grips.

Tensile testing was performed on a table model *Instron*, with a 2000 gm load cell. In the beginning, at least fifteen good specimens of each fiber sample were tested, but later on this number was decreased to four as the results were consistent ($\pm 5\%$) and the data obtained was mainly to be used for comparison of properties of different fibers. The property values obtained from these tests were then averaged to get the final values, and the results. Because of the variations in fiber diameter, a digital micrometer was used to measure the diameter of each fiber specimen at three to four places along its length. Fibers with excessive diameter variations (exceeding $\pm 5\%$ of mean value) were discarded.

In later experiments, fiber specimens were also conditioned in a controlled atmosphere maintained at 59% relative humidity and 19°C. The fibers were allowed to equilibrate under these conditions for 36 hours before testing. Conditioning of fiber specimens before tensile testing provides a better comparison of the data obtained from different tests. These fibers were then tested on a *United* tensile testing machine with a 10 lb load cell, located in the conditioning room. In this case, the diameter was measured on a continuous length of fiber at several places, and then cut into smaller sections for testing. In

general, at least seven specimens of each fiber sample were tested. The overall tensile testing conditions are summarized in Table 3.6. The tensile strength, elongation at break, and Young's modulus were measured following the procedures described in ASTM D2256. The reported values are accurate within $\pm 5\%$.

3.2.2 Birefringence:

For the birefringence measurements, the fibers were first mounted on precleaned microscope slides, fixing at both ends with adhesive tape. These fibers were then observed under a magnification of 10X to 40X in a Carl-Zeiss polarizing microscope. The retardation was measured using a 30 order Berek compensator, and the standard method prescribed in its manual was used to measure the retardation and calculate birefringence. The value of fiber diameter used in birefringence calculations was measured at the same time when measuring retardation.

3.2.3 Wide Angle X-ray Scattering:

Wide angle X-ray patterns of as-spun and spun and drawn fibers were obtained using Phillips Norelco X-ray generator with nickel filtered $\text{CuK}\alpha$ radiation of wavelength $1.542\text{\AA}$. The X-ray unit was operated at 35 KV and 15 mA. Fibers were mounted as a parallel bundle on a sample holder and then exposed to the X-ray beam with fiber axis normal to the

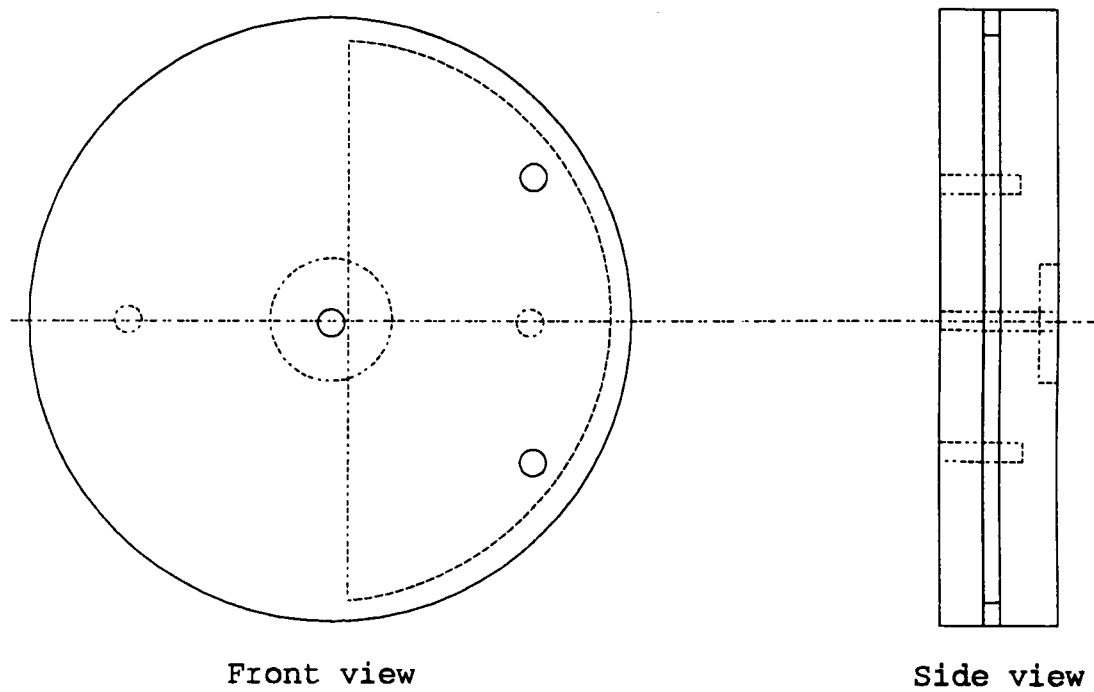
Table 3.6 Summary of experimental conditions for tensile testing.

Condition	Instron	United
Load cell	2000 gm.	10 lb.
Calibration load	500 gm, 1000 gm.	Precalibrated.
Gage length	50 mm.	50 mm.
Cross head speed	100 mm/min.	100 mm/min.
Conditioning	None.	At 59% R.H. and 19 C for 36 h.

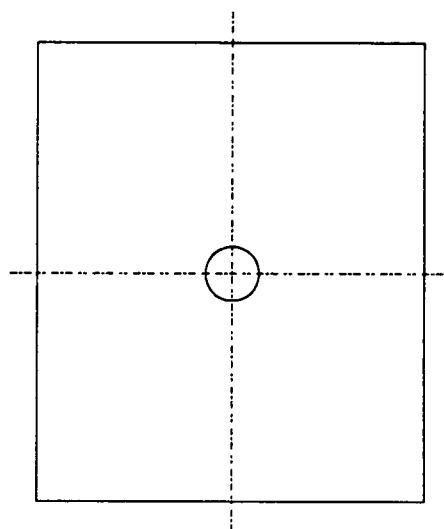
beam. Two different types of sample holders were used in these experiments as shown in Figure 3.5. Sample holder a was used in most of the experiments when sufficient fiber was available in continuous length. In a couple of cases, when sufficient length of fiber was not available, sample holder b was used. The distance between fiber specimen and X-ray film was maintained constant at 3.3 cm. Exposure times ranged typically between 60 to 180 minutes, depending on the thickness of fiber specimen. The films were then developed in KODAK industrex developer for six minutes, fixed in KODAK rapidfix for ten minutes, and washed and dried.

3.2.4 Density:

The density of as-spun fiber was determined using a density gradient column prepared according to ASTM standard D1505-68 (79). The solutions used to establish a density gradient were prepared by mixing carbon tetrachloride and toluene in proper proportion. The fiber specimens were first immersed in this solution and centrifuged in a clinical centrifuge for two minutes to remove any entrapped air. These specimens were then dropped into the density gradient column, and their position was measured after five hours. The density of the fiber sample was calculated from this position using the calibration curve for the column. Percent crystallinity in fiber samples was estimated using the relation



(a) 'D' type sample holder



(b) Plate type sample holder.

Figure 3.5 Fiber sample holders for X-ray.

$$X = \rho_c(\rho - \rho_a) / \rho(\rho_c - \rho_a)$$

where ρ is the density of fiber sample;

ρ_a is the density of amorphous phase;

and ρ_c is the density of crystalline phase.

Values of crystalline and amorphous densities were determined as described in the next section.

3.3 DETERMINATION OF AMORPHOUS AND CRYSTALLINE DENSITIES

The values of amorphous and crystalline densities for PEA-x,y polymers have not been previously published in the literature. In order to estimate the percent crystallinity in these fibers, the values of density of amorphous and crystalline phases are needed and an effort was made to determine these values for PEA 10,2 polymer. These experimental procedures are described below:

3.3.1 Specimen Preparation:

To determine the density of the amorphous phase, thin films with random orientation were prepared by melt pressing. Polymer pellets were placed between two thin sheets of Kapton® film and placed in a Wabash 12-ton melt press. The press platens were immediately closed without any pressure on the polymer pellets. Pellets were allowed to melt at 180 °C for three minutes and then pressed for two minutes. The resulting film was immediately quenched in brine maintained at -17 °C. Brine was prepared by mixing

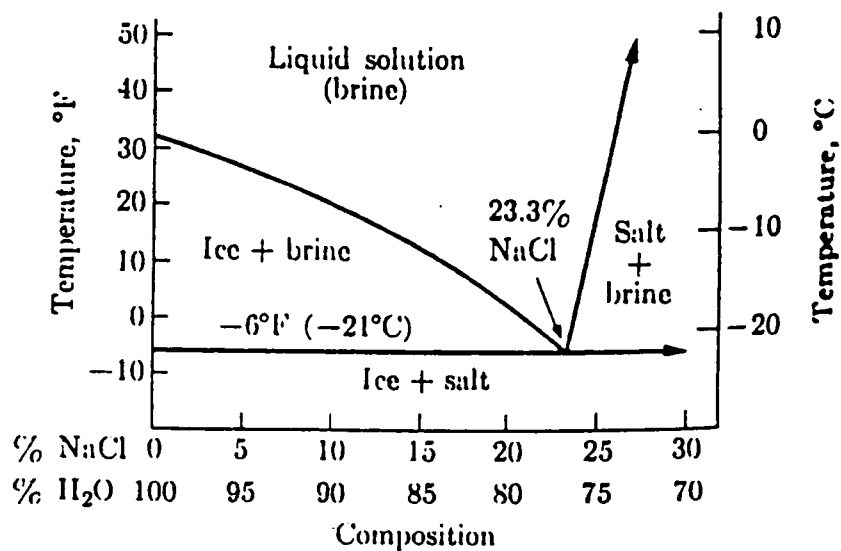
21.3% by weight of NaCl with water and then cooled to -17 °C with liquid nitrogen. The NaCl-H₂O phase diagram and arrangement of quench bath are shown in Figure 3.6. Six films were prepared using this method.

Films were also prepared by cooling the polymer melt slowly in the melt press. The polymer melt was cooled at ~5 °C/min to 125 °C, held at this temperature for 60 min, and then again cooled at ~5 °C/min to room temperature.

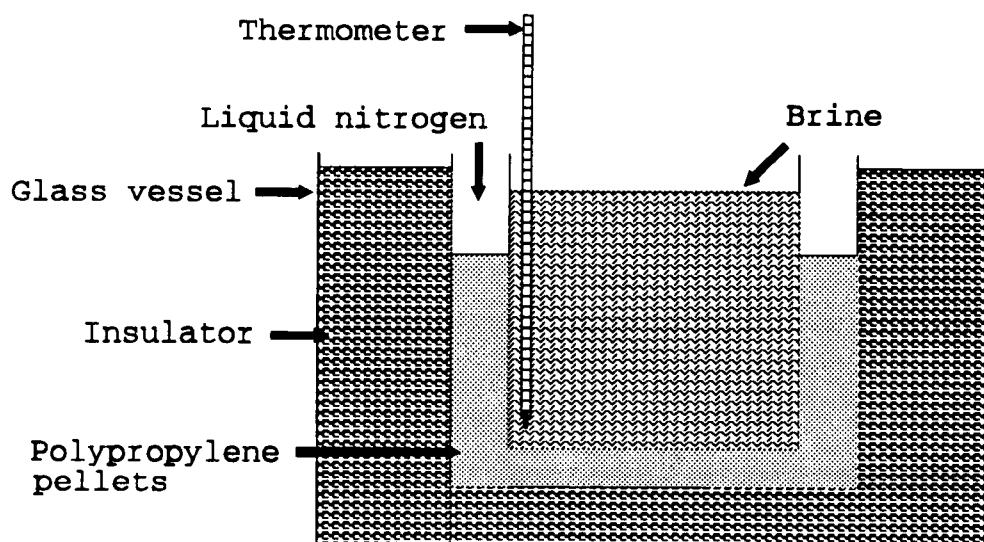
3.3.2 Amorphous Density:

Wide Angle X-ray Diffraction:

Wide angle X-ray diffraction scans on these films were obtained using a *Rigaku-Geigerflex* X-ray diffractometer in reflection mode with nickel filtered CuK α radiation. The 2 θ scans were taken from 5° to 35° interval. These diffraction patterns were then digitized by scanning the curve with a *APPLE* scanner connected to a *Macintosh* computer and then using *Datatheif* data extraction software. This method yields highly accurate data in very small increments, depending on the resolution of the input (475-500 data points were obtained in this case). Background intensity correction was made by subtracting the region below a straight line joining the points with minimum intensity on the two ends of curve; and parallel to X-axis. Data treatment and analysis was done using simple computer programs written in *Quick Basic*.



(a) NaCl-H₂O Phase Diagram



(b) Illustration of liquid bath for quenching films.

Figure 3.6 Quenching of PEA-10,2 films.

Wide angle flat film patterns were also prepared as described in section 3.2.3, to get a qualitative idea of the crystallinity in these films.

Density measurement:

Density of the above mentioned films was measured in a calibrated density gradient column with an accuracy of $\pm 0.0002 \text{ g/cm}^3$.

3.3.3 Crystalline Density:

Although polymers are never 100% crystalline, the value of crystalline density is normally calculated theoretically from the basic building block of a crystalline material; the unit cell of crystal structure. Determination of unit cell needs fiber patterns from highly oriented fibers with high crystallinity, and some expertise in X-ray crystallography.

The fiber patterns were obtained for as-spun fibers, spun and drawn fibers, and fibers with heat treatment after spinning and drawing. A *Phillips Norelco* X-ray generator with a *Statton* camera and nickel filtered $\text{CuK}\alpha$ radiation at 40 KV and 20 mA was used. It was first carefully aligned and calibrated using *Spectra*[®] polyethylene fibers. Wide angle fiber patterns were obtained with a specimen to film distance of 5 cm, and small angle fiber patterns were obtained with a specimen to film distance of 17 cm. Exposure time for wide angle patterns was typically 6 hours, and 28

hours for the small angle patterns. Air was sucked out of the camera with a vacuum pump to minimize the scattering by air.

Position of the reflections on fiber pattern was read using a film reader manufactured by *Ernest F. Fullam Co.*, which can read the distances on the film with an accuracy of 0.002 mm. The d spacings for each reflection were calculated by measuring the x and y coordinates for a given reflection with the center of pattern as origin. Interplanar spacing d was calculated using the relation

$$1/d^2 = |r^*|^2 = (\xi^2 + \zeta^2)/\lambda^2$$

where ξ and ζ are dimensionless quantities corresponding to cylindrical coordinates of a point hkl in reciprocal space, as shown in Figure 3.7 (80). ξ and ζ are calculated from the coordinates x and y , and the specimen to film distance D , using the following equations:

$$\zeta = y/(D^2 + x^2 + y^2)^{1/2}$$

$$\text{and} \quad \xi = [2 - \zeta^2 - 2(1 - \zeta^2)^{1/2}(D/(D^2 + x^2 + y^2)^{1/2})]^{1/2}$$

The values reported are accurate within ± 0.001 nm.

3.4 THERMAL DEGRADATION

The time and temperature dependence of the degradation of PEA-10,2 polymer was studied by maintaining the polymer

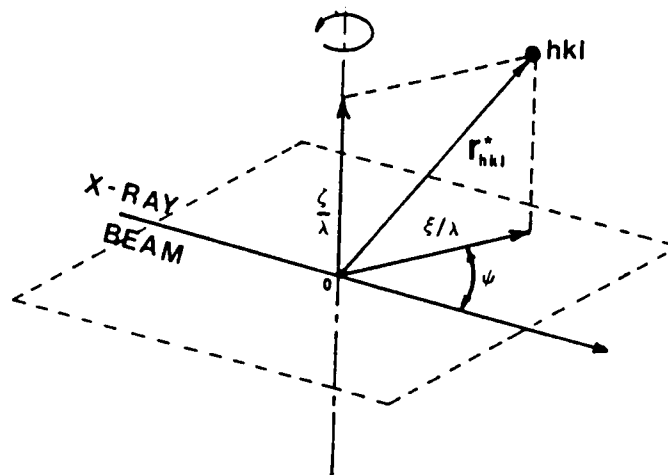


Figure 3.7 Cylindrical coordinates of the point hkl in reciprocal space.

Source: J. E. Spruiell, and E. S. Clark, in "Methods of Experimental Physics, Vol. 16B", Academic Press, 1980.

at an elevated temperature in an Instron capillary rheometer. Dry polymer was filled in the barrel of the rheometer maintained at a predetermined temperature, and a stopwatch was started at this instant. Slight pressure was then applied on the piston to extrude the polymer as soon as it melted. A sample of this extrudate was collected, and this time was recorded. More samples were collected by extruding the polymer melt at regular time intervals at each temperature. These samples were then sent to *LSS materials reserach laboratory* at 3M for GPC and IV measurements.

3.5 GLASS TRANSITION AND MOISTURE PLASTICIZATION

Glass transition temperatures of polymers PEA-10,2 and PEA-6,2 were measured, combined with the study of moisture plasticization of polymer PEA-6,2 using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). These experimental techniques are described in this section.

3.5.1 Specimen Preparation:

The Tg of fiber samples was measured in 'as-is' condition. For the study of moisture plasticization, the fiber specimens were first dried in a vacuum oven at 65 °C and 28 in of Hg for eight hours. One of these specimens was tested in dry state, one was tested after exposing it to atmospheric air for five hours, and one was tested after

dipping it in water at 38.5 °C for two hours. For DSC, the fiber samples were chopped into small pieces and filled in hermetic aluminum pans for DSC and dried. The sample to be tested dry was immediately sealed after taking it out of the vacuum oven, and another pan was left open in atmospheric condition for five hours before sealing it. Sample to be tested after wetting in water was dried in a glass veil and then immersed in water under controlled conditions before sealing it in the DSC pan. For DMA, fibers were cut into small lengths of about 35 mm and carefully aligned with the two ends pasted on a adhesive tape. For measuring the T_g of this fiber, it was tested in 'as-is' condition. Other specimens were placed in glass veils and dried. Specimen to be tested dry was immediately sealed, and the other two were tested after exposing to air and wetting in water.

3.5.2 Differential Scanning Calorimetry:

A Perkin-Elmer series 7 thermal analysis differential calorimeter connected to a Perkin-Elmer 7500 professional computer and TAS7 instrument controller was used to study the glass transition of PEA fibers. The instrument was first calibrated using a indium standard, and the baseline was optimized from -100 °C to 150 °C, as described in the user's manual. The fiber samples sealed in hermetic DSC pans were heated at a constant heating rate of 10 °C/min from -75 °C

to 100 °C. These scans were plotted on the HP 7470A plotter connected to the DSC7.

3.5.3 Dynamic Mechanical Analysis:

Dynamic mechanical analysis was done using a rheovibron model DDV-II-C manufactured by Toyo Baldwin Co. and connected to a Hewlett Packard computer. The alignment of specimen holder on this machine was first corrected, and the fiber specimen was mounted. The AVD 985A data acquisition program was then loaded and the heating rate was set at 1 °C/min. The temperature range for this test was set from -100 °C to 100 °C. The sample chamber was cooled to starting temperature using liquid nitrogen, and then covered with an insulator to avoid rapid heat gain. The experiment was performed under a constant flow of dry and cool nitrogen gas through the sample chamber. Data on storage modulus E' , loss modulus E'' , and loss tangent $\tan\delta$ was obtained as a function of temperature at the frequencies of 1.1 Hz, 11 Hz, and 110 Hz.

3.6 GEL SPINNING

Preliminary studies of the suitability of gel spinning technique for processing of PEA fibers was performed using Instron capillary rheometer for extrusion. PEA polymers with varying concentrations of n-methylpyrrolidone (NMP) were supplied by the 3M company for these studies. The polymer

was first divided into small batches of 30 ml in the dry box. Effect of solvent concentration on the melting behavior of polymer was studied using DSC7 in a similar way as described in section 3.5.2 in a temperature range of 30 °C to 190 °C and a heating rate of 10 °C/min. Extrusion of this polymer was performed using the capillary rheometer by adjusting the extrusion temperature in the neighborhood of peak melting temperature observed on the DSC. Some fiber was wound on the bobbin at a distance of about 1 m from die, using a variable speed D.C. motor.

Chapter 4

RESULTS AND DISCUSSION

4.1 DETERMINATION OF AMORPHOUS AND CRYSTALLINE DENSITIES

It was mentioned in the previous chapter that no technique has yet been developed to estimate the level of crystallinity in PEA polymers. An attempt was made to establish the amorphous and crystalline densities for polymer PEA-10,2 and estimate the crystallinity by measuring the density of fiber samples. The wide angle X-ray diffraction technique was also used to estimate crystalline fraction in a film with random orientation. Results obtained from both of these techniques are discussed in this section.

The density of PEA polymers was initially predicted to be $\sim 1.20 \text{ gm/cm}^3$, by comparing it with other polyesters (6). This was found to be surprisingly close when the density of quenched PEA-10,2 films was measured to be $1.2057 \pm 0.0004 \text{ gm/cm}^3$ using the density gradient column. The density gradient column (DGC) was first prepared with aqueous NaBr solution, and it was observed that the film and fiber samples continued to move downwards in the DGC (increasing density) for about 6-7 days, before reaching an equilibrium position. The increase in density with time was probably due to additional crystallization, and perfection in crystal structure because of the depression of T_g in the aqueous

medium. A slight increase in crystallinity was later confirmed from 2θ scans using a X-ray diffractometer. For this reason, another DGC was prepared using the toluene-carbon tetrachloride system as suggested in the ASTM D1505 (79) (for densities in the range of 0.87 gm/cm³ to 1.59 gm/cm³). The increase in density was still observed, but to somewhat lower extent. In order to avoid any variations in density measurements, the density of polymer samples was always measured five hours after dropping the sample into the DGC.

The density of quenched PEA-10,2 films was measured to be in the range of 1.2053 gm/cm³ to 1.2060 gm/cm³. The structure of these films was also examined by WAXD, by preparing flat film X-ray patterns and taking 2θ scans on the Rigaku diffractometer, as shown in Figures 4.1 and 4.2, respectively. These patterns consist of a single broad halo, indicative of an amorphous structure, with little or no indication of any crystallinity. One of these film samples was then annealed in a vacuum oven at 80 °C for eight hours, and also in boiling water for six hours. The WAXD patterns for these annealed films are shown in Figure 4.3 together with the pattern obtained for the same film before annealing. As can be seen from this figure, the crystallinity did not develop very well in the sample annealed at 80 °C, further confirming the amorphous

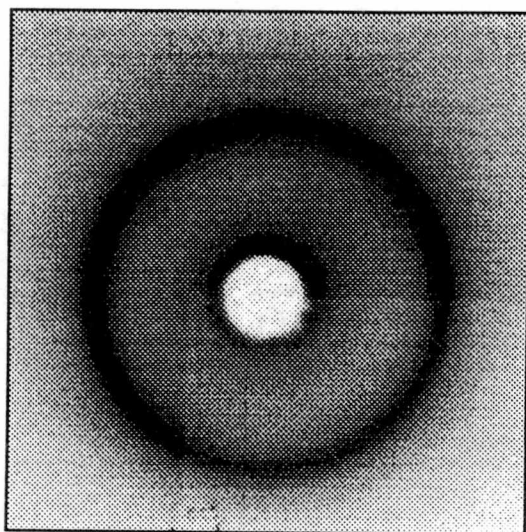


Figure 4.1 WAXS pattern of the quenched film.

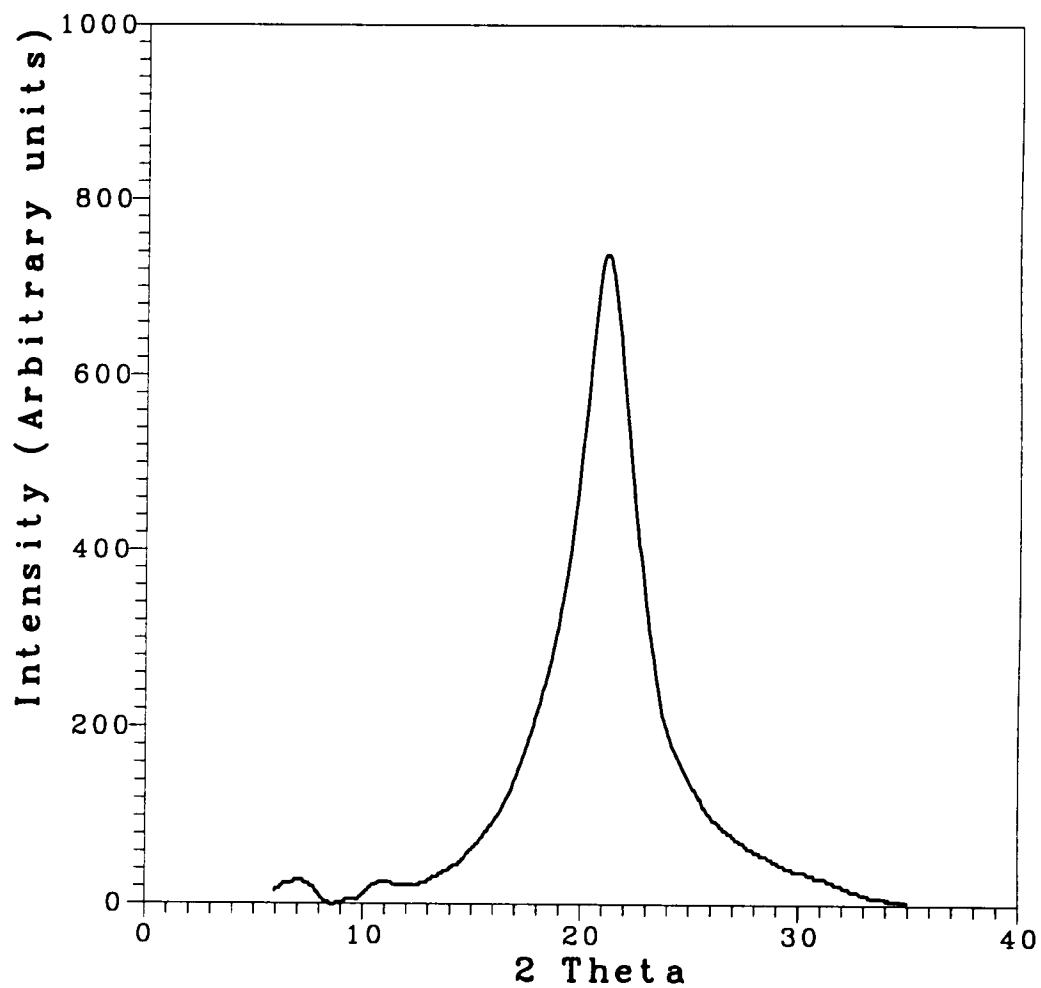


Figure 4.2 2 Theta scan for the quenched film.

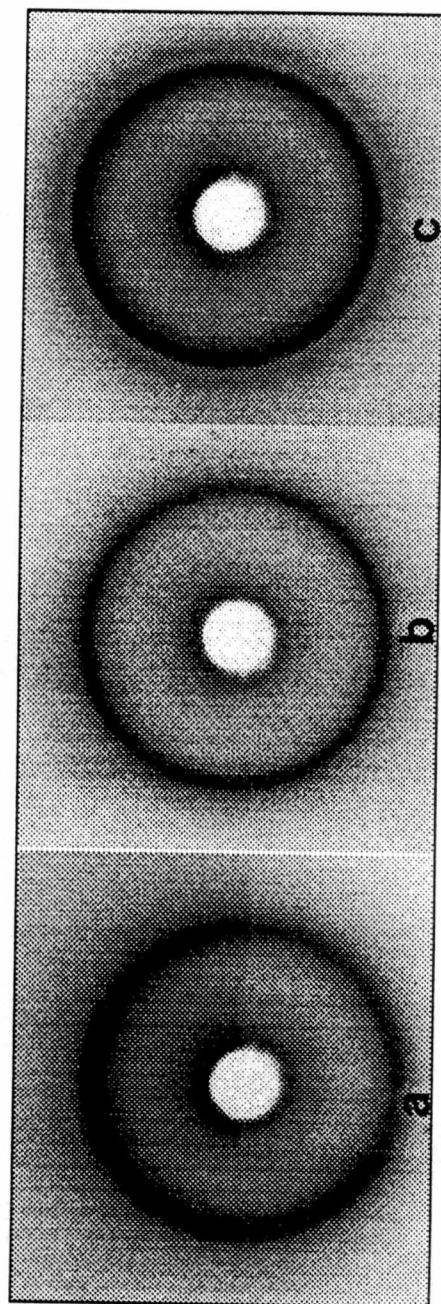


Figure 4.3 WAXS patterns showing the effect of annealing on the quenched PEA-10,2 film. (a) Quenched film, as is, (b) After annealing at 80 °C in vacuum for 8 h, and (c) After annealing in boiling water for 6 h.

structure of the original film. The amorphous density was thus confirmed to be $1.2057 \pm 0.0004 \text{ gm/cm}^3$.

The theoretical value of crystalline density of PEA-10,2 was calculated from fiber patterns of this polymer, taken with the specimen to film distance of 5 cm and 17 cm. These patterns are shown in Figures 4.4 and 4.5, respectively. As can be seen in these figures, the layer lines along the meridian are seen clearly in the fiber patterns W1 and S1. These reflections, however, seem to split in two symmetrical reflections along the meridian at higher draw ratios as seen in fiber patterns W2, S2, W3, and S3. Blackwell (81) has studied this type of fiber patterns in greater detail. He has proposed that this type of fiber pattern would be obtained if the *c* axis of unit cell is tilted with respect to the draw direction, forming an angle ϕ with the draw direction. Such tilting has also been reported in the case of poly(ethylene terephthalate) (82). These reflections are still assumed to represent the respective layer lines (81). An analogous approach can be taken in this case, and the repeat distance can be calculated.

The interpretation of these patterns was done starting with an assumption that the unit cell was trigonal, which would allow a good packing of the cylindrical polymer chains into a crystal. The approximate repeat distance was first

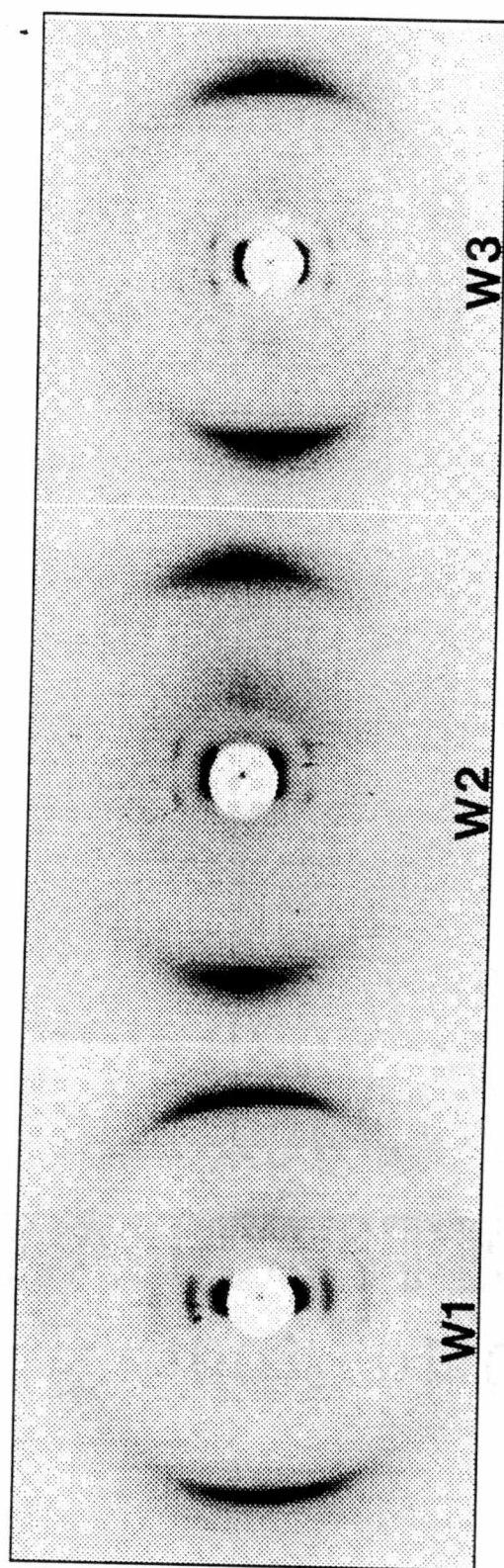


Figure 4.4 WAXS patterns obtained with $D=5$ cm for fibers MA111 (W1), MA111-3 (W2), and MI116-2.2H1 (W3).

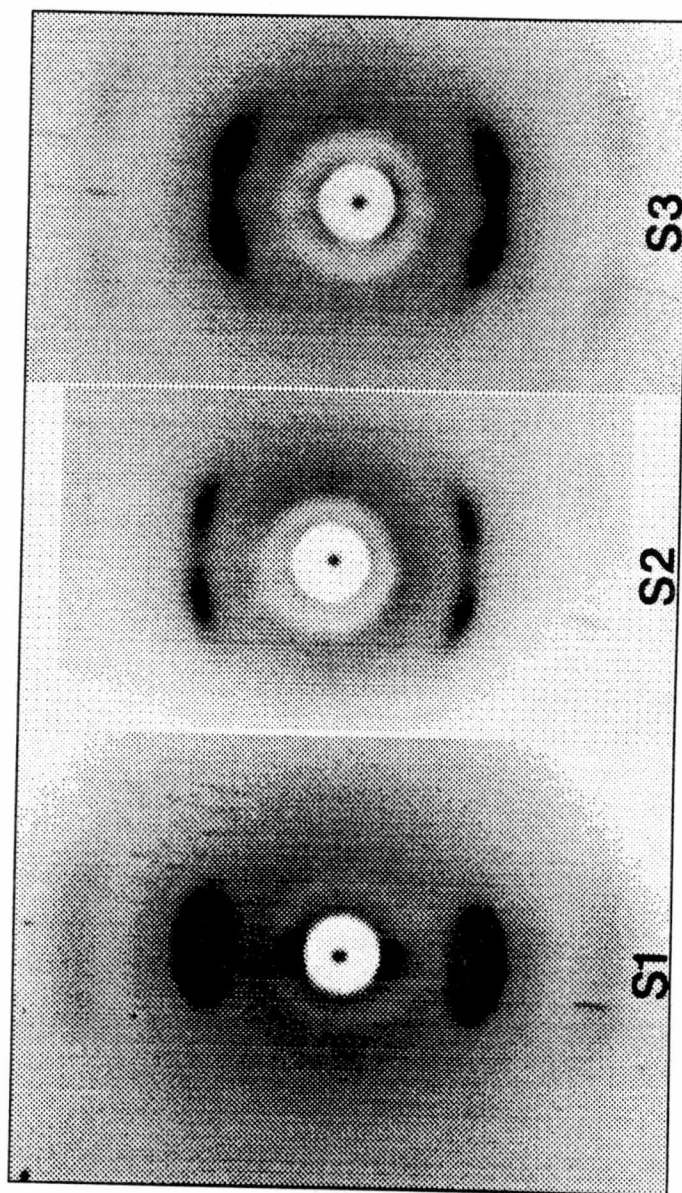


Figure 4.5 WAXS patterns obtained with $D=17$ cm for fibers MA111 (S1), MA111-3 (S2), and MI116-2.2H1 (S3).

calculated from chemical structure of PEA-10,2 using the *PC Model* software from *Serena Software*. The repeat distance was calculated to be 2.244 ± 0.018 nm for a few minimum energy conformations. As the patterns obtained for fiber MI116-2.2H1 (W3 and S3) were the best, these patterns were used to calculate the unit cell dimensions. The calculations were done as explained previously in Chapter 3, and the results are listed in Table 4.1.

The meridional reflections were indexed as 001, 002, and 003, corresponding to a chain axis crystallographic repeat of 2.2496 ± 0.0005 nm. This value agrees closely with the chemical repeat unit in an extended chain conformation. It can also be seen from fiber patterns W1, W2, and W3 in Figure 4.4, that only one equatorial reflection is seen clearly. This reflection was indexed as (100).

It can also be seen from fiber pattern W3 that the equatorial reflection is quite broad for the d spacing to be calculated precisely. This d spacing was also calculated from a 2θ scan previously taken on a randomized sample fiber FI109-2 after annealing it in vacuum at 100 °C for 24 hours. The peak in this scan is at $2\theta = 20.90^\circ$, and a corresponding d spacing of 0.425 nm, which matches closely with the value calculated from the pattern. The unit cell dimension a was calculated from this d spacing for the 100 planes.

Table 4.1 Calculations of d spacing from fiber patterns
of fiber MI116-2.2H2.

D	Line	x	y	ζ	ξ	d	2θ
169.45 mm	1	0.373	1.102	0.0649	0.0221	22.496	3.93
169.45 mm	2	0.729	2.144	0.1254	0.0435	11.614	7.61
169.45 mm	3	1.153	3.298	0.1906	0.0698	7.596	11.65
49.45 mm	Equator	1.898	0	0	0.3644	4.231	21.00

The unit cell for PEA-10,2 is proposed to be pseudo-hexagonal with $a=0.491$ nm and $c=2.2496\pm0.0005$ nm. The theoretical density calculated for this unit cell is $\rho_c=1.3095\pm0.0057$ gm/cm³, which is reasonable when compared with the experimentally measured amorphous density of $\rho_a=1.2057\pm0.0004$ gm/cm³.

The percent crystallinity in the slow crystallized film sample was calculated from its wide angle diffraction pattern, by overlaying a scaled diffraction pattern of amorphous film on it, as shown in Figure 4.6. The crystallinity as estimated from this technique is 36.1%, which is very high as compared to the crystallinity in fibers (the crystallinity measurements in fibers will be discussed in a later part of this chapter). The percent crystallinity in this film calculated from its density (1.2333 gm/cm³) is 28.2%. The flat film X-ray pattern for this film is shown in Figure 4.7, and this pattern also indicates well developed crystallinity in this film. The high level of crystallinity was produced in this film sample by holding it at 125 °C for 1 hour when cooling from the melt state.

As mentioned earlier, the film and fiber samples continued to move downwards in the DGC for a period of 6-7 days. This effect was more pronounced in quenched films and as-spun fibers, while the drawn fibers were relatively

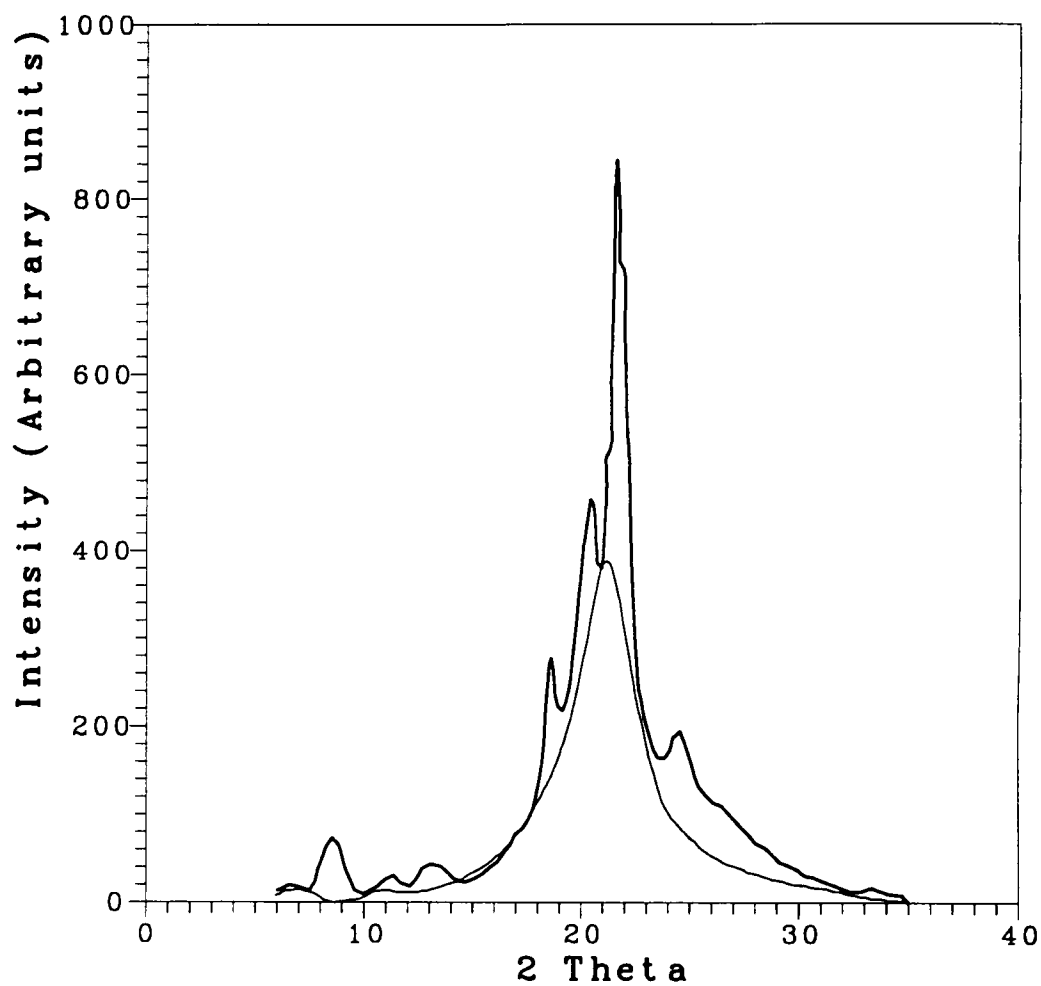


Figure 4.6 Scaled WAXD pattern of the amorphous film overlaid on the WAXD pattern of the slow crystallized film.

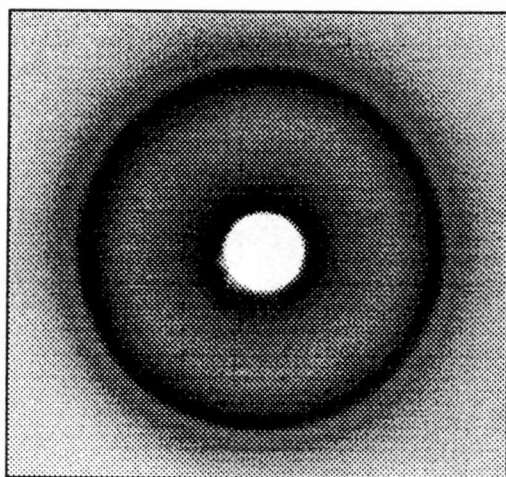


Figure 4.7 WAXS pattern of the slow crystallized film.

stable. It was observed that the density of as-spun fibers increased to values more than the density of drawn fibers after being put in the DGC. The density of fibers and films measured five hours after being put in the DGC, and the density after reaching a stable equilibrium position are compared in Table 4.2. It appears that the "annealing" effect in the DGC is more pronounced in specimen with little or no orientation as compared with specimen having high molecular orientation. It can also be noted that the density of a drawn and heat set fiber after annealing in boiling water is less than the density of the slow crystallized film.

The peak in a 2θ scan of amorphous film is seen at 21.25° . The most intense peak seen in the same film after annealing it in boiling water for 3 hours is at 21.6° , which shifts to 21.8° after annealing for 4 hours; and finally to 21.85° after annealing for 6 hours. This peak is seen at the same position for the slow crystallized film as well. These differences seen between the samples with a preferred chain orientation and samples with random orientation may be due to a possible difference in the crystal structure formation in the two cases. This can be further studied by stretching the quenched films either uniaxially or biaxially, and then annealing these films.

Table 4.2 The change in density with time for different
PEA-10,2 samples.

Description of sample	Time of Measurement	Density gm/cm ³	Percent Crystallinity
As-spun fiber drawn to 3X.	5h	1.2075	1.9
	7d	1.2109	5.4
Fiber drawn in-line to 3.8X.	5h	1.2076	2.0
	7d	1.2109	5.4
Fiber drawn in-line and redrawn to a overall draw ratio of 6.99X.	5h	1.2102	4.7
	7d	1.2133	7.9
Heat set fiber with a overall draw ratio of 7.26X.	5h	1.2127	7.3
	7d	1.2153	10.0
Fiber annealed in vacuum oven at 100 C for 24 h.	5h	1.218	12.7
Fiber annealed in boiling water for 6 h.	5h	1.2274	22.3
	7d	1.2313	26.2
Amorphous film	5h	1.2057	0.0
	7d	1.2138	8.4
As-spun fiber	5h	1.2075	1.9
	7d	1.2157	10.4
Slow crystallized film	5h	1.2333	28.2
	7d	1.2371	32.0

4.2 STUDIES OF GLASS TRANSITION AND MOISTURE PLASTICIZATION

The glass transition temperatures of PEA-10,2 and PEA-6,2 polymers were determined using the autovibron. The effect of moisture plasticization was also studied on PEA-6,2 fiber using the same technique. These results are tabulated in Table 4.3. The T_g was determined from the peak in loss tangent curve obtained from the dynamic mechanical analysis. An example of the data obtained at a frequency of 1.1 Hz is shown plotted in Figure 4.8.

The T_g of polymer PEA-6,2 is found to be about 10 degrees lower than that of PEA-10,2. This change is of the same order as the difference in the peak melting temperature of these polymers as measured using the DSC. As seen from Table 4.3, moisture has a substantial effect on the T_g of PEA-6,2. This polymer absorbs up to ~6% of moisture during the first two hours in water at 37 °C. This moisture acts as a diluent, and depresses the T_g. This plasticizing action naturally also affects the tensile strength, and normally a 15% to 20% drop in the initial tensile strength is observed with roughly 6% moisture content. This effect, however, could prove to be favorable if premoistening of PEA sutures before use would improve the handling characteristics, as has been found in polyamide-6 sutures (84).

DSC was also used to study the effect of moisture plasticization on the PEA-6,2 polymer. It was observed that

Table 4.3 Results of glass transition studies on PEA polymers
using dynamic mechanical analysis.

Sample Description	Tg		
	1.1 Hz.	11 Hz.	110 Hz.
PEA-10,2 as is	324 K	328 K	330 K
PEA-6,2 as is	313 K	318 K	329 K
PEA-6,2 dry	317 K	323 K	336 K
PEA-6,2 exposed to air	311 K	320 K	326 K
PEA-6,2 dipped in water	270 K	273 K	277 K

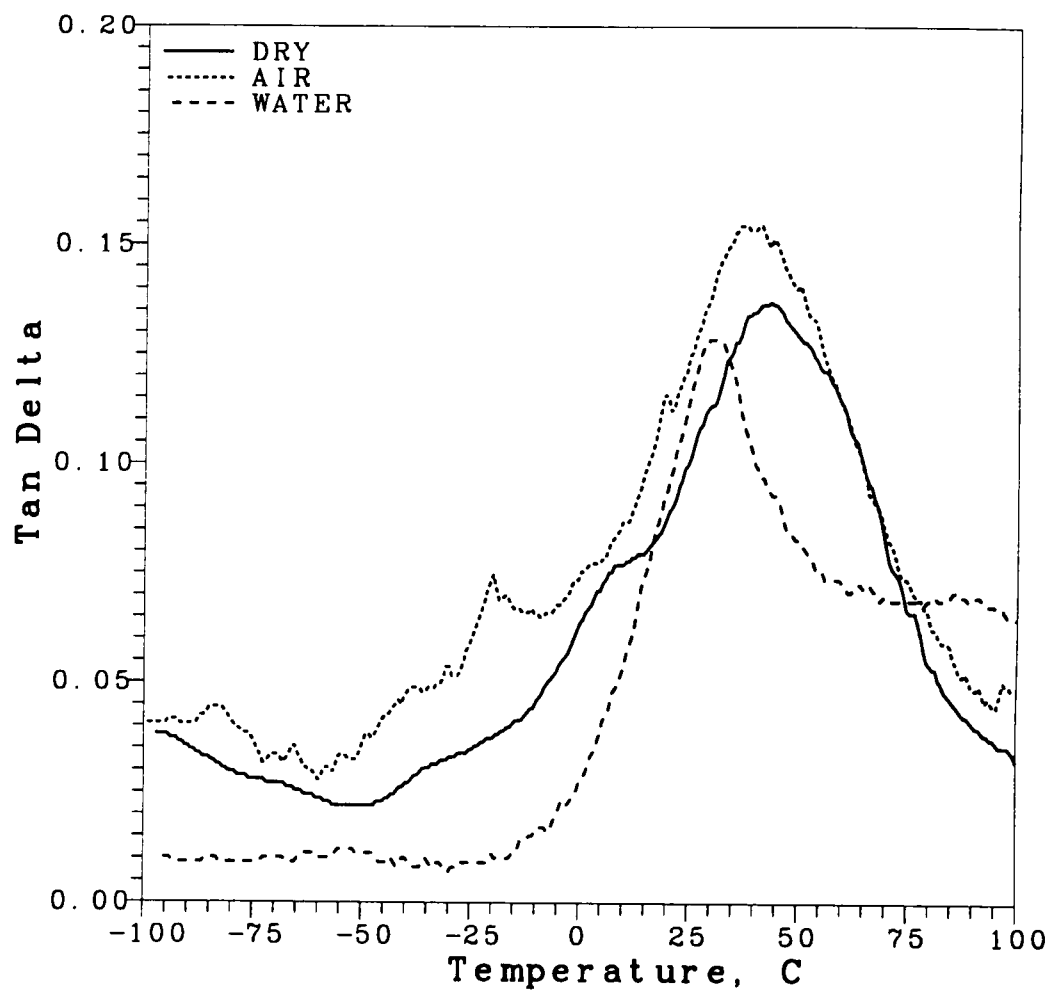


Figure 4.8 Loss tangent ($\tan \delta$) curves plotted against temperature for the different PEA-6,2 fiber samples.

the T_g could not be calculated very efficiently from the DSC due to the presence of other thermal effects in this region. One reason for this is that the difference between the glass transition and the onset of melting is only about $\sim 80^\circ\text{C}$, with the annealing effects present in this region. Although it is difficult to obtain an accurate numerical value of T_g from this technique, the shift in T_g with moisture uptake can clearly be observed as shown in Figures 4.9 and 4.10. The plasticizing action is more clear in Figure 4.10, where the sample conditioned in air is compared with the sample dipped in water ($\sim 6\%$ moisture).

4.3 FIBER PROCESSING

4.3.1 Preliminary Studies:

In this section, the results of fiber spinning using the *Fourne* extruder will be discussed along with the results of subsequent drawing of these fibers.

Melt spinning:

The extrusion conditions for PEA polymers were established easily with some preliminary studies using the *Instron* capillary rheometer. During the first melt spinning experiment it was observed that the filament remained tacky until it reached the drawdown device. Increasing the spinline length did not help very much, and an iced-water quench at the take-up was tried as an alternative. Quenching

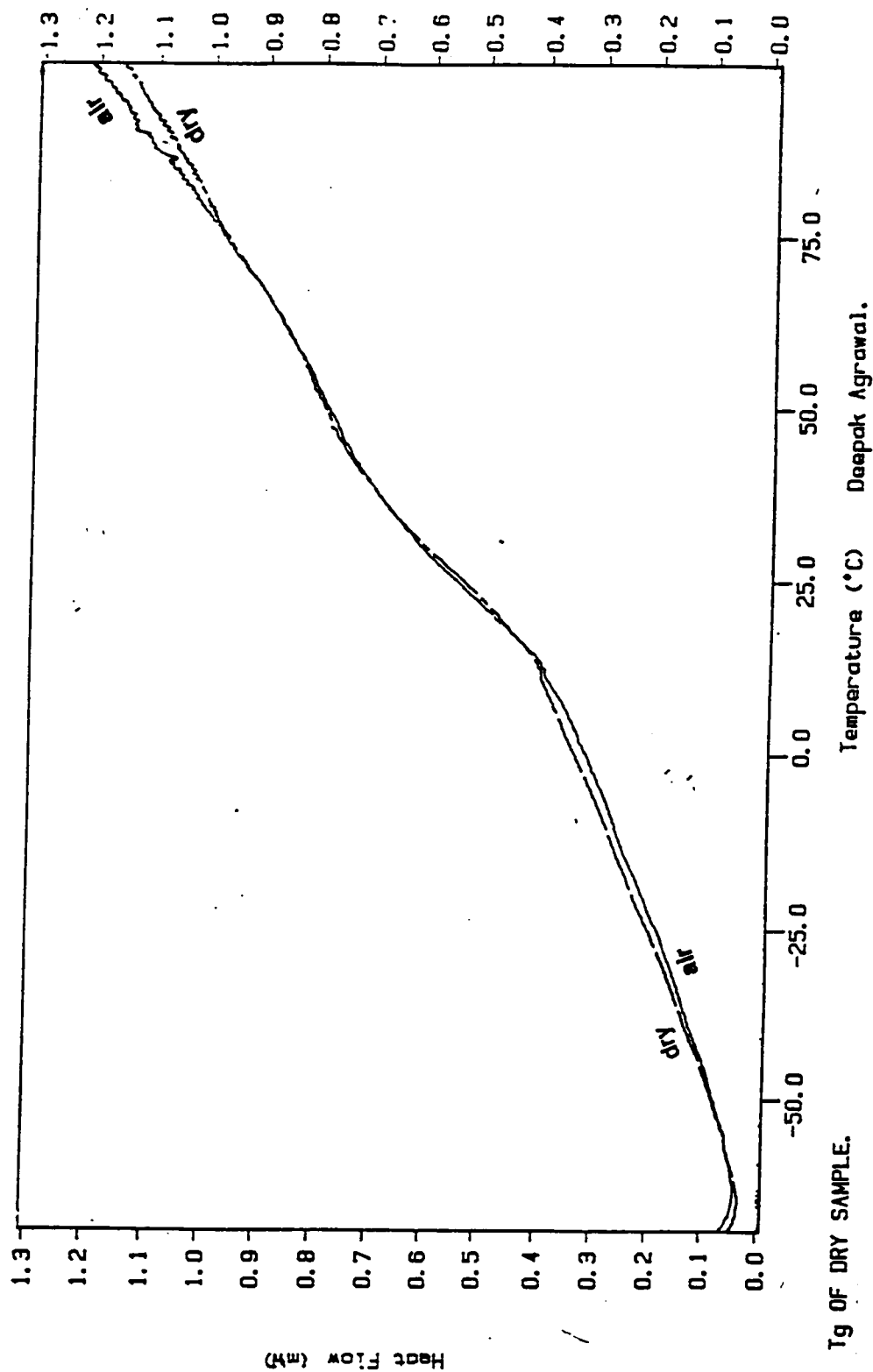


Figure 4.9 DSC scans for the dry fiber sample and fiber sample conditioned in atmospheric air.

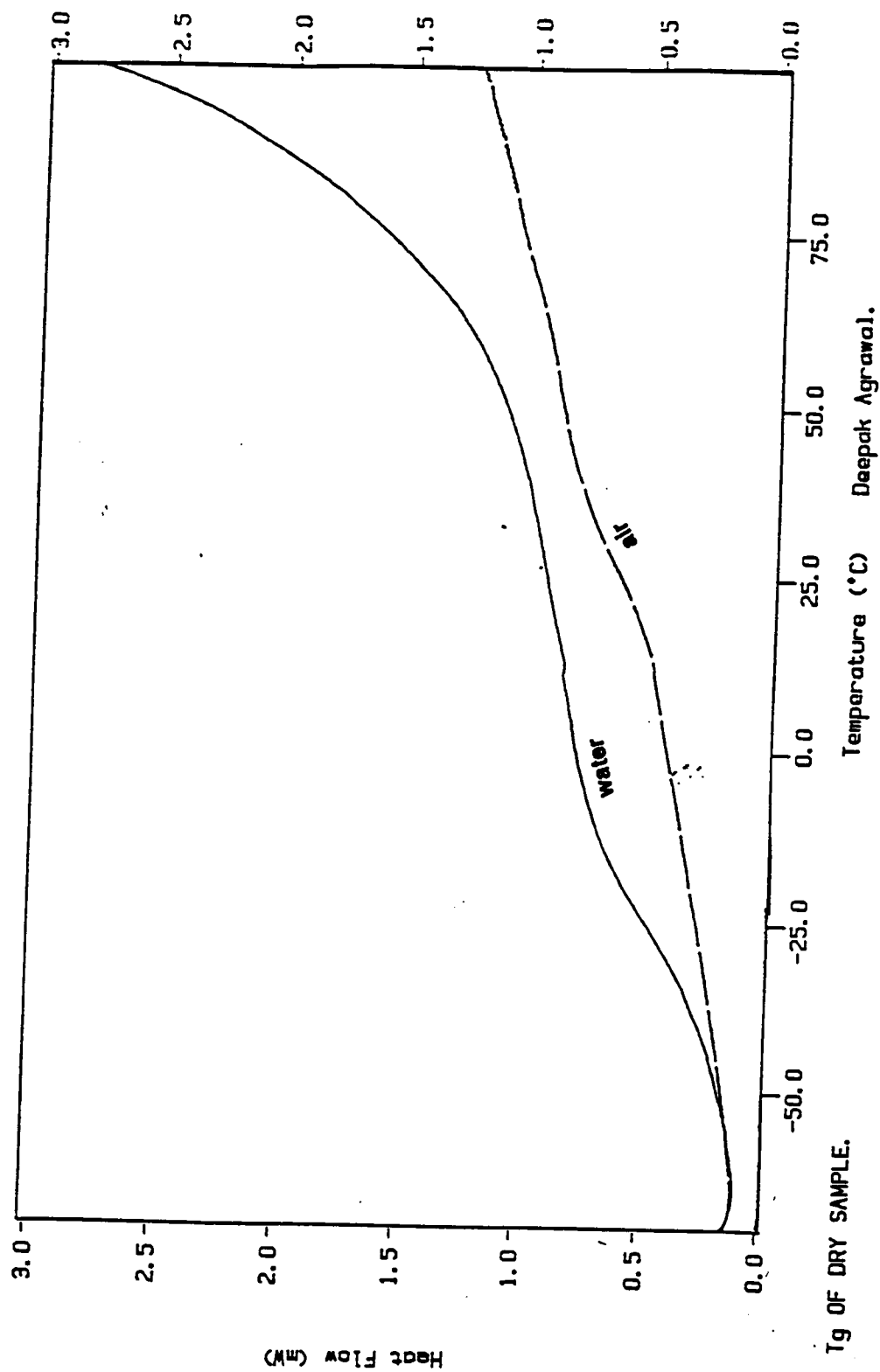


Figure 4.10 DSC scans for the fiber sample conditioned in air and the wet fiber sample (with ~6% moisture content).

helped to solidify the filament, and some good fiber was collected using this set up. The post extrusion IV of polymer processed in this experiment had dropped from 1.2 IV to 0.67 IV. As this drop was substantial, in the next experiment polymers with lower initial IV were processed to see if the percent drop in the IV could be decreased. Extrusion of polymer PEA-10,2 with 1.0 IV was satisfactory, but the drawdown of filament was faster because of the lower melt viscosity. The quality of these fibers did not appear to be as good as the fibers spun from PEA-10,2 with 1.2 IV. This was further verified by their drawing behavior and mechanical properties, as will be discussed later in this section. It was observed that the melt viscosity of polymer PEA-10,2 with 0.73 IV was too low for this material to be processed into fibers using the present setup. From the results of these experiments it was concluded that polymer PEA-10,2 with an initial $IV \geq 1.0$ was more suitable for fiber spinning, and attention was focused on preventing the molecular weight breakdown during processing. Polymer PEA-6,2 with 1.0 IV was also spun in this experiment, and it also formed good fibers with similar extrusion conditions as for PEA-10,2.

As the PEA polymers contain hydrolytically unstable ester linkages, a better cooling method was sought instead of the water quench method. A radial flow air cooling chimney was designed for this purpose. It was successfully

used in a later experiment, and the need for a cold water quench at the take-up was thus eliminated. Cooling of the filament was achieved by forced convection using well-diffused radial flow of ambient air over a length of one meter in the spinline. Air cooling did not appear to help very much in preserving the molecular weight, but still this technique was preferred over the water quench method. An additional band heater was placed directly below the spinneret to prevent cooling of the bottom surface of the spinneret, and maintain it at the extrusion temperature. This helped in decreasing the final zone temperature on the extruder, which is favorable for preventing the molecular weight breakdown.

Drawing:

To determine the optimum drawing conditions for PEA fibers, fibers FW101 and FW102 were first drawn at different draw temperatures. The effect of draw temperature on maximum draw ratio is shown in Figure 4.11. It can be observed that the optimum draw temperature is in the range of 50 °C to 70 °C for both of these fibers. The difference in the maximum draw ratio between the two filaments at each temperature is perhaps due to the different initial molecular orientations, as will be discussed later. The effect of different draw temperatures on the tensile strength of fibers FW101 and FW102 is shown in Figure 4.12. It can be seen from this

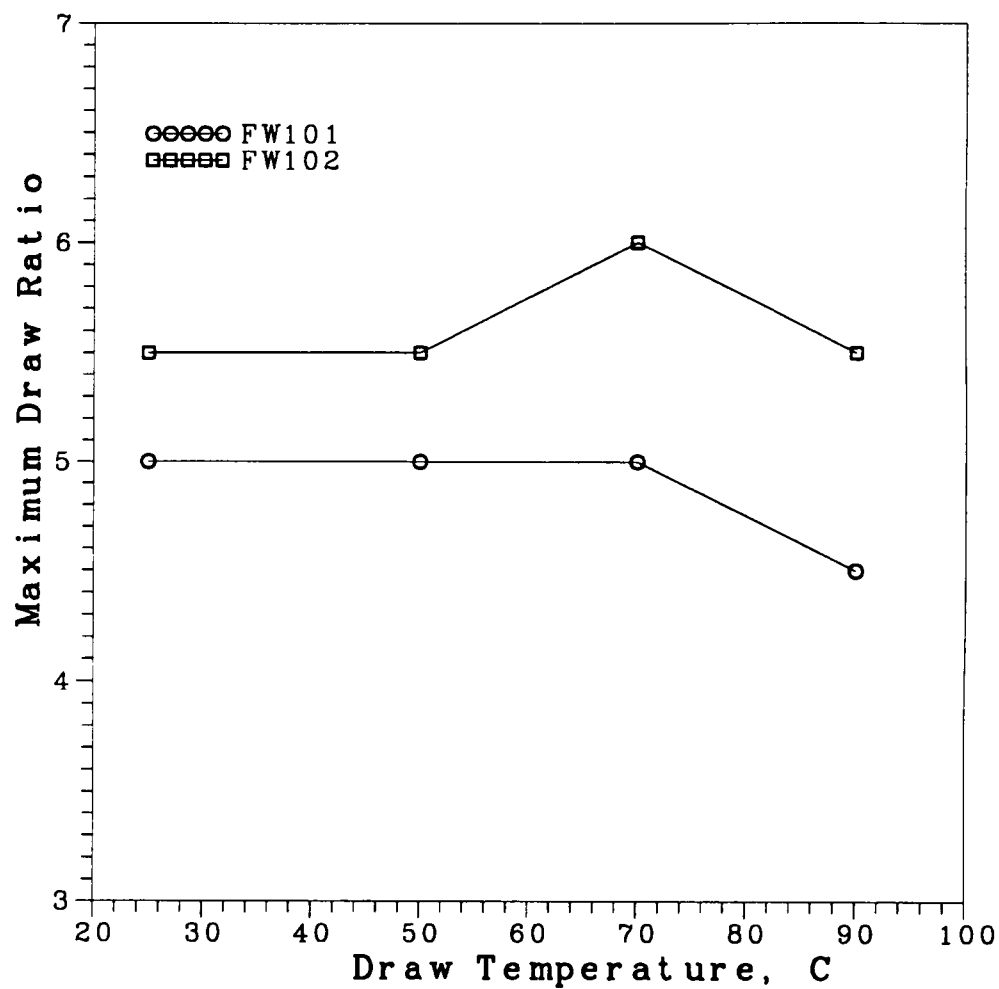
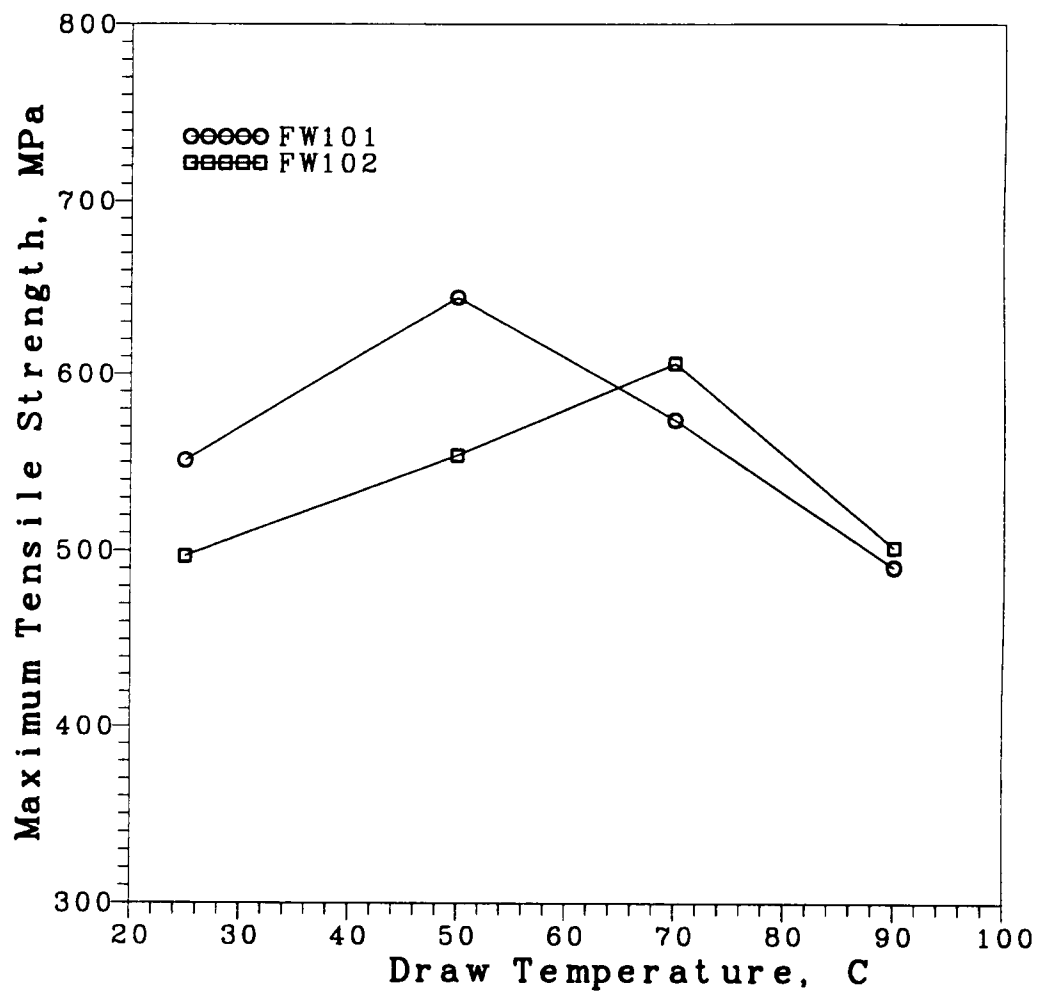


Figure 4.11 Plot showing the effect of draw temperature on the maximum draw ratio of PEA-10,2 fibers.



*Mean values of tensile strength are plotted. Variations observed during the tensile testing were within $\pm 5\%$ of this value.

Figure 4.12 Plot showing the effect of draw temperature on the maximum tensile strength obtained in PEA-10,2 fibers.

figure that better strength is obtained at draw temperatures of 50 °C and 70 °C in the two cases. As expected, the strength increases with increasing draw ratios at each draw temperature. These results are summarized in Table 4.4.

A few trials on drawing of fibers FW103 through FI109 revealed that the optimum draw temperature was in the range of 60 °C to 65 °C, and all of these fibers were drawn at a temperature of 60 °C. Some discrepancies were observed in the drawing behavior of these fibers, even among the fibers processed under similar conditions. These differences were not very well understood until some of these fibers were tested for their molecular weight and IV; these results are tabulated in Table 4.5. The difference in molecular weight of these fibers is probably due to the effect of different residence time of polymer in the extruder, and the different processing techniques. As can be seen from Figure 4.13, the maximum attainable draw ratio for each of these fiber samples is somewhat dependent on the molecular weight in this range.

Tensile Testing and Birefringence:

The results of tensile testing and birefringence measurements on fibers FW103 through FI109 are tabulated in Table 4.6. Tensile strength is plotted as a function of draw ratio for these fibers in Figure 4.14. There appears to be substantial scatter in this plot, which may be due to a

Table 4.4. Effect of draw ratio and draw temperature on the tensile strength of PEA-10,2 fibers.

Fiber ID	Draw Ratio	Draw Temp. C	Percent Elongation	Tensile Strength, MPa	Modulus GPa
FW101-1	5.0	25	61	551	-
FW101-2	3.0	50	176	255	-
FW101-3	4.0	50	104	385	2.02
FW101-4	5.0	50	58	644	-
FW101-5	5.0	70	52	574	3.89
FW101-6	4.5	90	56	491	-
FW102-1	5.5	25	53	497	-
FW102-2	5.5	50	38	554	-
FW102-3	6.0	70	44	606	-
FW102-4	5.5	90	58	502	-

Table 4.5 Molecular weight and IV of PEA-10,2 fibers processed using the Fourne extruder.

Fiber ID	Molecular Weight		Intrinsic Viscosity dl/g
	Mw	Mn	
FW101-4	6.33E+04	2.44E+04	0.67
FW103-1	5.12E+04	2.01E+04	0.6
FW103-3	5.07E+04	2.00E+04	0.6
FA104-3	5.83E+04	2.15E+04	0.67
FA106-1	5.14E+04	1.94E+04	0.67
FI109-2	6.64E+04	2.33E+04	0.71

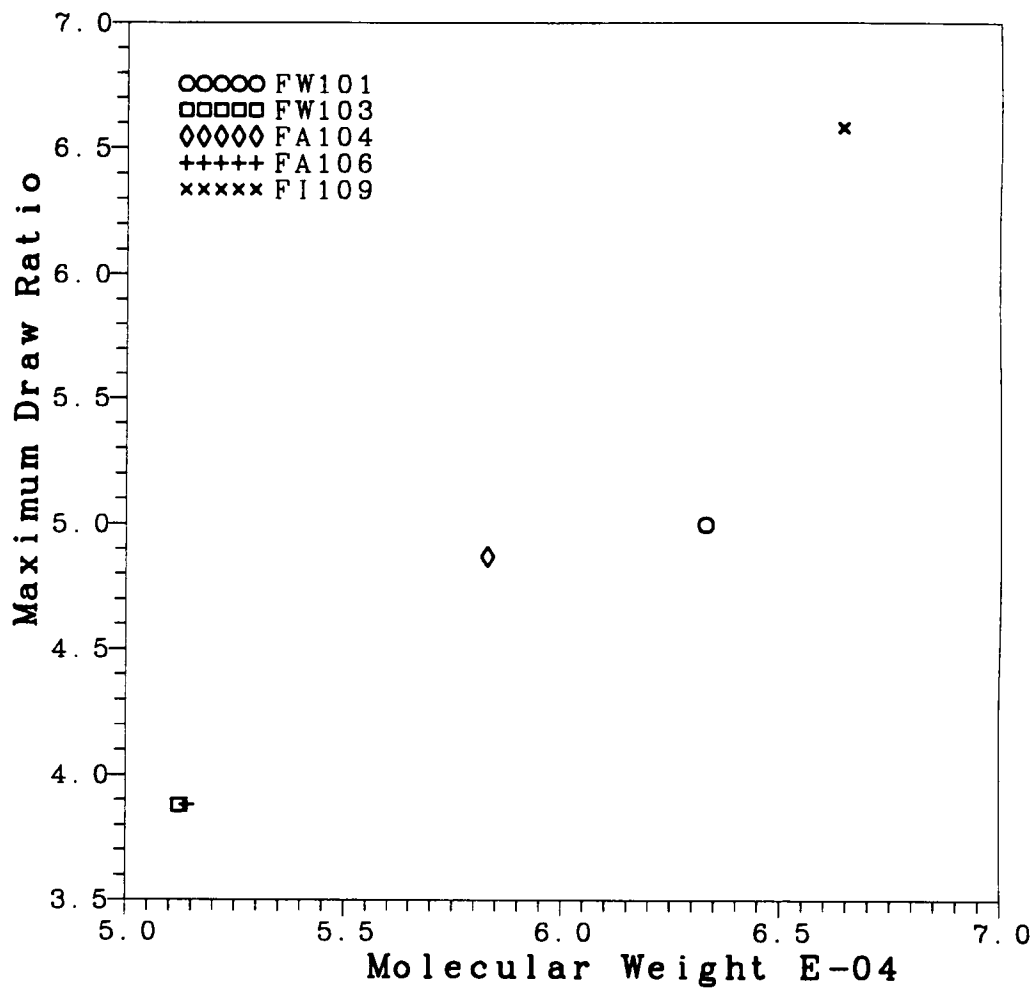
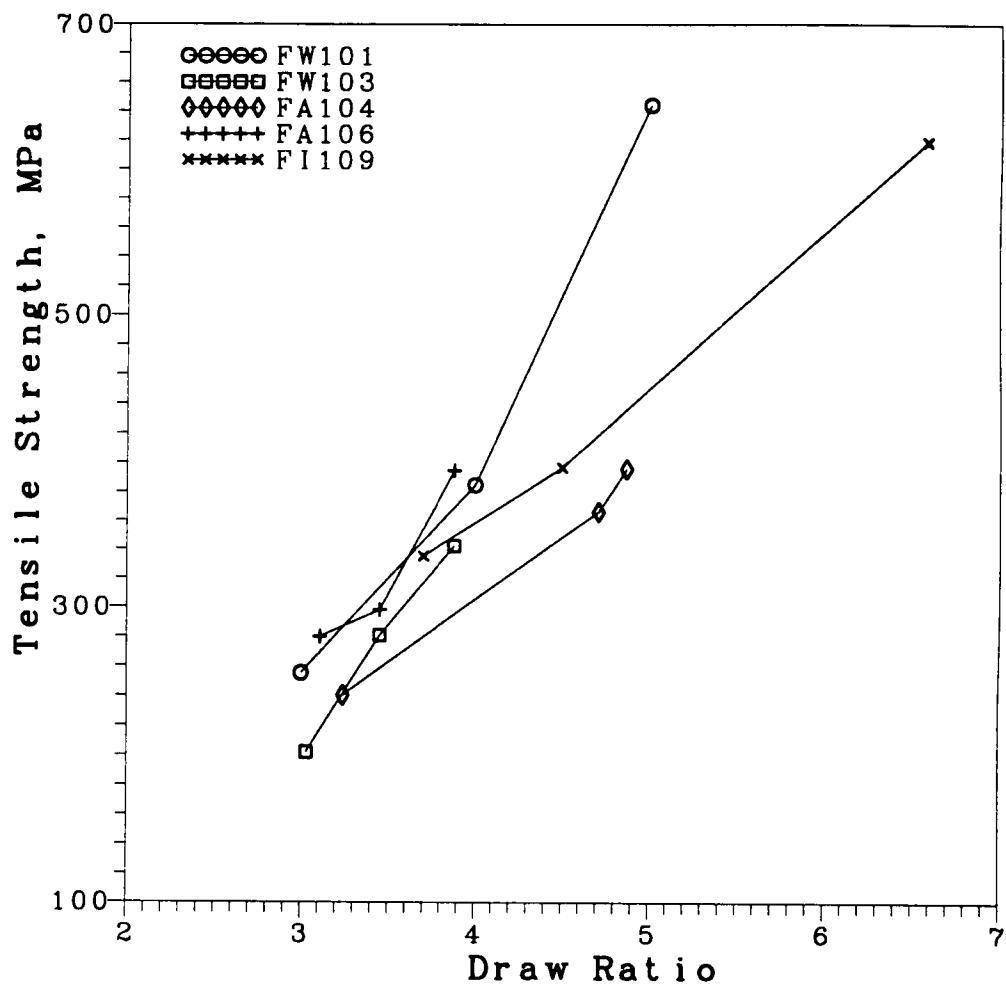


Figure 4.13 Plot showing the effect of weight average molecular weight on the maximum draw ratio obtained in the PEA-10,2 fibers.

Table 4.6 Strength and birefringence results for fibers FW103 through FI109.

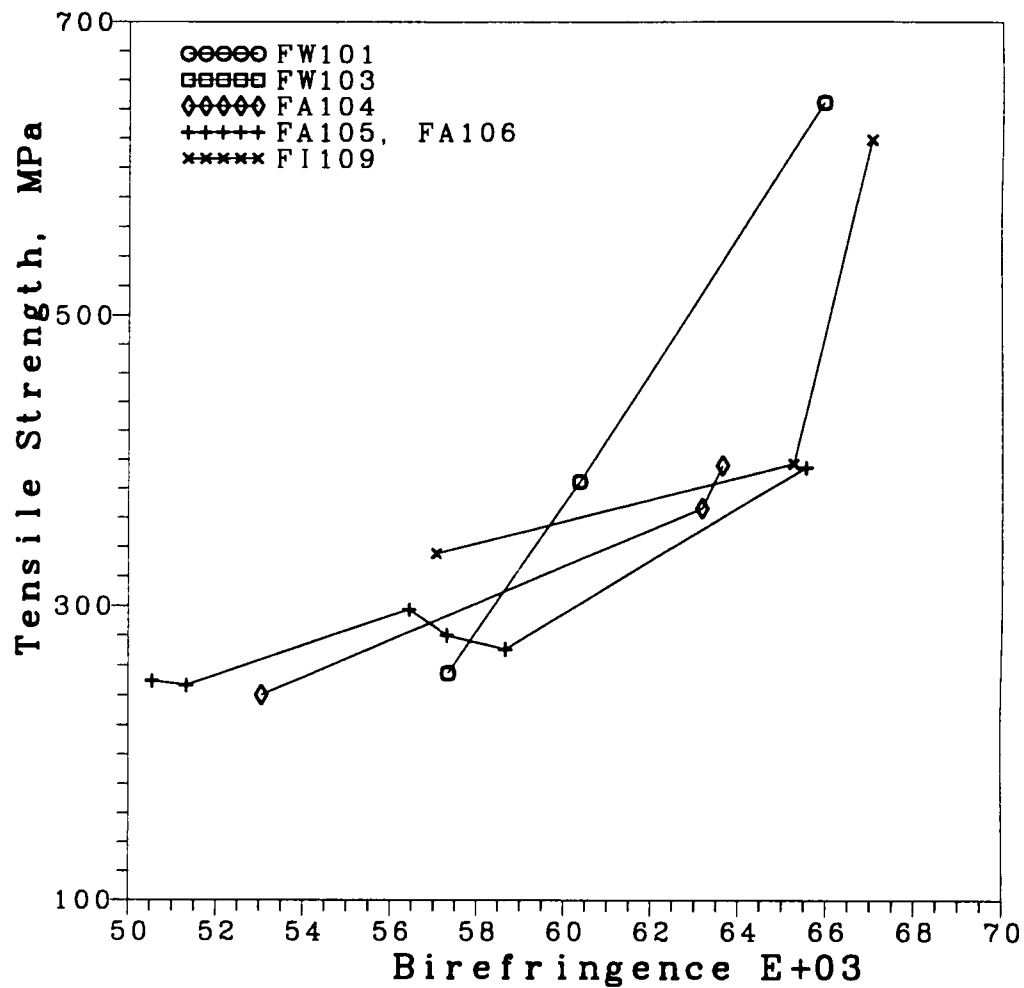
Fiber ID	Draw Ratio	Draw Temp. C	Birefringence	Percent Elongation	Tensile Strength, MPa
FW103-1	3.03	60	0.0635	55	202
FW103-2	3.45	60	0.0597	46	281
FW103-3	3.88	60	0.0653	22	343
FA104-1	3.24	60	0.0531	103	240
FA104-2	4.71	60	0.0632	74	367
FA104-3	4.87	60	0.0636	59	396
FA105-1	3.03	60	0.0513	113	247
FA105-2	3.11	60	0.0506	104	250
FA105-3	3.45	60	0.0587	78	271
FA106-1	3.11	60	0.0573	65	280
FA106-2	3.45	60	0.0564	62	298
FA106-3	3.88	60	0.0655	45	395
FI107	3.88	60	-	78	346
FI108	4.60	60	-	54	408
FI109	3.70	60	0.0571	123	335
FI109-1	4.50	60	0.0653	55	397
FI109-2	6.58	60	0.0670	52	619



*Mean values of tensile strength are plotted. Variations observed during the tensile testing were within $\pm 5\%$ of this value.

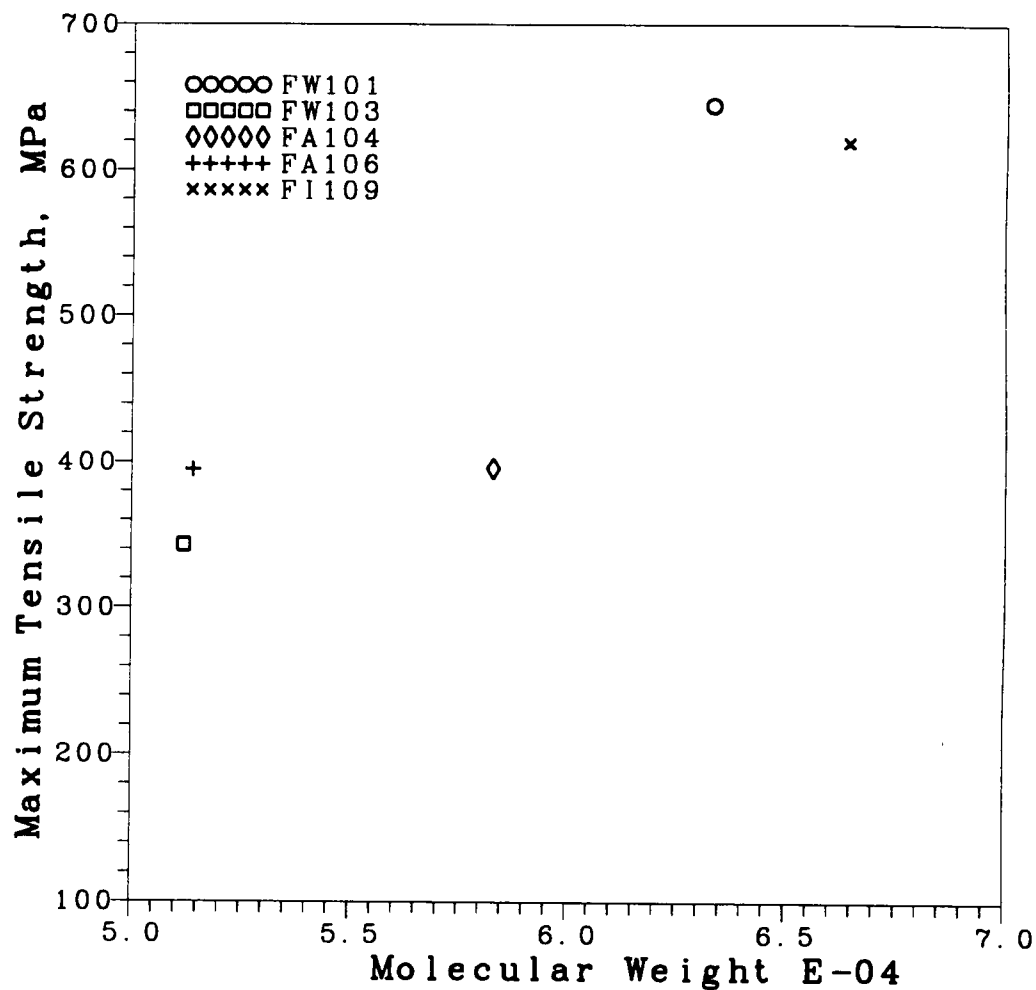
Figure 4.14 Plot showing the effect of draw ratio on the tensile strength of PEA-10,2 fibers.

number of reasons. One reason is that the tenacity is a function of molecular orientation in the fiber, and the orientation developed after drawing to a given draw ratio depends on the initial molecular orientation in the as-spun filament. In addition, the molecular weights of these samples are not the same, as shown previously in Table 4.5. Similar scatter is seen when the tensile strength is plotted against birefringence, a measure of overall molecular orientation, as seen in Figure 4.15. It can also be noted from this figure that the correlation of tensile strength with birefringence is somewhat better in the regime prior to reaching highest levels of molecular orientation. At higher levels of molecular orientation, it is known that the strength depends on other morphological features and not orientation alone (85-88). The maximum tensile strength attained in each fiber sample is plotted against its weight average molecular weight in Figure 4.16. From this figure it appears that the maximum tensile strength that can be obtained in a fiber sample is also associated with its molecular weight in this range. The explanation for this is more likely associated with the fact that polymers with longer molecular chains have more tie molecules, and consequently, higher strengths (89). This further emphasized on the need to preserve the molecular weight during processing. It was then decided to develop a better understanding of the degradation behavior of polymer PEA-



*Mean values of tensile strength are plotted. Variations observed during the tensile testing were within +5% of this value.

Figure 4.15 Plot showing the effect of overall molecular orientation on the tensile strength of PEA-10,2 fibers.



*Mean values of tensile strength are plotted. Variations observed during the tensile testing were within $\pm 5\%$ of this value.

Figure 4.16 Plot showing the influence of weight average molecular weight on the maximum tensile strength obtained in PEA-10,2 fibers.

10,2 at high temperatures, and try to improve the processing conditions so as to get better molecular weight retention.

4.3.2 Thermal Degradation Studies:

Time and temperature dependence of degradation of PEA-10,2:

The results of studies on thermal degradation of PEA-10,2 polymer are shown in Figure 4.17. Molecular weight of starting resin is plotted at time 0. It can be seen from this figure that the molecular weight drops rapidly in the first few minutes at elevated temperatures. The decrease in the molecular weight is also dependent on the temperature in processing range, but is more strongly associated with time. It is apparent from these results that decreasing the residence time of polymer at high temperatures during melt spinning would help in preserving the molecular weight. It has been shown by W. Michaeli and R. Von Oepen (89) that the drop in molecular weight for polylactides is also dependent on moisture content and shearing, in addition to the melt temperature and residence time during processing; and R. G. Sinclair (90) has reported a drop in tensile strength with increasing residence time for polylactide copolymers.

This degradation problem at high temperature could be reduced by either improving the thermal stability of the polymer, by decreasing the shearing and residence time

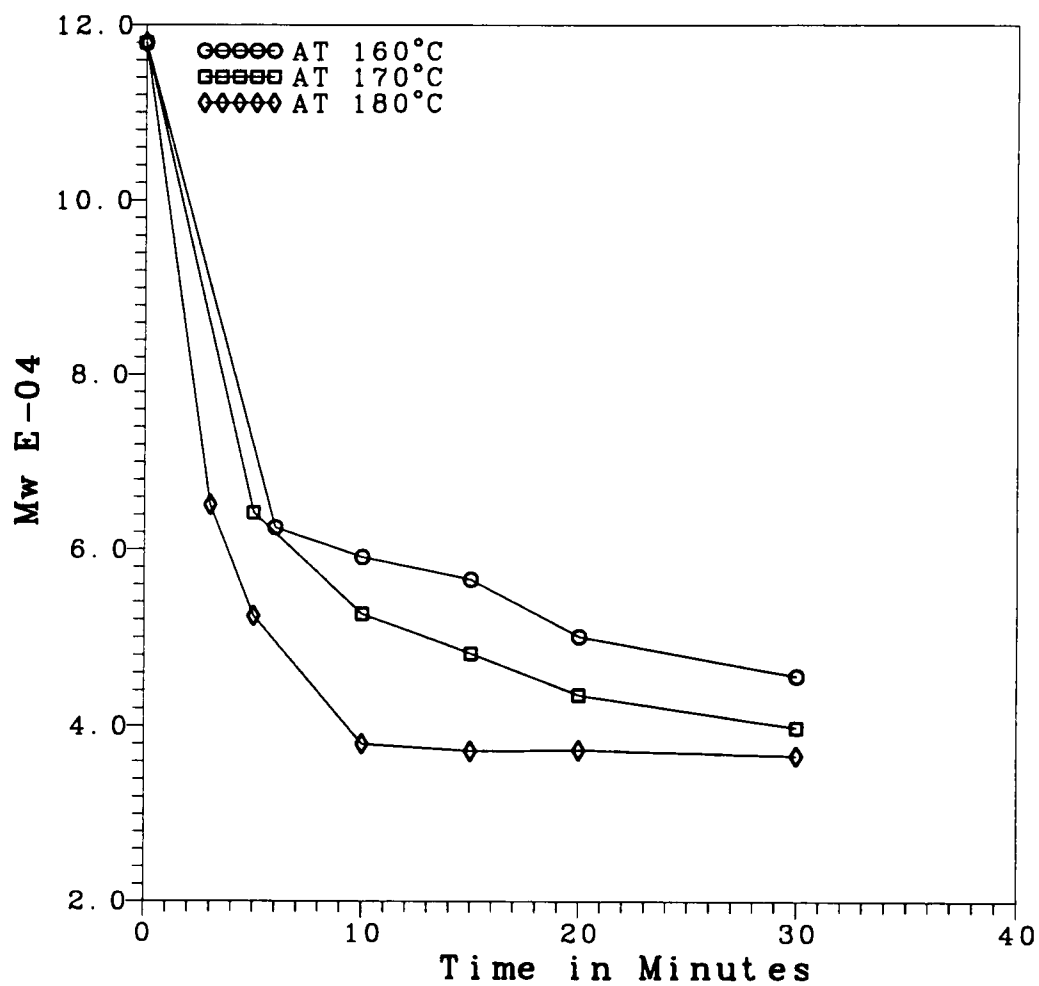


Figure 4.17 Plot showing the effect of residence time on the molecular weight degradation of PEA-10,2 polymer.

during processing, or by reducing the processing temperature.

Gel spinning studies:

The gel spinning experiments were performed primarily to study the extrusion of PEA polymer with the solvent (NMP), as an alternative processing technique. The extrusion of polymer with the solvent can be done at a lower temperature and this would help in preventing the thermal degradation resulting at high temperatures. The effect of solvent concentration on the melting of PEA polymers was first studied on the DSC and the results are tabulated in Table 4.7. It can be seen that the melting temperature decreases considerably with the increasing solvent concentration for both the polymers. The peak melting temperature seen on the DSC was also found to correlate well with the extrusion temperature listed in column 4 of the same table.

It was observed that the viscosity of extrudate decreased with increasing solvent content as anticipated, and extrusion of polymer filament with solvent concentration above 50% was just not feasible. It was learned from these experiments that the PEA polymers also formed good fibers by this technique. If the gel spinning technique is to be reviewed in the future, it is recommended to keep the

Table 4.7 Effect of solvent on the melting of
PEA polymers.

Polymer	Solvent Concentration (%)	Peak Melting Temperature (C)	Processing Temperature (C)
PEA-10, 2	0	161	175
PEA-10, 2	14	150	158
PEA-10, 2	40	118	137
PEA-10, 2	44	117	131
PEA-10, 2	53	99	-
PEA-10, 2	60	95	-
PEA-6, 2	0	147	170
PEA-6, 2	15	140	-
PEA-6, 2	19	135	140
PEA-6, 2	34	125	134
PEA-6, 2	57	92	-
PEA-6, 2	67	71	-

solvent concentration to about 20%, as it appeared to be close to the optimum solvent concentration for this method.

Melt spinning using the Maxwell extruder:

In an attempt to reduce the residence time and shearing during extrusion, the *Maxwell* extruder was considered as an alternative. The 3M company had also supplied us with PEA-6,2 polymer with improved thermal stability. The original PEA-10,2 polymer and the stabilized PEA-6,2 polymer were melt spun using the *Maxwell* extruder.

Extrusion of the PEA polymers using the *Maxwell* extruder aided in preserving the molecular weight as seen from the results in Table 4.8. It can also be seen in this table that the use of water quench for polymer PEA-6,2 did not affect the fiber IV very much. For better comparison, these results are shown plotted together with the results from previous experiments in Figure 4.18. It can be seen from this figure that the new extrusion technique helps a good bit in preserving the molecular weight, and improving the thermal stability of polymer further helps in this effort. These results are significantly better compared with similar biodegradable polyesters processed by melt spinning (92-95). Molecular weight retention of the heat stabilized PEA-6,2 is so far the best in any of the processing studies on this polymer (96). These results indicate that it would

Table 4.4 IV and GPC results for fibers processed
using Maxwell extruder.

Fiber ID	Molecular Weight		Intrinsic Viscosity dl/g
	Mw	Mn	
MA111	9.44E+04	2.53E+04	0.82
MI114-2	8.59E+04	2.50E+04	0.84
MA117	7.74E+04	2.28E+04	0.80
MI118-6H1	7.42E+04	2.44E+04	0.76
MA119	6.56E+04	2.36E+04	0.76
MA621	1.16E+05	3.09E+04	0.80
MW622	1.26E+05	3.05E+00	0.91
MA623	9.08E+04	2.68E+04	0.88
MW624	9.76E+04	2.81E+04	0.90

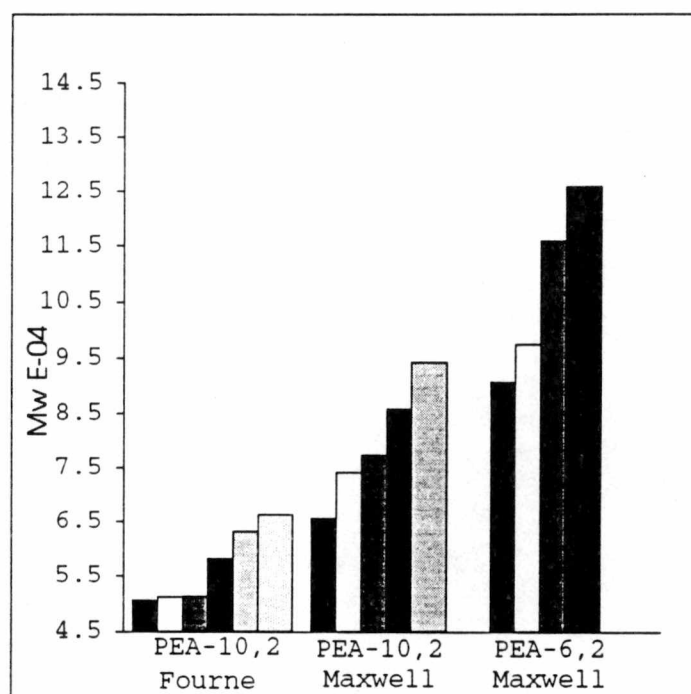


Figure 4.18 The weight average molecular weight plotted for each of the experiments. Each bar represents the molecular weight of a sample processed during that experiment.

be a good idea to consider use of special machinery for the processing of thermally unstable polymers.

4.3.3 Optimization of Processing Conditions:

As the use of *Maxwell* extruder helped in a significant reduction of the molecular weight, the melt spinning of PEA polymers was now performed using this extruder. The effect of several processing conditions on the structure and properties of PEA fibers was studied in an attempt to optimize the processing conditions to obtain the most desirable properties in the final fiber.

The effect of drawdown ratio during melt spinning on the initial molecular orientation of fiber was also studied, and the results for polymer PEA-10,2 are tabulated in Table 4.9. The WAXS patterns for these fibers are shown in Figure 4.19, and it can be seen that there is a slight increase in orientation at higher drawdown ratios, indicated by the shortening of the arcs. As expected, the birefringence increases with increasing drawdown ratio as seen in columns 2 and 3 of Table 4.9. The density of these fibers as measured from the density gradient column is given in column 4, and it can be seen that there is slight increase in density with increasing drawdown ratios. However, the spinline breaks at drawdown ratios exceeding 150 under the present extrusion conditions. This may be approximately the maximum feasible drawdown ratio during melt spinning. The

Table 4.9 Properties of the as-spun fibers.

Fiber ID	Drawdown Ratio	Birefringence	Maximum Draw ratio	Maximum Strength, MPa	Density gm/cm ³
MA119	22	0.0225	5.15	291	1.2065
MA111	45	0.0280	7.13	475	1.2074
MA113	95	0.0313	3.19	399	1.2075
MA117	138	0.0338	3.19	363	1.2077

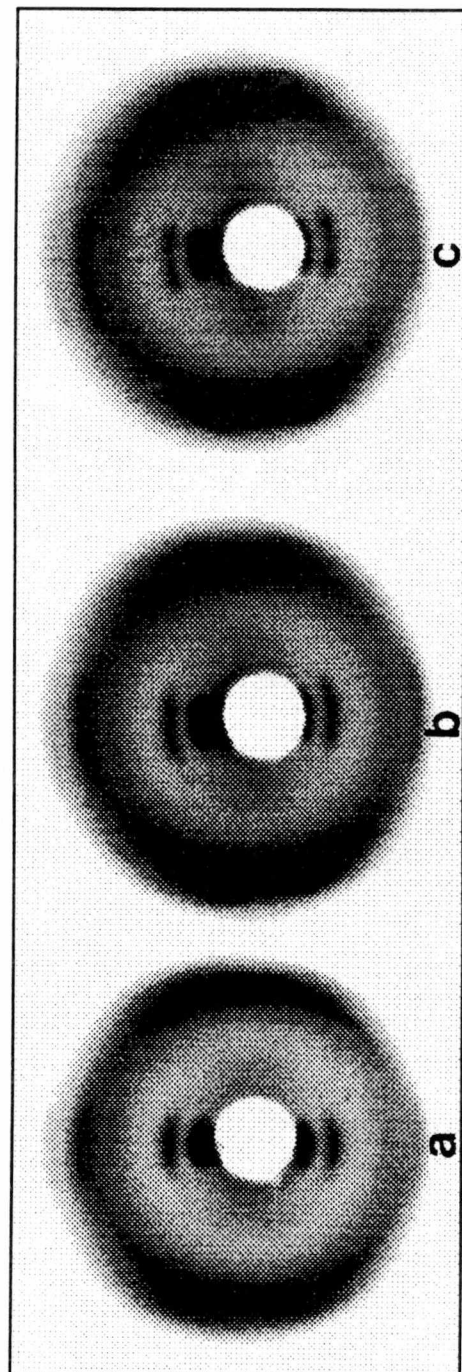


Figure 4.19 WAXS patterns for as spun fibers with increasing drawdown ratios.

(a) MA111 [DDR=22], (b) MA113 [DDR=95], and (c) MA117 [DDR=138].

maximum post-spinning draw ratios that could be attained at a draw temperature of 65°C, are listed in column 5 of this table. It appears from these data that drawdown ratios in the range of 20-50 would be optimal for good subsequent drawing.

As-spun fiber samples were then drawn to different draw ratios at 65°C, and the results are tabulated in Table 4.10. It can be seen from this table that the maximum draw ratio and maximum strength obtained from each fiber sample still show some dependence on its weight average molecular weight, and this is in good agreement with the results discussed earlier. Although the fiber MA117 is of higher molecular weight than MA119, the lower draw-ratio for this fiber may be due to the higher initial molecular orientation as reflected by its birefringence values. WAXS patterns for fiber sample MA111 in as-spun form and after drawing are shown in Figure 4.20. Increasing crystalline orientation can be seen with an increase in draw ratio, but any increase in crystallinity is not very obvious. The broad equatorial reflections could mean a smectic phase, and this can be confirmed only after a good understanding of the crystal structure development during the drawing (or deformation) process.

Additional trial experiments were performed on fiber MA119 to study the drawing under different conditions. These

Table 4.10 Strength and orientation in as-spun fibers after drawing at 65 deg. C.

Fiber ID	Draw Ratio	Birefringence	Tensile Strength, MPa	Modulus GPa	Percent Elongation
MA111-2.1	3.19	0.0543	216	0.73	109
MA111-1	3.50	0.0491	222	0.71	130
MA111-2	5.02	0.0599	439	1.71	22
MA111-3	7.13	0.0610	475	1.64	28
MA113-1	3.19	0.0428	399	1.50	47
MA117-1	3.19	0.0597	363	1.39	52
MA119-1	3.19	0.0494	244	0.69	114
MA119-2	4.44	0.0529	252	0.74	121
MA119-3	5.15	0.0584	291	0.80	99

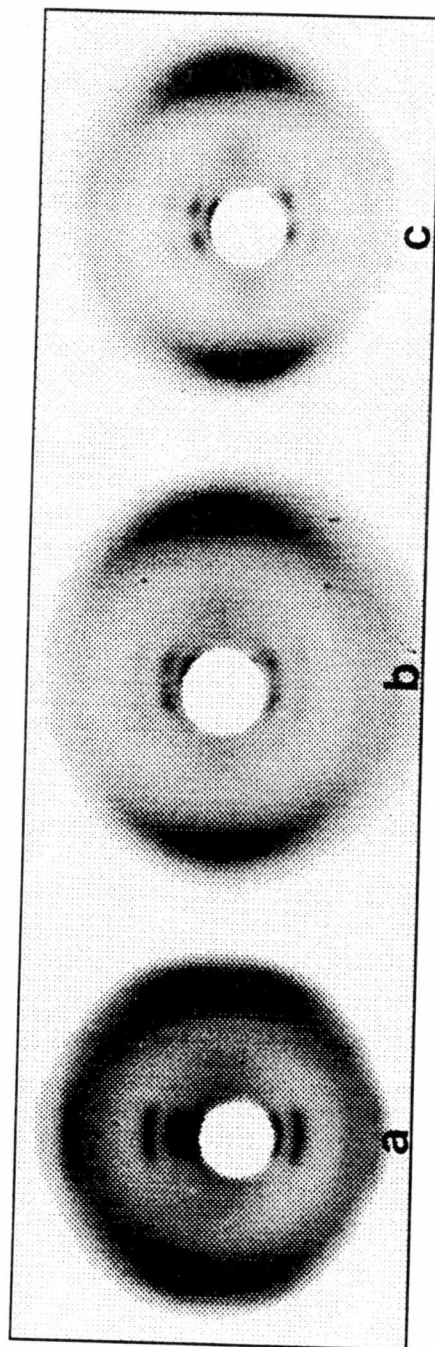


Figure 4.20 WAXS patterns showing the development of orientation during the drawing of fiber MA111. (a) MA111 as spun, (b) MA111 drawn 3.19X, and (c) MA111 drawn 7.13X.

results are tabulated in Table 4.11. It will be shown in a later part of this chapter, that moisture acts as a diluent and depresses the T_g of PEA polymers. As can be observed in Table 4.11, the plasticizing action of water permits drawing to higher draw ratios at room temperature. Although it does not seem to have a significant effect on the strength of fiber, the elastic moduli of these fiber samples are slightly lower than other fiber samples of similar strength. Drawing of the same fiber by exposing it to steam to get a combined effect of moisture plasticization and high temperature appears to give better strength, and again, with a lower elastic modulus. These results appear to be encouraging, but more experimental studies are needed to come to any such conclusions. It can be argued that the lower modulus may be due to presence of higher moisture content, but it should not make a large difference as all the fibers were conditioned under same humidity and temperature conditions prior to testing. Moisture uptake drops the tensile strength as well, and it is possible that it has a larger effect on the elastic modulus than on the tensile strength.

All the fibers have consistently exhibited some sort of 'aging' after being spun. The drawing of fibers becomes more difficult if stored for even small periods of time (2-3 days) after being spun, and the maximum attainable draw ratio also decreases. This phenomenon is not very well

Table 4.11 Comparison of tensile strength (<>) and Young's modulus ([]) of fiber MA119 after drawing under different conditions.

Drawing Conditions	Draw Ratio					
	3	3.19	3.66*	4.44	4.95*	5.15
Drawn at room temperature, 25 deg. C.	<245> [0.75]	-	-	-	-	-
Drawn at 65 deg. C.	-	<244> [0.69]	-	<252> [0.74]	-	<291> [0.80]
Drawn at room temperature, 25 deg. C, after immersing in water.	-	<251> [0.65]	-	<375> [0.67]	-	-
Drawn under a jet of steam at the feeding pulley.	-	-	-	<416> [1.1]	-	-
Drawn at room temperature to 3X, and then redrawn in second stage at 65 deg. C.	-	-	<370> [1.39]	-	<439> [1.53]	-

<> Strength is in MPa.

[] Modulus is in GPa

* Drawn in two stages.

understood at this point of time, but may relate to the influence of moisture absorption on the crystallization kinetics of the polymer at aging temperature. The possible existence of such effects can be examined in future studies.

In-line drawing of fibers was performed under several different conditions, and the results are tabulated in Table 4.12. It can be seen from this table that the in-line drawing at room temperature gives better results. The maximum attainable draw ratio during in-line drawing appeared to be decreasing with increase in draw temperature above room temperature. In-line drawing of fiber to 2.2X was tried at 65 °C, but a stable neck was not formed, resulting in varied fiber diameter. It can also be noted that in-line drawing using either of the two snubbing pins does not seem to affect the properties very much. The Young's modulus of these fibers as expected is increasing with increasing tensile strength and increasing draw ratio.

The WAXS patterns for two of these fibers, MI115 and MI120, are shown in Figure 4.21. The increase in crystalline orientation with increased draw ratio is accompanied by a slight increase in crystallinity, which can be seen clearly from these patterns.

Second stage drawing of the in-line drawn fibers was performed at 65°C, and the results are tabulated in Table 4.13. Fibers MI110, MI112, MI116, and MI120 were all drawn

Table 4.12 Strength and orientation in as-spun and in-line drawn fibers.

Fiber ID	Draw Ratio	Draw Temp. C	Birefringence	Percent Elongation	Tensile Strength, MPa	Modulus GPa	Snubbing Pin
MI110	3.00	50	0.0487	89	236	0.84	-
MA111	1.00	-	0.0280	355	90	-	-
MI112	3.00	60	0.0458	103	265	0.73	-
MA113	1.00	-	0.0313	325	99	-	-
MI114	3.73	R.T.	0.0450	100	333	1.07	Steel
MI115	3.80	R.T.	0.0450	63	379	1.27	Steel
MI116	3.00	R.T.	0.0454	105	273	0.73	Teflon
MA117	1.00	-	0.0338	346	96	-	-
MI118*	2.20	65	0.0444	249	167	0.41	-
MA119	1.00	-	0.0225	470	110	-	-
MI120	3.00	R.T.	0.0452	74	284	0.85	-

*Did not form a stable neck at this draw ratio.

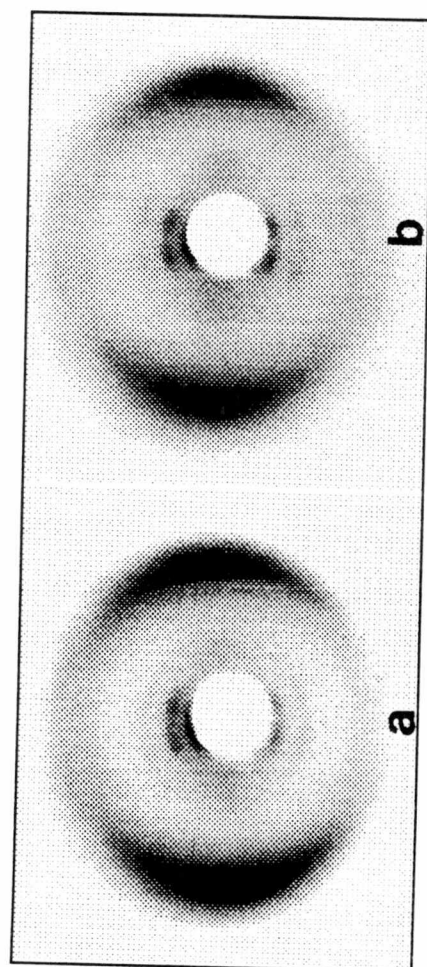


Figure 4.21 WAXS patterns showing the development of orientation during in-line drawing of fibers. (a) MI120 [ILD=3X], and (b) MI115 [ILD=3.8X].

Table 4.13 Strength and orientation in the in-line drawn fibers after redrawing at 65 deg. C.

Fiber ID	Overall Draw ratio	Birefringence	Percent Elongation	Tensile Strength, MPa	Modulus GPa
MI110-1	5.28	0.0586	36	459	1.56
MI112-1	3.97	0.0464	112	289	0.79
MI112-2	4.26	0.0559	40	395	1.49
MI112-3	5.40	0.0520	84	334	1.18
MI116-1	5.40	-	59	335	1.05
MI116-2	7.59	0.0602	71	323	1.19
MI116-3	8.40	0.0569	51	439	1.29
MI120-1	3.97	0.0551	96	291	0.88
MI120-2	5.38	0.0573	77	318	1.11
MI120-3	7.58	0.0557	79	366	1.16
MI120-4	8.40	0.0580	69	360	1.14
MI120-5	9.60	0.0555	32	420	1.65
MI116-1	4.94	0.0458	62	380	1.39
MI116-2	6.71	0.0633	46	501	1.60
MI117-1	5.03	0.0701	34	557	2.08

to 3X in-line, while fibers MI114 and MI115 were drawn in-line to 3.73X and 3.8X respectively. Comparison of the maximum tensile strength of these fibers shows that drawing in-line to a higher draw ratio helps in getting better strengths, although the overall draw ratio obtained may not be very high. This can also be supported by the fact that the maximum tensile strength obtained from fiber MI115 is higher than fiber MI114, in spite of having a lower molecular weight. As seen earlier, the elastic modulus of these fibers is also increasing with the tensile strength. It is noteworthy that the modulus of in-line drawn fibers increases very rapidly in the second stage drawing. This is not very much desirable for application as surgical sutures, and thus the draw ratio during in-line drawing needs to be carefully optimized. The highest draw ratio of 3.8X attained during in-line drawing was also confined due to the limitations of the present setup. In-line drawing to higher draw ratios may be possible with some other drawing apparatus.

As there were large diameter variations in fiber MI118, the results on secondary drawing of this fiber are presented separately in Table 4.14. These diameter variations were present until the fiber was drawn to the maximum draw ratio.

From the above results, it can be concluded that the best approach would be to draw the fiber in two stages, and

Table 4.14 Strength and orientation in fibers drawn in-line to 2.2X and redrawn at 65 deg. C.

Fiber ID	Draw Ratio	Birefringence	Percent Elongation	Tensile Strength, MPa	Modulus GPa
MI118-1	2.92	0.0463	143	234	0.62
MI118-2	3.95	0.0528	120	256	0.67
MI118-3	5.56	0.0590	135	274	0.77
MI118-4	6.16	0.0534	75	367	1.13
MI118-5	7.04	0.0500	107	234	0.71
MI118-6	8.40	0.0435	158	232	0.63
MI118-7	11.33	0.0604	65	487	1.48

the first stage drawing to be performed in-line at room temperature. This first stage draw should be at the highest draw ratio consistent with stable drawing process and desirable end properties.

Heat setting of fibers was contemplated to reduce the shrinkage that may occur due to high orientation, and to enhance the strength. It was observed that the fiber would melt and curl up if heated to a temperature of 120°C for heat setting. The maximum temperature for a stable heat setting process, as seen from the experiments, is 105°C. Heat setting of some fiber samples was done at 100°C and 105°C, and the results are tabulated in Table 4.15. Heat setting of these fibers appears to contribute more towards enhancement of modulus rather than the tensile strength as can be seen in the last two columns of this table. It can also be seen from the WAXS patterns in Figure 4.22, that the heat setting tends to perfect the crystal structure, and increase the crystallinity. Consequently if low modulus is desired, heat setting of these fibers may not be preferable. It would be a better idea to focus on optimizing a two stage drawing technique with first stage drawing performed in-line.

The percent crystallinity in PEA-10,2 fibers was calculated from their measured density using these values of crystalline and amorphous densities, as shown in Table 4.16.

Table 4.15 Comparison of strength and orientation after heat setting.

Fiber ID	Overall Draw ratio	Birefringence	Percent Elongation	Tensile Strength, MPa	Modulus GPa
MI115-2.1	4.64	0.0528	34.7	458	1.56
MI115-2.1H1	4.73	0.0545	34.8	465	2.20
MI116-2.1	3.66	0.0510	87.1	280	-
MI116-2.1H1	3.73	0.0546	66.9	271	-
MI116-2.2	6.99	0.0554	58.4	294	1.04
MI116-2.2H1	7.13	0.0605	45.6	369	1.48
MI116-2.2H2	7.13	0.0575	52.2	327	1.67
MI116-2.3	7.74	0.0573	35.5	426	-
MI116-2.3H1	7.89	0.0620	42.1	372	-
MI116-2.3H2	7.89	0.0576	52.4	359	-
MI118-6	8.40	0.0435	158	232	0.63
MI118-6H1	8.56	0.0542	68	341	1.26
MI120-4	8.40	0.0580	69	360	1.14
MI120-4H1	8.56	0.0605	60	363	1.51

H1- Heat set at 100 deg. C.

H2- Heat set at 105 deg. C.

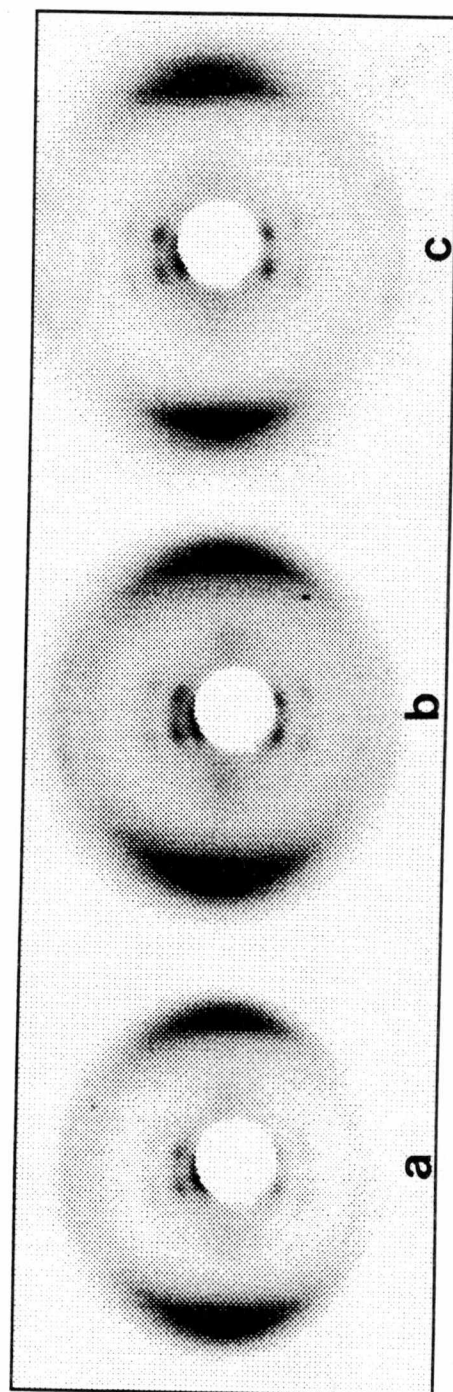


Figure 4.22 WAXS patterns for the fiber MI116-2.2 before and after heat setting. (a) MI116-2.2 as is, (b) MI116-2.2 heat set at 100 °C, and (c) MI116-2.2 heat set at 105 °C.

Table 4.16 Calculations of crystallinity in
PEA-10,2 fiber samples.

Fiber ID	Overall Draw ratio	Density gm/cm3	Percent Crystallinity	Modulus GPa
FW101-2	3	1.2076	2.0	-
FW101-3	4	1.2087	3.1	2.02
FW101-4	5	1.2089	3.3	-
FI109	3.7	1.208	2.4	-
FI109-1	4.7	1.2086	3.0	-
FI109-2	6.58	1.2092	3.7	-
MA111	[45]	1.2074	1.8	-
MA111-1	3.19	1.2075	1.9	0.71
MA111-3	7.13	1.2091	3.5	1.64
MA113	[95]	1.2075	1.9	-
MA117	[138]	1.2077	2.1	-
MA119	[22]	1.2065	0.8	-
MI120	3	1.2077	2.1	0.85
MI115	3.8	1.2076	2.0	1.27
MI116-2.2	6.99	1.2102	4.7	1.04
MI116-2.2H1	7.26	1.2127	7.3	1.48
MI116-2.2H2	7.26	1.2139	8.5	1.67

Values in [] are drawdown ratios.

The crystallinity estimations in a few fibers spun using the Fourne extruder are also presented in the same table for the sake of comparison. It can be seen that the crystallinity values for all these fibers are very consistent. However, the crystallinity in all of these fiber samples is fairly low. The crystallinity does not increase very much during drawing, but increases significantly during the heat-setting step. This also explains the increase in modulus observed after the heat setting of these fibers as shown in column 4 of the table.

A few fiber samples were also tested without conditioning in order to compare the present values of tensile strength with previous results. These results are in Table 4.17. The strength of fibers appears to decrease slightly after conditioning, which may be simply due to higher moisture content. The drop in strength for the heat-set fibers is comparatively lower, but more information is needed to confirm these results.

During the spinning of polymer PEA-6,2, it was observed that the fibers remained tacky when they reached the godet. Additional cooling obtained by blowing air upwards along the spinline helped to some extent, but did not completely eliminate this problem. Some fiber was collected with air-cooling, and another fiber sample was collected with the water quench technique. These preliminary results are

Table 4.17 Effect of conditioning on the tensile strength.

Fiber ID	Tensile Strength, MPa	
	As is	Conditioned
MI116-2.1	313	280
MI116-2.1H1	277	271
MI116-2.2	374	294
MI116-2.2H1	395	369

tabulated in Table 4.18. Although these results are inconclusive, it can be seen that fiber MA621 which was spun with a low drawdown ratio, exhibits good elongation to break during the tensile testing. This fiber after being drawn during tensile testing, was again tested for its strength, and it surprisingly gave the highest strength of all the fibers tested. This indicates that the optimum drawdown ratio for PEA-6,2 fibers would be lower than that for PEA-10,2 fibers, together with a very low initial molecular orientation. The WAXS patterns for fiber MA624 in as-spun form and after drawing are shown in Figure 4.23. It can be seen from these patterns that the crystalline orientation is somewhat more as compared with PEA-10,2 fibers of similar draw ratio. It can also be seen that the crystalline orientation increases rapidly at relatively low draw ratios, combined with increasing crystallinity.

The in-line drawing experiments could not be performed on this polymer as the quantity of polymer was insufficient. All of the PEA-6,2 fibers were processed from only 200 gm of starting material, using the present setup.

Table 4.18 Strength and orientation in PEA-6,2 fibers.

Fiber ID	Draw ratio	Draw Temp. C.	Birefringence	Tensile Strength, MPa	Modulus GPa
MA621	1	-	0.0024	54	-
MA622	1	-	0.0181	84	-
MA623	1	-	0.0149	65	-
MA624	1	-	0.0170	84	-
MA623-1	2.4	60	0.0377	139	1.54
MA623-2	3	60	0.0504	238	2.08
MA623-3	3	80	0.0459	169	1.7
MA623-4	2.5	25	0.0357	191	1.62
MA624-1	2.5	60	0.0393	165	1.44
MA624-2	3	60	0.0455	147	1.31
MA624-3	3	80	0.0586	316	2.93
MA624-4	2.5	25	0.0460	179	0.92
MA621-1	~5.7	19	-	355	-

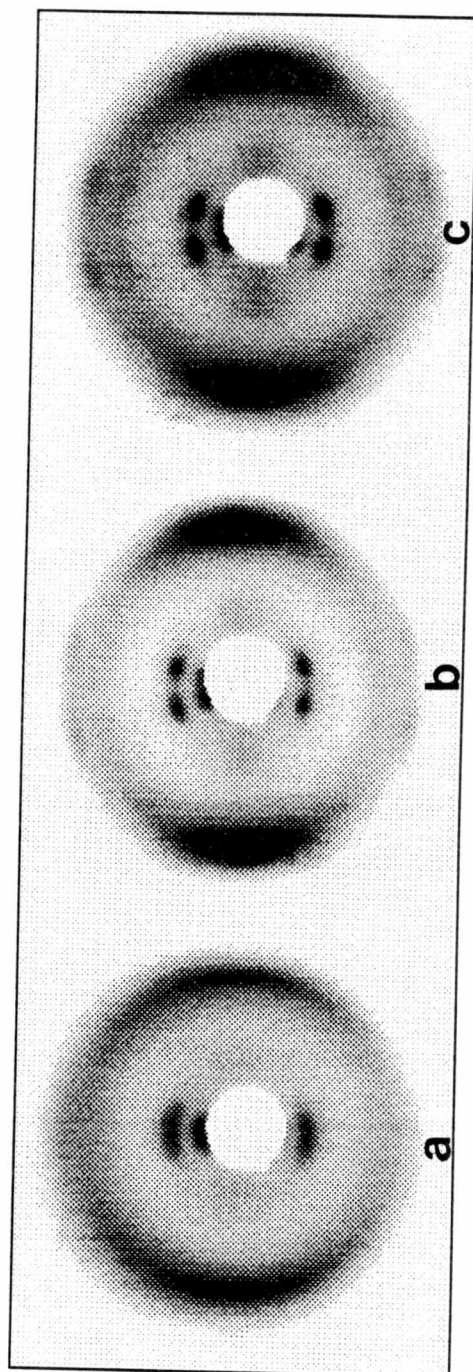


Figure 4.23 WAXS patterns for the fiber MA624 showing the development of orientation and crystallinity during drawing. (a) MA624 as spun, (b) MA624 drawn 2.5X, and (c) MA624 drawn 3X.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

The results obtained from the present work are the first in the studies of processing and characterization of PEA monofilaments. In most cases, a thorough understanding and careful investigation of all the aspects is required to come to any *conclusion* from the experimental results. However, there is always some starting point, and the conclusions in this chapter follow largely from the results obtained during the present study. Appropriate recommendations are made for further research, based on these conclusions.

5.1 CONCLUSIONS

- The densities of amorphous and crystalline phases of polymer PEA-10,2 are found to be 1.2057 ± 0.0004 gm/cm³ and 1.3095 ± 0.0057 gm/cm³, respectively. The unit cell in the crystal structure of PEA-10,2 fibers is proposed to be pseudo-hexagonal, with $a = 0.491 \pm 0.001$ nm, and $c = 2.2496 \pm 0.0005$ nm. There appears to be another form of crystal structure present in randomly oriented PEA-10,2 films.
- Moisture absorption decreases the glass transition temperature of the PEA-6,2 polymer. This drop is about 47 °C for ~6% moisture content.

- Good monofilaments can be produced by melt spinning and drawing of PEA polymers with an initial of $IV \geq 1.0$. These filaments solidify very slowly on the spinline, and an efficient cooling method has to be adopted to overcome this problem. A radial flow air cooling chimney can be used for this purpose. A cold water quench before take-up also works equally well, and does not seem to have any direct effect on the filament structure and properties. Another alternative would be quenching in a dry ice-acetone bath to eliminate any contact with water.
- The molecular weight of the PEA polymers drops substantially during the melt spinning process. This is due to the instability of the polymer at high temperatures, and is dependent on its residence time at high temperatures, other conditions being same. Decrease in molecular weight tends to adversely affect the drawability and the tensile strength of PEA-10,2 fibers, in the range of molecular weights studied. Reducing the residence time during extrusion helps in preserving the molecular weight of these polymers, and the Maxwell extruder can be used for this purpose. The use of this technique together with a thermally stable grade of polymer PEA-6,2 yields significantly higher molecular weights in fibers. The molecular weight retention in this case is much superior as compared with the results of melt spinning of other biodegradable polyesters. This

indicates a need for specialized machinery for processing of thermally degradable polymers.

- PEA polymers containing up to 50% NMP can be extruded easily, but the optimum solvent concentration seems to be around 20% NMP. The extrusion temperatures correlate well with the melting peak on the DSC.
- The weight average molecular weight and the initial molecular orientation have a combined influence on the drawability of PEA fibers. Drawdown ratios in the range of 20-50 (Birefringence of 0.02-0.03) during spinning seem to be the optimum for subsequent drawing of polymer PEA-10,2. However, the optimum drawdown ratio for polymer PEA-6,2 seems to be much lower. PEA-6,2 fibers with very low initial molecular orientation (Birefringence ~0.002) exhibit better drawability.
- The best approach to achieve higher tenacities in PEA-10,2 fibers would be to perform the drawing in two stages, with the first stage drawing done in-line at room temperature. Higher temperatures above room temperature adversely affect the in-line drawing process. The use of steel or Teflon snubbing pins during in-line drawing does not seem to alter the properties very much. Higher draw-ratios during in-line drawing yield higher strengths after subsequent drawing, at least in the range of draw-ratios attained in present experiments. The elastic

modulus of fibers processed in this manner increases rapidly during the second stage drawing, but this may not be desirable for application as surgical sutures. This technique thus needs to be optimized carefully, with the first stage draw at the highest draw ratio consistent with a stable drawing process and desirable end properties.

- Heat setting of PEA-10,2 fibers does not improve their tensile strength very much, for the fibers having higher initial strength. It does increase the elastic modulus and the crystallinity in these fibers.

5.2 PROPOSED RESEARCH

Further studies should be performed to determine the optimum processing conditions for PEA-6,2 polymer. The effect of several processing variables has already been studied for PEA-10,2 polymer, and this knowledge would be helpful in these studies. The drawing of PEA fibers with moisture plasticization seems to give encouraging properties as discussed in Section 4.3, and it would be worthwhile to study this aspect. PEA-6,2 fibers also show a higher elastic modulus compared to the PEA-10,2 fibers, which is contrary to the expectations. The suitability of these materials for application as surgical sutures can be studied with more specialized test methods, which directly reveal the information on the properties of interest. As the moisture

acts as a diluent and depresses the T_g , it would tend to soften the material. Thus the premoistening of PEA sutures may improve their handling characteristics during a surgery.

The value of theoretical density should be calculated for the PEA-6,2 polymer. A similar approach as used for the calculation of theoretical density of PEA-10,2 polymer, can be used. The value of amorphous density should also be determined for PEA-6,2 polymer, for use in calculation of the crystallinity in this polymer by measuring its density. The crystal structure(s) in PEA-10,2 and PEA-6,2 polymers could also be studied in detail. The possible existence of different structures in PEA-10,2 fibers and films should also be investigated.

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