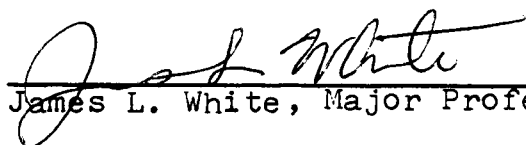
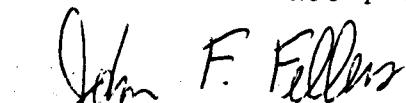
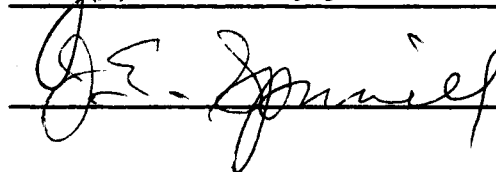


To the Graduate Council:

I am submitting herewith a thesis written by John Edmond Flood, entitled "The Formation and Characterization of Biaxially and Uniaxially Oriented Poly (p-Phenylene Terephthalamide) Films from Liquid Crystalline Solutions." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.


James L. White, Major Professor

We have read this thesis and
recommend its acceptance:

Accepted for the Council:


Vice Chancellor
Graduate Studies and Research

THE FORMATION AND CHARACTERIZATION OF BIAXIALLY AND
UNIAXIALLY ORIENTED POLY (p-PHENYLENE
TEREPHTHALAMIDE) FILMS FROM LIQUID
CRYSTALLINE SOLUTIONS

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

John Edmond Flood

June 1982

3060765

DEDICATION

This thesis is dedicated to my wife, Alice, my mother, Marie, and to the memory of my father, Sergeant Major John J. Flood.

ACKNOWLEDGMENTS

The author wishes to thank professors John F. Fellers and James L. White for giving him the chance to work under them and for their guidance and understanding throughout this project.

The author is indebted to the Department of the Navy for their financial support in this research.

The author wishes to thank the Polymer Engineering faculty and students, in particular Carl Wust and Daniel Harwood for their useful advice throughout the course of his work.

The author also wishes to thank Ted Long and his co-workers in the Electronics Shop, Tommy Thompson and his co-workers in the Machine Shop, and Al Carter and his co-workers in the Facilities Shop.

ABSTRACT

An annular die and oil coated mandrel in conjunction with a wet extrusion operation is used to produce biaxially oriented poly (para-phenylene terephthalamide) PPD-T film. Extruded and uniaxially drawn films are also produced without the mandrel. The PPD-T is dissolved in 100% sulfuric acid at a concentration of 17% by weight. Water, methanol, ethanol, and combinations of water and alcohol are used as coagulants for the above process. At 17% by weight, PPD-T/H₂SO₄ solutions are liquid crystalline.

It is shown through mechanical testing and wide angle x-ray diffraction techniques using orientation functions and pole figures that a relatively high level of biaxial orientation is achieved using the mandrel process. The above techniques were also used to characterize extruded and uniaxially drawn films. Indications of fairly high tensile strengths were found, as high as 16,000 psi for mandrel processed films and 37,000 psi for uniaxially drawn films. It is believed that the liquid crystalline nature of the PPD-T/H₂SO₄ solutions contribute greatly to the high levels of orientation and good strength characteristics achieved in PPD-T films.

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CHAPTER I

INTRODUCTION

In 1972, Kwolek (49) of DuPont was issued her now famous patent dealing with the synthesis of Kevlar^R, PPD-T. In the same patent, PPD-T dissolved in sulfuric acid was wet spun to produce heat resistant, very high strength, high modulus fibers. She determined that her solutions were anisotropic or liquid crystalline at certain temperatures and concentration ranges. It was believed that the liquid crystalline nature of these solutions led to the very high levels of orientation and strength in Kevlar^R fibers. Rapid development by DuPont led to Kevlar^R fibers being used as tire cord, bullet proof vests, and composites for airplane and automobile parts to reduce weight and add strength. The market appears to be expanding rapidly with new uses being found daily.

Fibers give strength and orientation in only one direction. The only way to achieve biaxial strength would be to weave the fiber. Therefore, the next logical step for this new technology would be to produce high strength, high modulus biaxially oriented Kevlar^R films. Some possible uses for these films would be as composites with other polymers to produce high strength, light weight parts for automobiles, airplanes, and military vehicles.

The films by themselves would be a relatively high strength fabric for use as protection against heat and other injuries in hazardous occupations. Certainly many other uses could be found for such a material.

There were attempts at the University of Tennessee to produce a biaxially oriented Kevlar^R film (5) using a blown film process. The resulting films had a great deal of uniaxial orientation, since high blow up ratios were difficult to achieve. These early failures led to the development of the present mandrel process which is believed to be the most effective method for the production of biaxially oriented, high strength Kevlar^R film. The following chapters attempt to explain the mandrel process and its history in detail as well as explain how uniaxially oriented films may be produced. There will also be chapters dealing with molecular orientation as determined through WAXS techniques and mechanical properties of the films. The superstructure of the films, as seen using scanning electron microscopy, will also be the subject of a chapter.

CHAPTER II

BACKGROUND

A literature survey is necessary to understand the developments leading up to the present mandrel process. It is important to understand the nature of polymer liquid crystal systems, and, hence, their possible applications in terms of industrial processes. There will be a review of the kinematics and dynamics of the blown film and mandrel film processes in order to better understand how these processes induce orientation into polymer films. Also, included is a survey of X-ray diffraction techniques to determine orientation in polymer film.

A. Classification of Polymer Liquid Crystals

Liquid crystals are categorized into three groups: nematic, smectic, and cholesteric (27). Nematic liquid crystals exhibit one dimensional order while cholesteric liquid crystals possess order similar to nematic, but with a superimposed twist. The smectic state is a layered structure with two dimensional order. Variations exist within the smectic state involving tilting or twisting within the liquid crystal. Examples of all three may be seen in Figure 1.

Low molecular weight liquid crystals exhibit all three forms (27). Some pure low molecular weight organic

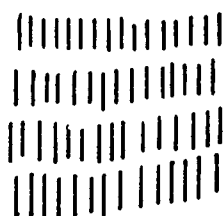
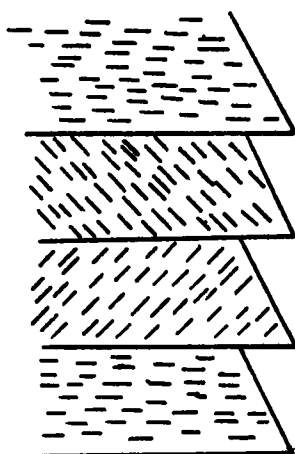
**NEMATIC****SMECTIC****CHOLESTERIC**

Figure 1. The Three Liquid Crystal States; Nematic, Smectic, and Cholesteric.

compounds may exhibit a smectic and nematic state dependant on temperature. Polymer liquid crystals seem to always be nematic or cholesteric.

Liquid crystal systems may also be classified as being thermotropic or lyotropic (27). Thermotropic liquid crystals form through the action of heat alone on pure substances or mixtures of substances. Lyotropic liquid crystals are the result of a two component system in which liquid crystalline behavior occurs in a certain concentration range. Most of the known polymer liquid crystals are lyotropic.

B. Synthetic Polymer Liquid Crystals and Their Fibers

Polypeptides

The first synthetic polymer liquid crystal to be discovered was poly (γ -benzyl-L-glutamate), P γ BLG (20). Elliott and Ambrose of Courtaulds (20), preparing oriented films of P γ BLG, observed the formation of a spontaneously birefringent liquid phase in a chloroform solvent. The birefringent phase consisted of large numbers of spherulites.

Investigations by Robinson (75, 76, 77) with P γ BLG confirmed the results of Elliott and Ambrose. It was found that the birefringent region was due to liquid crystal formation. Robinson expanded these observations and noted a similarity between the supramolecular structures

of polypeptides in solution and thermotropic low molecular weight cholesteric liquid crystals. He proposed an arrangement involving planes of parallel polypeptide helices. The planes were equidistant from each other with a slight angular displacement relative to adjacent planes; see Figure 1 .

In order for the anisotropic phase to form from P γ BLG in solution, the polymer must be in a semi-rigid α helix form (4). The form consists of helical polypeptide chains. Hydrogen bonding between the CO and NH groups add to the rigidity (67, 90). Studies by Downie et al. (19) confirmed the existence of the α helix in concentrated solutions in most solvents.

Later investigations by Robinson et al. (76) found that the critical concentration of P γ BLG was dependant on the molecular weight. As molecular weight increased, the critical concentration decreases. This was in accordance with a theory proposed by Flory (23) involving the ability of rigid rodlike macromolecules to arrange themselves randomly in a concentrated solution.

Ballard, of Courtaulds, (8) describes a method for the wet and dry spinning of polypeptide solutions to produce artificial fibers. The polypeptides he used most extensively were poly (γ -methyl-L-glutamate) and poly (γ -methyl-D-glutamate). The resulting fibers, following a subsequent drawing step, consisted mostly of

polypeptides in the β configuration, that is, the fully extended form. The spun fibers formed were mainly in the α configuration. Stretching the thread resulted in a transformation of the polymer fibers to the β form.

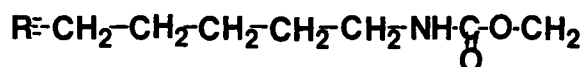
Uematsu and Uematsu and their co-workers (92) have investigated the optical properties of cholesteric polypeptide solutions in more recent years. Miller and Wee (52) have developed phase diagrams for P γ BLG and its solvents.

Other polypeptides that have been investigated for liquid crystalline characteristics are:

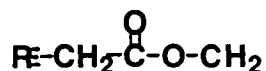
poly (glutamic acid) (83)



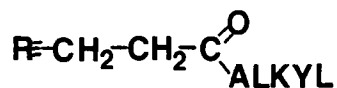
poly (E-carbobenzyloxy-L-lysine) (78)



poly (β -benzyl-L-aspartate) (77)



poly (γ -alkyl-L-glutamate) (77)



where the alkyl is methyl (P γ MLG), ethyl (P γ ELG), propyl, butyl, amyl, hexyl, or cyclohexyl.

Cellulose Derivatives

Panar and Willcox (65) first reported liquid crystalline characteristics in a variety of cellulose derivative solutions. In the same period, Werbowyj and Grey (96) reported studies for hydroxypropylcellulose, HPC, solutions which were later confirmed and extended by Onogi et al (62). These observations were extended to other systems by Bheda, Fellers, and White (9, 10), and Aharoni (1). It was shown by Onogi, White, and Fellers (63), and Asada et al. (6) that high levels of birefringence and orientation could be achieved during flow in solutions of HPC and water. Bheda et al. (9) made similar studies for cellulose acetate butyrate. He spun fibers from several liquid crystalline solutions involving cellulosic derivatives.

Rheological and birefringence studies have been done on bulk HPC by Shimamura, White, and Fellers (81) which served to indicate thermotropic liquid crystal behavior. Extruded filaments had skin-core structures with highly oriented outer layers. This was believed due to orientation achieved during flow in the die and reservoir. Fibers were also melt spun.

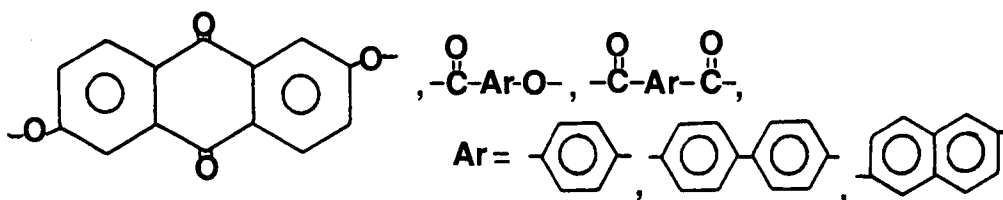
Polyesters

Kuhfuss and Jackson (36, 37, 38) of Tennessee Eastman have prepared copolymers by acidolysis of poly (ethylene terephthalate), PET, with poly (acetoxymethoxybenzoic acid and

by reacting PET copolyester with methyl-p-hydroxybenzoate which exhibit liquid crystalline behavior.

At DuPont, Pletcher (72) and Kleinshuster (43) have developed largely aromatic copolyesters similar to the Eastman polyesters which exhibit liquid crystalline behavior.

Warner and Jaffe (94) and Warner (93) of Celanese describe polymers based on the structures listed below which exhibit similar characteristics:



Calundann, also of Celanese (15), describes aromatic polyester fibers with tensile strength of 17,000 psi, a tensile modulus of 9.9×10^5 psi, and percent elongations of 2.7.

Aromatic Polyamides

1. Synthesis

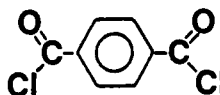
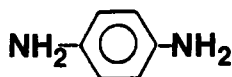
DuPont, from the early sixties to the early and mid-seventies, was issued a series of patents dealing with the synthesis of wholly aromatic polyamides (33, 48, 49, 87). In many cases, a flame resistant material was the main objective. Most synthesis processes involved a low

temperature, aqueous, polycondensation method using aromatic amines and aromatic acid halides.

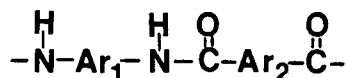
In 1972, Kwolek (49) of DuPont, was issued her now famous patent involving the polymerization and processing of poly (p-phenylene terephthalamide) PPD-T. Her method of polymerization involves reacting an aromatic diamine, p-phenylenediamine, and an aromatic diacid chloride, terephthaloylchloride. The amine groups in the aromatic diamine and the acid chloride groups in the diacid chloride must be attached in the para position on the benzene rings.

p-phenylenediamine

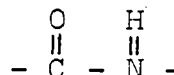
terephthaloylchloride



The polymer was obtained by agitating an aqueous solution of the above two monomers in a cyclic non-aromatic oxygenated organic solvent. The reaction proceeds at temperatures below 100°C. The polymer structure produced was:



where, in the case of PPD-T, Ar_1 and Ar_2 are para linked benzene rings. The term aromatic polyamide is due to the repeat units linked by the following group:



Examples of solvents used were hexamethylphosphoricamide and N-methyl-2-pyrrolidone.

2. Dilute Solutions of P-Linked Amides

Schaeffgen et al.(79) found that in dilute solutions the intrinsic viscosity-molecular weight relationship, the Mark-Howink equation, gives an "a" value of 1.7 for low molecular weight poly (p-benzamide) and 1.08 for high molecular weight samples. Their values suggest a semi-rigid model for p-linked aromatic chains. Kwolek (49) derived similar results in her patent. Strazielle's and Arpin's (86) investigation of dilute solutions of p-linked aromatic polyamides revealed results similar to Kwolek (49) and Schaeffgen et al. (79).

3. Characteristics of Concentrated PPD-T/H₂SO₄ Solutions

Kwolek (49), in her 1972 patent, found that when PPD-T is dissolved in 100% sulfuric acid at the appropriate concentrations, an optically anisotropic solution resulted. She demonstrated the transition from an isotropic solution to an anisotropic solution for poly (p-benzamide) in HF by plotting viscosity as a function of polymer concentration by weight percent. The result was a maximum in solution viscosity as the solution passes into the anisotropic region. This maximum was representative of the critical concentration at a particular temperature and inherent viscosity; see Figure 2.

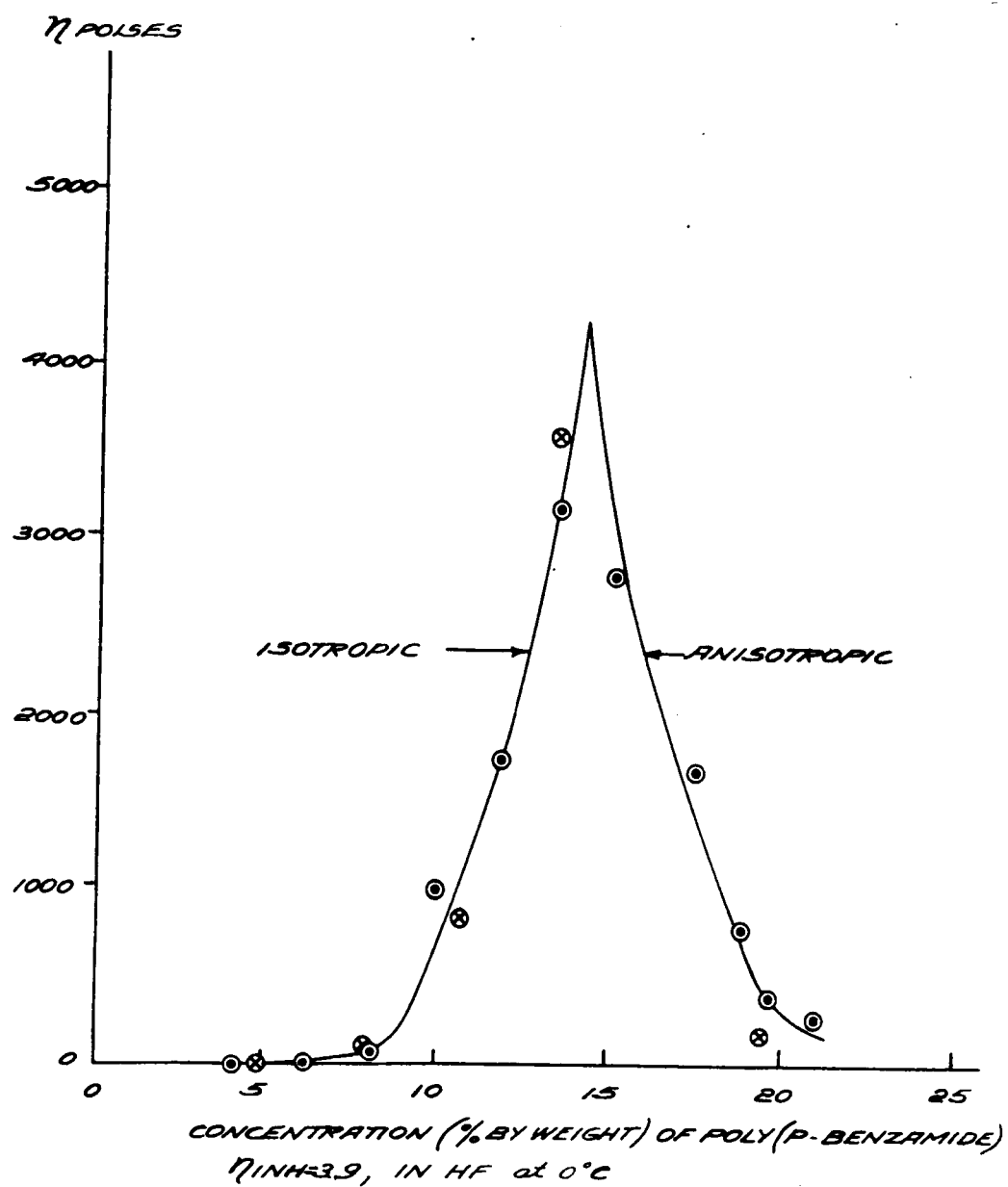


Figure 2. Kwolek's Plot of Viscosity Versus Concentration for poly (p-Benzamide).

In Figure 3, Kwolek presents a phase diagram for PPD-T and sulfuric acid indicating a need for acid concentrations of at least 99% to produce optically anisotropic solutions. The critical concentration is also represented in the same diagram as 8.7 weight percent PPD-T.

Blades' 1973 and 1975 patents (11) discuss degradation problems associated with PPD-T/H₂SO₄ dopes. He suggests a sulfuric acid concentration of 99.8% to keep water content down and to reduce hydrolysis. Mixing temperatures should be kept below 90°C. Higher PPD-T concentrations also tend to reduce the activity of the sulfuric acid.

In the second of these patents, Blades discusses melting temperatures of PPD-T/H₂SO₄ solutions at different concentrations. The melting temperature was found to increase as polymer concentration increases. Polymer dopes of 17%, 21%, and 25% by weight were shown to melt at the temperatures 40°-50°C, 63°-65°C, and 72°-82°C respectively.

The temperatures at which the solutions begin to go from an anisotropic state to an isotropic state were determined. For concentrations of 17%, 21%, and 25%, the temperatures were 80°-100°C, 82°-135°C, and 110°-122°C respectively. Even at these higher temperatures, the solutions were still mostly anisotropic.

In a more recent paper, Kulichikhin et al.(44) gave phase diagrams for PPD-T in sulfuric acid. They plotted

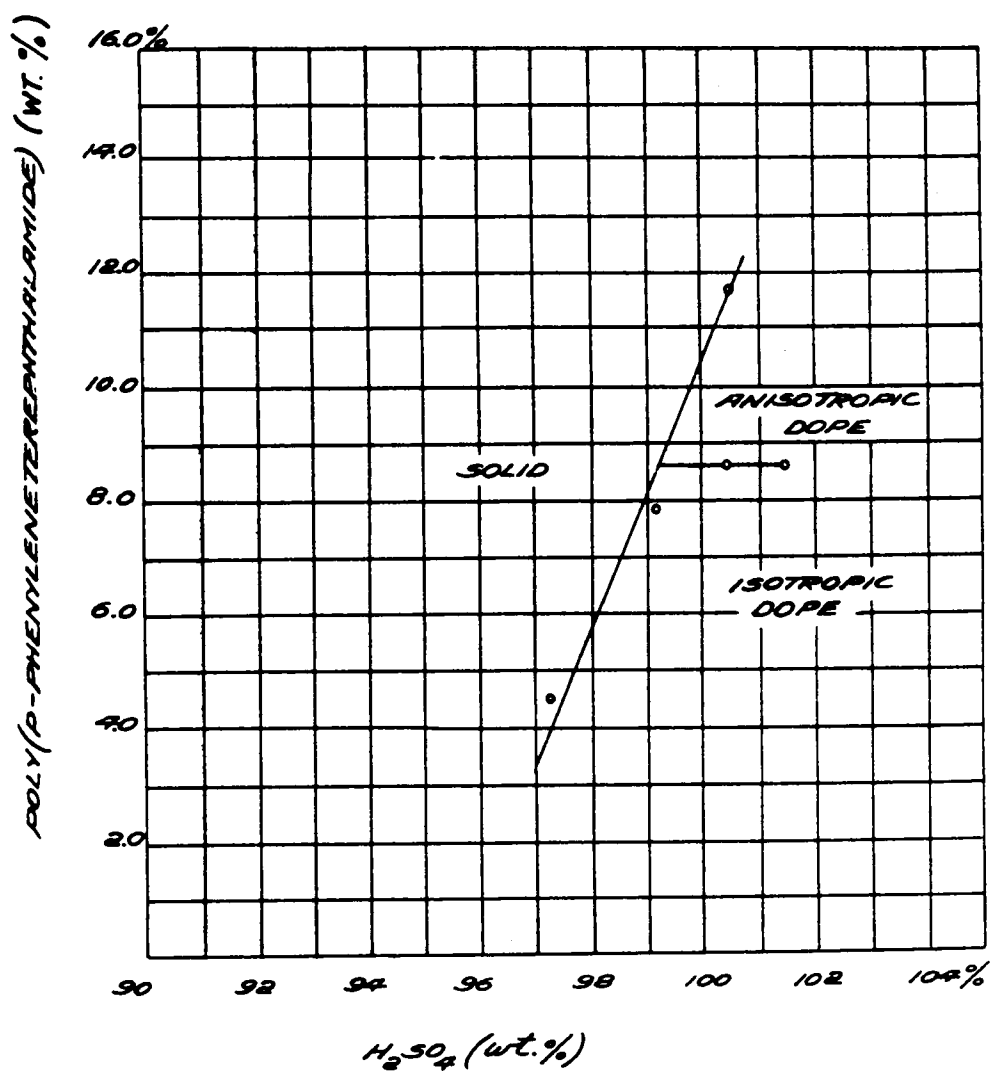


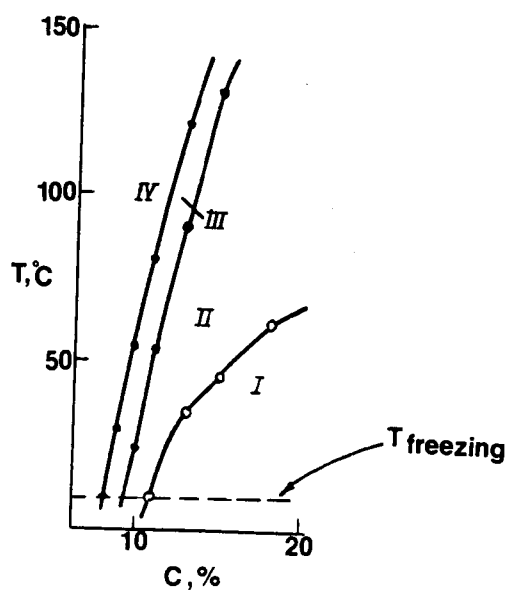
Figure 3. Kwolek's Phase Diagram of PPD-T and H_2SO_4 .

temperature versus polymer concentration and noted the temperatures at which the anisotropic to isotropic transition was taking place; see Figure 4.

Observations by Kwolek (49) and Panar and Beste (64) of PPD-T/ H_2SO_4 solutions tell of the existence of birefringent spheres in the transition regions and nematic or threadlike structures in wholly anisotropic solutions. Onogi et al. (62) and Aoki et al. (5), using a polarizing microscope, show the existence of negative spherulites in the transition regions of PPD-T and Cl-PPD-T solutions. Negative spherulites suggest that the macromolecules are oriented in a circumferential or tangential manner in relation to the spherulite radius. In solutions of 9% PPD-T/ H_2SO_4 , the average size of the spherulites was about 50 microns. Observations of wholly anisotropic solutions agreed with Panar and Beste (64), that is, nematic crystals were observed.

4. Rheological Properties

Kulichikhin et al. (44) studied the flow of anisotropic solutions of PPD-T and sulfuric acid. Figure 5 is a plot of viscosity versus polymer concentration. The transitions from the isotropic to anisotropic phase may be seen as a sharp decrease in viscosity. The large increase in viscosity past this transition point was attributed to the onset of a solid phase.



The solid anisotropic region is I, the liquid anisotropic region is II, the two phase region is III, and the isotropic region is IV.

Figure 4. Kulichikhin et al.'s Plot of Temperature Versus Polymer Concentration for PPD-T/H₂SO₄ Solutions.

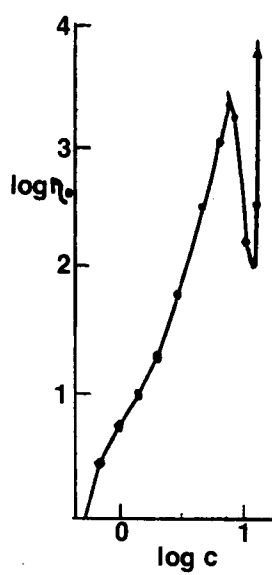


Figure 5. Kulichikhin et al.'s Plot of Viscosity Versus Polymer Concentration for PPD-T/H₂SO₄ Solutions.

Aoki et al.(4) have done studies of aromatic polyamides in solution. Using Kwolek's DDA test (49), they found Kevlar/H₂SO₄ solution's critical concentration to be between 9 and 9.5 percent by weight; see Figure 6a. Viscosity shear rate data reveals a largely Newtonian response for solutions below 10% and a non-Newtonian response for those solutions above 10% by weight; refer to Figure 6b. In plots of viscosity versus shear stress for anisotropic solutions in flow, it was observed that shear stresses never went below a critical value; see Figure 7a. Viscosity versus concentration plots, as seen in Figure 7b, demonstrates the transition from the isotropic to anisotropic phase.

5. Fiber Formation from Aromatic Polyamides

Patents dealing with fiber formation from aromatic polyamides may be found as early as 1961 (33). One of the first patents describing a wet spinning process in detail involving aromatic polyamides is King's 1963 patent (42). One of the polymers he used was poly (m-phenylene-isophthalamide), MPD-T, which he spun from an 18% solution of MPD-T, dimethylacetamide, DMA, and calcium chloride. The solution was spun from a 100 hole spinneret, with each hole having a .003 inch diameter, into aqueous coagulation baths with varying amounts of calcium thiocyanate and DMA, usually around 50% and 10% respectively. The coagulation bath temperatures ranged

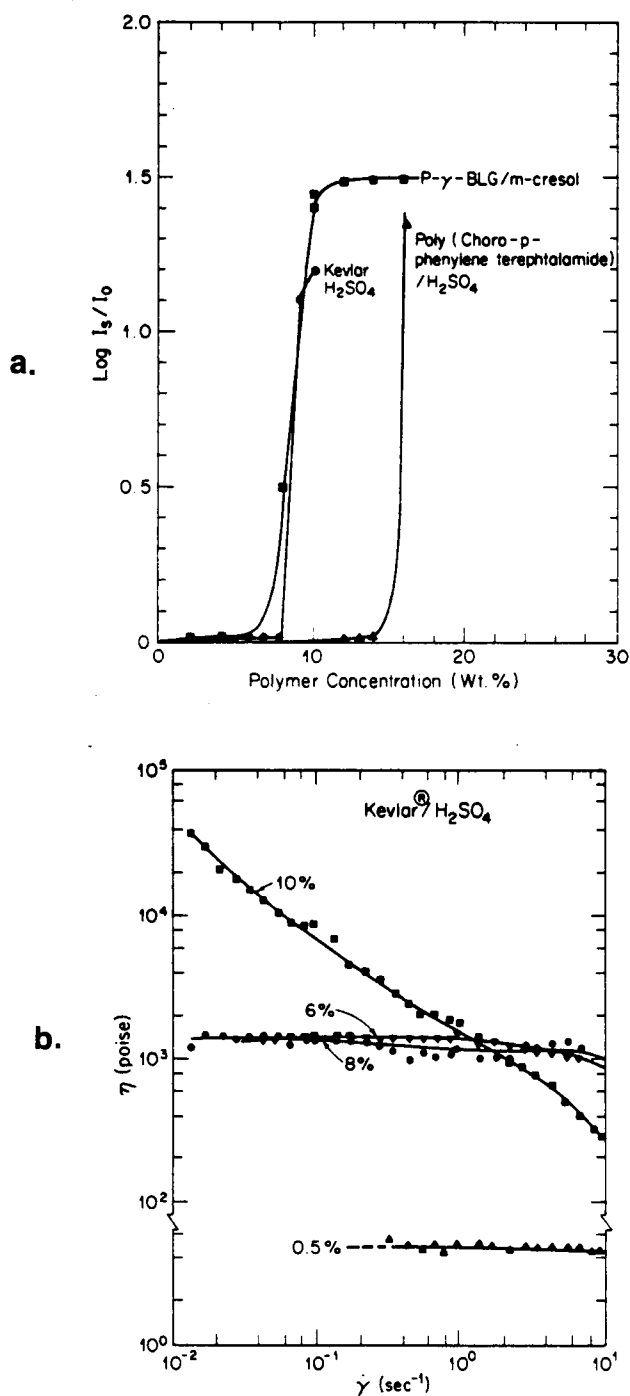


Figure 6. Aoki et al.'s Plots of (a) Light Intensity Versus Polymer Concentration and (b) Viscosity Versus Shear Rate for PPD-T/ H_2SO_4 Solutions.

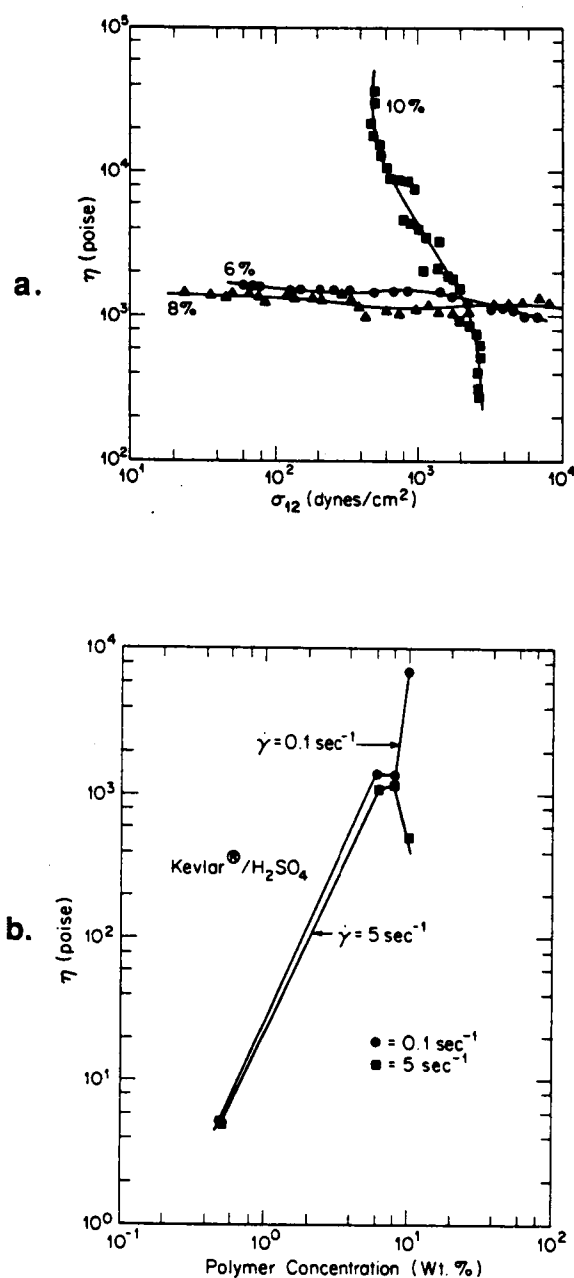


Figure 7. Aoki et al.'s Plots of (a) Viscosity Versus Shear Stress and (b) Viscosity Versus Concentration for PPD-T/H₂SO₄ Solutions.

from 50° to 110°C. Extrusion temperatures for the polymer solution ranged from 15° to 30°C. Following coagulation, the polymer was drawn over a heated surface of about 300°C to further "crystallize" it. The mechanical properties of the resulting fibers were: modulus 150-180 gpd, tenacity 8 gpd, and percent elongations 10% to 13%.

Morgan of Monsanto (55) developed a dry-jet wet spinning process in which the extruded fiber is spun through a gaseous medium 1/8 to 1 1/2 inches into a coagulation bath. According to the patent, the gaseous medium allows for instantaneous skin-core formation to begin before the fiber enters the coagulation bath. Polymer concentrations ran from 10% to 30% by weight, with extrusion temperatures ranging from 30° to 120°C. Some examples of the polymers used were poly (m-phenylene-isophthalamide) and poly (4'-4-diaminobenzanilide terephthalamide). Solvents used were dimethylformamide and dimethylacetamide containing up to 10% metal salts such as lithium chloride and calcium chloride. The coagulation bath consisted of 0% to 40% of dialkylamide in water. The temperatures in the coagulation bath ranged from 10°C to 50°C, preferably 15°C to 25°C.

Following the coagulation of the fiber was an orientation step in which the fiber was relaxed or stretched as much as four times its length in a hot water or boiling water bath. Temperatures ranged between 50°C and 100°C. The fiber was then taken through a washing step in water.

Kwolek's (49) 1972 patent involving the synthesis of PPD-T also discusses a wet spinning process. An anisotropic solution of PPD-T and H_2SO_4 is spun through a thick precious metal spinneret into an aqueous coagulating bath near 40°C . Coagulation baths consisted of water, ethylene glycol, and methanol. The yarn was drawn through the bath around rollers, usually making more than one pass through the bath. It was then taken up on a bobbin and washed with cool running water. Heat treatment involved passing the wet, washed yarn through a tube at temperatures between 400°C and 600°C and speeds of 25 ft/min. PPD-T fibers from this invention exhibited high degrees of crystallinity and tensile moduli as high as 900 gpd and tenacities close to 15 gpd.

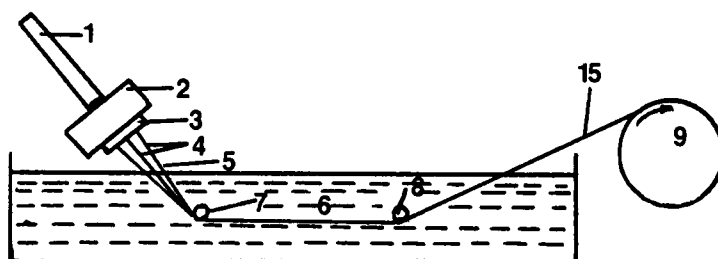
Blades' (11) 1972 and 1975 patents for DuPont are similar to Kwolek's except that a jet-dry wet spinning process was used to induce higher levels of orientation; see Figure 8.

Fibers from the above patents had tenacities as high as 32 gpd, a modulus as high as 950 gpd, and percent elongation values of around 3%.

C. Tubular Film Formation

General

The most widely used methods for thin film production is the blown film process. In a tubular blown-film process,



The spin dope is pumped through transfer line 1 through a spinning block 2, through the orifices of the spinneret 3, through the layer of gas 5, and into the coagulating liquid 6, where the filaments, 4, are conducted under guides 7 and 8 and as spun yarn, 15, is wound upon a bobbin 9.

Figure 8. Blades' Dry Jet Wet Spinning Process for Kevlar^R Fibers.

the polymer melt is extruded upward from an annular die onto nip rollers which draw the film upward and provide an air-tight seal. Air is blown into the tube through the die to provide a small pressure gradient across the film surface, thereby expanding the bubble and providing stress in the radial direction. An air ring is used to cool the hot bubble rapidly to solidify the film below the nip rolls; see Figure 9.

Two early patents from the Visking Corporation (24, 80) describe two film blowing methods in which a screw extruder is used to extrude the molten polymer and large rotating nip rollers are used to take up the tubular film. In the same year as the above patents, Modern Plastic Machinery Corporation (91) was issued a patent dealing with tubular film blowing. In this case, the film was extruded downward with air being supplied from below the film and not through the die. Some other patents of interest during this period were issued to W. J. Johnson (39, 40), R. C. Kress (45), and C. A. Kronholm (47).

In 1965, G. W. Cheney and F. Hughes of Dow (16) were issued a patent describing a method for blown tubular film production in which air pressure is supplied to the inside of the film by means of a "centrally located distributor." One of the main objectives of this patent was to provide a method to efficiently control temperature, that is, cooling, and still induce orientation into the film.

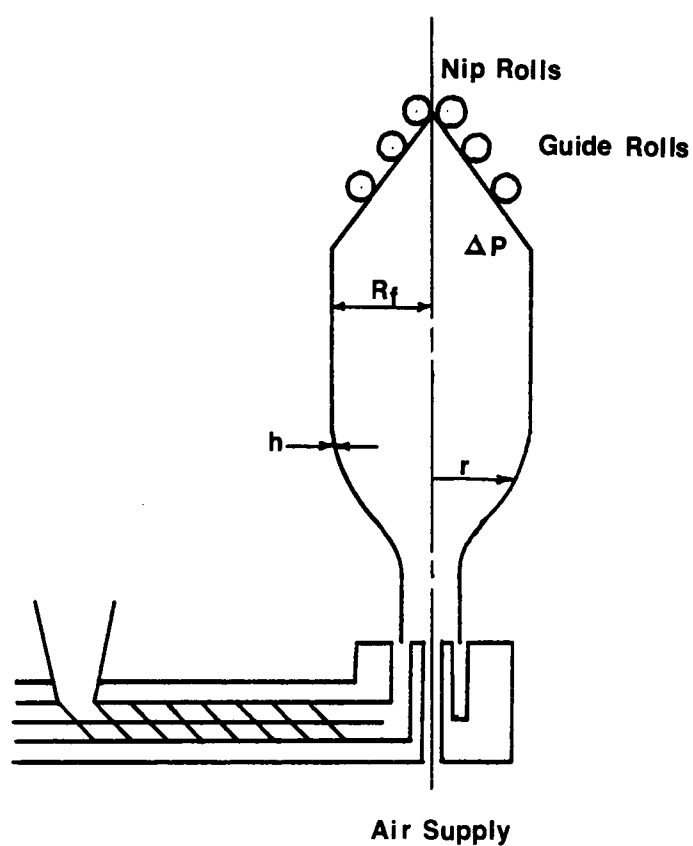


Figure 9. Schematic of a Typical Blown Film Process for Polymer Melts.

Kinematics of Blown Films

Pearson and Petrie (69, 70), Han (29), and White (100) have made kinematic studies of the film blowing process. They use the theory of thin shells in which the film thickness h is considered much smaller than other film dimensions, that is, $h \ll r$, where r is the film radius. All velocities were expressed in terms of r , h , and z , where z is the distance along the machine direction. The coordinate system used may be seen in Figure 10.

The rate of deformation tensor may be presented in the following form:

$$\|d\| = \begin{vmatrix} d_{11} & 0 & 0 \\ 0 & d_{22} & 0 \\ 0 & 0 & d_{33} \end{vmatrix} \quad (\text{II.1})$$

where $d_{11} = \partial V_1 / \partial \xi_1$, $d_{22} = \partial V_2 / \partial \xi_2$, and $d_{33} = \partial V_3 / \partial \xi_3$

Shear components are considered negligible. The above three equations are usually defined in terms of r and h as a function of z .

$$d_{22} = V_1 \cos \theta \frac{1}{h} \frac{dh}{dz} \quad (\text{II.2})$$

$$d_{33} = V_1 \cos \theta \frac{1}{r} \frac{dr}{dz} \quad (\text{II.3})$$

$$d_{11} = -V_1 \cos \theta \left(\frac{1}{h} \frac{dh}{dz} + \frac{1}{r} \frac{dr}{dz} \right) \quad (\text{II.6})$$

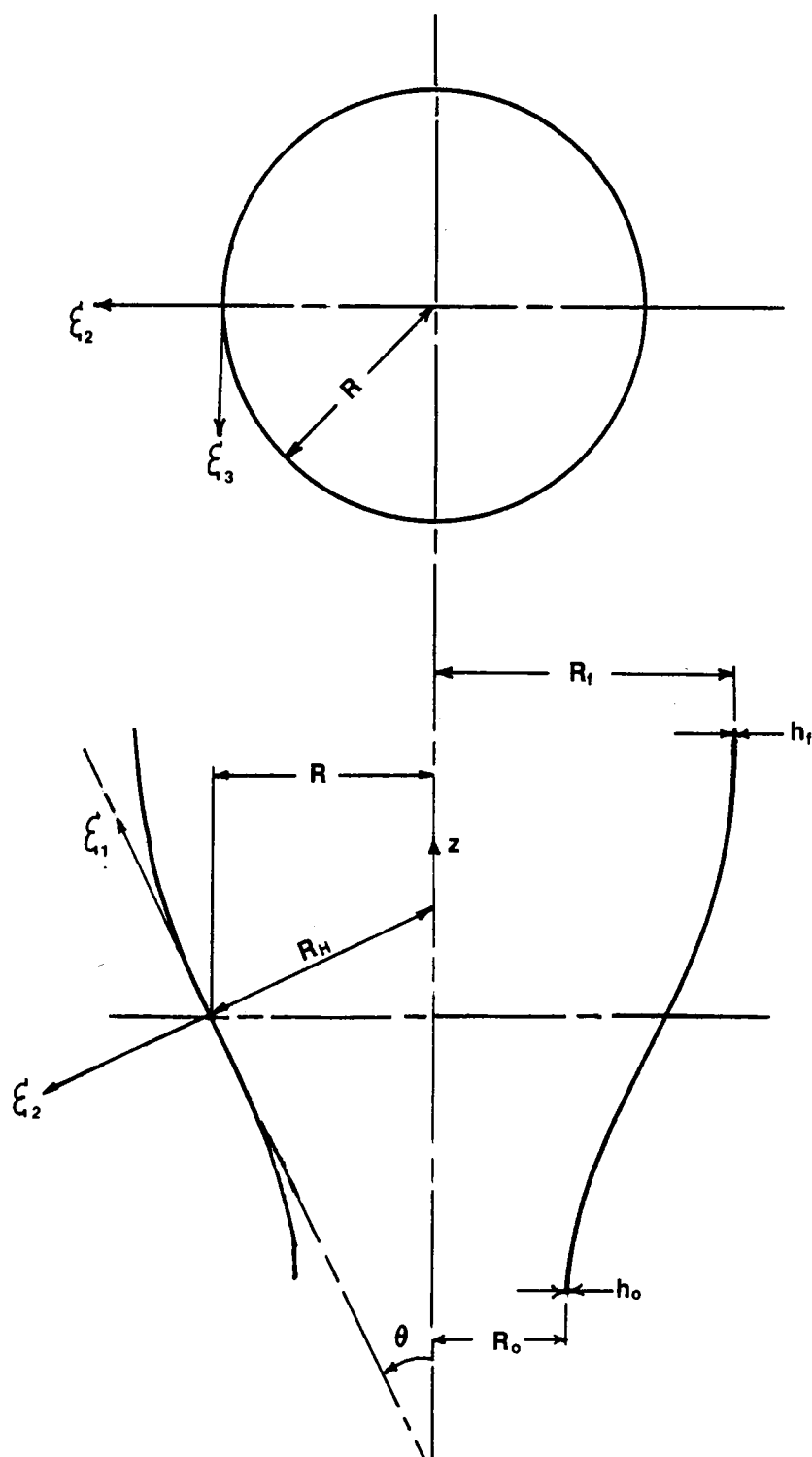


Figure 10. Coordinate System for the Blown Film Process.

Conditions for uniaxial stretching are that $d_{22} = d_{33}$ or that

$$\frac{V_L}{V_0} = \frac{1}{B^2} = \frac{R_0^2}{R_f^2} = \frac{h_0^2}{h_f^2} \quad (\text{II.5})$$

For planar extension, either $d_{33} = 0$, or $d_{22} = 0$, resulting in the following conditions:

$$\frac{V_L}{V_0} = \frac{R_0}{R_f} = \frac{1}{B} \text{ for } d_{22} = 0 \text{ and} \quad (\text{II.6})$$

$$\frac{V_L}{V_0} = \frac{h_0}{h_f} \text{ for } B = 1 \text{ and } d_{33} = 0 \quad (\text{II.7})$$

Conditions for equal biaxial stretching are that the deformation rates in the transverse direction are equal to those in the machine direction $d_{11} = d_{33}$, eventually leading to this equation for equal biaxial stretching:

$$V_L/V_0 = R_f/R_0 = \sqrt{h_0/h_f} \quad (\text{II.8})$$

Ast (7), Farber and Dealy (22), Han and Park (29), and Iwakura et al. (35) have reported experimental studies involving the kinematics of the blown film process. Furber and Dealy used motion pictures to follow the deformation history. Han and Park studied the effects of varying air pressure on the bubble using photographic techniques. Iwakura et al. made an analysis of films extended in the transverse direction without deformation in the machine directions.

Dynamics of Blown Films

Development of a force balance for the expanding tubular bubble has usually involved applying thin shell theory and its resulting equations. Alfrey (2) and Pearson (68) were the first to use this type of analysis. Further developments were made by Pearson and Petrie (69, 70), Han and Park (29), and Pearson and Gutteridge (28, 71).

Pearson's and Petrie's (69, 70) analysis involved using the coordinate system in Figure 10. A force balance using these coordinates gives the following equation:

$$2\pi r \cos \theta P_L + \pi \Delta p [R^2 - r^2] + 2\pi \rho g \int_z^Z r h \sec \theta dz = F_z \quad (\text{II.9})$$

in which r and R are bubble radii at z and Z ; the freezing line, h , is the film thickness at z , P_L the force acting in the direction of flow, Δp the pressure difference across the film, ρ the density of the melt, g the gravitational acceleration, and F_z the tensile force at $z = Z$.

D. Mandrel Process

General

In the mandrel process, a tubular film is extruded downward over a mandrel, which may be one of a variety of shapes, where it is expanded to the desired radius while still in the molten state during a drawing process. Air

pressure is usually used to support the film prior to being drawn over the mandrel. In most cases, the film is cooled as it passes over the mandrel. Take up is provided by nip rollers.

In an 1878 patent, J. W. Hyatt (34) describes a mandrel process involving extruding cellulose solutions over a mandrel and then coagulating the solution on the mandrel. More recently, Gerow (26) developed a mandrel process, mainly for polyethylene, and in a later paper describes it in more detail. He discusses optimal mandrel to die distances, mandrel shape, mandrel temperatures, extrusion rates, and film speeds. Gerow finds that bubble instability occurs when mandrel distances are greater than $1/2$ the mandrel diameter with blow-up ratios in excess of 3:1. He claims that the optimum mandrel distance is $1/2$ the mandrel diameter with blow ratios of 2.5 to 1.

The mandrel design involves four dimensions: shoulder radius, skirt length, taper, and diameter; see Figure 11. The shoulder radius is important in introducing the polymer tube to the mandrel surface. The size of this radius is very important since it partially determines the quantity of air pumped over the mandrel by the sliding action of the plastic tube. As the radius increases and the angle of incidence decreases, a larger layer of air will flow past the mandrel causing the secondary bubble to burst due to increases in unreleased air pressure.

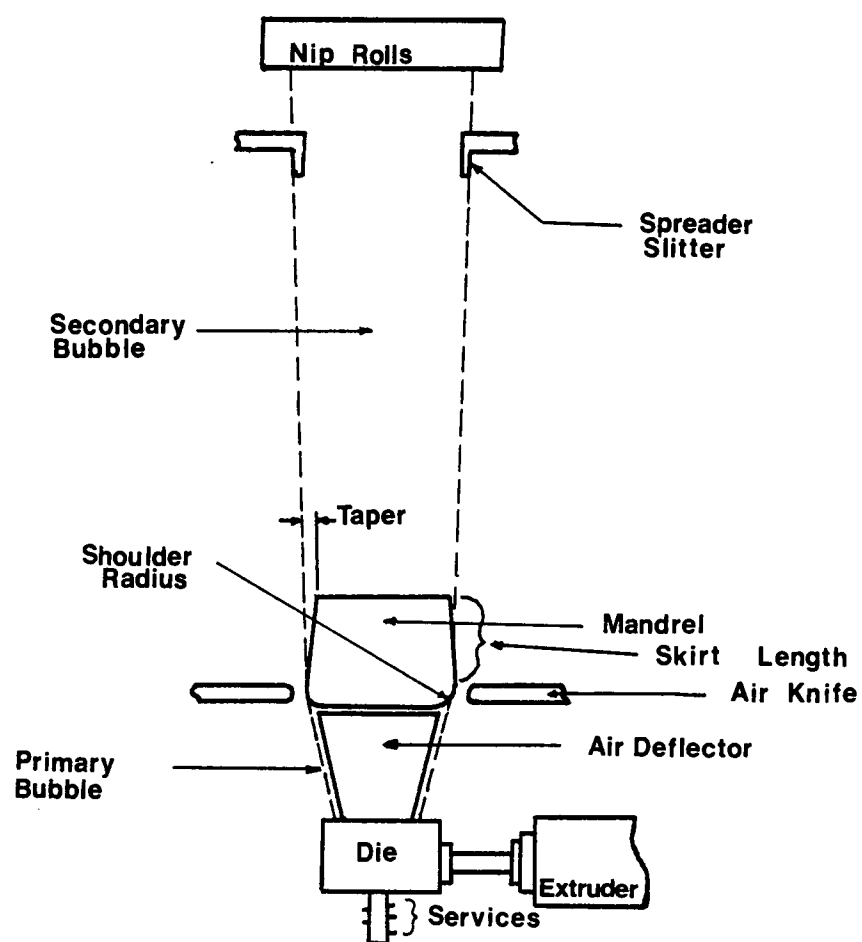


Figure 11. Mandrel Process for Polymer Melts Developed by Gerow.

Optimum mandrel temperatures for polyethylene were found to be between 150° - 200°C . These temperatures result in higher film modulus and a reduction in film stickage to the mandrel surface.

Lower extrusion rates are more desirable because of the increased dwell time of the film on the mandrel surface, resulting in higher quench rates and better film properties.

Cichelli (17) describes a mandrel process using a mandrel with a gradually increasing radius and air as a lubricant and method of heat transfer between the mandrel and film surface. Fallwell (21) developed a method similar to that of Cichelli.

In 1964, Richie and Scalora (74) introduced an apparatus similar to that of Gerow's with the addition of a spreader in order to facilitate take up of film. The shape of the film bubble was changed from circular to elliptical by the spreader just prior to film take up.

Kinematics and Dynamics of the Mandrel Process

The mandrel process involves drawing an extruded film in tubular form over a mandrel to induce orientation in the radial and machine direction. Wessling and Alfrey (97) and Wessling (98) made a study of biaxially stretching elastic and viscous tubes over rotationally symmetric mandrels. In a recent paper, Gutteridge (28) describes

film-stretching over a conical mandrel using elastic and visco-elastic models.

In Wessling's and Alfrey's study of the elastic case, a thin walled tube of vulcanized rubber was drawn slowly over a conical Teflon mandrel; see Figure 12. It was assumed in this example and in all of the above examples that $r \gg h$. The drawing motion was opposed by friction which is a factor used to define the stretching pattern in addition to the mandrel shape.

All forces involving bending and twisting were excluded, once again, a condition common to all of the above cases. Two forces were assumed to be acting on the membrane: normal forces per unit area, P_N , and tangential forces per unit area, P_T , acting in the meridional direction; see Figure 12. These forces vary with position.

The coordinate system for all cases was cylindrical; refer to Figure 12. R_m was defined as equal to infinity when a conical mandrel was used. The equations for equilibrium are listed below.

$$P_N = h\sigma_H/R_H + h\sigma_M/R_M \quad (\text{II.10})$$

$$\alpha r P_N = \frac{d}{dz} (rh\sigma_M \cos \theta) \quad (\text{II.11})$$

where $\alpha = \tan \theta$

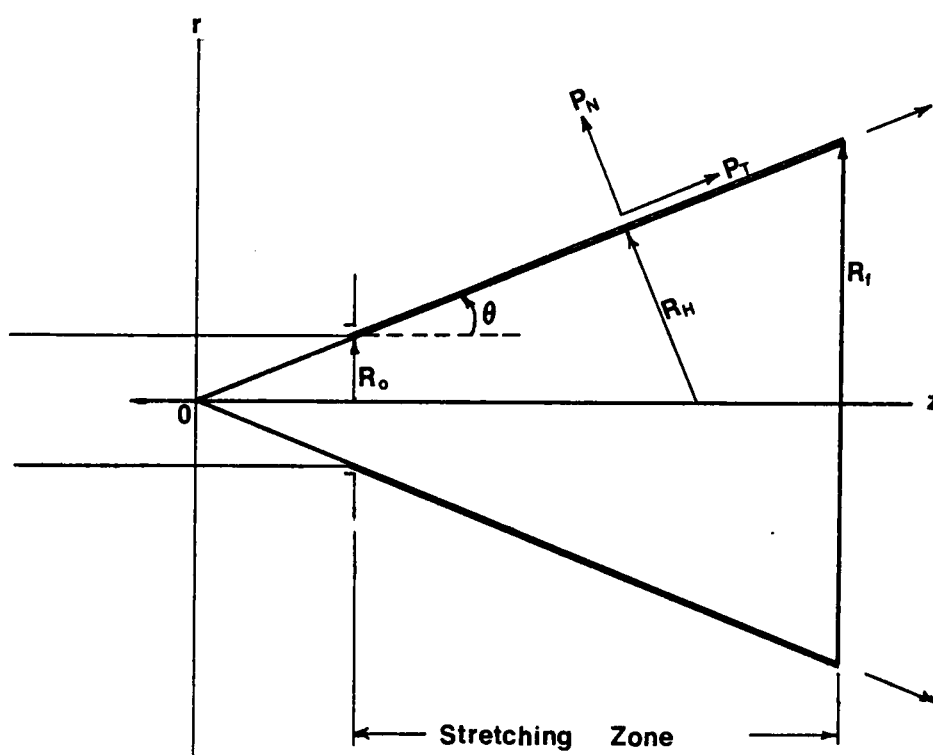
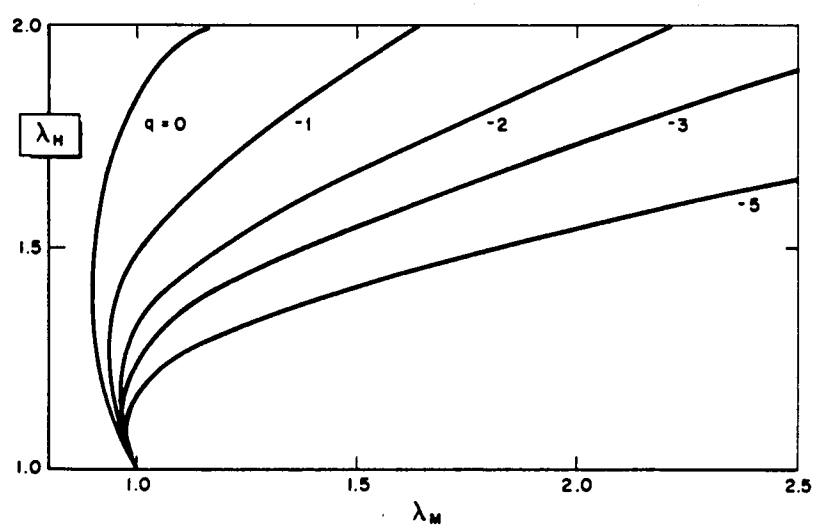


Figure 12. Coordinate System for the Mandrel Film Process.

Material properties for Wessling's and Alfrey's case were defined for large elastic deformation, that is, the Mooney-Rivlin theory of rubber elasticity.

Accelerations involved in this analysis and all cases previously mentioned are considered very small due to the small velocities used. Therefore, the problem is assumed to be one of steady state.

The material properties equation and equilibrium equations were combined to give the elastic model. Wessling and Alfrey looked at a variety of conditions for stretching tubes over conical mandrels. An example may be seen in Figure 13, which is a plot of the extension ratio in the hoop direction λ_H versus the extension ratio in the machine direction λ_M for different values of q , where increasing values of $-q$ may be obtained by increasing the frictional drag on the film or by reducing the cone angle. Reducing the cone angle increased the surface area of cone in contact with the membrane at any λ_H . All the trajectories in Figure 13 exhibit an initial contraction in the meridional direction followed by biaxial stretching. Stretching in the meridional direction increases more rapidly as the tube moves further down the cone. This additional stretching in the meridional direction is claimed "due to the nature of the resisting forces," that is, the axial components of P_N and P_T . The result is a sharply curved trajectory with the amount of curvature dependent on q .



$q = K/\mu$ where $-K$ = the coefficient of sliding friction.

Figure 13. Biaxial Extension Ratio Trajectories Calculated from the Large Deformation Theory: $T = 0.1$.

Wessling's interpretation for the viscous case uses the constitutive equation for a viscous Newtonian fluid:

$$e_{ij}(t) = (1/2\eta) s_{ij}(t) \quad (\text{II.12})$$

The term η is the shear viscosity and $e_{ij}(t)$ and $s_{ij}(t)$ are the deviatoric strain rate and stress tensors respectively.

Some conclusions reached by Wessling are that for nonisothermal stretching, the viscosity increases as the tube proceeds down the cone, therefore, making stretching more difficult as the tube reaches the end of the cone. The cone shape creates all the stretching in the hoop direction while stretching in the meridional direction in the frictionless case is achieved through the velocity ratio, which is the velocity of the film at the end of the cone over the velocity of the film at the beginning of the cone. He further demonstrates that on shorter cones, the hoop stress is large enough to maintain tension on the film and reduce the chance of inducing compressive forces, and the buckling that results, because the resisting force is small. Longer cones require higher velocity ratios due to build up of resistant forces.

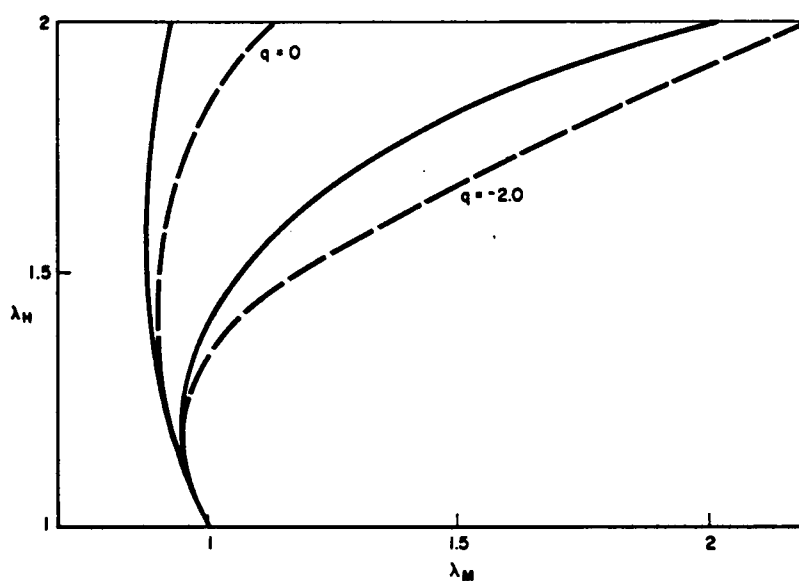
In a comparison of the elastic and viscous examples, it was shown that the viscous case exhibited a wide range of biaxial stretching patterns dependent on viscosity, friction, and the velocity ratio. The elastic case didn't

demonstrate this versatility. According to Wessling and Alfrey, there is no operating condition which will produce uniform biaxial stretching in the elastic case.

Wessling, using both models, made a comparison of conditions for which the two cases would be similar. He found that the freely feeding tube in the elastic case and isothermal stretching with maximum velocity in the viscous case were most alike. The extension ratio trajectories can be seen in Figure 14. It was observed that at small strains, the differences were small. The stress ratio plot, Figure 15, demonstrated another difference: that under comparable conditions, the stress ratio was larger in the elastic case.

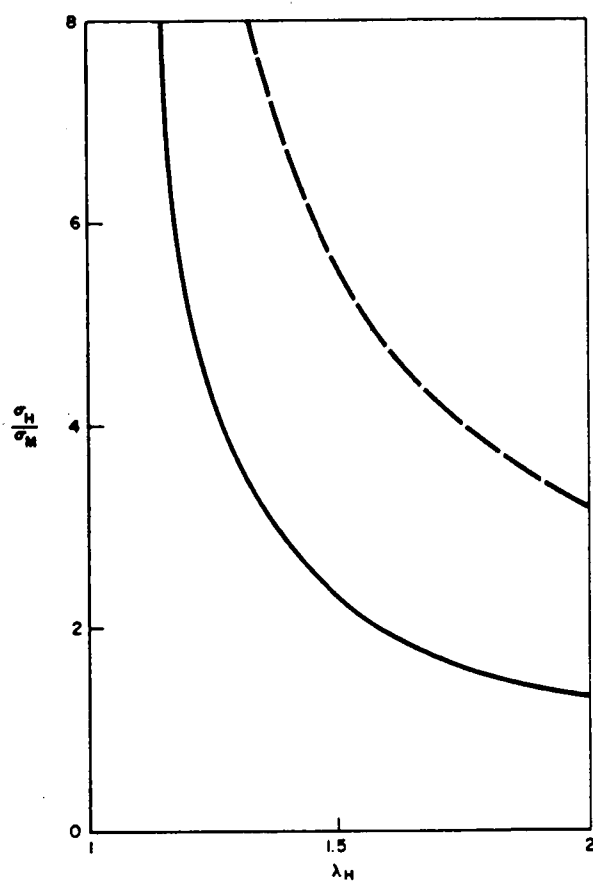
For stretching of a viscous tube, it was found that stretching patterns depend mainly on the mandrel geometry and friction but not on the material properties or velocity. Therefore, the viscoelastic case would approach the viscous or Newtonian solutions when flow or friction were present. When flow isn't present, the viscoelastic case approaches that of the large strain elastic case.

Gutteridge (28) discusses film stretching over a conical mandrel using both an elastic and viscoelastic rheological model, with polypropylene as the theoretical material. The model involved heating a plastic tube just below its melting temperature and drawing it over a conical mandrel. The lower temperatures were used in the



The solid line represents the viscous case for isothermal stretching under minimum velocity conditions. The broken line represents the elastic case for $\bar{T} = 0.1$.

Figure 14. A Comparison of the Extension Ratio Trajectories Predicted for Mooney-Rivlin Elastic and Newtonian Viscous Material Properties.



The solid line represents the viscous case and the broken line the elastic case.

Figure 15. A Comparison of the Stress Ratios for the Elastic and Viscous Solutions.

hope of inducing stresses resulting in a higher degree of molecular orientation, preferably biaxial orientation. Isothermal and nonisothermal conditions were taken into account.

The constitutive equation for viscoelastic conditions was presented by Funt (25) using a Kelvin-Voigt model

$$\sigma_i(t) = \epsilon(t) G(T) + G(T)\tau(T)d\epsilon_i/dt \quad (\text{II.13})$$

where $\eta = G\tau$, $G(T)$, a temperature dependent elastic modulus, η , the viscosity, and τ , a retardation time.

As was in earlier models, the constitutive equation was combined with the equations of equilibrium in order to define the elastic and viscoelastic models using various conditions of stretching.

Gutteridge's conclusions were that under isothermal and limited stretching conditions, a high degree of equal biaxial extension can be obtained. By using a viscoelastic material at a low temperature and applying a linearly decreasing temperature profile, an elastic material can produce equal biaxial extension over a range of the stretching conditions. It was further stated that for the mandrel process, sequential drawing takes place first in the radial direction followed by meridional direction stretching.

E. Solution Fabricated Film

One of the earlier patents involving solution spun films was issued to W. P. Cohoe (18) in 1915. It involves extruding a cellulose solution through an annular opening and coagulating it as the tube issues from the die to produce sausage casings. J. E. Brandenbergers (12, 13), in 1925 and 1926, was issued two patents dealing with the manufacture of viscose films. His process was comprised of extruding through a slit die a solution of sodium cellulose xanthate in film form into a coagulant of caustic soda to produce cellulose films.

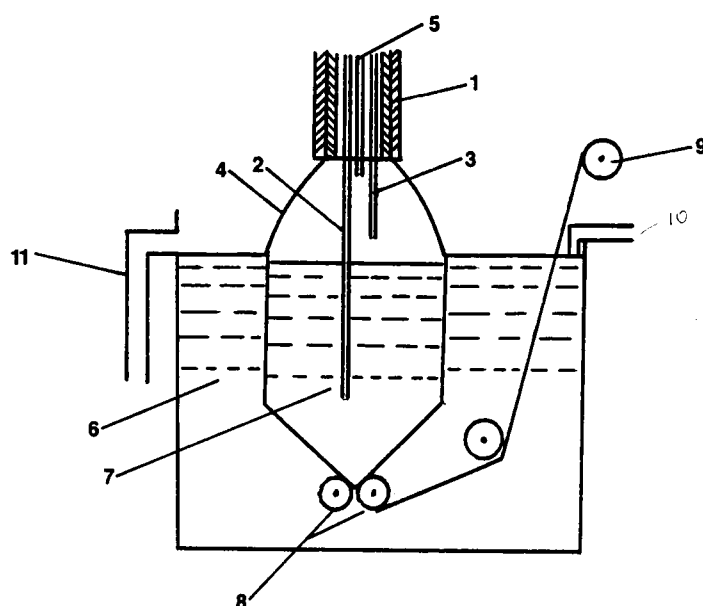
In some of the early DuPont patents (87) dealing with the synthesis of aromatic polyamides, films were made by casting the solutions and then flashing the solvents off. Hill and Kwolek (33) made films from 15% solutions of poly (m-phenylene isophthalamide), MPD-I, dissolved in dimethylformamide and lithium chloride using the above casting process. Properties of the film at 20°C in the casting or machine direction were: modulus, 500,000 psi; tensile strength, 12,000 psi; and percent elongation, 3%-5%. Hot rolled samples revealed the following properties in the machine direction: modulus, 900,000 psi; tensile strength, 30,000 psi; and 10% elongation. Properties in the transverse direction were: modulus, 200,000 psi; tensile strength, 30,000 psi; and 10% elongation. In 1966, Sweeny (88) made cast films from solutions of MPD-I, dimethylacetamide, and lithium chloride.

Recently, tubular film blowing processes have been developed to make film from aromatic polyamides. Miyoshi et al.(53) of Unitika Ltd. filed a Japanese patent describing such a process. In their patent, they use a dry-jet wet spinning method with a coagulant to solidify the film; see Figure 16. The annular die dimensions are: diameter, 100 mm, and slit width, 0.5 mm. The air gap length was 200 mm. Film blow up ratios were claimed to be three times the original diameter. Water at room temperature was used as a coagulant. Claims are made of high strength, on the order of 40,000 psi tensile strength in the machine and transverse direction for films of PPD-T. Unblown film was found to be brittle and weak.

At the University of Tennessee, Aoki et al.(5) have produced ribbons and blown films from isotropic and anisotropic solutions of PPD-T/ H_2SO_4 . The process for blown film formation was similar to that of Miyoshi et al; see Figure 17. Ribbons were made using a slit die.

Examination of ribbons using scanning electron microscopy revealed a scale like structure which diminishes when films were made from higher concentration solutions. High concentration solutions produce samples which appeared as bundles of fibrils.

The blown films demonstrated preferential orientation in the machine and transverse direction. Wide angle X-ray diffraction studies indicated orientation of the (110)



Number 1 is the annular slit, 2 the extruded film, 3 the access tube for the coagulant, 7, and 4 the recirculation tube for used coagulant. Number 5 is the tube for introducing an inert gas, 6 the coagulant outside the tube introduced through 10 and removed by 11, and numbers 8 and 9 are winding rollers.

Figure 16. The Tubular Film Blowing Process for Aromatic Polyamides Developed by Miyoshi et al.

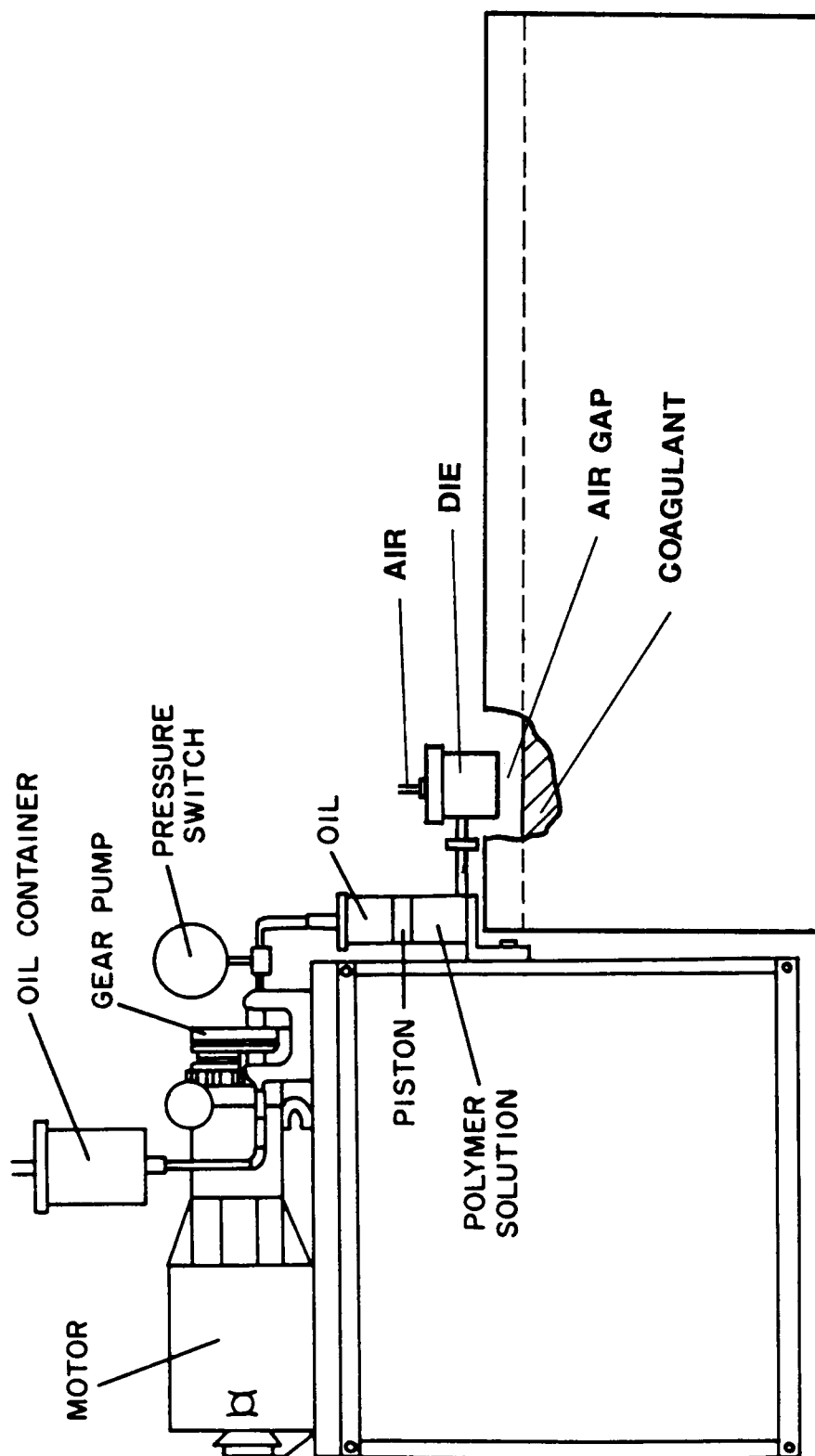


Figure 17. The Tubular Film Blowing Process Developed by Aoki et al.

planes in the transverse direction from samples coagulated in water. From the known model of PPD-T's unit cell (58), it was suggested that the b-axis tends to become oriented perpendicular to the machine direction. Annealing resulted in sharpened and increased diffraction intensity. The annealed samples also show a new diffraction ring at $7.63\text{\AA}$. Orientation was found to increase with annealing.

F. Wide Angle X-Ray Diffraction Studies

The Determination of PPD-T Unit Cell

Northolt and van Aartsen (60, 61) determined PPD-T's unit cell to be orthorhombic using wide angle X-ray diffraction. The dimensions are $a = 7.87\text{\AA}$, $b = 5.18\text{\AA}$, and c (the fiber axis) $= 12.9\text{\AA}$ with β being approximately 90° . They indexed the reflections by assuming a monoclinic unit cell. Some of the strong reflections are the (004), (006), (110), and (200). The observed extinctions are (hko) with h and k odd and (hol) with l odd. The (hol) extinction is believed due to the "pseudosymmetry" of the unit cell. The calculated crystallographic density is 1.48 g/cm^3 for two monomeric units per cell. The experimental value is 1.43 g/cm^3 ; see Figure 18.

The initial model for PPD-T had a space group of $P2_1/n$ as determined by extinctions and comparisons of WAXS patterns of PPD-T to poly (p-phenylene oxide), POL, and poly (p-phenylene sulphate) patterns. Diffraction

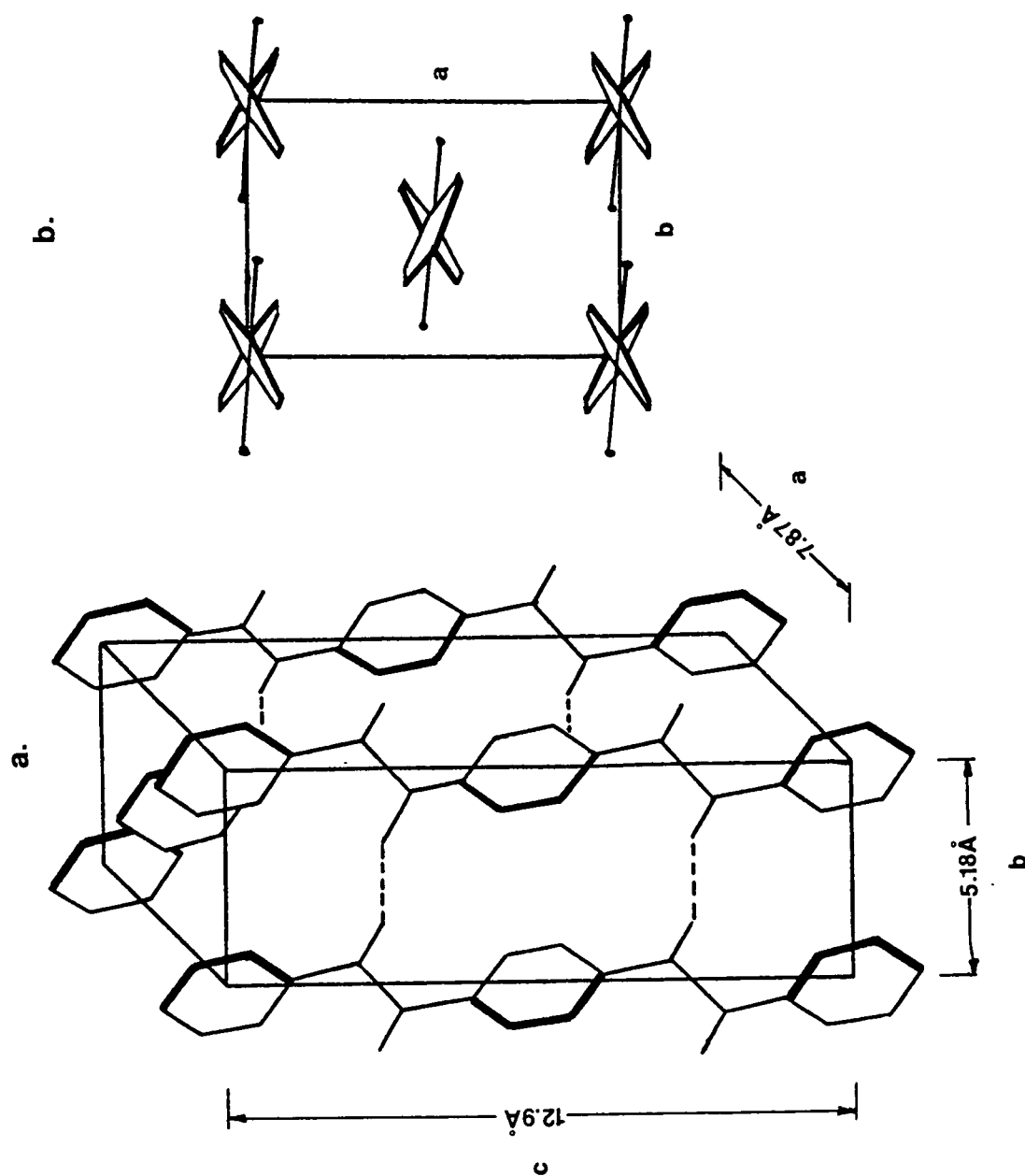


Figure 18. (a) The Northolt Model for PPD-T's Unit Cell and (b) the c-axis Projection of the Northolt Model.

patterns taken with the fiber axis tilted relative to the camera introduced two reflections, the (104) and (106), that suggested the space group may be Pn. This space group fits with the above reflections and the (004) and (006) reflections if there is a small displacement parallel to the c-axis between the hydrogen bonded planes. The results indicate that a heat treated fiber tends to exhibit a Pn space group and the untreated fiber a $P2_1/n$ space group. The $P2_1/n$ space group is the favored model due to the presence of chain segments which are "steriochemically centrosymmetric" and due to the suggested model for hydrogen bonding between the chains; see Figure 18.

Tadakoro (88) suggested essentially the same model for PPD-T as Northolt. Hancock et al (30) found that the WAXS reflection for wet spun coagulated PPD-T fiber differs from Northolt's prediction; the strong (110) is missing and extra reflections at 5.1Å and 7.6Å are present.

Two recent papers by Haraguchi, Kajiyama, and Takayanagi (31, 32) discuss the effect of the coagulant on the crystalline structures of uniplanar films of PPD-T. Water, as a coagulant, was found to have an effect on the film regardless of the solution concentration. Through X-ray and infrared studies, they determined that the resulting crystalline structure differed

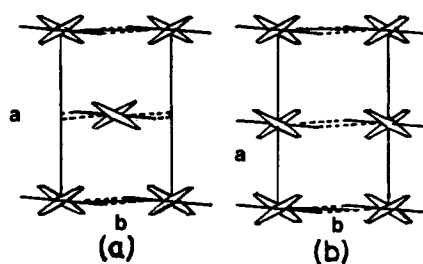
considerably from the Northolt (61) and Tadakoro (88) model. The original structure, given by Northolt and Tadakoro, was called modification I and the new structure modification II.

The big differences in WAXS patterns of modification II were as follows: 1. The absence of the strong (110) reflection; 2. The appearance of a strong inner reflection with a Bragg spacing of $5.1\text{\AA}$; 3. The Bragg spacing of the (200) reflection is larger by $.01\text{ nm}$. 4. Reflections with a spacing between $2.0\text{\AA}$ and $3.2\text{\AA}$ are not observed.

Infrared absorption bands at 720 and 730 cm^{-1} were found to be sensitive to crystal modification. The band at 730 cm^{-1} is sensitive to modification I and the band at 720 cm^{-1} is sensitive to modification II.

Films from solutions of PPD-T, 3% by weight, upon coagulation with water were found to exhibit the modification II crystalline structure; see Figure 19.

Annealing these films resulted in a 3% weight loss and a return to the crystalline structure of modification I. The density went from 1.385 g/cm^3 to 1.420 g/cm^3 . What these results and the disappearance of water related absorption bands suggest is that water molecules are tightly bound in the original PPD-T films coagulated with water. Films coagulated in water from concentrated solutions of PPD-T 15% by weight, upon annealing, essentially stayed in the crystalline form of modification II.



Modification I has the unit cell dimensions $a = 7.87 \text{ \AA}$, $b = 5.18 \text{ \AA}$, and $c = 12.9 \text{ \AA}$. Modification II was reported by Northolt and has the dimensions $a = 8.0 \text{ \AA}$, $b = 5.1 \text{ \AA}$, and $c = 12.9 \text{ \AA}$.

Figure 19. c-Axis Projections of the Crystal Structures of PPD-T for (a) Modification I and (b) Modification II.

The proposed crystalline structure of modification II has the same a and c unit cell dimensions and the same molecular packing along the a and c axis as modification I. The b dimensions and the molecular packing along the b-axis are different from modification I; see Figure 19. From this model it was shown that the inner 5.1A reflection resulted from the (010) plane.

PPD-T thin films coagulated with water exhibit modification II, uniplanar orientation with the hydrogen bond direction perpendicular to the film surface. Film coagulated with organic liquids exhibit modification I, uniplanar orientation with the hydrogen bond direction parallel to the film surface; see Figure 20.

Orientation Functions

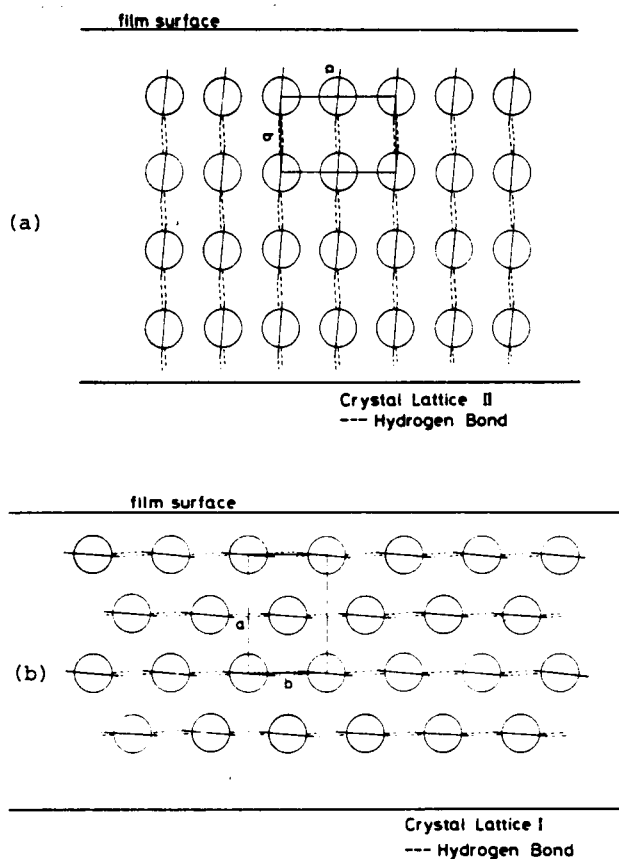
Stein (84, 85) appears to be the first to consider the problem of biaxial orientation in polymers. He developed a method for determining the average orientation of a biaxially oriented sample with orthorhombic symmetry. Figure 21 is the coordinate system that Stein used. The orientation functions are defined below.

$$f_{a,z} = \frac{1}{2}(3\langle \cos^2 \theta_{a,z} \rangle - 1) \quad (\text{II.14})$$

$$f_{b,z} = \frac{1}{2}(3\langle \cos^2 \theta_{b,z} \rangle - 1) \quad (\text{II.15})$$

$$f_{c,z} = \frac{1}{2}(3\langle \cos^2 \theta_{c,z} \rangle - 1) \quad (\text{II.16})$$

$$f_{\sigma,a} = 2\langle \cos^2 \sigma_a \rangle - 1 \quad (\text{II.17})$$



(a) is the water coagulated film representing a Modification I structure. (b) is the organic liquid coagulated film exhibiting a Modification II structure.

Figure 20. Schematic Representation of Uniplanar Orientation in PPD-T Thin Films.

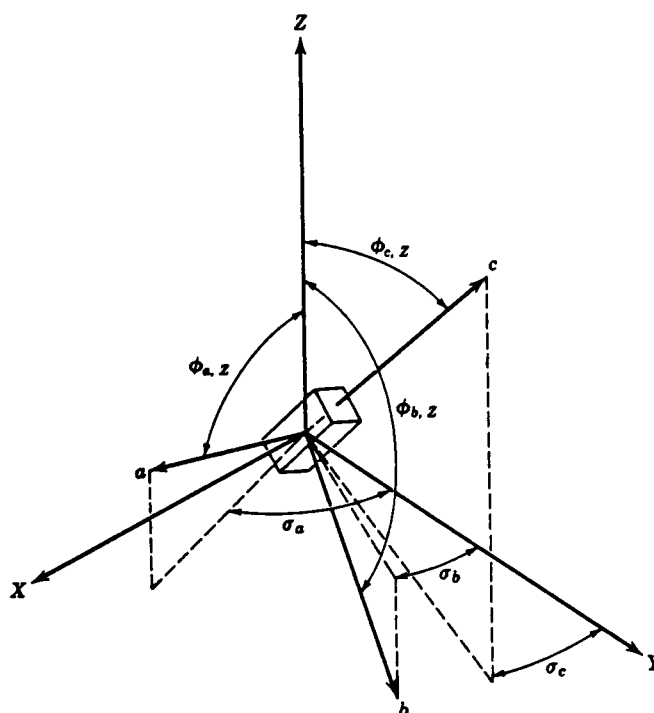


Figure 21. Stein's Coordinate System for Biaxial Orientation Functions.

$$f_{\sigma,b} = 2\langle \cos^2 \sigma_b \rangle - 1 \quad (\text{II.18})$$

$$f_{\sigma,c} = 2\langle \cos^2 \sigma_c \rangle - 1 \quad (\text{II.19})$$

From orthogonality

$$f_{a,z} + f_{b,z} + f_{c,z} = 0 \quad (\text{II.20})$$

also

$$f_{\sigma,a}(1-f_{a,z}) + f_{\sigma,b}(1-f_{b,z}) + f_{\sigma,c}(1-f_{c,z}) = 0 \quad (\text{II.21})$$

The previous equations were checked by Krigbaum et al.(46) in determining orientation distributions of biaxially oriented poly (ethylene). It was found, using their own orientation distribution functions, that equation (II.20) doesn't always equal zero and wasn't correct.

Nomura, Kawai, Kimura, and Kagiya (58, 59, 41), using an analysis similar to Stein's, developed a more general case than above.

One of the problems associated with Eulerian angles is that they are prejudiced in favor of a single specific direction in the material, that is, the machine direction. Eulerian angles do not allow an adequate representation of orientation in the transverse direction.

White and Spruiell (99) developed a method for defining biaxial orientation functions. They used the polarizability tensor, which was defined as a second order tensor with nine components. It may be utilized

to express the behavior of a molecule of a material and its interaction with electromagnetic phenomena.

Two equations were developed for a general analysis using the coordinate system shown in Figure 22.

$$f_z^B = 2 \overline{\cos^2 \phi_{1z}} + \overline{\cos^2 \phi_{1y}} - 1 \quad (\text{II.22})$$

$$f_y^B = 2 \overline{\cos^2 \phi_{1y}} + \overline{\cos^2 \phi_{1z}} - 1 \quad (\text{II.23})$$

Equations 22 and 23 may be developed further for orthorhombic crystals to give these orientation functions

$$f_{z,a}^B = 2 \overline{\cos^2 \phi_{a,z}} + (\overline{\cos^2 \phi_{a,y}} - 1) \quad (\text{II.24})$$

$$f_{y,a}^B = 2 \overline{\cos^2 \phi_{a,y}} + (\overline{\cos^2 \phi_{a,z}} - 1) \quad (\text{II.25})$$

$$f_{z,b}^B = 2 \overline{\cos^2 \phi_{b,z}} + (\overline{\cos^2 \phi_{b,y}} - 1) \quad (\text{II.26})$$

$$f_{y,b}^B = 2 \overline{\cos^2 \phi_{b,y}} + (\overline{\cos^2 \phi_{b,z}} - 1) \quad (\text{II.27})$$

$$f_{z,c}^B = 2 \overline{\cos^2 \phi_{c,z}} + (\overline{\cos^2 \phi_{c,y}} - 1) \quad (\text{II.28})$$

$$f_{y,c}^B = 2 \overline{\cos^2 \phi_{c,y}} + (\overline{\cos^2 \phi_{c,z}} - 1) \quad (\text{II.29})$$

The above functions, 24-29, are related by these two relationships:

$$\overline{\cos^2 \phi_{a,z}} + \overline{\cos^2 \phi_{b,z}} + \overline{\cos^2 \phi_{c,z}} = 1 \quad (\text{II.30})$$

$$\overline{\cos^2 \phi_{a,y}} + \overline{\cos^2 \phi_{b,y}} + \overline{\cos^2 \phi_{c,y}} = 1 \quad (\text{II.31})$$

which leaves four independent orientation factors.

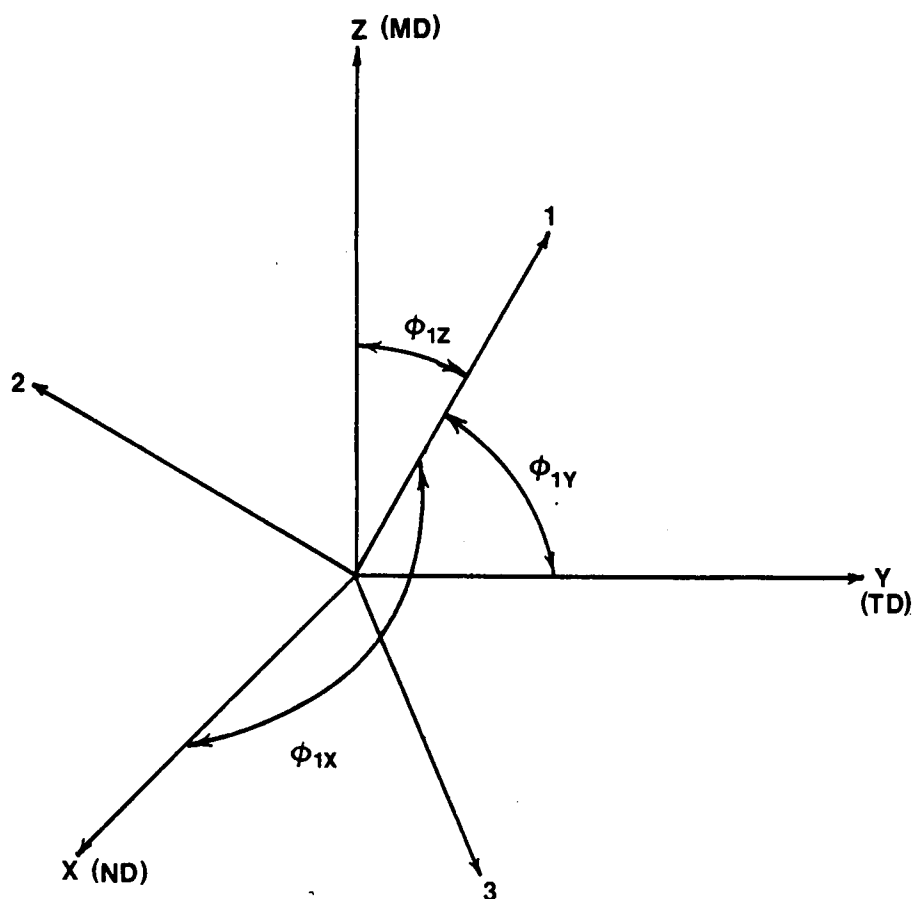


Figure 22. White and Spruiell's Coordinate System for Biaxial Orientation Functions.

The orientation function found through equations 24-29 may be plotted on a graph to determine the degree and type of orientation each set of coordinates represents; see Figure 23.

Pole Figures

Angles from equations 24-29 may be found through pole figure analysis. Pole figures give a three dimensional orientation distribution of the crystals in a polycrystalline sample, that is, the spacial distribution of poles, normal to certain crystallographic planes.

Pole figures from several planes are needed to determine all the $\cos^2 \phi_{jz}$ and $\cos^2 \phi_{jy}$, ($j = a, b, c$), values in equations 24-29. Diffracting (hkl) planes perpendicular to a crystallographic axis are used in the above case. For example, (hkl) planes perpendicular to the a-axis may be represented as a pole figure for those planes showing the distribution of the a-axis in space with:

$$\cos^2 \phi_{az} = \frac{\int_0^\pi \int_0^{2\pi} I_{hkl}(\phi_z, \beta_z) \cos^2 \phi_z d\beta_z d\phi_z}{\int_0^\pi \int_0^{2\pi} I_{hkl}(\phi_z, \beta_z) d\beta_z d\phi_z} \quad (\text{II.32})$$

where I_{hkl} is the intensity diffracted from the (hkl) planes and ϕ_z and β_z are the spherical coordinates. Values for $\cos^2 \phi_{jy}$ may be found using the same method as above except that integrations are taken over ϕ_y and β_y .

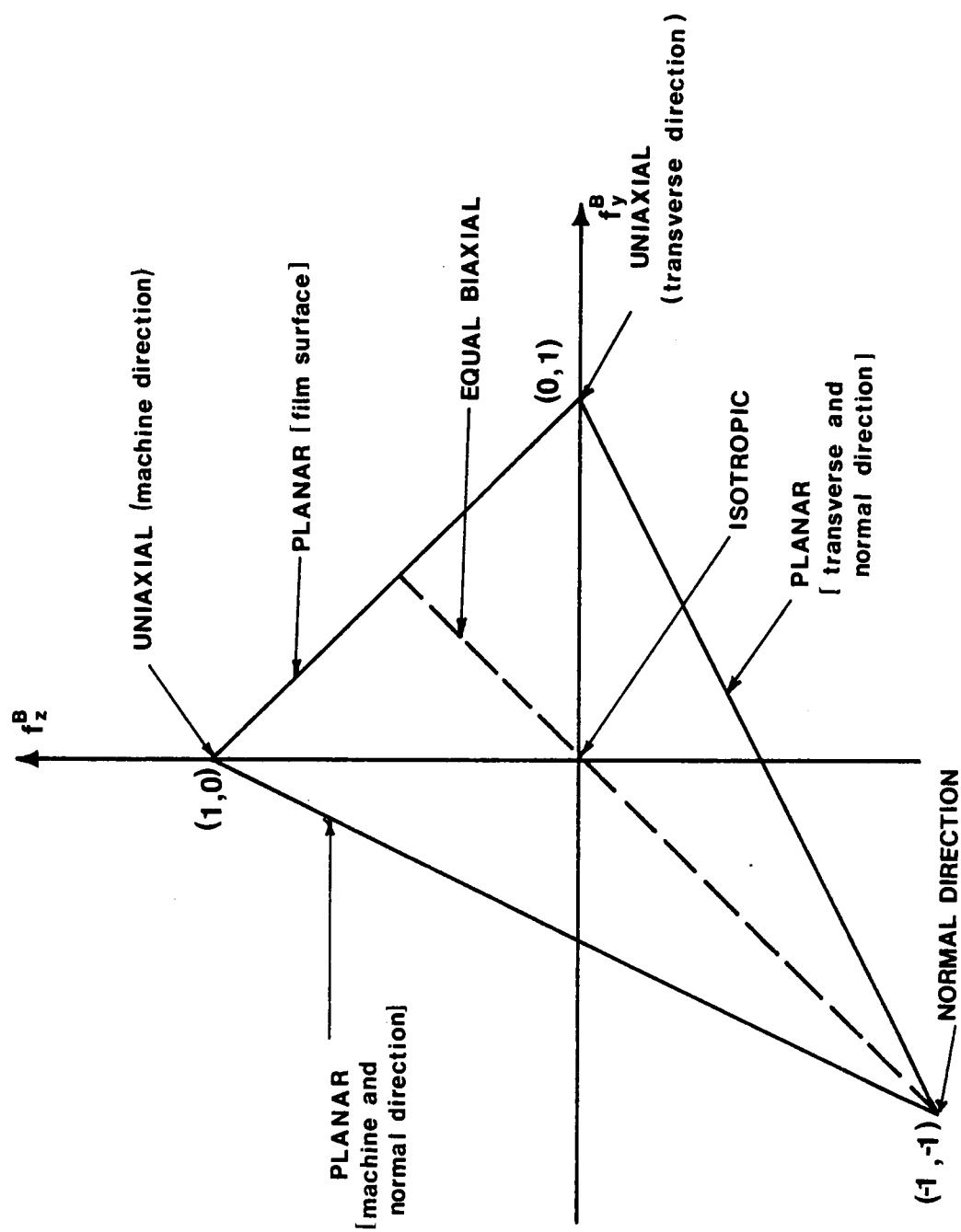


Figure 23. White and Spruiell's Orientation Triangle.

Wilchinsky (3) describes a procedure for the situation when no diffracting planes are perpendicular to the crystallographic axes.

CHAPTER III

EXPERIMENTAL

The experimental procedures leading up to the production of Kevlar^R films are explained in detail in this chapter. It was found during the development of these procedures that to obtain good results, strict guide lines should be followed. Seemingly small details, if not followed, usually lead to failure of the film process.

The first section deals with materials used in the experimental procedures. The following sections deal with solution and film production. The final sections explain methods used for film characterization.

A. Materials

Kevlar^R, which we shall consider PPD-T, in the form of Kevlar^R 29 quarter inch staple fiber, was provided by E. I. DuPont de Nemours. The fibers were washed with Fisher Scientific's purified carbon tetrachloride to remove surface treatments.

Fisher reagent grade 96% sulfuric acid and fuming sulfuric acid with 30% excess SO₂ were mixed to produce 100% sulfuric acid.

The coagulants were denatured ethanol and ethylene glycol from Fisher Scientific, and methanol from Ashland Chemical and water. Table 1 summarizes the concentrations used in the different experiments.

Table 1. Coagulant Types and Concentrations Used for the Different Film Processes

Coagulant Concentration Volume %	Applicable Film Processes
H ₂ O	Ex*, Uni**
45% H ₂ O 55% EtOH	Ex, Uni
25% H ₂ O 75% EtOH	Ex, Uni, Man***
5% H ₂ O 95% EtOH	Ex, Uni, Man
45% H ₂ O 55% MeOH	Ex, Uni
25% H ₂ O 75% MeOH	Ex, Uni, Man
5% H ₂ O 95% MeOH	Ex, Uni, Man
Ethylene Glycol	Ex, Uni

*Ex represents extruded films or the film process with no mandrel and no drawdown.

**Uni represents the film process with no mandrel but with a drawdown.

***Man represents the film process in which the films are allowed to extrude over a mandrel.

The oils used for the mandrel process were Sears 10w-40 and 15w-50 "weight" and Dow Corning 200 silicone oils in the 100 and 350 centistoke range. The viscosity of these oils in SI units are summarized in Table 2.

B. Preparation of PPD-T/H₂SO₄ Solutions

Solvent History

In order to prepare a solution of Kevlar^R and sulfuric acid, the solvent, 100% sulfuric acid, must first be prepared. This is accomplished by adding fuming sulfuric acid to concentrated (96%) sulfuric acid.

The procedure for determining the percent concentration of concentrated sulfuric acid is as follows:

1. Place a 400 ml beaker with 150 ml of distilled water and stir bar onto a magnetic stirrer.
2. Introduce four to five drops of phenolphthalein indicator into the beaker and turn on the stirrer.
3. Draw 3 ml of concentrated sulfuric acid into a 5 ml glass syringe fitted with a #18 needle.
4. Remove the #18 needle and replace it with a Teflon^R stopcock fitted with a #23 needle.
5. Weigh the needle, stopcock, and syringe assembly.
6. Introduce into the beaker, while stirring, about one ml of concentrated sulfuric acid from the syringe. The tip of the needle should be just below the water surface. After delivering the acid, remove the needle

Table 2. Oil Types and Viscosities* Used in the Mandrel Process

Oil Type	Viscosity Centipoise
Duo Seal Vacuum Pump Oil	200
Sears 10w-40	177
Sears 15w-50	313
Dow Corning (200)	102
Dow Corning (200)	370

*All viscosities were measured by a Brooksfeld Viscometer at 25° C.

from the water, close the stopcock valve, and touch the needle to the side of the beaker to remove excess water and acid.

7. Weigh the needle, stopcock, and syringe assembly.
8. Titrate the acid/water solution using 0.5N NaOH.
9. Usually three titrations are sufficient with all samples agreeing to within 0.4 percent.
10. The equation used to calculate percent concentration is:

$$\text{percent H}_2\text{SO}_4 = \frac{(\text{ml base}) (N) (4.9039)}{(\text{wt of PPD-T})}$$

Upon determining the concentration of sulfuric acid, the appropriate amount of fuming sulfuric acid should be added to bring the concentration to 100%.

Preparation of PPD-T Fiber

Kevlar^R 29 fiber has an oily coating which must be removed prior to contact with sulfuric acid for two reasons. First, the oil probably contains water. Second, the oil seems to react with the sulfuric acid creating a reddish colored solution which may result in polymer degradation. The procedure for fiber preparation is as follows:

1. Pack as much fiber as possible into a 2000 ml beaker.
2. Pour carbon tetrachloride into the beaker until

full. This should be carried out under a ventilated hood using rubber gloves.

3. Allow the fibers and carbon tetrachloride to sit for thirty minutes and then agitate by hand using rubber gloves.

4. Remove large clumps of fiber and squeeze out the excess carbon tetrachloride.

5. Place the fibers in a 2000 ml beaker half full with fresh carbon tetrachloride and repeat step 4.

6. Upon completion of step 5, place the fibers under a blanket of paper towels and allow them to dry for twenty four hours.

7. Washed and dried fibers are stored in clean, dry bottles in a dark, dry place.

Solution Preparation

PPD-T/ H_2SO_4 solutions are prepared in 800 ml jars. Concentrations are determined by weight percent. All of the mixing takes place within a dry box made of poly (vinyl chloride), PVC, and poly (methyl methacrylate) PMMA, under a nitrogen atmosphere. Figure 24 is a photograph of the dry box. The top is PMMA and the sides are PVC to prevent corrosion. The mixer is a 1/2 horsepower General Electric AC motor, contained within the dry box. The procedure for preparing Kevlar/ H_2SO_4 solutions is as follows:

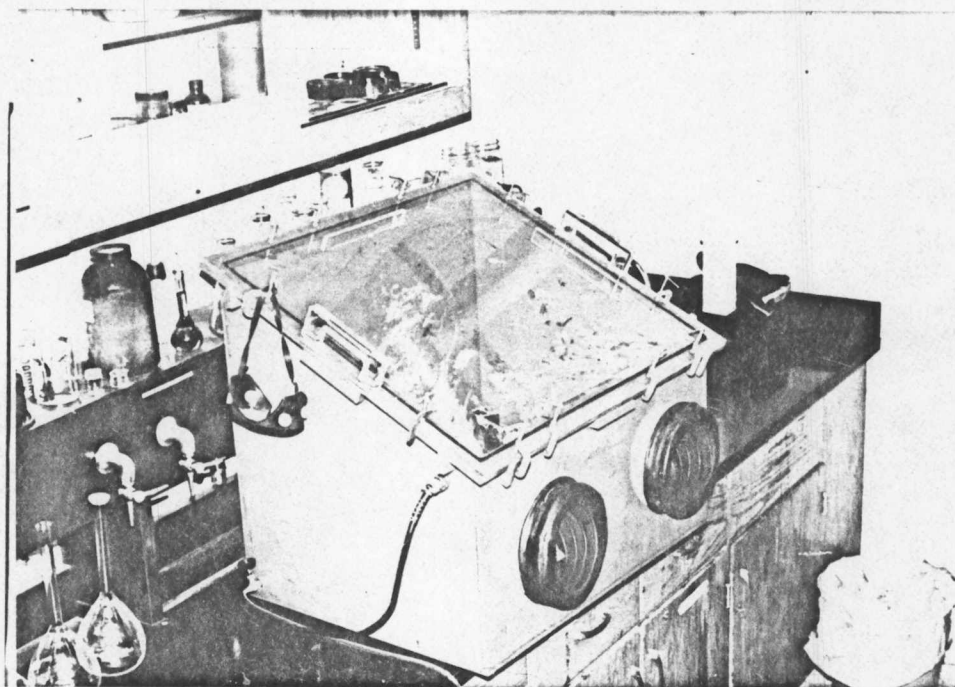


Figure 24. Dry Box Used in Preparation of PPD-T/H₂SO₄ Solutions.

1. Weigh an 800 ml jar with Teflon^R lid.
2. Introduce about 375 ml of 100% H₂SO₄ into the jar and weigh.
3. Determine the amount of PPD-T to be added. For example, a 17% solution with 300 grams of 100% H₂SO₄ would require 61.4 grams of PPD-T.
4. Weigh out the PPD-T needed, usually in 30 gram increments.
5. Place into the dry box the 800 ml jar, the PPD-T wrapped in aluminum foil, two osterizer eight ounce stir jars with blades and caps, two Fisher Scientific Scoopulas with the handles wrapped in electrical tape, and one 1000 ml Erlynmeyer flask with stopper. Fill the dry box with nitrogen for a period of three minutes and then shut it off. Periodically introduce nitrogen into the dry box for thirty second periods throughout the mixing process.
6. Using the Scoopula, mix the PPD-T in by hand, preferably by adding large chunks until all of the PPD-T is in the jar. Stir by hand until a fairly, though not totally, homogenous solution is achieved. The solution will begin to heat up as it is stirred. It is important during this stage not to allow the solution to cool below 50°C or mixing becomes much more difficult due to the viscosity increase.
7. Upon completion of the procedure described in 6, place about two thirds of the polymer solution into

one of the eight ounce stirring jars, filling it to the top. Attach the jar to the blender and mix the solutions for periods of two minutes with stirring by hand in between each mixing period until a totally homogenous solution is reached, that is, no PPD-T fibers can be seen.

8. Pour about one-third of the newly mixed solution into the remaining stirring jar and introduce the remaining polymer-solvent mixture from the 800 ml jar into the stirring jar. Mix using the same procedure as described above.

9. Upon completion of step 8, blend the contents of both stirring jars thoroughly and then pour into the 1000 ml flask using the Scoopulas to assist the process.

Bubble Removal

Bubble removal is accomplished by applying a vacuum to a fluid PPD-T solution. Figure 25 is a photograph of the apparatus used. Nitrogen is bled into the flask containing the solution to prevent water contamination and to keep the solution at the desired level. The vacuum pump used is manufactured by Duo-Seal and has a 1/5 horsepower motor.

For solutions over 12% by weight, a silicone oil bath heated by a Corning magnetic stirrer/hotplate, model number PC-351, was used to keep the solutions in a molten

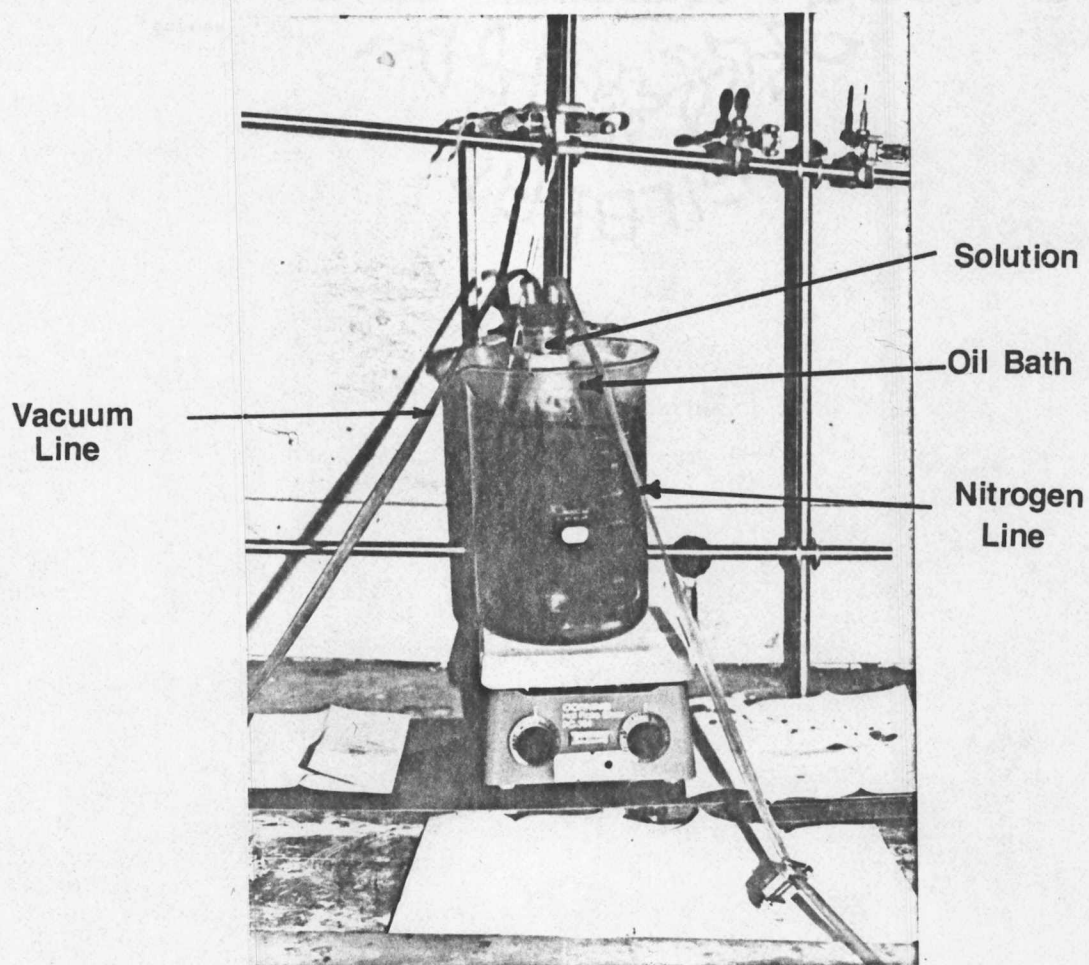


Figure 25. Apparatus for Removal of Air Bubbles from PPD-T/H₂SO₄ Solutions.

state. The silicone oil is Dow-Corning 200 with a viscosity of 100 cs.

Complete removal of bubbles usually requires about twenty-four hours.

C. Film Processing

Operation Description

Oil is pumped using a gear pump into a reservoir in which sits a piston with the polymer solution below the piston; see Figures 26 and 27. Oil pressure forces the polymer solution into the annular die where it emerges as an annular tube. The film may then be drawn over a cone shaped mandrel into a coagulation bath to provide biaxial orientation (see Figure 28) or drawn directly into the bath without the use of a mandrel to give uniaxial orientation; see Figure 29. When the mandrel is used, oil is pumped from an overhead separatory funnel with air pressure. The oil passes through the center of the die and onto the mandrel surface. This gives the polymer film a medium on which it may be drawn without sticking to the mandrel, thereby providing elongational flow; refer to Figure 30. The coagulating film may then be taken up around rollers through the bath by hand.

Equipment

The extrusion pump is made by Zenith Laboratories. It involves a 1/4 horsepower low speed General Electric

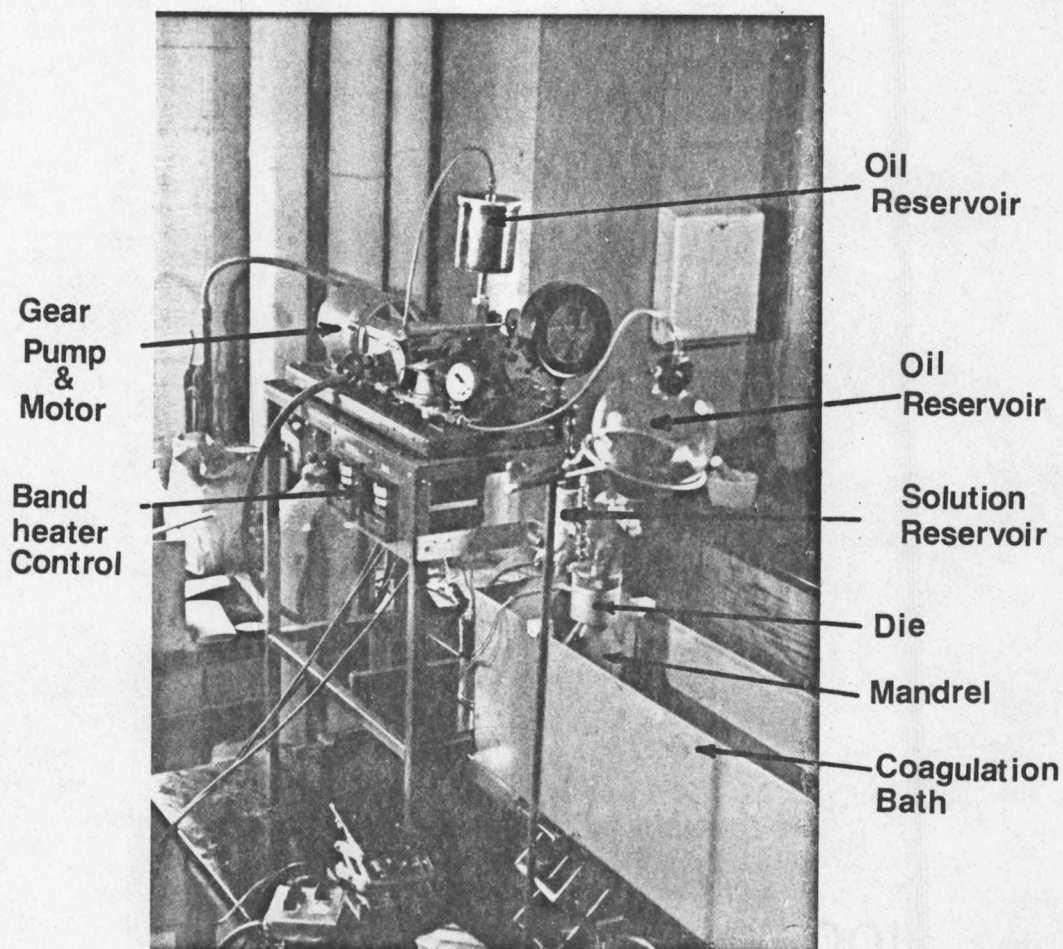


Figure 26. Photograph of the Present Mandrel Apparatus for the Production of Biaxially Oriented PPD-T Film.

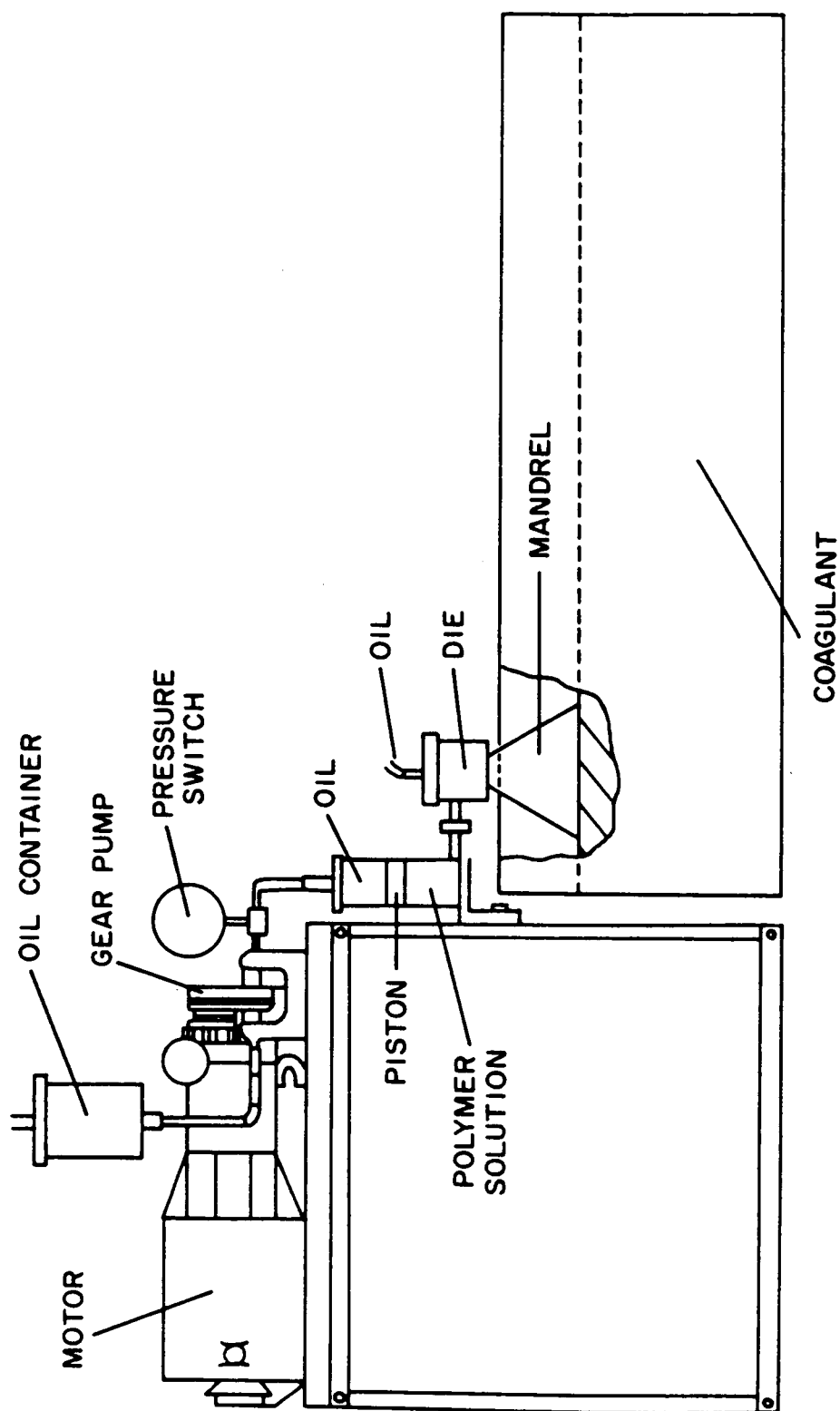


Figure 27. Schematic of the Mandrel Apparatus.

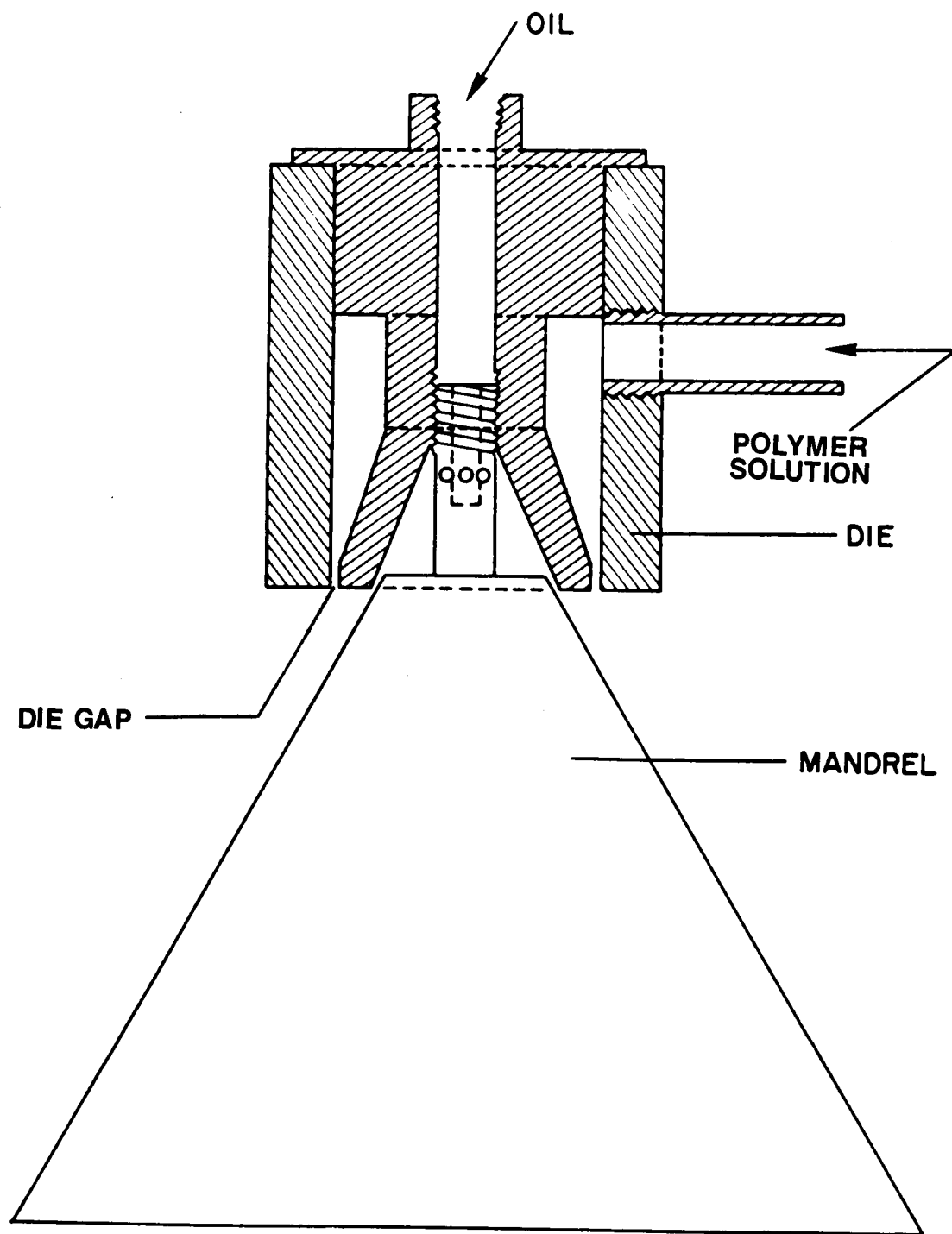


Figure 28. Schematic of Annular Die Cut Away and Mandrel.

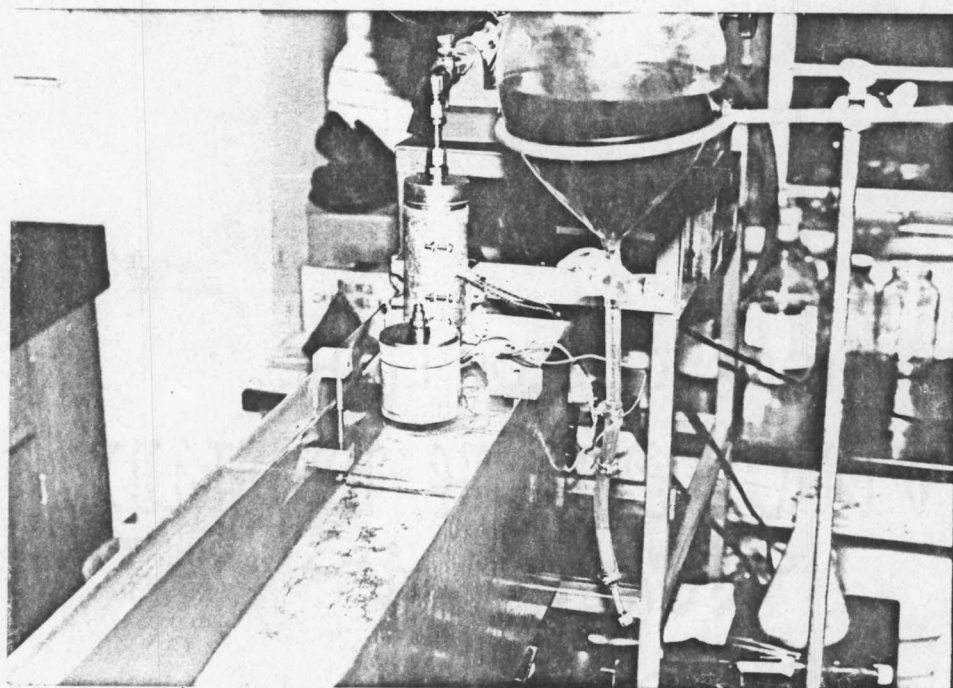


Figure 29. Photograph of the Uniaxial Film Apparatus.

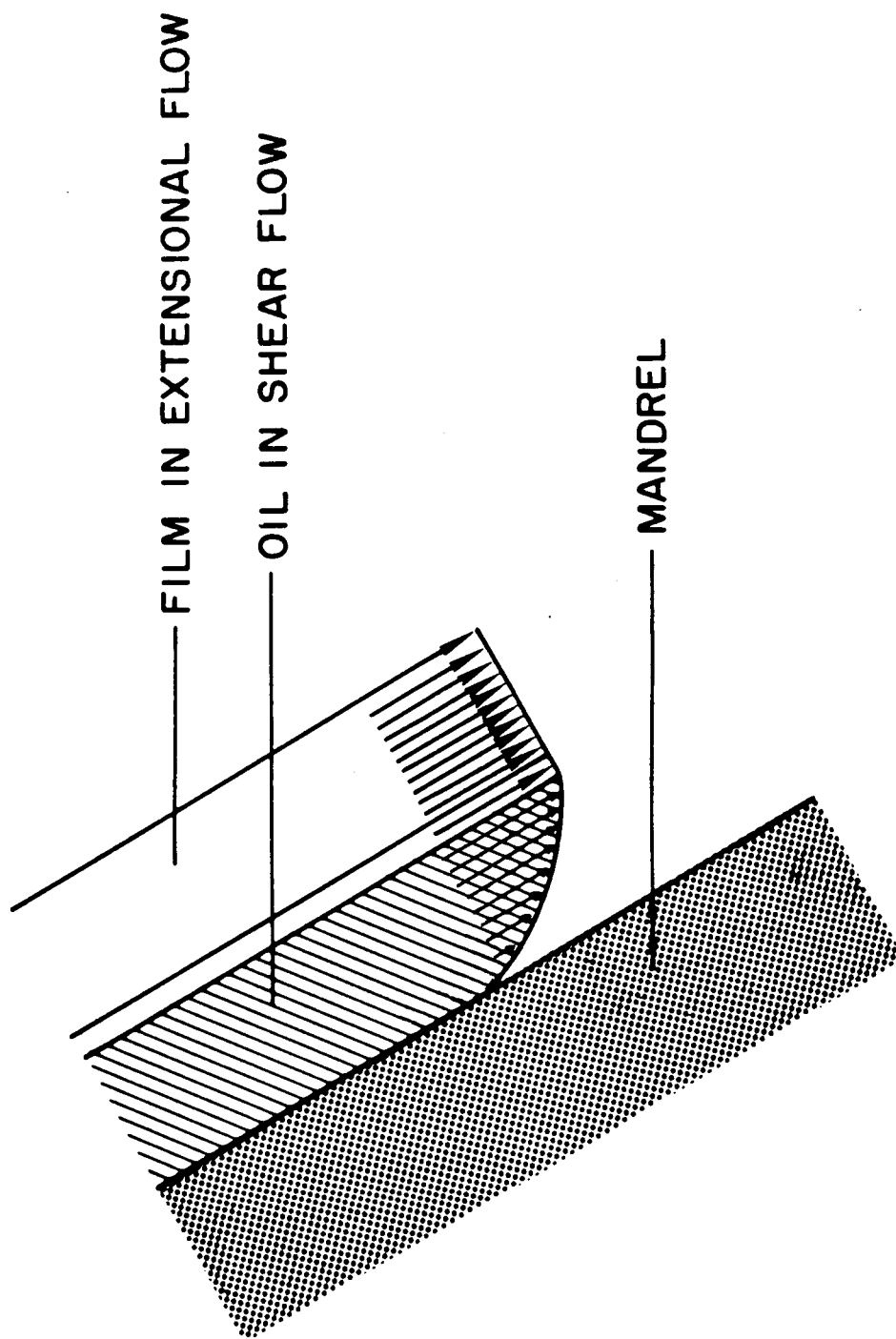


Figure 30. Schematic of the Type of Elongation Flow Taking Place on the Mandrel Surface.

motor which operates a gear pump used to pump oil from the reservoir above the motor; see Figures 26 and 27. Different extrusion rates may be achieved by changing the motor speed. A plot of pump setting versus flow rate is shown in Figure 31. Pump setting versus velocity in the annular die is plotted in Figure 32.

The die and solution reservoir are made of type 304 stainless steel and were designed by Aoki et al. (5) with further modifications in dimensions by the author. The current dimensions of the reservoir and die are shown in Table 3. The piston is made from stainless steel and Teflon^R. The Teflon^R provides a seal against the reservoir wall to prevent oil leakage into the polymer solution.

Heating of the die and reservoir is accomplished by specially fitted band heaters made by Hotwatt of 120 volt, 200 watt and 120 volt, 120 watt respectively. Temperature control for the band heaters is provided by two Athena controllers with a range of 30°C to 300°C. Thermocouples are iron-constantan coated with Teflon^R to prevent corrosion.

The mandrel is made of poly (vinyl chloride) to prevent corrosion; see Table 3 for dimensions. The cone design was chosen because of its simplicity both to make and to interpret in terms of film kinematics and dynamics.

The coagulant for the film is contained in a twenty gallon rectangular stainless steel container. Take up

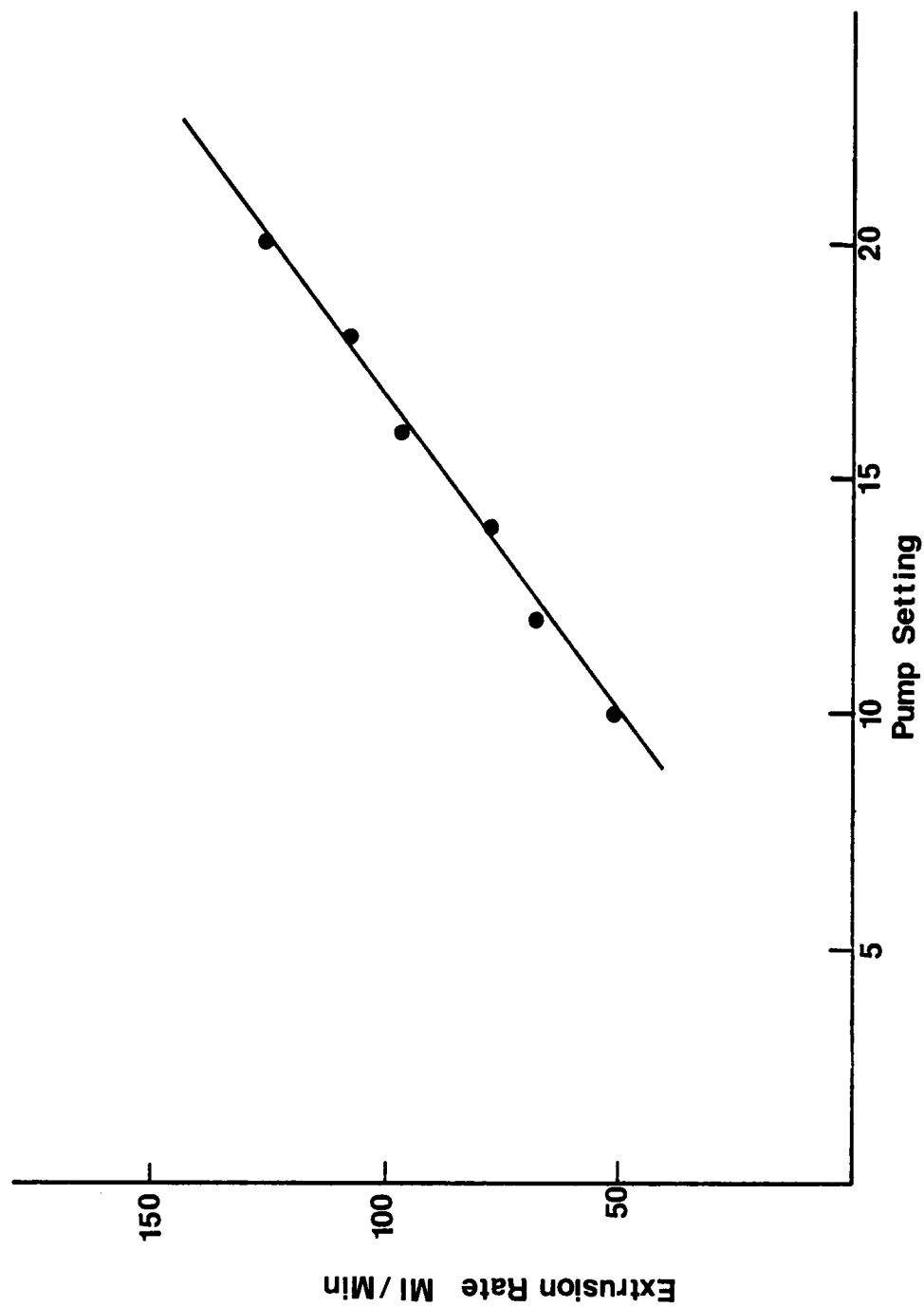


Figure 31. Plot of Pump Setting Versus Flow Rate.

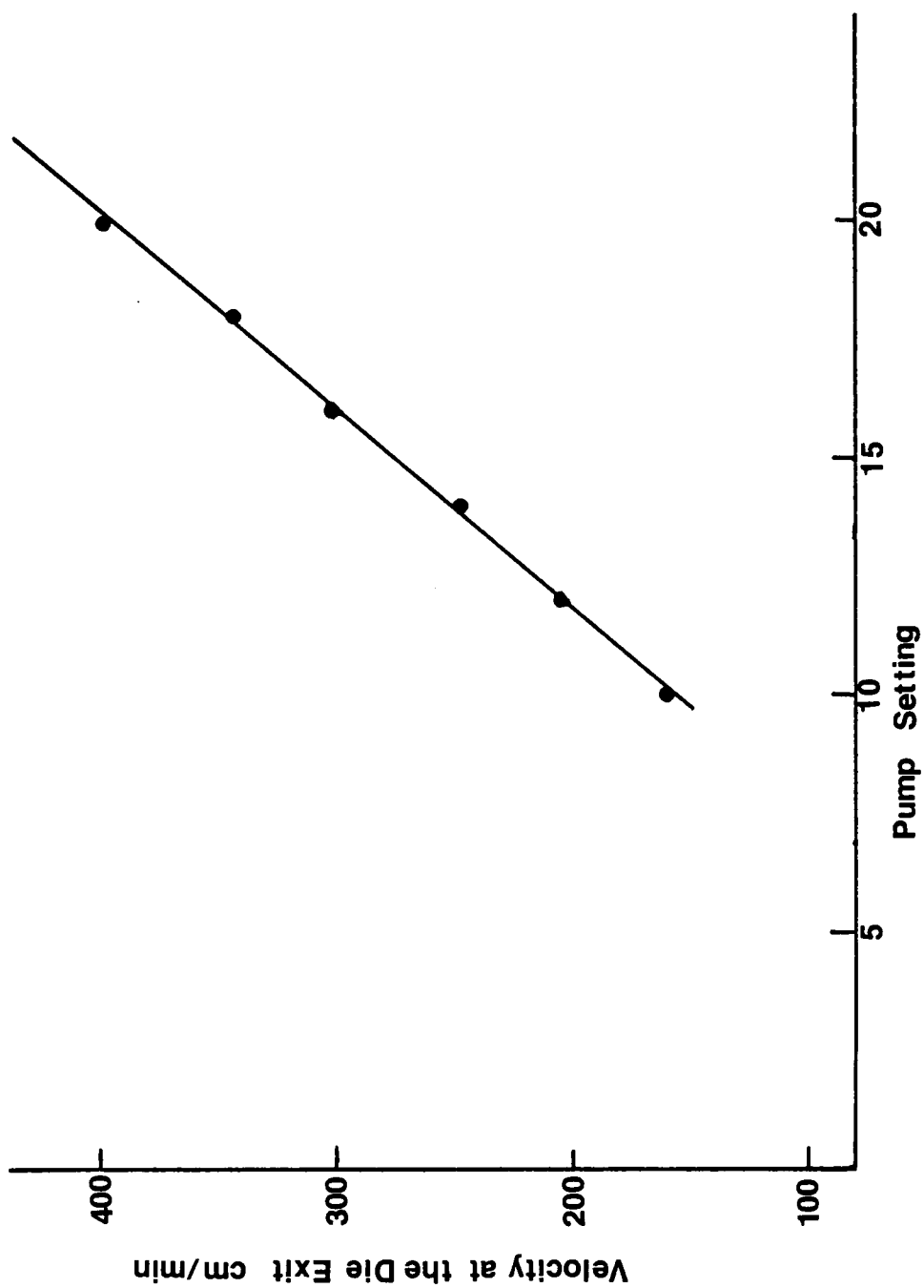


Figure 32. Plot of Pump Setting Versus Extrusion Velocity.

Table 3. Important Dimensions of the Die, Mandrel, and Reservoir

Die Dimensions		Mandrel Dimensions		Reservoir Dimensions	
Height	80 mm	Height	112 mm	Height	30.7 cm
Radius	34.83 mm	Initial Radius	16.5 mm	Length	126.0 cm
Annular Radius	25.4 mm	Final Radius	80 mm	Width	20.0 cm
Gap	0.03 mm	Angle from Vertical	30°	Volume	7.62 x 10 ⁴ ml

rollers, also made of stainless steel, may be fitted to the coagulant bath, usually under the mandrel, to aide in drawing the film without ripping it.

Oil is pumped over the mandrel surface from a 2000 ml sepratory funnel suspended above the die and mandrel. Oil flow rates are controlled by varying the air pressure to the sepratory funnel. See Figure 27, page 72.

Preparation and Operation of the Film Process

After the removal of bubbles from the polymer solution, preparations for film processing should be made. This involves the steps listed below and the equipment previously described.

1. Make sure all passages in the die and reservoir are clear of obstructions, however small they may be, to reduce the chance of gap blockage and to allow for a good seal between the piston and reservoir wall.
2. Insert a 56 square/in 3.5 by 3.5 cm wire mesh screen into the joint connecting the reservoir and die. This is to trap impurities; see Figure 33.
3. Connect the thermocouple to the annular die using Teflon^R tape.
4. Place band heaters on the reservoir and die and connect the reservoir band heater and thermocouple into the heating control. Set temperature control to desired temperature and turn it on.

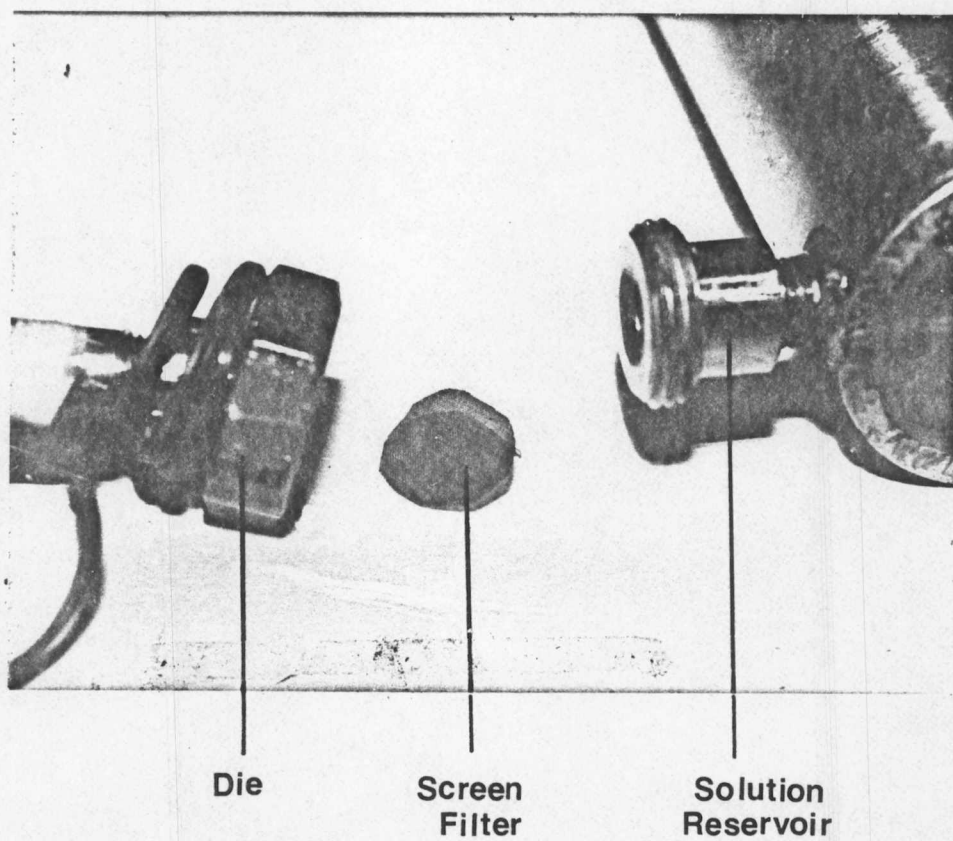


Figure 33. Photograph of Screen Insert Between the Die and Reservoir.

5. Upon reaching the desired temperature, remove the solution from the oil bath and pour the solution, with the reservoir angled about 30° from the table, down the side of the reservoir. About four centimeters should be left in the top of the reservoir to allow for insertion of the piston. This procedure is performed in the open air, not under a nitrogen blanket; see Figure 34.

6. Immediately after inserting the piston, place the top on the reservoir, turn off the temperature control, and disconnect the thermocouple and band heater. Then, wearing asbestos gloves, connect the reservoir die assembly to the extrusion pump. Reconnect the thermocouples and band heaters to the temperature control for both the reservoir and die. Turn on the temperature control for the reservoir.

7. Coat the bottom of the die around the gap with 10W-40 weight oil to stop the film from sticking to the die as it extrudes out.

8. If a biaxial film is to be made, screw the mandrel into the bottom of the die leaving a 0.4 cm gap between the top of the mandrel and the die.

9. Turn on the temperature control to the annular die.

10. Fill the coagulant bath till the coagulant just touches the bottom of the mandrel. Further adjustment of the coagulant level may be made by raising or

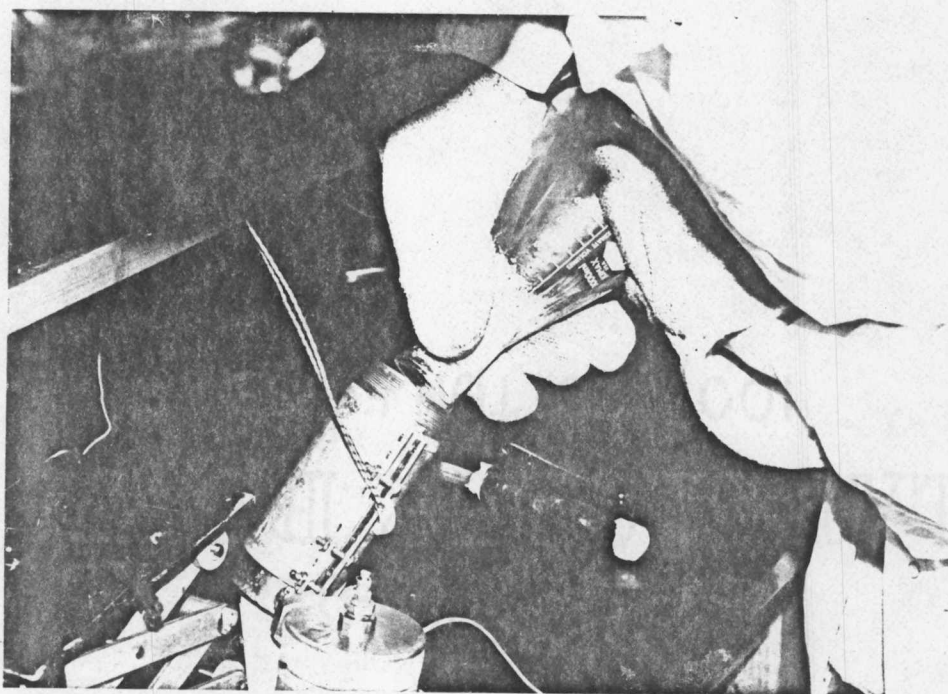


Figure 34. Photograph of Transfer Procedure of PPD-T/
 H_2SO_4 Solution into the Reservoir.

lowering the adjustable platforms on which the coagulant bath sits.

11. Fill the pump reservoir and the separatory funnel with oil. The pump reservoir should be filled with 10W-40 oil; the separatory funnel's oil type is dependent on factors which will be discussed later. The separatory funnel is stoppered and hooked into a nitrogen tank; the stopper is held down by electrical tape.

12. Connect the draw rollers to the coagulant bath.

13. When the annular die reaches the desired temperature, allow an additional five minutes of heating to ensure that the whole apparatus is at that temperature.

14. Set the pump for the desired extrusion rate and open the stopcock to the separatory funnel, allowing the oil to flow over the cone. Oil flow rate may be controlled through nitrogen pressure.

15. Once oil completely covers the mandrel surface, open the reservoir oil supply and turn on the pump.

16. When the film begins to emerge over the mandrel, a high oil flow rate (at least faster than the extrusion rate) over the mandrel surface is desirable in order to obtain complete coverage of the polymer dope over the mandrel surface. This flow rate may be reduced once coverage is achieved. See Figures 35 - 38.

17. Take up for this process was done by hand. If the film isn't being drawn faster than or equal to the

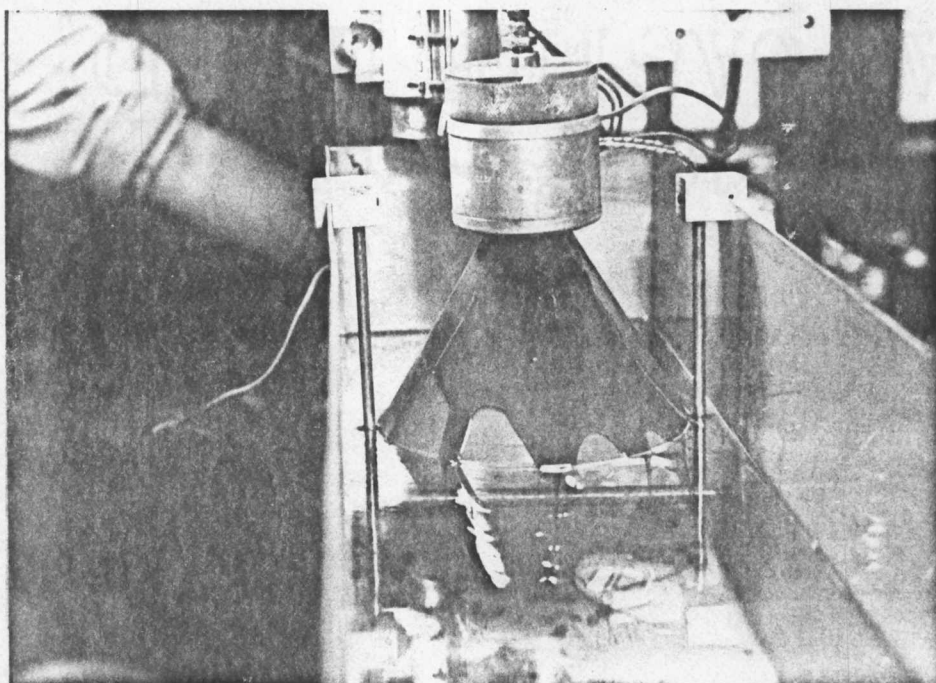


Figure 35. Oil Beginning to Extrude Over the Mandrel.

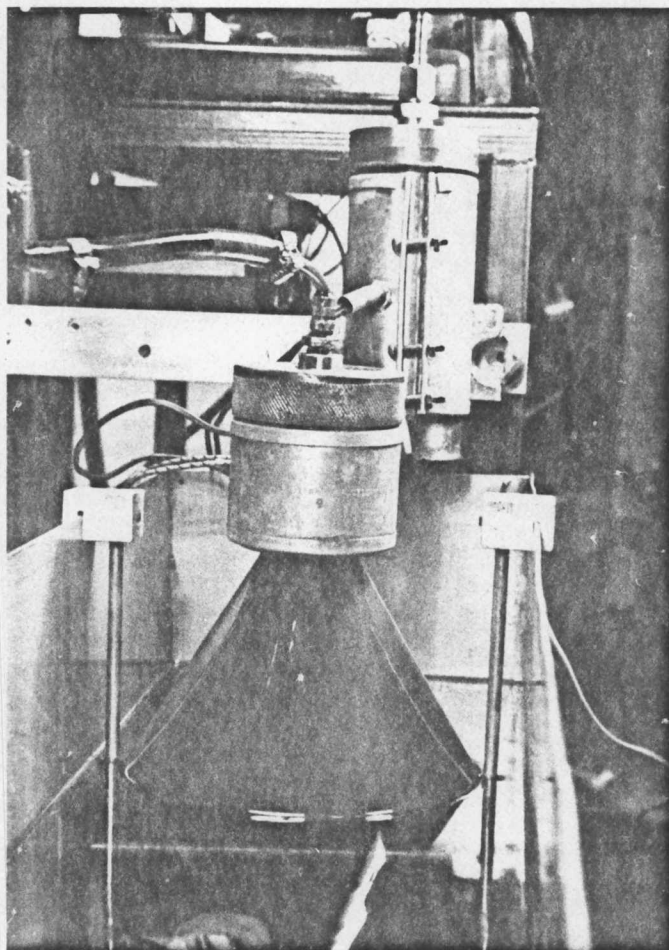


Figure 36. Oil Covering the Entire Mandrel Surface.

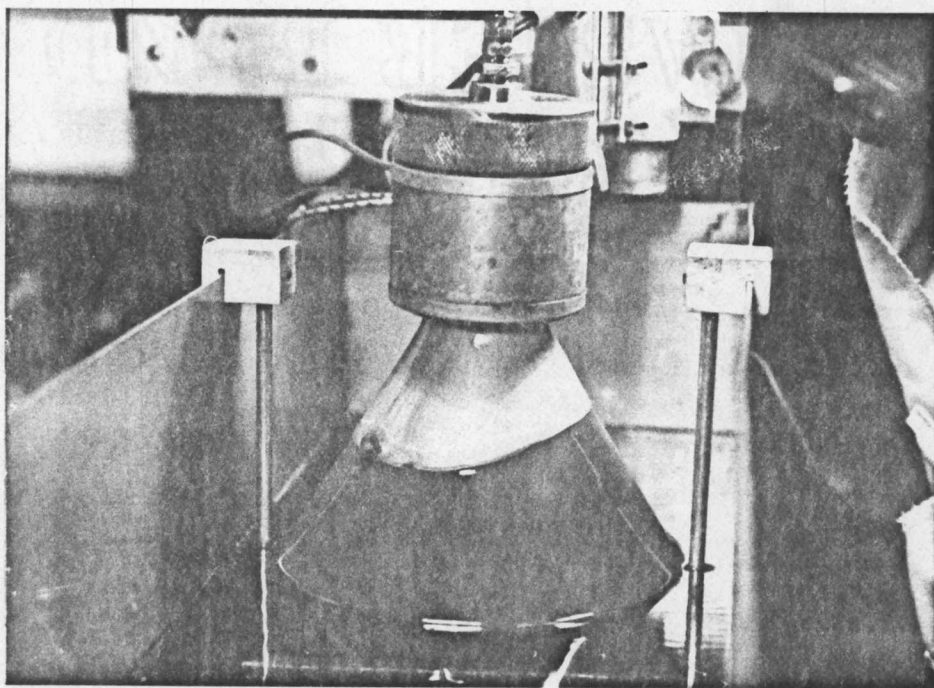


Figure 37. PPD-T Film Beginning to Extrude Over the Oil and Mandrel Surface.

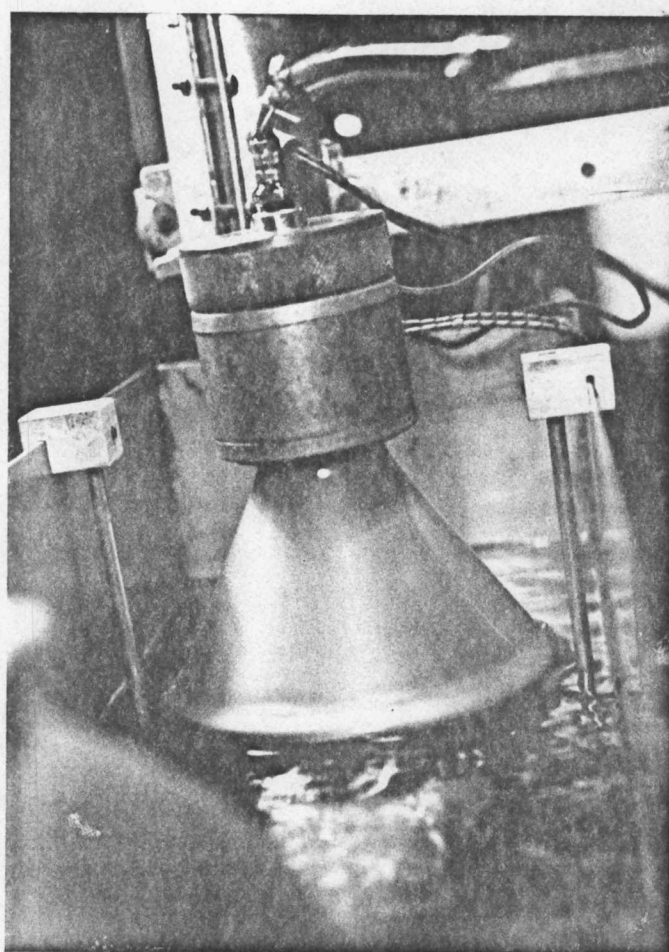


Figure 38. PPD-T Film Covering the Entire Oil and Mandrel Surface.

extrusion rate, buckling of the film immediately takes place on the cone surface.

18. Upon termination of the extrusion process, turn off the pump and band heaters and allow the film to stay in the coagulation bath for about five minutes. Then transfer the film to a water bath. Change the water at least twice during the first two hours. After the last water change, the film may be allowed to stay in the water for periods of up to a week.

Uniaxial films may be made without the use of the mandrel or oil by extruding the polymer solution directly into the coagulant with or without an air gap; see Figure 29, page 74.

All equipment should be cleaned immediately after usage has occurred in order to reduce the damaging effect of the sulfuric acid. The piston should be taken apart and cleaned every third run.

D. Film Characterization

WAXS Technique and Equipment

Wide angle X-ray diffraction patterns were made using a Philips X-ray generator with a copper target tube and nickel filter. X-ray wave length for the $\text{CuK}\alpha$ beam is $1.542 \text{ \AA}$.

Film samples were prepared by gluing films together with 3-M epoxy until a thickness of at least 1.2 mm and

less than 2.5 mm is achieved. Film directions are marked with felt tip pens.

X-ray patterns generated through the transverse and machine direction are taken using the sample holder designed by E. S. Clark (3). Patterns through the normal direction are made by taping the sample directly to the sample holder. A typical pattern for PPD-T films requires between two and three hours for good results.

Pole Figures and Orientation Functions

Pole figures are a two dimensional picture depicting a three dimensional sphere, which indicates orientation of a single crystal plane in space in reference to the three directions of the polymer sample. In the case of PPD-T films, the three directions are the machine, transverse, and normal directions; see Figure 39.

A single crystal orientor in conjunction with a General Electric X-ray generator and PDP-15 computer was used to produce pole figures from PPD-T films. The planes used were the (110), (200), and (006) (61).

Orientation functions were obtained from $(\cos^2\theta)$ values generated from intensity data of the (110) and (200) pole figures using methods developed by Wilchinsky (3) and White and Spruiell (99); see pages 55 and 57. Appendix I for further details. The (004) plane wasn't used in this analysis due to overlap from the (211) plane.

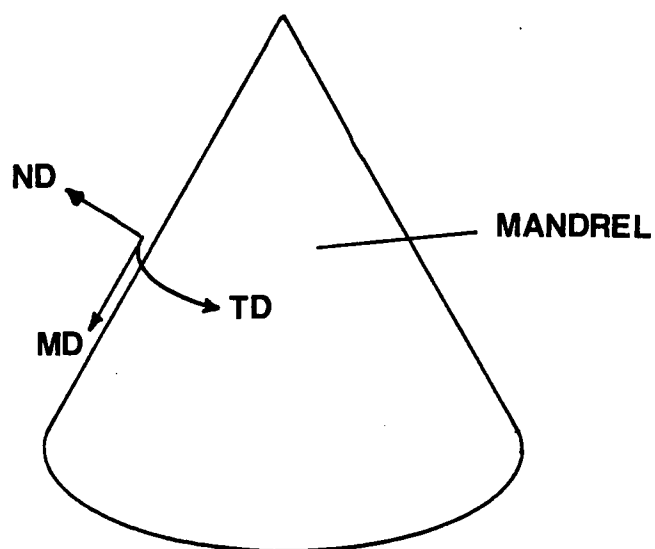
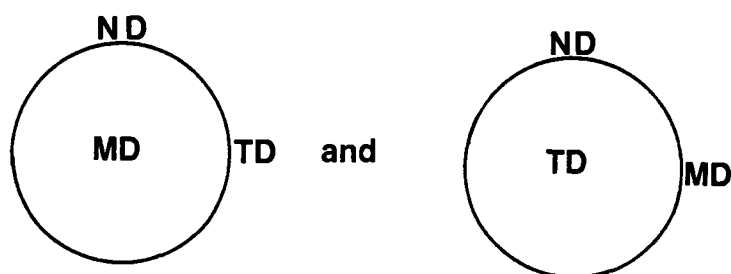


Figure 39. Schematic of the Film Directions on the Mandrel Surface.

This will be discussed later in more detail. The (006) reflection was too weak for use in determining orientation functions.

Samples were made by gluing films together using 3-M epoxy and applying a weight to the sample to ensure proper adhesion. To obtain the desired size, usually between 1.2 and 1.7 mm³, the samples were cut with a razor blade. Sample thickness was made larger in the normal direction because of the presence of glue, usually by about 0.2 mm. Alexander (3) describes a method for determining optimum sample thickness for wide angle X-ray diffraction. Once the samples are made, two are required, a polystyrene stick is glued to a machine direction face for one sample and to a transverse direction face for another. The pole figures generated are respectively:



Scanning Electron Microscope

SEM photographs of film cross sections and film surfaces normal to the film plane were taken using an AMR High Resolution Electron Microscope model number 900.

Samples were cut on a Teflon^R sheet using a scalpel. The samples to be used for cross section photomicrographs were mounted in slotted sample holders with epoxy glue. Other samples were glued flat onto the sample holder surface. All samples were coated with gold.

Film Shrinkage Measurements

Upon complete coagulation of the film, a small section of the film was removed from the coagulant and cut into two-inch square pieces. The stretching directions were noted with a felt tip marker on the film surface. The film was allowed to dry in the air for twenty-four hours. Film dimensions were then remeasured. The difference between the two measurements was translated to a percent shrinkage.

Determination of Mechanical Properties

Uniaxial stress strain measurements were made on PPD-T films using an Instron Tensile Tester model number 1122. Razor blades and straight edges were used to cut the samples. Sample size was usually 1 cm by 5 cm for biaxial and uniaxial film and 0.7 cm by 3 cm for undrawn films. Samples were cut in three directions, machine, transverse, and forty-five degrees between the machine and transverse directions.

Cross head speeds were 2 mm/min while chart speeds were 200 mm/min. Instron air clamps, with a clamping

force of 15 pounds, were used to clamp the sample. Gauge lengths were 2 cm.

CHAPTER IV

PROCESSING CONDITIONS

Since experimental procedures were discussed in the last chapter, it now becomes important to explain how and why certain parameters for both the uniaxial and mandrel processes were arrived at.

A. Results

Undrawn and Uniaxial Film Processing Conditions

Both the undrawn and uniaxial film processes used exactly the same equipment; see page 74, Chapter III. The difference between the two was the existence of a drawdown for the uniaxial film process that wasn't present for the undrawn film. Therefore, processing conditions for both methods will be explained together with emphasis on the uniaxial film process. The undrawn film process was used mainly as a control to demonstrate films where no attempt was made to induce orientation. The main objective of the uniaxial film process was to induce a high degree of molecular orientation in the machine or pulling direction.

Table 4 summarizes the range of processing conditions available for the undrawn and uniaxial film processes. The following sections expound upon the conditions in Table 4.

Table 4. A Summary of Processing Conditions for the Undrawn and Uniaxially Drawn Film Process

Processing Conditions	
Solution Concentration	2-5% and 12-23% by weight
Solution Temperature	65°-80°C for 17% concentration*
Die Gap	0.2 mm on up
Transverse Draw Ratio	1
Extrusion Velocity	85-400 cm/min**
Takeup Rate	1 to 8 times the extrusion rate
Coagulant Concentration	From 100% H ₂ O to 100% alcohol (alcohol is either methanol or ethanol)
Coagulant Density	Not applicable
Oil Viscosity	Not applicable

*Higher concentrations require higher temperatures.

**This was the range of extrusion velocities attempted. Probably much lower and much higher rates could be used.

1. Die Gap

The die gap was the gap made by the annular opening in the die; see Figure 28, page 73. A die gap of 0.3 mm was chosen for the undrawn and uniaxial film processes. Probably a large variety of gaps could be used for both processes with relative success. Neither method was particularly sensitive in terms of film rippage, etc., to the size of the die gap.

2. Solution Concentrations

Concentrations as low as 5% by weight could be used to make uniaxial films. Almost no drawdown could be used because the film split as soon as it was stressed. Concentrations above 12% were processed with relative ease. It was found that higher concentrations resulted in a higher degree of processability. Solutions 17% by weight were chosen because of their processability as compared to lower concentrations and because of the low temperatures at which they could be extruded, that is, 60° to 75°C as compared to higher concentrations. Processability would be defined as the ability of the polymer dope to stretch or expand under conditions of elongational flow.

It was also important that the solution concentration be in the anisotropic region, which has been proven to aid in producing higher degrees of orientation in PPD-T fibers (49). Therefore, concentrations below 10% weren't really considered for this process.

3. Solution Temperatures

Temperatures ranging from 60° to 75°C could be used for uniaxial film production. Film splitting wasn't a problem within the above temperature range. Seventy degrees centigrade was chosen as the processing temperature to help reduce polymer degradation as compared to higher temperature (11), and to keep the polymer within the anisotropic region; see Figure 4, page 16.

4. Air Gap

The air gap is the distance between the die opening and the coagulant; see Figure 17, page 45.

Initially, uniaxial films were made by extruding through the annular opening into an air gap between one-half and one inch. When drawdown was required, the film usually ripped, with long tears in the pull or machine direction, in the air gap. Smaller air gaps, between one-fourth and one-half inch, were attempted; still the films ripped. The next step was to use no air gap. The end of the die was placed just below the coagulant surface. The results were fairly successful with drawdown ratios as high as eight being achieved with little ripping. Drawdown was measured by dividing the initial film thickness by the final average film thickness. Due to the effects of coagulation, that is, swelling or shrinking, this was a relative measurement.

5. Extrusion and Take Up Rates

A variety of extrusion rates could be used for this process ranging from 85 cm/min on up to 400 cm/min. Take up rates were on the order of five to eight times the extrusion rates. Take up rates were determined by measuring the final film thickness and comparing it to the initial thickness and the extrusion rate. Take up was usually accomplished by hand drawing. Specific take up velocities were difficult to determine.

6. Coagulants

A large variety of coagulants could be used for the undrawn and uniaxial process. Fast coagulants such as water and solutions of water and alcohols, such as methanol, tend to give the best results in terms of mechanical properties, etc. Table 4 summarizes the coagulants used.

Blown Film Process

Early attempts by the author to produce a biaxially oriented film involved a blown film process. The process is the same as the mandrel film process up until emergence of the polymer solution from the annular die.

The film was extruded as a tube through an air gap between one-half and one inch into a coagulation bath; see Figure 17, page 45. Air was pumped through the die into the bubble created by the film and coagulant.

Inflation of the bubble was attempted to produce stress in the transverse direction. Problems resulted when longitudinal rips appeared in the inflating bubble causing the bubble to deflate. Other problems associated with this process were related to the small bubble volume, resulting in poor air pressure control and the effects of gravity causing the film to draw down prematurely and rip.

The above results lead to development of the present mandrel process.

Mandrel Film Process

Following the failure of the blown film process, it was decided that a different approach was needed. This led to the development of the mandrel process to produce biaxially oriented films. The basic premise of the mandrel process was to extrude the polymer solution through an annular opening and over a mandrel, conically shaped in this case, to induce molecular orientation in both the machine and transverse directions. That elongational flow and not shear flow should take place on the mandrel was considered a necessity in order to induce higher degrees of orientation. For the above situation to be accomplished, oil was extruded through the center of the die onto the mandrel to give a relatively frictionless surface for the polymer film to be drawn over.

Table 5 summarizes the range of the processing conditions used for the mandrel process. The following sections explain the processing conditions in more detail.

1. Mandrel Design

A conically shaped mandrel was chosen for its simplicity of design and interpretation. Dimensions of the mandrel were based on the initial film diameter, 50.5 mm, and the coagulation bath dimension, that is, as large a final diameter as the bath dimensions would allow, in this case 200.1 mm. The diameter at the top of the mandrel, 31 mm, was chosen to allow for uniform oil distribution over the mandrel surface and to allow for a gradual radius increase for the extruding polymer tube. An inclination angle of 30° to the vertical was chosen in order to produce gradual stretching. It also reduced gravity effects as opposed to a small angle.

The mandrel was attached to the die to avoid slitting the film. The support for the mandrel also doubles as an access point for the oil to the mandrel surface; refer to Figure 28, page 73.

2. Die Gap

Initially, a die gap of 0.2 mm was used in conjunction with the mandrel. The resultant film thinned out rapidly and ripped prematurely. A 0.25 mm gap was attempted with similar results. The tendency to rip

Table 5. A Summary of Processing Conditions for the Mandrel Film Process

Processing Conditions	
Solution Concentration	15-23% by weight*
Solution Temperature	68-80°C for a 17% solution**
Die Gap	A minimum of 0.3 mm
Transverse Draw Ratio	3.3
Extrusion Velocity	160-270 cm/min***
Takeup Velocity	Equal to extrusion velocity
Coagulant Concentration	From 5-25% H ₂ O by volume in methanol or ethanol
Coagulant Density	Less than or equal to 0.87 gm/cm ³
Oil Viscosity	177-314 cp
Oil Type	Hydrocarbon based
Oil Density	Greater than 0.87 gm/cm ³

*A 17% solution was the highest concentration attempted. Higher values would probably work better.

**Increasing concentrations require higher temperatures.

***270 cm/min was the highest rate attempted. Rates lower than 160 cm/min resulted in film splitting.

wasn't as pronounced. Gaps above 0.3 mm worked relatively well with the present mandrel design. In most cases, the films stayed together for the full stretch ratio. Occasional ripping, however, still occurred.

3. Solution Concentration

Early work with uniaxial and blown films determined that the higher the solution concentration, the easier the solution was to process into a film. Concentrations below eight percent formed gels and became very inelastic, resulting in very poor spinnability regardless of temperature.

While bubble removal, though important, wasn't critical for the extruded and uniaxial film, it was a necessity in order for the mandrel process to work. This was found to be impossible with the vacuum method of bubble removal for concentrations above 5% and below 8%. Solution viscosities were too high and increased temperatures, 70°-80°C, resulted in rapid degradation. Degradation was observed as a large decrease in viscosity and a color change from amber to black.

Seventeen percent solutions were chosen for their high degree of processability in relation to the mandrel process, that is, they stretched easier under elongation flow as compared to lower concentrations. They were also chosen because of the low processing temperatures used during the extrusion process, 60°-75°C, and because

of the ease involved in making them up relative to higher concentrations. It was also important as stated earlier for the concentration of the solution to be in the an-isotropic region.

4. Solution Temperature

A variety of temperatures were attempted for 17% solutions ranging from 60°-85°C. Temperatures below 65°C resulted in early failure in the film, that is, ripping, before the full stretch ratio could be reached. Temperatures from 68° to 85°C worked well with temperatures between 70° and 75°C chosen as the operating temperatures. Degradation and transitions to the isotropic phase were brought about by temperatures above 90°C (11, 44).

5. Lubricating Oil

Oil was introduced to the mandrel surface to provide an essentially frictionless surface for the stretching polymer film. Viscosity, density, and chemical structure (including impurities) were the three most important criteria in choosing the correct oil.

Too low a viscosity, at or below 100 centipoise at 23°C, resulted in premature film splitting on the mandrel surface prior to reaching the full stretch ratio. Splitting took place about a quarter of the way down the mandrel. The result was a relatively thick, 0.3 to 0.5 mm, uniaxially oriented film.

Greasing the mandrel surface with Dow Corning Silicone grease resulted in very slow movement and sticking of the extruding film to the mandrel. Upon sticking, the film would immediately begin to buckle and overlap. Low extrusion rates couldn't cure the problem.

High viscosity oils such as Sears 90W gear oil usually weren't consistent in covering the mandrel surface, that is, pitting of the oil film occurred allowing the polymer dope to stick to the mandrel.

A medium weight oil such as Sears 15W-50 gave the best results. In most cases the film reached the end of the mandrel, though occasional splitting still occurred, usually towards the bottom of the mandrel. Another oil used with relative success was Sears 10W-40. In this case, splitting occurred more often than with 15W-50 oil and usually further up on the cone. See Table 6 for a list of oil viscosities.

Oil density is important because the oil must sink in the coagulant. Otherwise, the oil spreads out on the coagulant surface taking the film with it, causing film splitting before coagulation takes place. Likewise, the density of the coagulant was regulated to accommodate the oil. Table 7 contains the combinations of oils and coagulants that meet the above requirements.

Table 6. Viscosities* and Effectiveness of Oils Used in the Mandrel Process

Oil Type	Viscosity Centipoise	Oil Effectiveness**
Duo Seal Vacuum Pump Oil	200	Fair
Sears 10w-40	177	Fair
Sears 15w-50	313	Good
Dow Corning (200)	102	Poor
Dow Corning (200)	370	Poor

*All viscosities were measured by a Brooksfeld Viscometer at 25°C.

**Poor: PPD-T film can't cover the mandrel surface and splits.

Fair: Frequent film splitting but the PPD-T film covers the mandrel.

Good: Occasional splitting but the PPD-T film always covers the mandrel.

Table 7. Oil and Coagulant Compatibility for the Mandrel Process

Oil Type	Coagulant Concentrations by Volume				
	100% H ₂ O	45% H ₂ O 55% MeOH	25% H ₂ O 75% MeOH	5% H ₂ O 95% MeOH	Ethylene Glycol
Dow Corning (200) 370 cp	no*	yes**	yes	yes	no
Duo Seal Vacuum Pump Oil	no	no	yes	yes	no
Sears 10w-40	no	no	yes	yes	no
Sears 15w-50	no	no	yes	yes	no

*No implies that the PPD-T film will follow the oil spreading out on the coagulant surface and split. Oil density is less than the coagulant density.

**Yes implies that the oil will sink far enough into the coagulants to keep the PPD-T film from spreading out on the coagulant surface. Oil density is greater than the coagulant density.

Carbon based oils such as Sears 10W-40 and 15W-50 worked well with the mandrel process. Silicon based oils such as Dow Corning 300 with a similar viscosity as the above oils resulted in failure of the stretching film. Failure or ripping developed relatively early on the mandrel surface, about a quarter of the way down, resulting in thick, 0.3-0.5 mm, uniaxial films.

6. Coagulants

The original criterion for choosing a coagulant was to use those in the Kwolek and Blades patents (49, 11). They were water, methanol, ethanol, and ethylene glycol. When oil density became a factor, coagulant density also became important. It was found that water, an excellent coagulant, was difficult to work with because oils that flow in a satisfactory manner on the mandrel floated on the surface of the water. Combinations of water and alcohol were attempted; refer to Table 7. Seventy-five percent methanol or ethanol and 25% water were found to work well with the oils used. Ninety-five percent methanol and ethanol with 5% water were also used. Pure ethylene glycol was found to be too dense for the oils used. Table 8 is a list of coagulant densities.

Dow Corning 300 silicon oil sinks in coagulants made up of 55% ethanol or methanol and 45% water. The oil itself doesn't lend itself well to the mandrel process.

The temperature of all coagulants was room temperature.

Table 8. Coagulant Densities for Different Combinations of Alcohol and Water

Coagulant Volume %	Density gm/cm ³
H ₂ O	1
[45% H ₂ O] [55% EtOH]	0.9139
[25% H ₂ O] [75% EtOH]	0.8676
[5% H ₂ O] [95% EtOH]	0.8013
[45% H ₂ O] [55% MeOH]	0.9156
[25% H ₂ O] [75% MeOH]	0.8715
[5% H ₂ O] [95% MeOH]	0.8089
[Ethylene] [Glycol]	1.0765

7. Extrusion and Take Up Rates

The mandrel process operated satisfactorily for a variety of extrusion rates ranging from 50 ml/min on up to 150 ml/min. Usually extrusion rates below 50 ml/min caused early thinning and failure of the stretching film. An extrusion rate of 80 ml/min was chosen for the process because it appeared to work well.

Take up was accomplished by hand. If the take up rate was below the extrusion rate, buckling in the film resulted at the mandrel base. Buckling induces the film to break through the oil layer and stick to the mandrel. Drawdown ratios, defined as take up rates/extrusion rates, are fairly easy to control due to the buckling effect. Higher drawdown ratios were achieved by increasing the take up rates over extrusion velocity. Control of constant higher drawdown ratios was difficult for two reasons. First, take up was accomplished by hand. Second, the small amount of polymer available made steady state conditions difficult to achieve.

There were attempts to use a take up roll to give a controlled drawdown ratio. The quantity of solution available for each run, between 300 and 400 ml, wasn't enough to allow establishment of steady state conditions. By the time the film reached the reel, the quantity of polymer was beginning to run low.

Film Thickness Variations

All of the films produced had some thickness variation in the transverse direction. Biaxial films exhibited a greater degree of variation than either the uniaxially drawn or undrawn films. Typical values for undrawn uniaxial and biaxial films were 0.5 - 1.0 mm, 0.025 - 0.2 mm, and 0.005 - 0.1 mm respectively. Undrawn films exhibited thicknesses larger than the die opening.

Film Shrinkage

Upon coagulation, the film appeared to be in a swollen state. After washing the film with water, the film was allowed to dry at room temperature. The shrinkage for four coagulants, from the time the film is coagulated to the time it dries (about twenty-four hours), was measured. Table 9 is a list of film shrinkage as a function of film direction drawdown, blowup, and the coagulant used for some typical films.

Experimental Runs

Table 10 is a list of experimental runs. The coagulant, drawdown ratio, and blowup ratios are the changing variables. Solution concentration, processing temperatures, and extrusion rates were kept constant in all cases.

Table 9. Film Shrinkage as a Function of Film Direction, Processing History, and Coagulant Used

Coagulant Volume %	Percent Shrinkage					
	Undrawn		Uniaxially Drawn		Biaxially Drawn	
	MD*	TD**	MD	TD	MD	TD
100% H ₂ O	73	73	0	20	--	--
45% H ₂ O 55% MeOH	5.9	38	1.3	17	--	--
25% H ₂ O 75% MeOH	24	33	0	28	2	0
5% H ₂ O 95% MeOH	15	30	5.7	30	0	0

*MD - Machine direction shrinkage

**TD - Transverse direction shrinkage

Table 10. A Table of Experimental Runs and Their Process Conditions

Experimental Run Number	Coagulant	Transverse		Machine Draw Ratio	Temperature °C	Extrusion Rate ml/min	Percent Concentration
		Direction	Draw Ratio				
1	[5% H ₂ O] [95% MeOH]	1	D = 1		70	85	17
2	[25% H ₂ O] [75% MeOH]	1	D = 1		70	85	17
3	[45% H ₂ O] [55% MeOH]	1	D = 1		70	85	17
4	[50% MeOH] [50% EtOH]	1	D = 1		70	85	17
5	[100% H ₂ O]	1	D = 1		70	85	17
6	[25% H ₂ O] [75% EtOH]	1	D = 1		70	85	17
7	[5% H ₂ O] [95% MeOH]	1	D > 1		70	85	17
8	[25% H ₂ O] [75% MeOH]	1	D > 1		70	85	17
9	[45% H ₂ O] [55% MeOH]	1	D > 1		70	85	17
10	[50% MeOH] [50% EtOH]	1	D > 1		70	85	17
11	[100% H ₂ O]	1	D > 1		70	85	17
12	[25% H ₂ O] [75% EtOH]	1	D > 1		70	85	17
13	[5% H ₂ O] [95% MeOH]	3.3	D = 1		70	85	17
14	[25% H ₂ O] [75% MeOH]	3.3	D = 1		70	85	17

Table 10 (continued)

Experimental Run Number	Coagulant	Transverse		Machine Draw Ratio	Temperature °C	Extrusion Rate ml/min	Percent Concentration
		Direction	Draw Ratio				
15	[50% MeOH] [50% EtOH]	3.3	D = 1	70	85	17	
16	[50% MeOH] [50% EtOH]	3.3	D = 1	70	85	17	
17	[50% MeOH] [50% EtOH]	3.3	D = 1	70	85	17	
18	[25% H ₂ O] [75% EtOH]	3.3	D = 1	70	85	17	
19	[50% MeOH] [50% EtOH]	3.3	D > 1	70	85	17	

B. Discussion

Certain conditions such as air gap, coagulants used, etc., need further explanation in terms of what is happening to the stretching film during the film process. The following sections deal in a qualitative way with some possible answers and raise more questions as to what is taking place.

Uniaxial Film Processing Conditions

1. Air Gap

Since there is no air gap in the uniaxial process, all stretching takes place in the coagulant. The conditions are nonisothermal. Because of the low temperature of the coagulation bath, viscosity builds up rapidly as do stresses. At the same time, coagulation is taking place contributing largely to viscosity and stress increases. Stretching under these conditions is very complicated and no attempt will be made to explain it from a dynamic point of view, except to say that an air gap would probably enable higher levels of orientation to be achieved and also allow more shrinkage. Higher drawdown ratios can be achieved in an air gap because coagulation isn't taking place.

2. Coagulant

For the present uniaxial film process, additional drawing in the machine direction could be achieved with a

slower coagulant such as ethylene glycol. Fast coagulants such as water tend to retard the drawing process.

3. Kinematics of the Uniaxial Process

From a kinematic viewpoint, there were two possibilities which partially describe the type of stretching present. The first involved the film thickness becoming smaller but at the same time the radius was also reducing. The second case involved planar extension in which the film radius remained constant as the film thickness reduced. Both of the above examples were explained in Chapter II under the heading of Kinematics of Blown Films. The stretching conditions were listed as $d_{33} = d_{22}$ and $d_{33} = 0$ respectively.

Which of the above two cases is correct is hard to determine. There is a reduction in the film radius during uniaxial stretching for PPD-T film. The degree of wrinkling in the film prevents accurate measurement, thus leading us to the conclusion that the reduction in film radius isn't simply explained by kinematics. It is also due to the huge mass transfer of H_2SO_4 from the polymer solution and to the large temperature changes taking place.

Mandrel Process

1. Advantages of the Mandrel Film Process Over the Blown Film Process

Failure of the blown film process resulted in development of a new method for biaxial film production without the drawbacks of the blown film process. Use of a mandrel to induce biaxial orientation doesn't involve air pressure and gravity effects aren't as dominant due to support provided by the mandrel.

Stretching, according to Gutteridge's (28) models, takes place first in the transverse direction and then in the machine direction for a cone shaped mandrel. The opposite is true for a blown film process. If the above situation can be applied to nematic liquid crystal solutions, which may not be a valid assumption, there would be definite advantages in using a mandrel process over the blown film process. That is, that a large amount of orientation in the machine direction isn't introduced to the expanding film prior to transverse stretching using the mandrel process. Due to the easily oriented nematic character of PPD-T/ H_2SO_4 solutions, additional orientation in the machine direction is undesirable. The reason for this is due to machine direction orientation induced during flow through the die. The result of all this uniaxial orientation would be rips in the film when transverse orientation is attempted. The blown film process

for Kevlar^R solutions demonstrated longitudinal rips, or machine direction rips, upon inflation of the film. This indicated a high degree of uniaxial orientation in the machine direction prior to transverse stretching. The mandrel process didn't usually rip. When it did rip, the holes were circular indicating biaxial orientation. From a qualitative viewpoint, the Gutteridge models appear to work for Kevlar^R solutions.

2. Kinematics of the Mandrel Process

Upon reaching the mandrel surface, the polymer film begins to undergo elongational flow due to stresses in the transverse and machine direction and the lubricating oil. Since the film isn't twisting on the mandrel surface, the flow is irrotational. The oil beneath the film is undergoing shear flow. Figure 30, page 75, is an approximate diagram of the two types of flow present.

The kinematics of a mandrel process are the same as that of a film blowing process; see pages 26-28. The exception is that θ is constant. Therefore, the resulting equations are essentially the same.

For unequal biaxial stretching, which wasn't explained in Chapter II, Equation II.8 from Chapter II becomes

$$\frac{h_f}{h_o} < \frac{1}{B^2} \quad (\text{IV.1})$$

where stretching in the machine direction is greater and

$$\frac{h_f}{h_o} > \frac{1}{B^2} \quad (\text{IV.2})$$

where stretching in the transverse direction is greater
 where $B^2 = \frac{R_f}{R_o}$.

3. Film Nonuniformities in the Mandrel Process

In the case of the mandrel process, real values may be substituted into Equation II.8 to determine the type of stretching that the film undergoes, but the results would be deceptive. The reason for this is because of large thickness variations about the film's circumference; refer to the section on film thickness variations, page 111.

The large range in film thickness indicates different degrees of stretching taking place around the film's circumference. Uniaxial films also demonstrate a thickness variation, though not quite as drastic as those in the biaxial film.

Existing kinematics are dependent on an initial uniform extrusion rate through the die gap and a final uniform thickness. The possibility exists that extrusion rates are different about different positions on the die gap. The variations in film thickness have already been reported.

Nonuniformity both in extrusion rates and film thickness may be attributed to several conditions:

1. Variations in the annular die gap.
2. Polymer starvation in the die due to die design.
3. Polymer starvation in the die due to nonsteady state conditions.
4. For the mandrel process only, the frictionless surface created by the lubricating oil and transverse stresses induced by the mandrel.
5. Any combination of the above conditions.

4. Effects of Die Design on Film Formation

Die gap variations, by themselves, causing such large changes in film thickness are unlikely. They could instigate an initial flaw in the film resulting in a rapid thinning in the flawed section of the film during the drawing process. Large gap variations weren't present in the existing die.

The possibility of polymer starvation to various parts of the die is very real considering the die design. In this case, that section of the die opposite to the die entrance would be the region under suspicion; see Figure 28, page 73. Biaxial films were always thicker in those sections extruded below the die entrance and thinner in those sections opposite the die entrance. Uniaxial films made with the same extrusion rates show the same effect but not as extensively.

The above effect could be attributed to exit velocities below the entrance being higher than exit velocities

opposite the die entrance. The result, for the mandrel process, would be a film tending to draw itself to the side of the mandrel with the higher exit velocities creating thick and thin spots. For the uniaxial process, higher drawdowns result where the exit velocities are lowest.

Two reasons that could explain the variations in extrusion rates around the die exit's circumference are die design and nonsteady state conditions. Because polymer enters the die from the side and circles around the die, back pressures may never be high enough to create uniform polymer distribution to parts of the die opposite the die entrance before it exits. A die with less open space within the die might improve the situation, as would higher extrusion rates. The best solution would involve entering the die from the top, but in this case, die designs would become complicated.

5. Effect of Nonsteady State Conditions of Film Formation

Nonsteady state conditions due to the small amount of polymer used, 300 to 400 ml, also would result in polymer starvation and variations in the extrusion rates. The obvious solution would be to use larger amounts of polymer. With the current polymer reservoir, that was impossible. A larger reservoir should be designed or another method of extrusion used. Larger quantities would also result in the need for a more efficient bubble removal method.

6. Effects of Oil Viscosities on Biaxial Film Formation

Oil viscosities above 170 cp were found to reduce the incident of film splitting for 17% solutions at 70°C. This effect can be related to friction. The higher the viscosity, the higher the amount of friction present. Obviously, too much friction results in film stickage on the mandrel surface. A frictionless surface, low oil viscosity aided by uneven extrusion rates, allows the film to move and stretch unevenly about the mandrel surface resulting in film splitting or thinning. A certain amount of friction is necessary to reduce the gathering and thinning effect in the stretching film and to reduce film splitting.

7. Effects of Oil as a Coagulant

The ability of the lubrication oil to coagulate the polymer solution must also be taken into account. If a high degree of coagulation is taking place while the film is on the mandrel, the ability of the film to stretch decreases because of a reduction in "solution elasticity." This decrease in elasticity is a result of the solvent, sulfuric acid, being removed from the solution causing an increase in polymer concentration and solution viscosity. The end result is that internal stresses would build up and cause film rippage on the mandrel.

The coagulating ability of the oil could be related to a variety of factors. These are oil viscosity, water content, and chemical structure. A low oil viscosity could induce diffusion of the acid from the solution into the oil. The degree of diffusion is probably low due to the affinity of acid for the Kevlar^R, that is, hydrogen bonding. Water content and chemical structure may be closely associated, that is, the amount of water in a particular oil may be dependent on the chemical structure. Chemical structure in this context is either a carbon or silicon based oil. Carbon based oils with viscosities over 170 cp work well with the mandrel process; silicon based oils with viscosities over 170 cp don't.

The implication is that silicon oils may have a higher affinity for water than carbon based oils. Since water is a good coagulant, even small amounts, such as moisture absorbed from the air, would induce coagulation and early film rippage.

8. Effects of Nonisothermal Stretching Conditions and Processing Temperature on Film Formation

The biaxial film process is a nonisothermal process when the film is on the mandrel and in the coagulant. The film begins to cool immediately after emerging from the die. Upon reaching the coagulant, it is quenched

to room temperature and coagulated. The lubricating oil, after traveling through the heated die, is close to the same temperature of the polymer solution. In both cases, for the solution and the oil, viscosity increases as a function of mandrel position, that is, the further down the mandrel, the higher the viscosity.

Wessling (98), for his solutions involving stretching of a viscous tube over a conical mandrel, allowed viscosity to vary according to the following relationship

$$\eta = Cr^n \quad (\text{IV.4})$$

where η is the viscosity, C is a constant, r the mandrel radius, and n a temperature related constant. In the same paper, he discusses stretching in a temperature gradient on a frictionless mandrel. He suggests that initial stretching for a decreasing temperature profile is in the machine direction. Wessling and Alfrey's (97) elastic model, which is an isothermal model with and without friction present, suggests that first transverse stretching and then meridional or machine direction stretching take place.

Gutteridge (28) uses a linearly decreasing temperature profile to describe biaxial stretching for the elastic and viscoelastic cases. Equations IV.5 and IV.6 represent the temperature profiles for her elastic and viscoelastic models respectively.

$$T_x = \frac{dT/da}{(165-T_1)} \quad (\text{IV.5})$$

where a is equal to r/r_0 , r_0 is equal to the initial film radius, and T_1 is equal to the temperature at $r = r_0$.

$$T = \frac{dT}{da} (a-a_1) \quad (\text{IV.6})$$

where a_1 is equal to r_1/r_0 and r_1 is equal to the initial mandrel radius.

Both the elastic and viscoelastic models for non-isothermal drawing indicate initial stretching in the transverse direction. Gutteridge also found that the elastic case gives a range of conditions under which equal biaxial stretching takes place. The viscoelastic model doesn't give a range, just a single point at a particular value of longitudinal draw ratio and radial draw ratio in a linearly decreasing temperature profile.

For the present mandrel process, there are indications, as was previously mentioned, that stretching initially takes place in the transverse direction. This implies that Gutteridge's elastic and viscoelastic models are at least qualitatively describing the type of stretching taking place on the mandrel.

It is obvious that there are increased stresses in both the machine and transverse directions resulting from the decreasing temperatures and increasing viscosities. Certainly the nonisothermal conditions contribute

to orientation in the film in addition to stresses introduced by pulling the film over the mandrel. Later, through WAXS and mechanical properties, it will be shown that biaxial orientation is developed in the stretching film.

Higher stresses also contribute to the likelihood that the film will rip while stretching on the mandrel surface. As was previously stated, temperatures below 60°C for 17% solutions caused early failure in the stretching film. This was probably a result of temperatures decreasing too rapidly, causing a rapid increase in viscosity, and hence, stress increases in the stretching film. Higher temperatures, above 70°C, result in lower viscosities and stresses thereby allowing the film to stretch over the mandrel without ripping.

9. Effect of Coagulant on the Mandrel Film Process

For the mandrel process, a relatively quick or strong coagulant such as water is more desirable. The reason for this is that a fast coagulant prevents additional drawing, hence, orientation, and ripping of the film after it is drawn over the mandrel. It also may be the most efficient coagulant for total removal of H_2SO_4 . Since water couldn't be used, ethanol and methanol were chosen.

Taeratanachi et al. (89) discuss the effect of coagulant polarity, molecular size, and viscosity on coagulation rate. Their conclusions are that coagulant molecular

size, and hence viscosity, is the important variable in determining coagulation rate. For example, the smaller the molecular size, the lower viscosity is and the faster the coagulation rate is. Figure 40 demonstrates relative coagulation rates for a variety of coagulants. Water, acetone, and ethanol were considered the fastest. Methanol would also be considered a fast coagulant.

Film Shrinkage

Table 9 indicates that film shrinkage is more a function of orientation than of coagulant. Highly drawn uniaxial films exhibited very little shrinkage in the machine direction as compared to the transverse direction. Biaxial films exhibited essentially no shrinkage in either direction. Undrawn films in general exhibited a relatively large amount of shrinkage in all directions with less shrinkage in the machine direction than in the transverse direction. This indicates orientation taking place in the machine direction due to the die.

Undrawn films coagulated in water exhibit a higher degree of shrinkage than those films coagulated in combinations of water and alcohol. Taeratanachi's work agrees with these results; see Figure 41. The mechanism for this phenomenon isn't clearly understood. Haraguchi et al. (32) indicate that water tends to get trapped between the PPD-T molecule creating a swelled structure (31, 32). Organic coagulants such as methanol and ethanol in solutions with less than 50% water didn't exhibit a swelled structure.

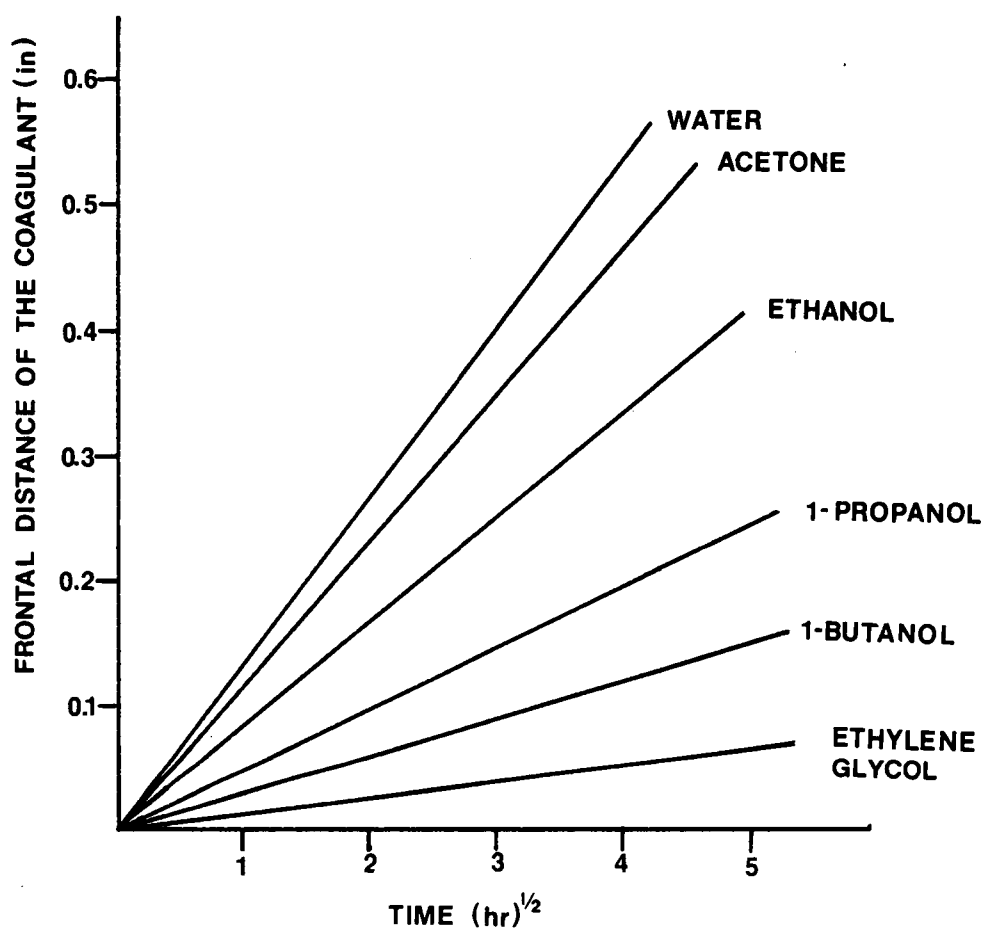


Figure 40. Taeratanachi et al.'s Plot of Frontal Distance of Coagulants Versus Time for Different Coagulants.

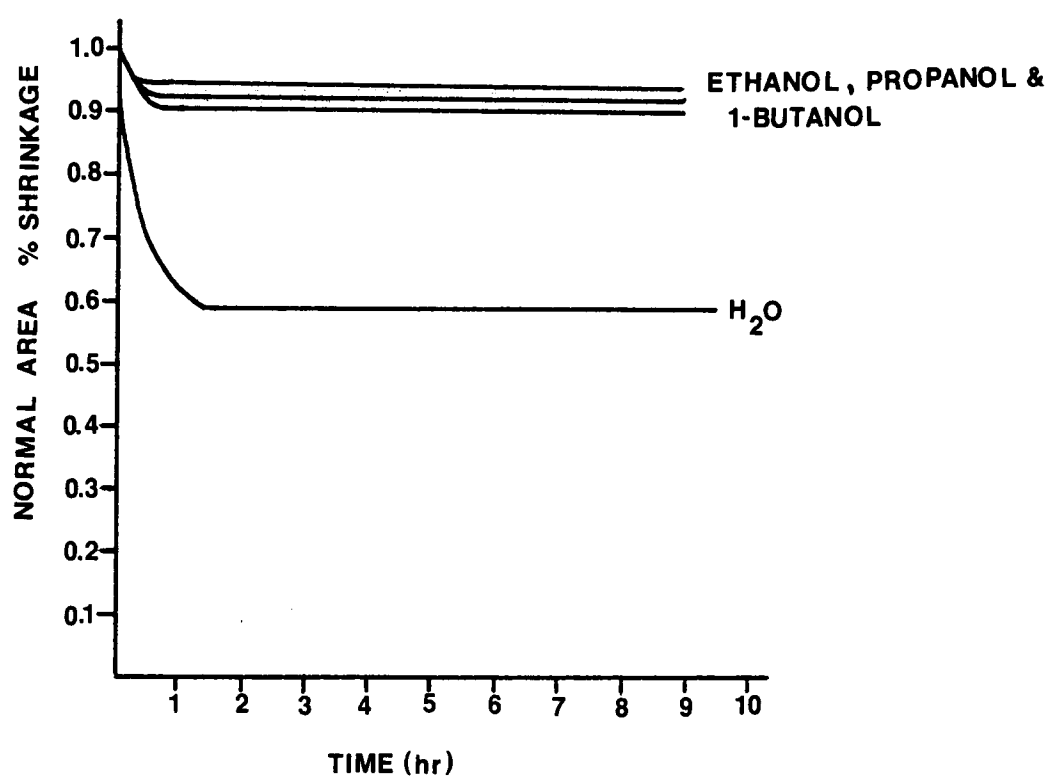


Figure 41. Taeratanachi et al.'s Plot of % Shrinkage in PPD-T Films Versus Time for Different Coagulants.

CHAPTER V

DETERMINATION OF MOLECULAR ORIENTATION IN PPD-T FILMS
THROUGH WIDE ANGLE X-RAY DIFFRACTION TECHNIQUES

This chapter begins with a brief explanation of the important crystallographic planes used to determine orientation and their relationship to the Haraguchi et al. (31) Modification II unit cell and the Northolt (61) unit cell for PPD-T. Later sections deal with determining molecular orientation in extruded, uniaxially drawn, and biaxially drawn films using WAXS patterns, pole figures, and orientation functions.

A. Important Crystallographic Planes

Haraguchi et al. (31) found that PPD-T films coagulated in solutions with water contents above 50% by volume resulted in a different unit cell from the Northolt (61) determined unit cell. They realized that two different unit cells were present, the Northolt unit cell when less than 50% water was used, and the Haraguchi et al. unit cell when more than 50% water was used. It was also found that the presence of certain strong reflections, in particular the (010), was dependent on the coagulant (31); see Chapter II, pages 48 through 52 for more detail.

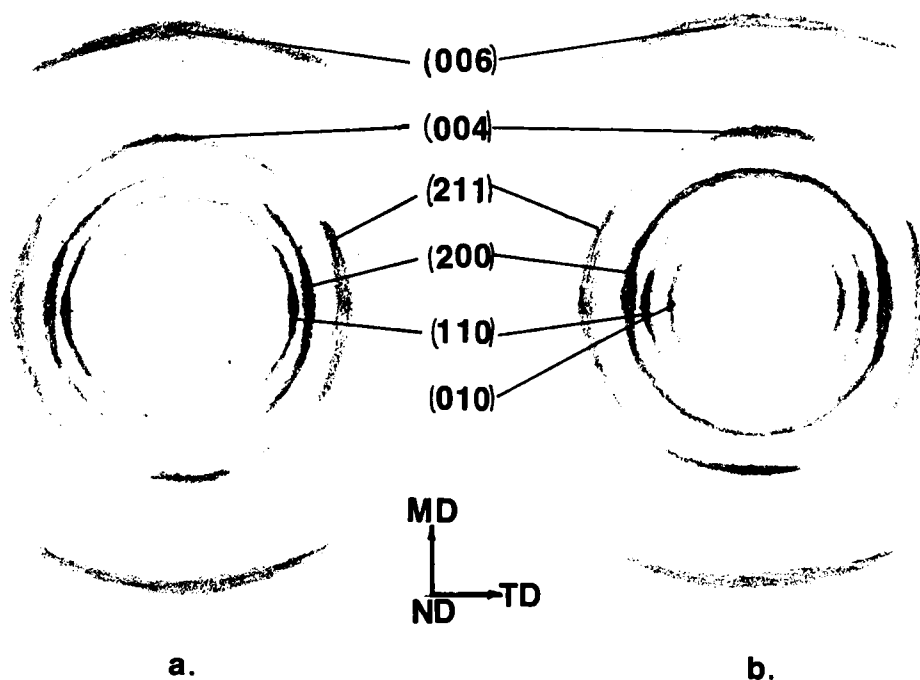
Results

When uniaxially drawn films were coagulated with a water content of 45% or less, a unit cell similar to the Northolt model resulted; see page 50, Figure 19. Table 11 is a comparison of the Northolt model and experimental results. It should be noted, once again, that the strong crystallographic reflections were the (110), (200), (004), (006), and (211). Figure 42 is a WAXS pattern demonstrating these reflections. Note that the (004) and (211) reflection overlap considerably; this situation didn't allow the use of the (004) plane in determining C-axis orientation.

Uniaxially drawn films coagulated in 100% water exhibit diffraction patterns similar to the Haraguchi et al. Modification II model; see Figure 42. Table 12 is a comparison of the Bragg spacing and 2θ angle of Haraguchi et al.'s model and the experimental results. The important crystallographic reflections were the (010), (200), (211), (004), and (006). Note the additional reflection due to the (010) plane.

Discussion

The one big difference between films coagulated in water and those coagulated in alcohol is the appearance of the (010) plane in the water coagulated film's diffraction patterns. This is in agreement with Haraguchi et al.'s Modification II model unit cell; see Figure 19,



The films were coagulated in (a) alcohol and water and (b) 100% water.

Figure 42. Schematic of Typical WAXS Patterns Taken Through the Normal Direction for Uniaxially Drawn Films.

Table 11. A Comparison of Northolt's Model's d Spacing and 2θ Values to the Experimental Values for Film Coagulated in Alcohol and Water

Strong Reflections	<u>Northolt</u>		<u>Flood*</u>
	d Spacing	2θ Degrees	2θ Degrees
(110)	4.33	20.5	20.85
(200)	3.94	22.57	23.16
(006)	2.15	41.7	42.9

*Values for 2θ angles were obtained from a combination of 2θ scans and WAXS patterns using uniaxially oriented films.

Table 12. A Comparison of Haraguchi et al.'s Modification I Model's d Spacing and 2θ Values to the Experimental Values for Water Coagulated Uniaxial Films

Strong Reflections	<u>Haraguchi et al.</u>		<u>Flood*</u>
	d Spacing	2θ Degrees	2θ Degrees
(010)	5.1	17.36	17.65
(110)	4.3	20.63	20.8
(200)	4.0	22.19	22.8
(006)	2.15	41.97	42.9

*Values for 2θ angles were obtained from a combination of 2θ scans and WAXS patterns using uniaxially oriented films coagulated in water.

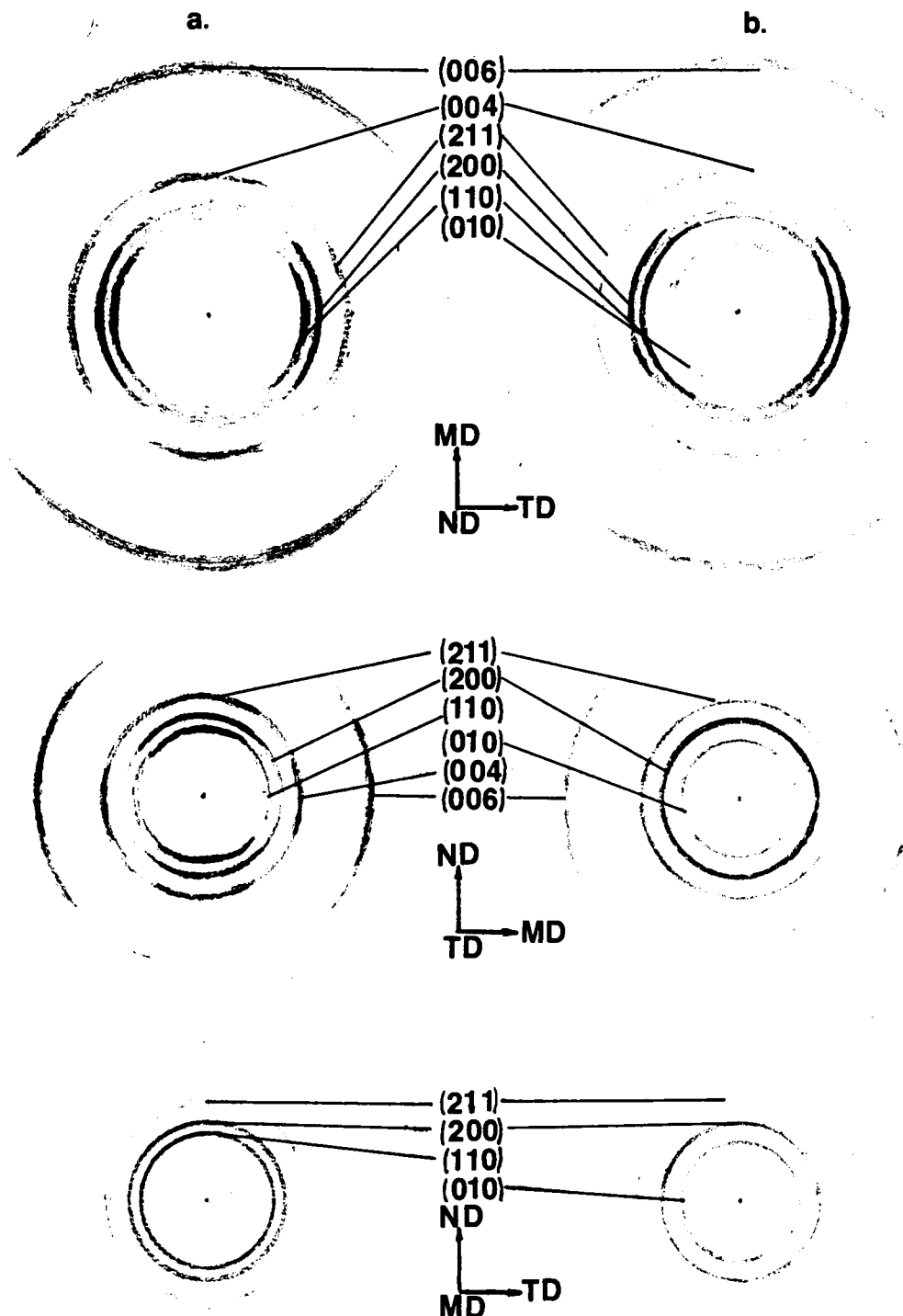
page 50 , that is, films coagulated in mostly water exhibit the Modification II model. Films coagulated in mostly alcohol exhibit the Modification I model or the Northolt model; see Figure 19.

There also appears to be some discrepancies between 2θ angles of both models and the experimental results. This could be due to inaccuracies in the equipment. Also, it is due to the relatively low orientation of the uniaxial films as compared to fibers and the inherent problems associated with taking measurements off the WAXS patterns.

B. Molecular Orientation in Undrawn Films

WAXS Patterns

Figure 43 presents WAXS patterns taken with the X-ray beam through different film directions for films coagulated in alcohol/water solutions and in pure water. In both cases, the (006) reflections indicate orientation of the c-axis to be partially in the machine direction. The degree of orientation, as determined by the width of the arcs, doesn't appear to be very high in either case. The (110) and (200) reflections indicate orientation of the a- and b-axis mainly in the transverse, normal direction plane and perpendicular to the machine axis for alcohol/water coagulated films. The (110) and (200) reflections for water coagulated films are blurred and the type of orientation present is hard to distinguish.



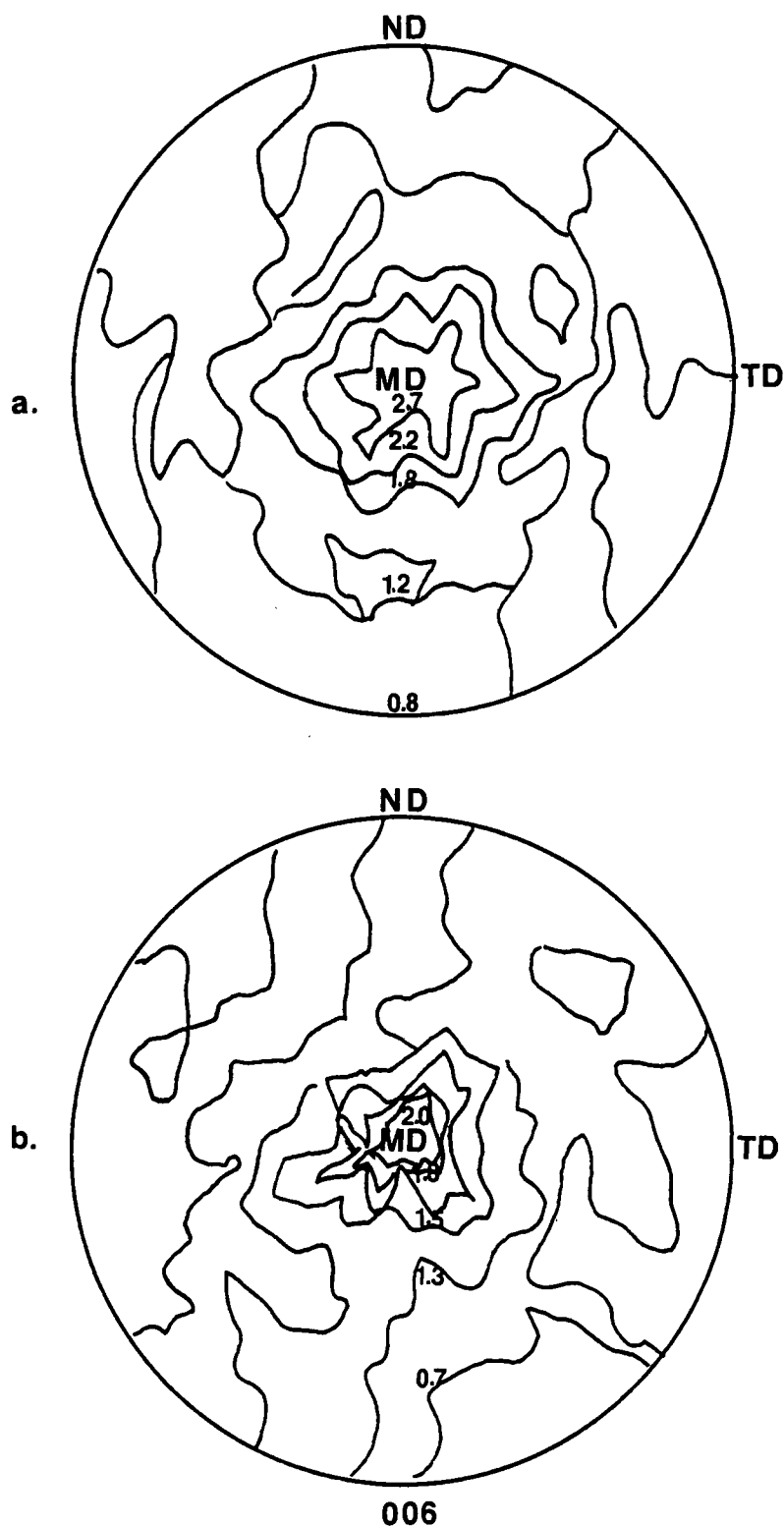
The films were coagulated in (a) alcohol and water and (b) in 100% water.

Figure 43. Schematic of Typical WAXS Patterns Taken Through the ND, TD, and MD for Undrawn or Extruded Films.

The WAXS pattern through the normal directions appears to be partially in the transverse direction. The other patterns don't show any orientation of the a-axis; refer to the (200) plane. The (010) reflection is weak and doesn't appear to show much orientation. The (110) reflection has disappeared or is very weak in the patterns taken through the machine direction and transverse direction. It is difficult to draw a conclusion about the disappearance of the (110) reflection because of overlap from the (200) reflection and (010) reflection, that is, it may not have disappeared, it is just covered by the other two reflections. This usually indicates a lack of orientation. Pole figures give a clearer picture of the type of orientation present in undrawn water coagulated films.

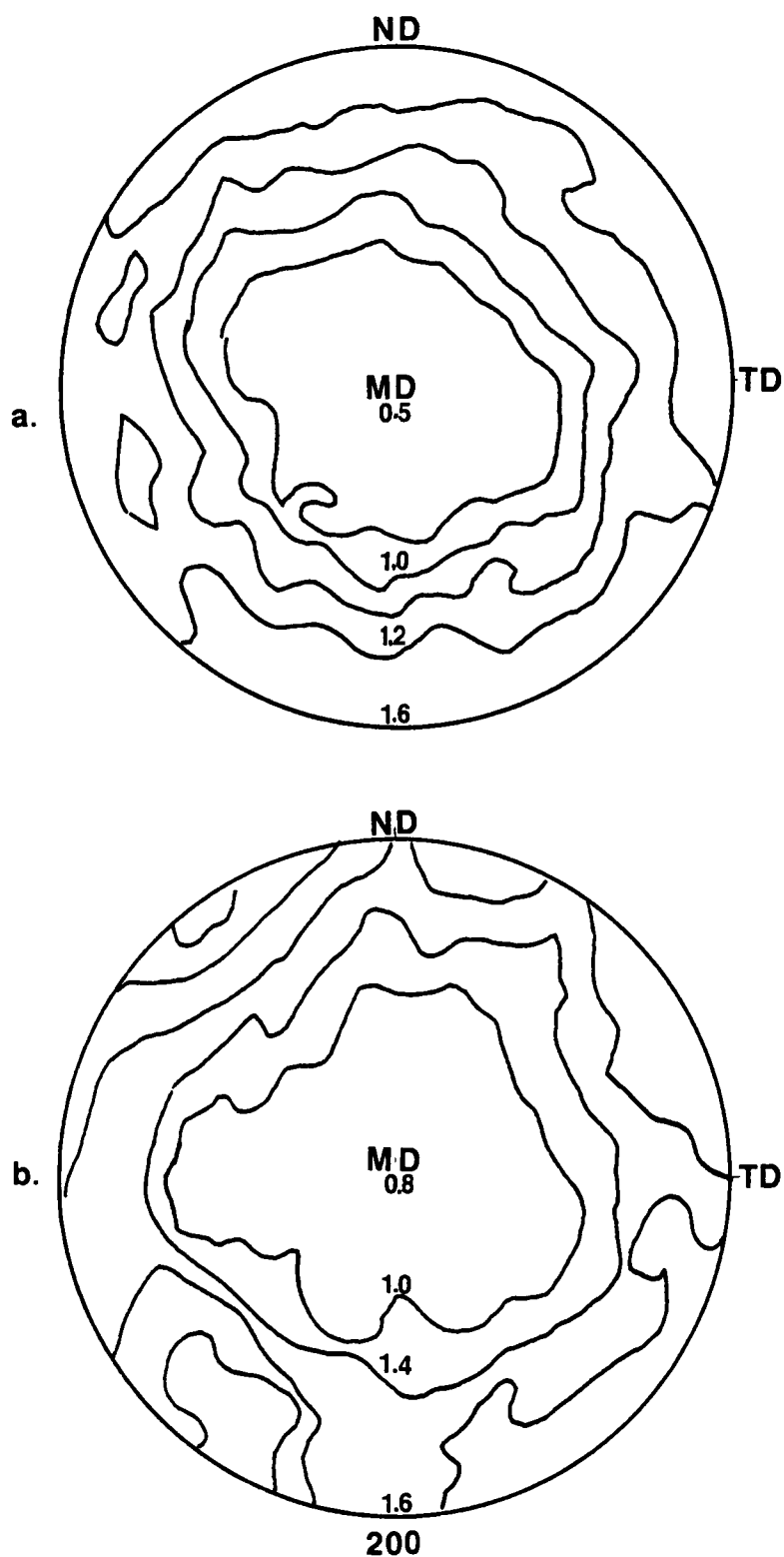
Pole Figures

Pole figures for the (006) plane for some typical undrawn films may be seen in Figures 44-46. Orientation of the (006) poles, which is equivalent to orientation of the c-axis, is mostly in the machine direction. Orientation of the (200) poles or the a-axis is mainly in the transverse, normal direction plane with tilting in and out of that plane. The (110) pole figure indicates orientation of the (110) poles similar to that of the (200) pole figure. The water coagulated films appear to show a slightly higher degree of orientation than the water/alcohol coagulated films.



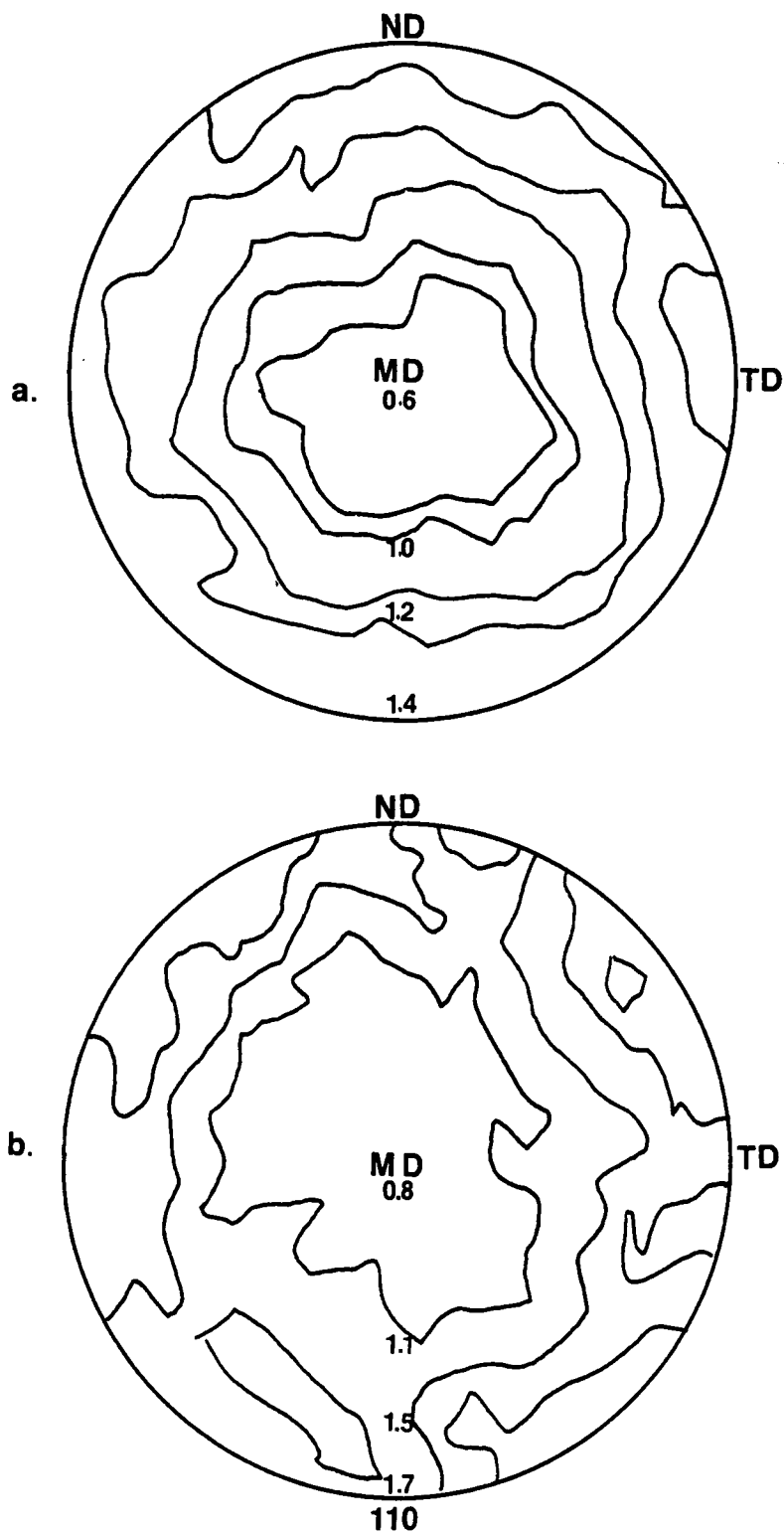
Films were coagulated in (a) alcohol and water and (b) in 100% water.

Figure 44. Typical (006) Pole Figures for Extruded Films.



Films were coagulated in (a) alcohol and water and (b) in 100% water.

Figure 45. Typical (200) Pole Figures for Extruded Films.



Films were coagulated in (a) alcohol and water and in (b) 100% water.

Figure 46. Typical (110) Pole Figures for Extruded Films.

Orientation Functions

Table 13 is a list of orientation functions for the a-, b-, and c-axis of the PPD-T unit cell relative to the z and y reference directions. The z-axis represents the machine direction and the y-axis the transverse direction; see Figure 23, page 58.

The c-axis orientation functions for undrawn films are listed in Table 13. Values for f_{zc}^B are always larger than f_{yc}^B values, an average of 0.3 versus 0.12 respectively. This indicates orientation of the c-axis mainly in the machine direction. Figure 47 is a plot of the c-axis orientation functions on the orientation triangle.

Orientation functions for the a-axis indicate f_{za}^B values that are larger or more negative than f_{ya}^B values. An average value of -0.17 for the f_{za}^B function versus -0.07 for the f_{ya}^B function was obtained. Plots of the orientation functions for the a- and b-axis on the orientation triangle may be seen in Figures 48 and 49. In both cases the resulting points are situated near the line indicating orientation perpendicular to the machine direction. Higher values on the line would indicate orientation of the a- or b-axis in the transverse, normal direction plane.

Orientation functions for run number six were disregarded in all of the averages because they were unusually low and also because mechanical properties were low. These were considered indications of above normal degradation in the film.

Table 13. Orientation Functions for Undrawn or Extruded Films, Uniaxially Drawn Films, and Biaxially Drawn Films

Experimental Run Number	Film Process	Orientation Functions					
		f_{za}^B	f_{ya}^B	f_{zb}^B	f_{yb}^B	f_{zc}^B	f_{yc}^B
1	Extruded	-0.16	-0.08	-0.15	-0.07	0.29	0.16
2	Extruded	-0.20	-0.11	-0.15	-0.09	0.35	0.20
3	Extruded	-0.14	-0.02	-0.09	-0.02	0.22	0.04
4	Extruded	-0.18	-0.04	-0.19	-0.00	0.33	0.04
5	Extruded	-0.15	-0.08	-0.15	-0.08	0.30	0.16
6	Extruded	0.019	0.06	0.03	0.07	-0.05	-0.13
7	Drawdown	-0.23	-0.08	-0.25	-0.09	0.48	0.17
8	Drawdown	-0.23	-0.08	-0.17	-0.10	0.40	0.18
9	Drawdown	-0.30	-0.11	-0.23	-0.10	0.52	0.21
10	Drawdown	-0.28	-0.04	-0.23	-0.05	0.51	0.01
11	Drawdown	-0.29	-0.11	-0.17	-0.06	0.46	0.18
12	Drawdown	-0.08	-0.03	-0.08	-0.03	0.16	0.00
13	Mandrel	-0.15	-0.20	-0.04	-0.04	0.19	0.22

Table 13 (continued)

Experimental Run Number	Film Process	Orientation Functions					
		f_{za}^B	f_{ya}^B	f_{zb}^B	f_{yb}^B	f_{zc}^B	f_{yc}^B
14	Mandrel	-0.17	-0.20	-0.06	-0.07	0.23	0.27
15	Mandrel	-----	-----	-----	-----	-----	-----
16	Mandrel	-0.14	-0.21	-0.03	-0.04	0.16	0.25
17	Mandrel	-0.18	-0.14	-0.04	-0.03	0.21	0.17
18	Mandrel	-0.23	-0.31	-0.16	-0.14	0.35	0.45
19	Mandrel Drawdown	-0.27	-0.13	-0.07	-0.04	0.27	0.16

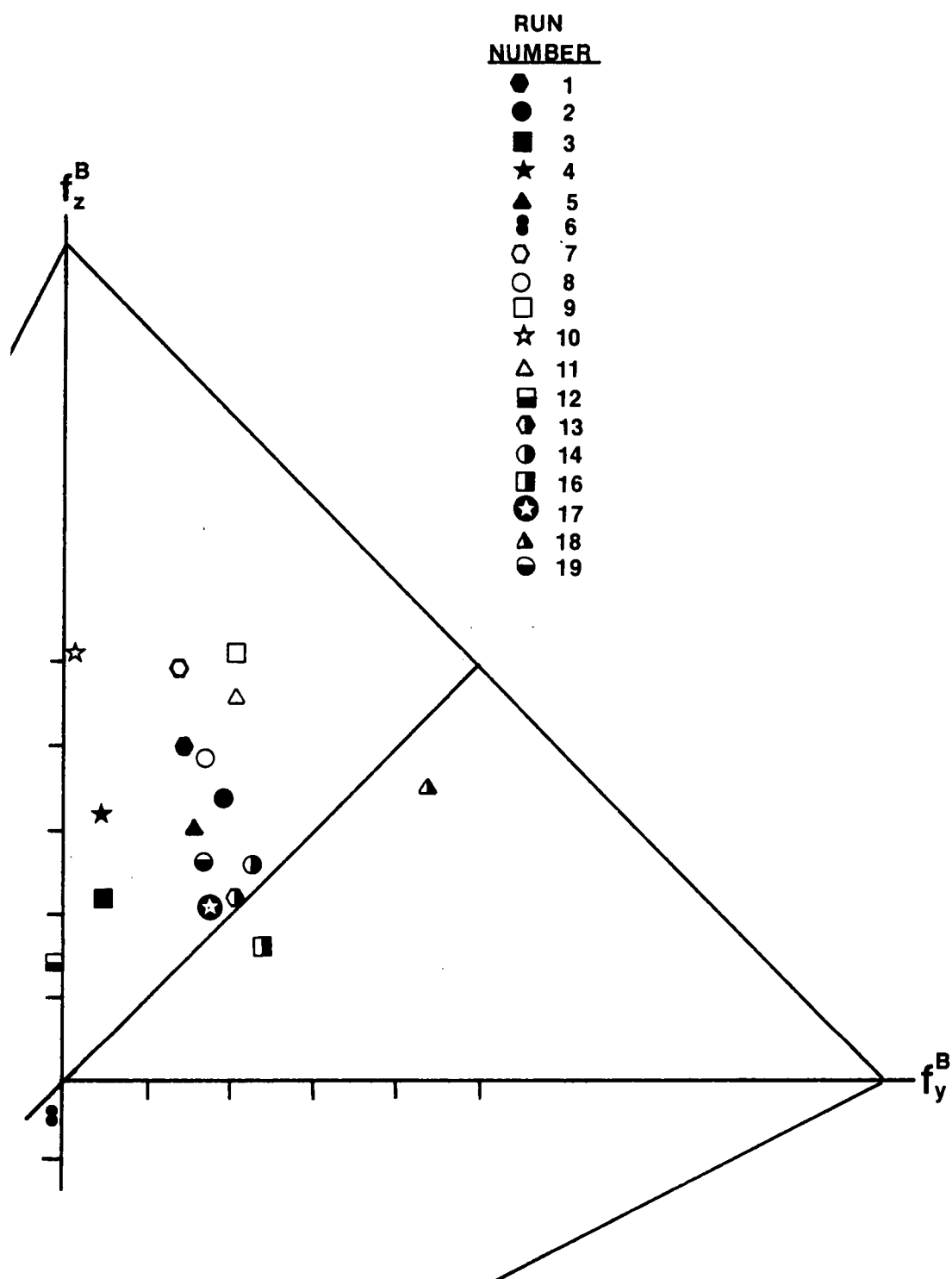


Figure 47. Orientation Triangle with c-axis Orientation Functions Plotted for Extruded, Uniaxially Drawn, and Mandrel Processed Films.

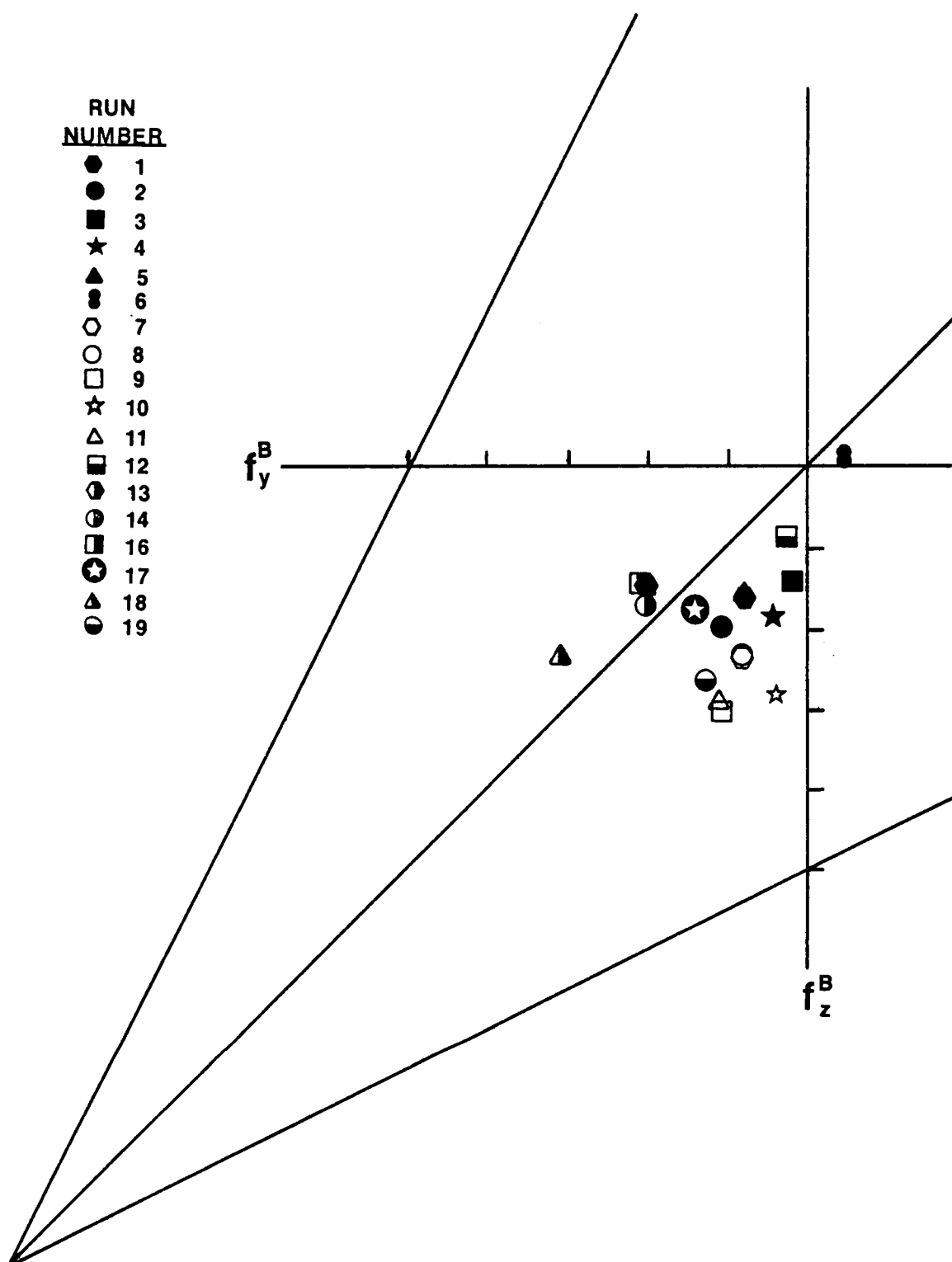


Figure 48. Orientation Triangle with a-axis Orientation Functions Plotted for Extruded, Uniaxially Drawn, and Mandrel Processed Films.

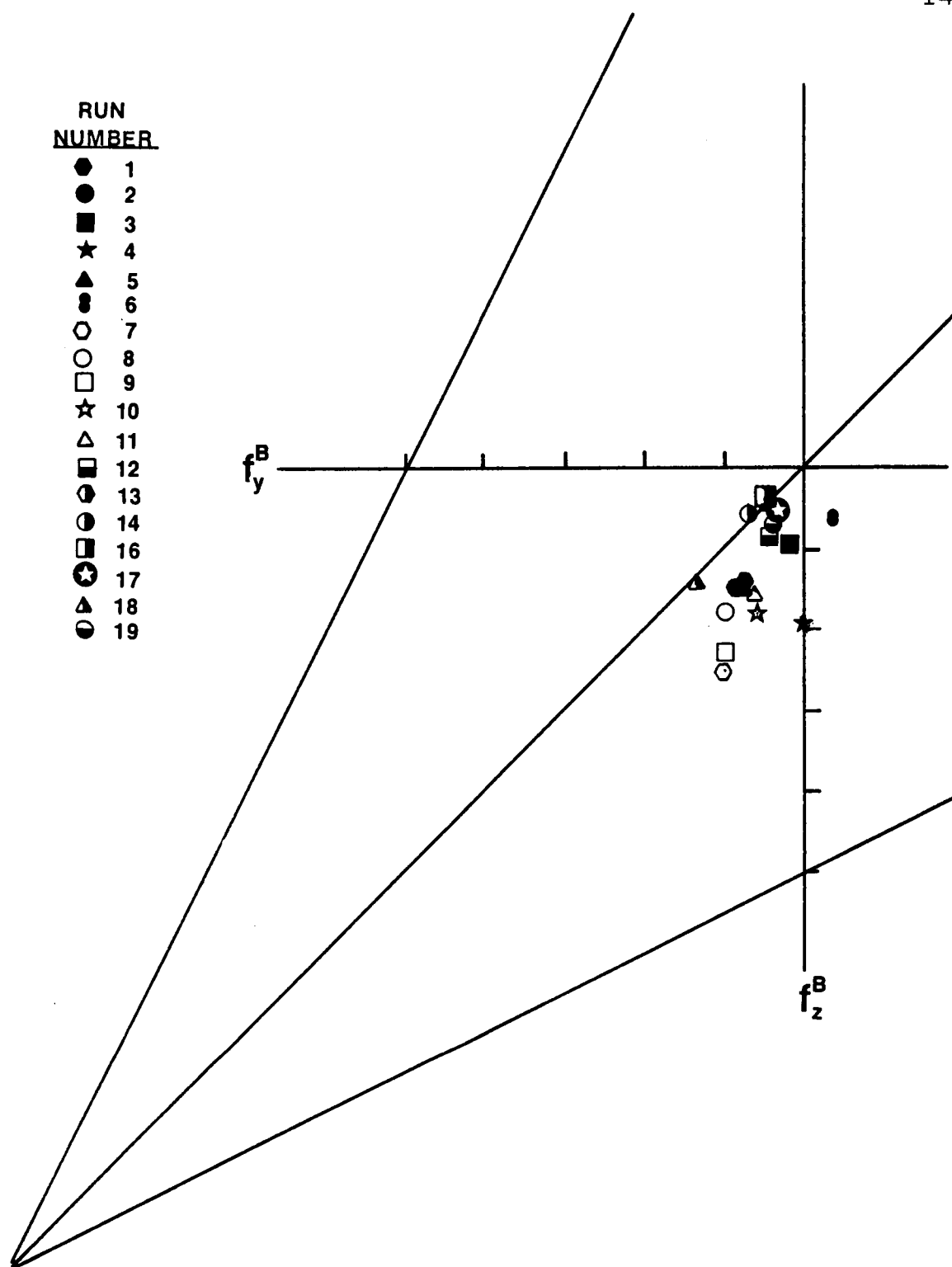


Figure 49. Orientation Triangle with b-axis Orientation Functions Plotted for Extruded, Uniaxially Drawn, and Mandrel Processed Films.

Discussion

The WAXS patterns, pole figures, and orientation functions all demonstrate the same type of orientation in undrawn or extruded films, which is the c-axis is mainly pointed in the machine direction with the a- and b-axis rotating about the c-axis. This is a fiber like texture, without the high degree of orientation obtained in a fiber.

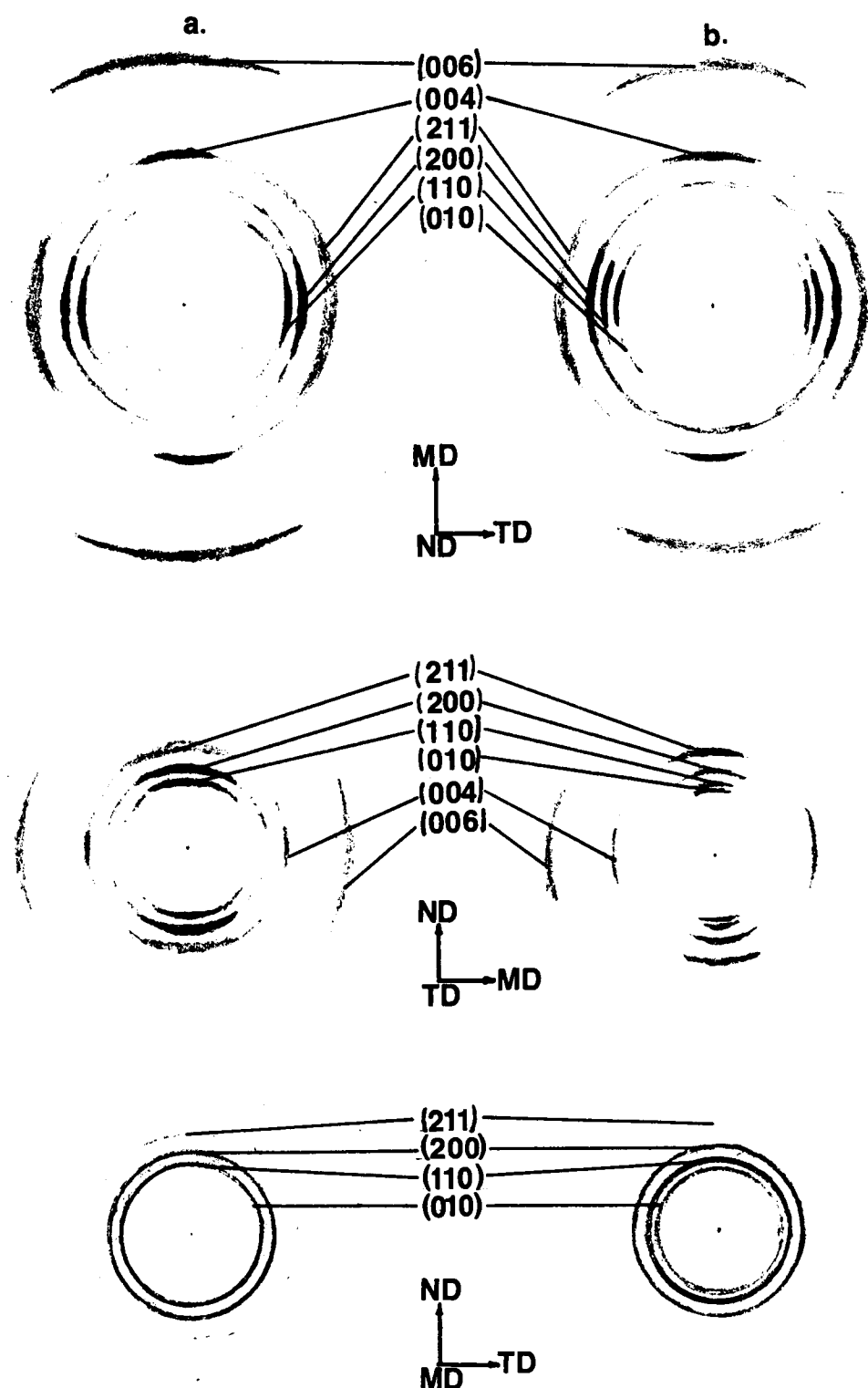
It is important to note here that these films were just extruded and that no drawdown was placed on them. The degree of orientation is relatively high considering the extrusion conditions. This situation can probably be attributed to the easily oriented nature of the liquid crystalline solutions.

Shimamura et al.(81) in their rheological and birefringence studies of bulk hydroxypropylcellulose, HPC, found that extruded filaments had skin-core structures with highly oriented outer layers. HPC was considered to be a thermotropic liquid crystal and the orientation was believed to be achieved during flow through the reservoir and die. A similar situation may be happening with extruded PPD-T film.

C. Molecular Orientation in Uniaxially Drawn Films

WAXS Patterns

In Figure 50 the (006) reflection as seen through three different film directions may be seen. The c-axis



The films were coagulated in (a) water and alcohol and (b) in 100% water.

Figure 50. Schematic of Typical WAXS Patterns Taken Through the ND, TD, and MD Directions for Uniaxially Drawn Films.

is oriented mainly in the machine direction. In the same figure, it can be seen that the a- and b-axis are rotating about the c-axis in the normal, transverse direction plane; refer to the (200), (110), and (010) reflections. Both the water coagulated films and alcohol coagulated films demonstrate the same type of orientation.

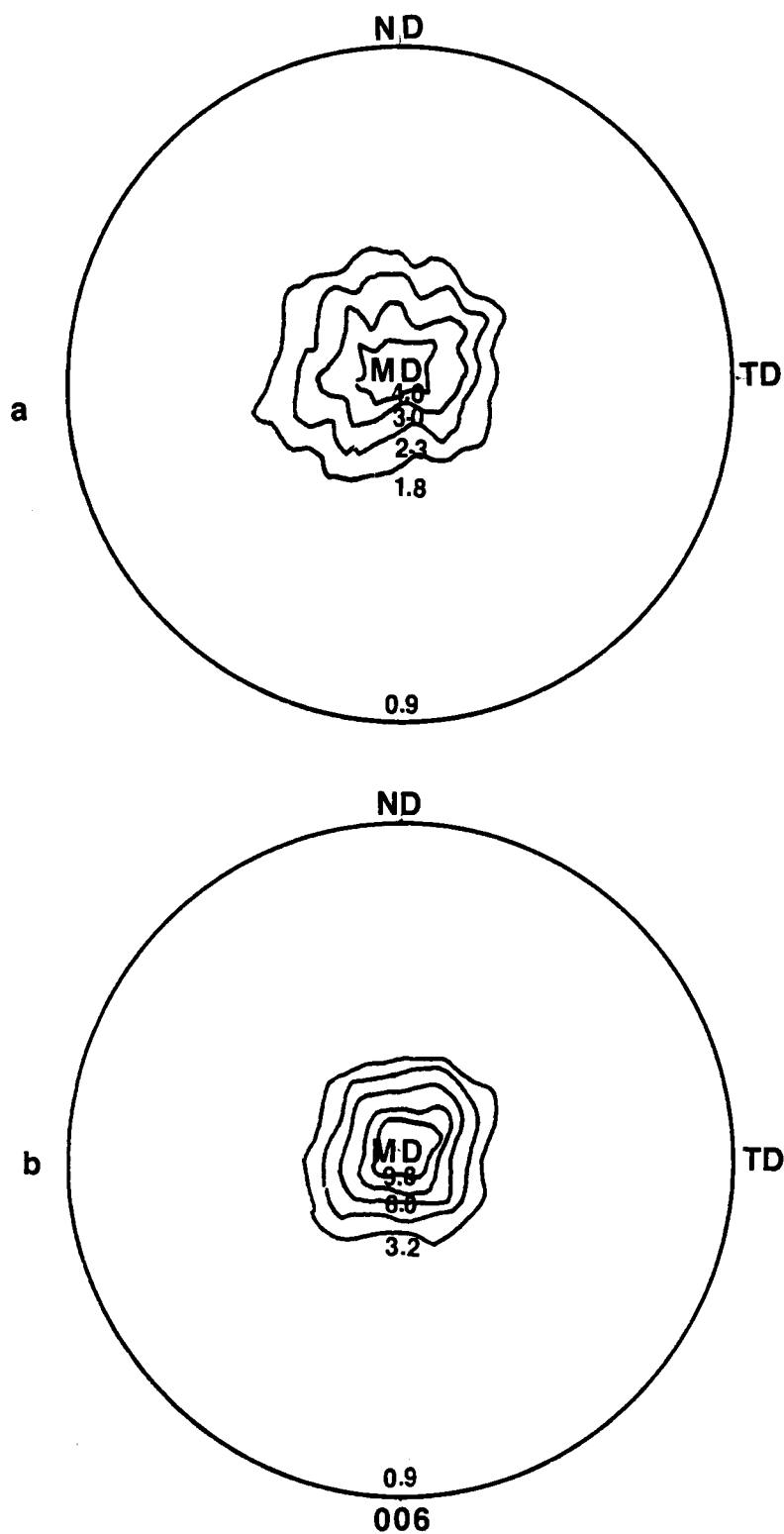
Pole Figures

Figures 51 through 53 present typical pole figures for some uniaxially drawn films. In Figure 51, it can be seen that orientation of the (006) poles, which is equivalent to orientation of the c-axis, is almost totally in the machine direction. Orientation of the (200) poles or the a-axis is mostly in the normal direction, transverse direction plane, and about the c-axis. Orientation of the (110) poles indicates similar orientation to that of the (200) poles, though not as sharp.

Orientation Functions

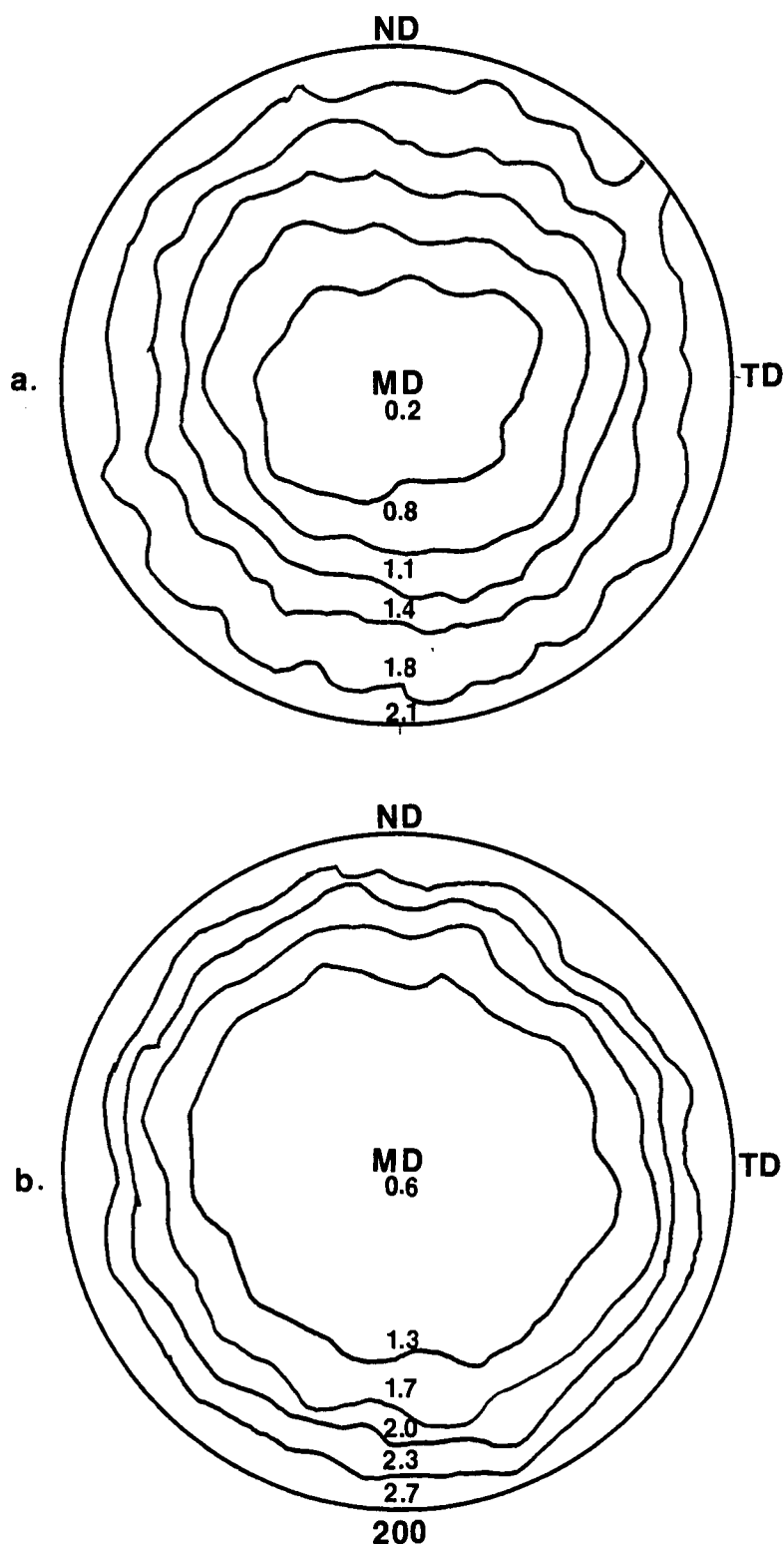
Values for the c-axis orientation functions may be seen in Table 13. They averaged for f_{zc}^B and f_{yc}^B 0.47 and 0.15 respectively. Plotting the c-axis functions clearly indicates orientation of the c-axis as being mostly in the machine direction; see Figure 47, page 144.

The orientation functions for the a-axis averaged -0.27 for f_{za}^B and -0.08 for f_{ya}^B . Figure 48, page 145, is a plot of a-axis orientation functions. It can be



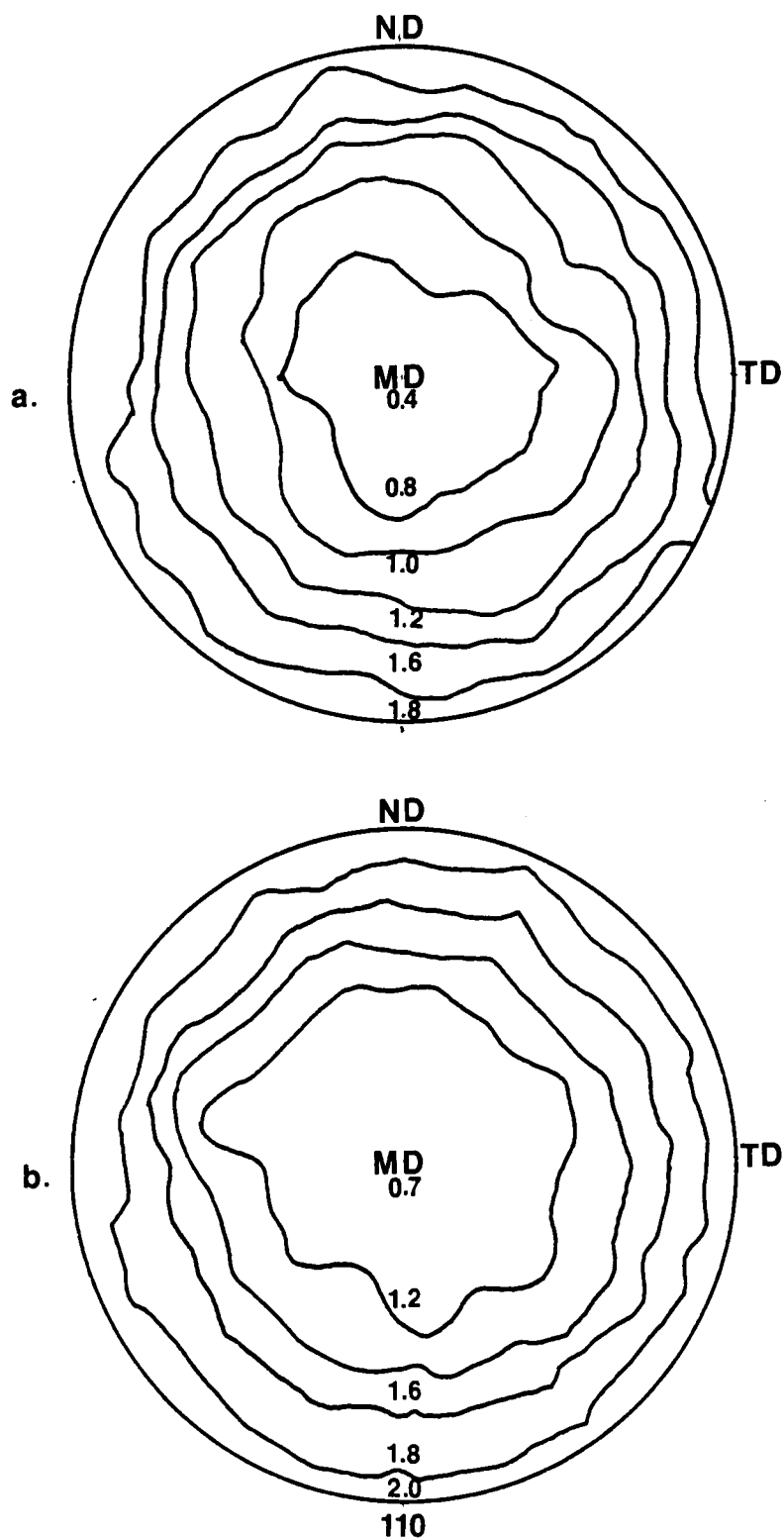
Films were coagulated in (a) alcohol and water and (b) in water.

Figure 51. Typical (006) Pole Figures for Uniaxially Drawn Films.



The films were coagulated in (a) alcohol and water and (b) in water.

Figure 52. Typical (200) Pole Figures for Uniaxially Drawn Films.



Films were coagulated in (a) alcohol and water and (b) in water.

Figure 53. Typical (110) Pole Figures for Uniaxially Drawn Films.

seen from the positions of the above values that the a-axis is lying mostly in the normal-transverse direction plane, perpendicular to the machine direction.

Orientation functions for the b-axis as seen in Table 13 and plotted in Figure 49 on page 146 indicate the same type of orientation as that of the a-axis. Values for f_{zb}^B averaged -0.21 versus -0.08 for f_{yb}^B .

Run number 12 was deliberately left out in all of the averages because it gave unusually low orientation functions and because the mechanical properties were very low. The above situation was attributed to degradation. Both runs number 6 and 12 came from the same batch of polymer solution. Since the solutions were degraded, high drawdowns were difficult to achieve due to a reduction in the elasticity of the solution.

Discussion

WAXS patterns typically show a higher degree of orientation than patterns taken from the undrawn films. The type of orientation is the same, that is, a fiber-like texture.

Pole figures exhibit the same situation, that is, orientation is enhanced, but still of the same type.

Orientation functions averaged higher values, which is indicative of increased orientation, than orientation functions for undrawn films; see Table 13, page 142.

Increased orientation would be defined as the c-axis oriented closer to the machine direction with the a- and b-axis being mostly in the normal, transverse direction plane. In other words, the undrawn films exhibit much more tilting of the a- and b-axis in and out of the normal direction, transverse direction plane because the c-axis is less aligned, at a larger angle, with the machine direction than the uniaxially oriented film.

Except for the appearance of the (010) plane in WAXS patterns, water coagulated films demonstrated the same type of WAXS patterns, pole figures, and orientation functions as the alcohol/water coagulated films.

D. Molecular Orientation in Biaxially Drawn Films

WAXS Patterns

Typical diffraction patterns for a biaxially drawn film may be seen in Figure 54. Figure 54 also represents patterns taken through different film directions. All mandrel drawn films demonstrate orientation of the c-axis in the machine direction, transverse direction plane; refer to the (006) reflection. Orientation of the a-axis was normal to the film plane; refer to the (200) reflection.

The diffraction patterns from biaxially drawn films indicate that the type of orientation is planar biaxial. This means that the c-axis is oriented mainly in the machine direction, transverse direction plane and the

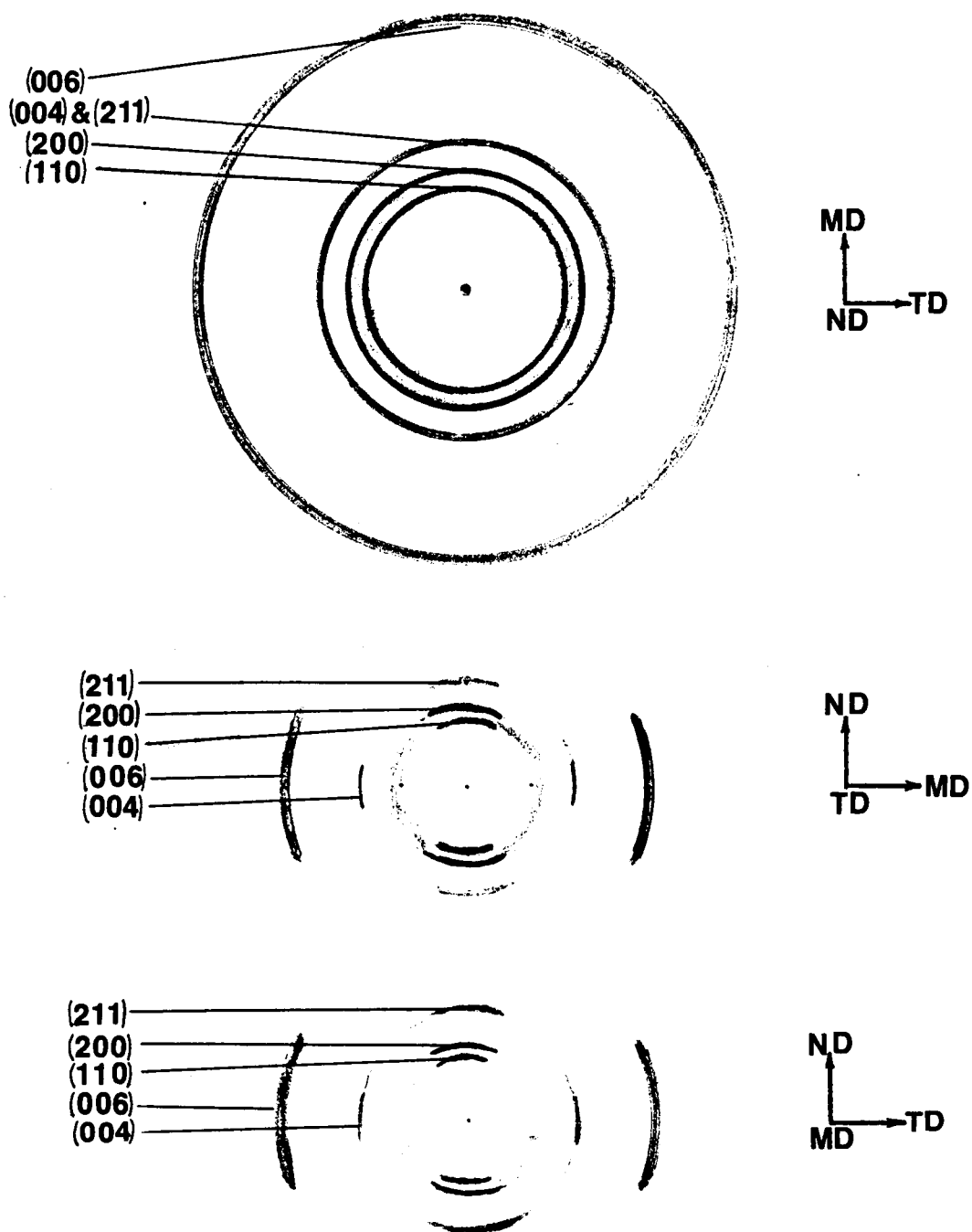


Figure 54. Schematic of Typical WAXS Patterns Taken Through the ND, TD, and MD Directions for Mandrel Processed Films.

a-axis is oriented mainly perpendicular to the film plane. It follows from the unit cell that the b-axis must also be situated in the machine direction, transverse direction plane, or film plane in a biaxial mode.

There seemed to be no particular effects on orientation, either degree or type, from the different coagulants used.

Films drawn over the mandrel with drawdown ratios greater than one indicated a return to the uniaxial orientation previously discussed. Pole figures in the following section will demonstrate this.

Pole Figures

Biaxially drawn films exhibit orientation of the (006) poles, which represents the c-axis, in the transverse direction, machine direction plane and about the normal direction; see Figure 55.

Pole figures for the (200) and (110) planes may be seen in Figures 55 and 56. The a-axis represented by (200) poles is oriented normal to the film plane. Poles from the (110) plane, though oriented mostly in the normal direction, don't exhibit the same degree of orientation as the (200) planes.

Orientation as demonstrated by the pole figures is the same as that demonstrated by the WAXS patterns. The c-axis is mostly in the plane of the film rotated through the machine and transverse directions, that is, planar

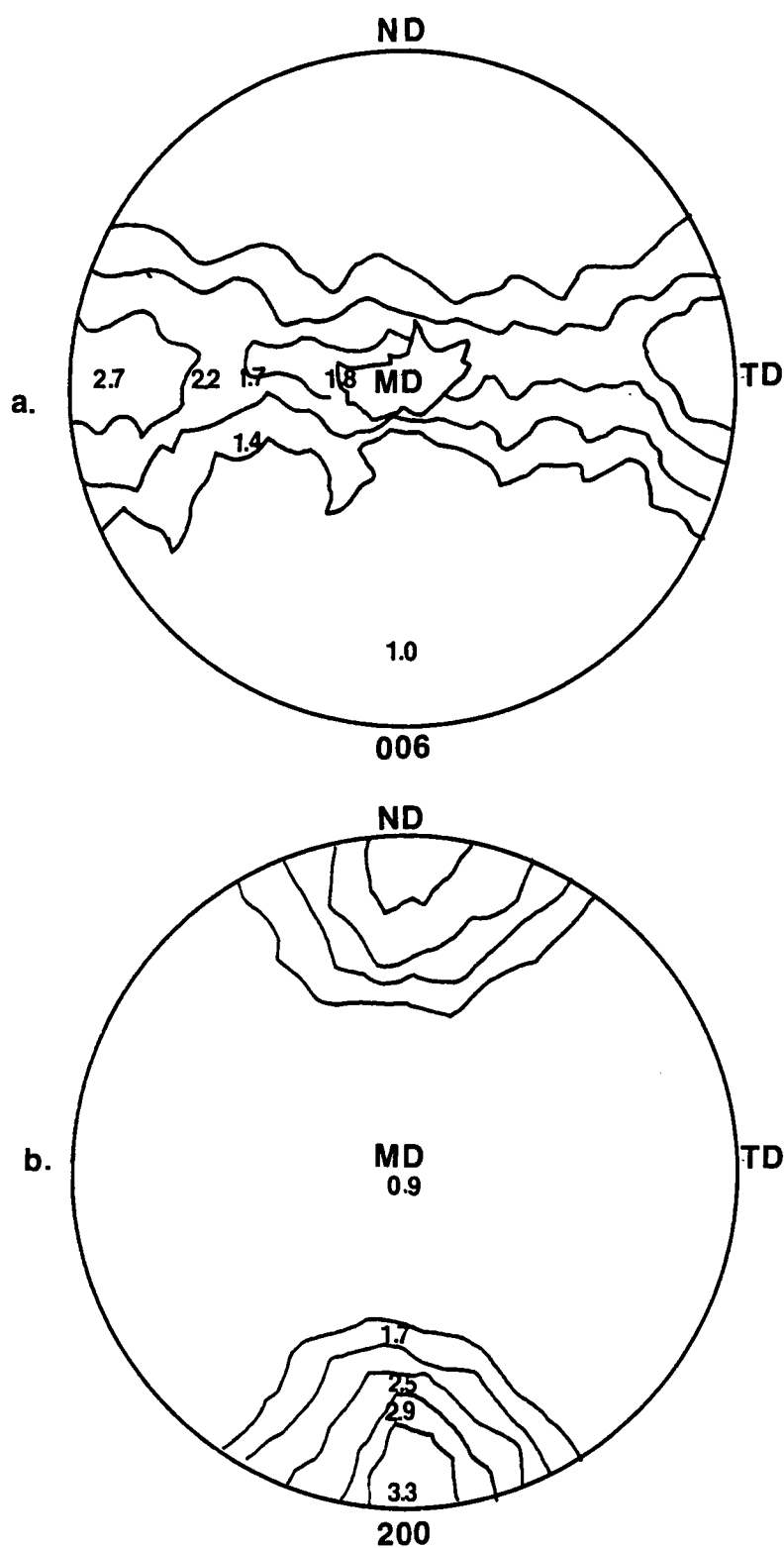


Figure 55. Typical (006) and (200) Pole Figures for Mandrel Processed Films.

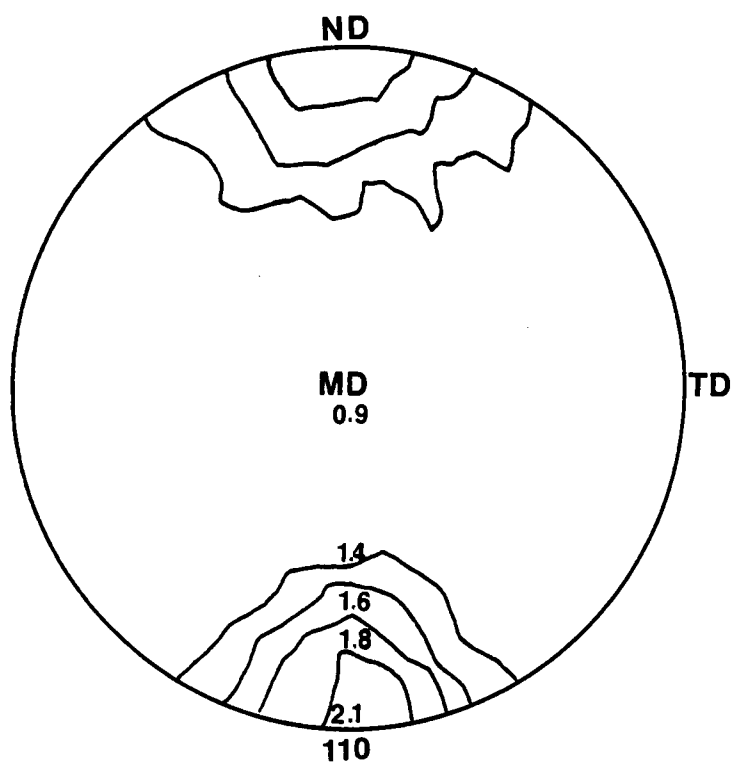


Figure 56. Typical (110) Pole Figure for Mandrel Processed Films.

biaxial. The a-axis is pointed normal to the film plane. The b-axis should be in the film plane orienting through transverse machine direction plane in a manner similar to the c-axis.

The one example of a pole figure for a film drawn over the mandrel, that is, with a drawdown ratio greater than one, may be seen in Figures 57 and 58. Orientation of the c-axis as exhibited in the (006) pole figure is seen to be uniaxial in the machine direction. Orientation of the a-axis, (200) pole figure, is seen to be mainly in the normal direction with some spread towards the transverse direction. The (110) pole figure is similar but with less orientation than the (200) pole figure.

The best way to describe the above type of c-axis orientation would be that it is between planar biaxial orientation and a fiber like orientation.

Orientation Functions

Orientation functions for the c-axis are shown in Table 13 and plotted in Figure 47, pages 142 and 144. These points are near the biaxial line indicating similar values for f_{zc}^B and f_{yc}^B , an average of 0.24 and 0.28 respectively. Points falling on the biaxial line indicate biaxial orientation of the c-axis in the machine and transverse direction. High values such as run number 19 indicate less tilting of the c-axis in and out of the machine,

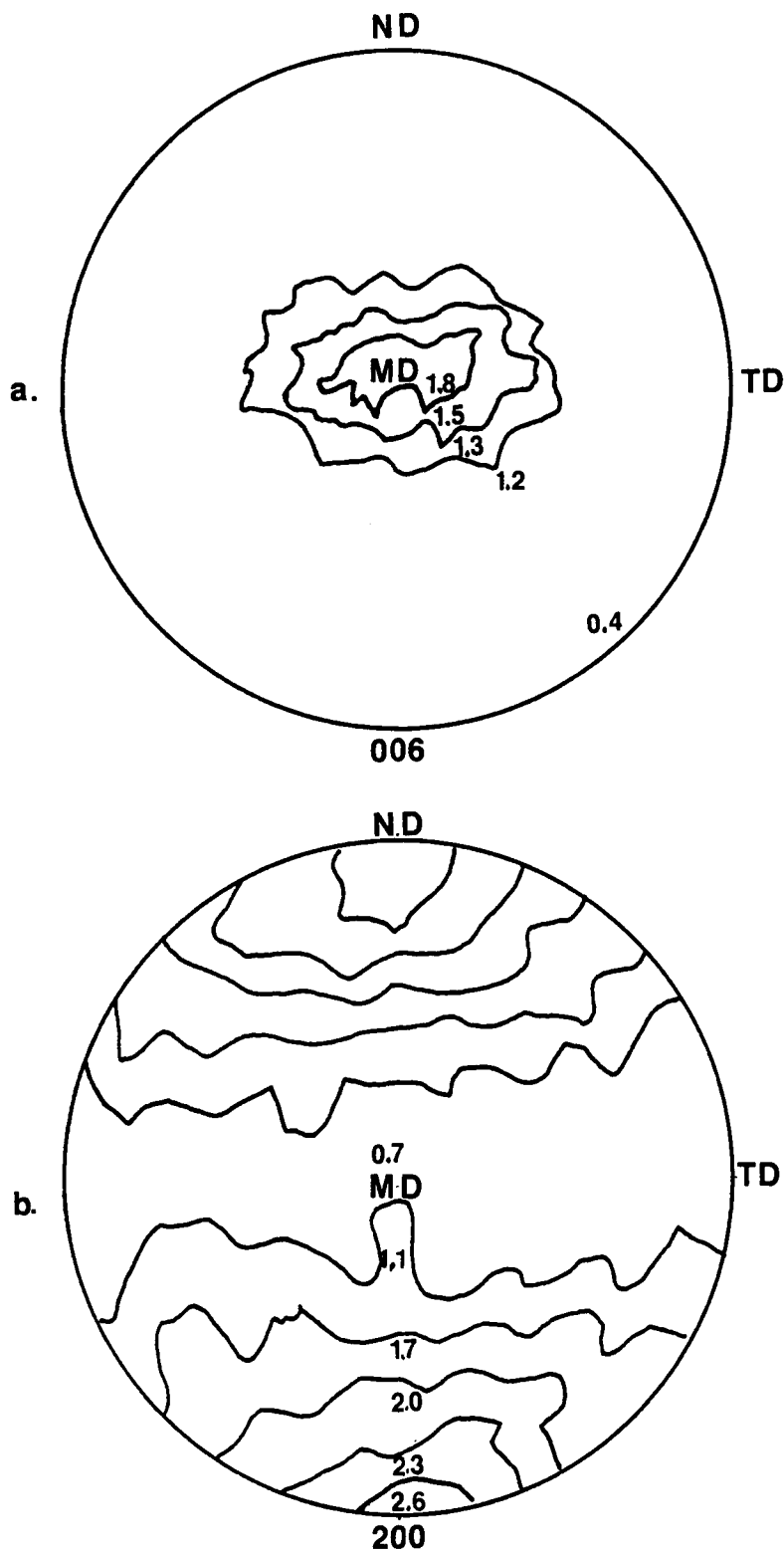


Figure 57. The (006) and (200) Pole Figures for a Mandrel Processed Film with a Drawdown Greater than One.

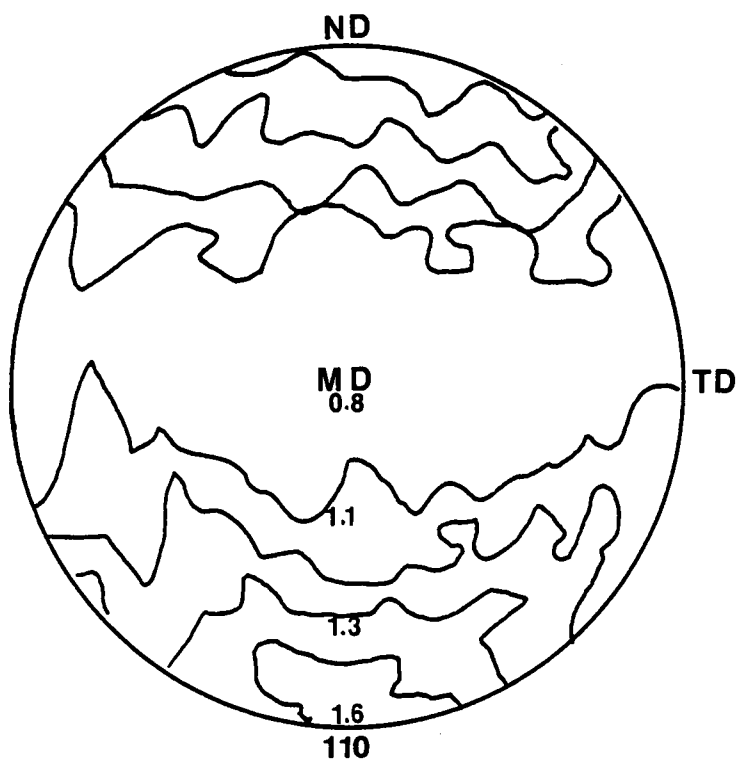


Figure 58. The (110) Pole Figure for a Mandrel Processed Film with a Drawdown Greater than One.

transverse direction plane and a more even distribution within the plane, that is, more highly planar biaxial.

The example of a film drawn over the mandrel with a drawdown greater than one indicates c-axis orientation functions between those of undrawn and mandrel drawn films; see Table 13 and Figure 47, pages 142 and 144.

Biaxially drawn films indicate the a-axis orientation function along the biaxial line in the third quadrant of the orientation triangle; see Table 13 and Figure 48. This means that the a-axis is preferentially pointed normal to the film plane. Values for f_{za}^B and f_{ya}^B averaged -0.17 and -0.21 respectively. The film with a drawdown greater than one exhibited a-axis orientation functions similar to those of the uniaxially drawn films; see Table 13 and Figure 48, pages 142 and 145.

Values for the b-axis orientation function f_{zb}^B and f_{yb}^B averaged -0.06 and -0.064 respectively, considerably lower than the average for a-axis orientation functions. This implies that the b-axis is more isotropically oriented as compared to the a- and c-axis. Still, most of the points are on or near the normal direction line; see Table 13 and Figure 49, pages 142 and 146.

Point 15 for the film drawn over the mandrel indicates b-axis orientation functions similar to those for undrawn films; see Table 13.

Discussion

There is good agreement between WAXS patterns, pole figures, and orientation functions. All three methods indicate biaxial orientation of the c-axis in the machine, transverse direction plane. They also show that the a-axis for the most part is oriented normal to the film plane. It follows from the unit cell that the b-axis, the hydrogen bond direction, is in the film plane, and also biaxially oriented.

Orientation functions pertaining to the b-axis are not easily explained. They lie on the biaxial line in the third quadrant, near the isotropic point. This indicates a random orientation which is contrary to data obtained from pole figures and WAXS patterns, that is, the b-axis should be biaxially oriented in the film plane. The b-axis orientation function could be explained in terms of tilting of the b-axis in and out of the film plane, while at the same time being rotated about the film plane. Of course the above situation prevents the a-axis from pointing exactly in the normal direction.

The film drawn over the mandrel exhibited a- and b-axis orientation functions similar to the extruded and uniaxial films. Orientation of the c-axis appears to be intermediate between the undrawn films and the biaxially oriented films.

Once again there seems to be no correlation between degree of orientation and coagulant. Run 19 is very high

for all the orientation functions, but it is only a single point and the pole figures and WAXS patterns weren't very different from the other biaxial films. Therefore, the coagulant for run number 19, 75% EtOH and 25% H₂O, can't be considered exceptional.

Comparing orientation functions for the three main types of films, extruded, uniaxially drawn, and biaxially drawn, gives the results in Table 14 and Figure 59. As can be seen, the c-axis orientation functions for both the undrawn and uniaxially drawn films lean towards the machine direction line while the biaxial film's orientation function is on the biaxial line.

Table 14. Average Orientation Functions for the Different Film Processes

Film Process	Orientation Functions					
	f_{za}^B	f_{ya}^B	f_{zb}^B	f_{yb}^B	f_{zc}^B	f_{yc}^B
Extruded	-0.17	-0.07	-0.15	-0.06	0.3	0.12
Drawdown	-0.27	-0.08	-0.21	-0.08	0.47	0.15
Mandrel	-0.17	-0.21	-0.06	-0.06	0.24	0.28

FILM PROCESS	ORIENTATION FUNCTIONS		
	f_a^B	f_b^B	f_c^B
UNDRAWN	■	▲	●
UNIAXIAL	□	△	○
MANDREL	▣	▴	◉

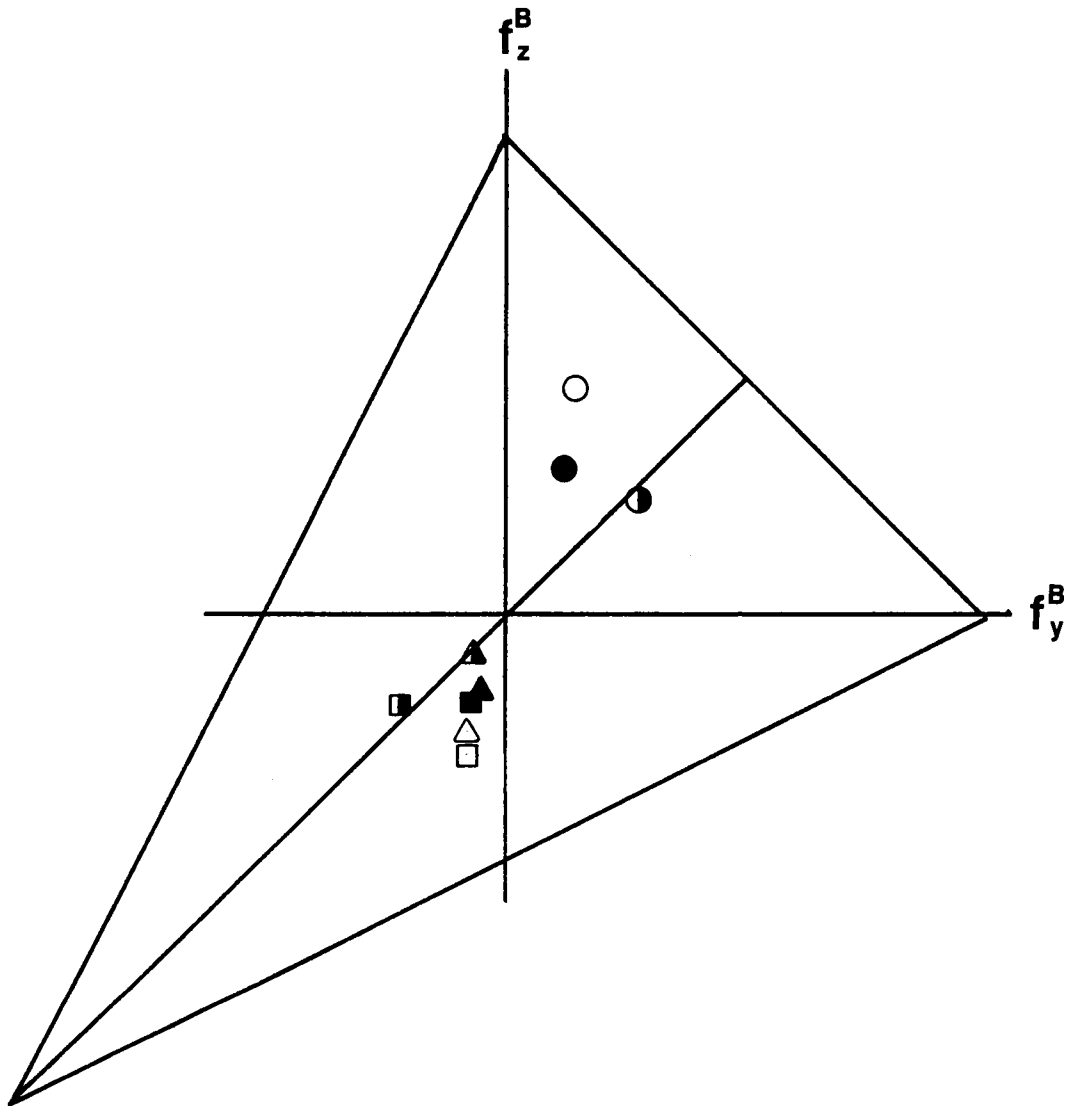


Figure 59. Average a-, b-, and c-axis Orientation Functions for the Three Film Processes Plotted on the Orientation Triangle.

CHAPTER VI

MECHANICAL PROPERTIES OF UNDRAWN, UNIAXIALLY DRAWN,
AND MANDREL PROCESSED PPD-T FILMS

A. Undrawn Films

Results

Undrawn films, as indicated in the stress strain curves in Figure 60, demonstrate a variation in tensile strength and modulus and, to some extent, percent elongation at break as a function of film direction. Modulus and tensile strengths are always greater in the machine direction than the transverse direction. Percent elongations are low indicating the brittle nature of these films. The shape of the curves don't indicate well defined yield points, and always result in a brittle fracture. Some of the films were so brittle they broke in the clamp upon being clamped.

Table 15 gives the tensile strengths moduli and percent elongations at break as a function of film directions for the three film processes. Tensile strengths in the machine direction averaged 6.4×10^3 psi versus 6.6×10^2 psi for the transverse direction for undrawn films. Modulus values in the machine direction averaged 1.7×10^5 psi versus 2.0×10^4 psi for the transverse direction. Percent elongation values as a function of the direction demonstrate a lot of scatter but also show the brittle

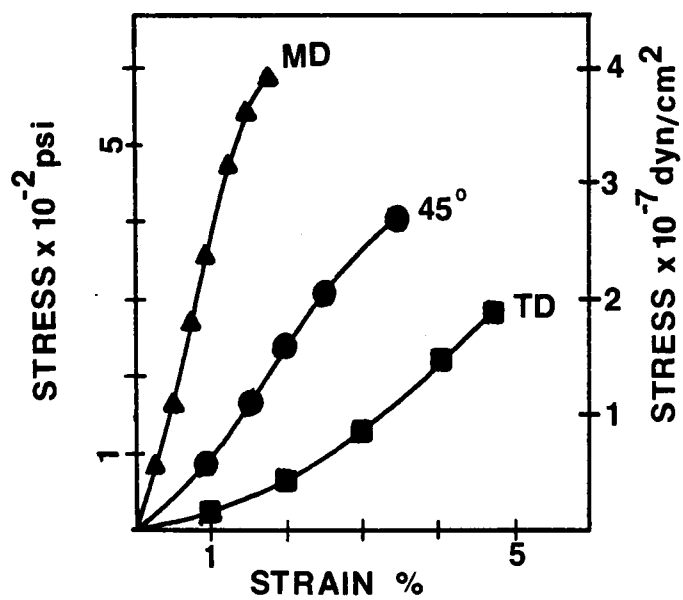


Figure 60. Typical Stress Strain Curves for Extruded Films as a Function of Film Direction.

Table 15. Mechanical Properties as a Function of Film Process and Direction

Run #	Film Process	Modulus (psi)		Breaking Stress (psi)		% Elongation		
		MD*	45°	TD	MD	45°	TD	0° 45° 90°
1	Extruded	6.6×10^4	4.6×10^4	1.9×10^4	2.2×10^3	1.2×10^3	7.9×10^2	5.9 4.7 6.5
2	Extruded	3.1×10^4	2.0×10^4	1.0×10^4	4.5×10^2	3.1×10^2	2.1×10^2	1.8 2.0 2.9
3	Extruded	5.5×10^5	SAMPLE BROKE IN CLAMP		1.7×10^4	-----	-----	4.2 ----
4	Extruded	1.6×10^5	3.43×10^4	7.3×10^4	4.2×10^3	1.1×10^3	2.1×10^3	3.3 4.4 2.9
5	Extruded	2.0×10^5	1.6×10^4	1.7×10^4	1.3×10^4	4.6×10^3	9.0×10^2	16.8 5.7 12.0
6	Extruded	3.9×10^4	SAMPLE BROKE IN CLAMP		1.3×10^3	-----	-----	4.0 ----
7	Drawdown	7.0×10^5	8.4×10^4	2.8×10^4	2.2×10^4	1.3×10^3	7.8×10^2	12.4 1.8 3.5
8	Drawdown	4.7×10^5	4.2×10^4	1.2×10^4	1.7×10^4	1.1×10^3	1.1×10^3	3.0 10.0 5.3
9	Drawdown	8.8×10^5	1.3×10^4	1.4×10^4	2.2×10^4	9.7×10^2	1.3×10^3	5.3 0.82 2.0
10	Drawdown	4.7×10^5	1.6×10^5	9.0×10^4	1.6×10^4	3.4×10^3	1.0×10^3	7.9 3.8 3.0
11	Drawdown	1.2×10^6	7.3×10^5	8.7×10^4 ✓	3.7×10^4	1.9×10^4	2.2×10^3	9.5 7.1 3.9
12	Drawdown	1.5×10^5	3.1×10^4	1.1×10^4	6.2×10^3	1.4×10^3	4.8×10^2	11.0 8.0 7.5
13	Mandrel	1.6×10^5	1.7×10^5	1.7×10^5	7.7×10^3	7.4×10^3	4.9×10^3	7.5 6.7 6.0
14	Mandrel	2.1×10^5	3.8×10^5	4.0×10^5	9.8×10^3	1.6×10^4	1.3×10^4	6.5 3.5 5.9
15	Mandrel	MECHANICAL TESTING NOT DONE ON THESE SAMPLES						
16	Mandrel	MECHANICAL TESTING NOT DONE ON THESE SAMPLES						
17	Mandrel	1.5×10^5	2.2×10^5	1.8×10^5	7.1×10^3	8.4×10^3	8.0×10^3	10.0 5.5 7.0
18	Mandrel	1.2×10^5	1.3×10^5	8.7×10^4	9.6×10^3	1.1×10^4	1.3×10^4	9.5 7.1 3.9
19	Mandrel Drawdown	3.0×10^5	1.01×10^5	1.0×10^5	1.4×10^4	3.4×10^3	3.9×10^3	7.8 9.3 5.7

*MD represents the machine direction or 0° angle, 45° is the direction 45° between the MD and TD direction where TD represents the transverse direction or 90° angle.

nature of these films. In all but one case, the percent elongation was no higher than 6.5% and as low as 1.8%. Water coagulated undrawn films show unusually high percent elongation values, which can't really be explained.

Plotting percent elongation as a function of direction gave very inconsistent results and was not done for any of the films including uniaxially drawn films and films extruded over the mandrel.

Plotting breaking stress as a function of film direction demonstrates the uniaxial character of extruded films. The general shape of these plots is oval with the long axis in the machine direction; see Figures 61 through 66.

In many cases the strength in the 45° direction is less than that of the transverse direction giving a star shape to the plot. This phenomena is the opposite of what would be expected and may be due to some internal flaw which shows up only on the 45° samples.

Plots of initial modulus as a function of direction may be seen in Figures 67 through 72 and in Table 15. The general shape of these plots is also an oval, once again with the long axis in the machine direction. These plots are similar to the breaking stress plots, indicating uniaxial orientation in the machine direction.

There is an experimental problem associated with undrawn films; an extreme amount of wrinkling occurs in the machine direction upon drying. This makes measuring

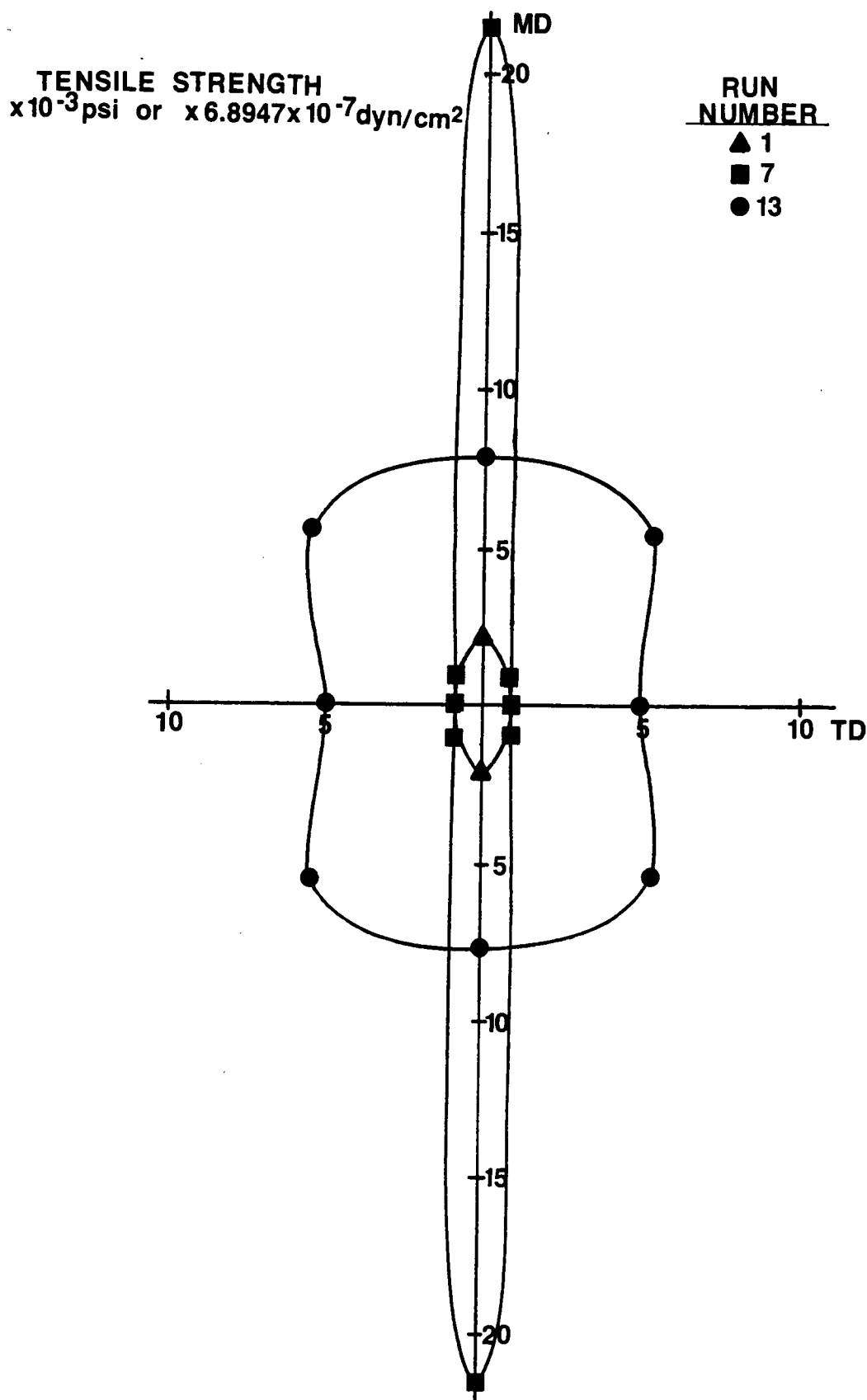


Figure 61. Radial Plots of Tensile Strength as a Function of Film Direction for Extruded, Uniaxially Drawn, and Mandrel Processed Films Coagulated in 5% Water and 95% Methanol.

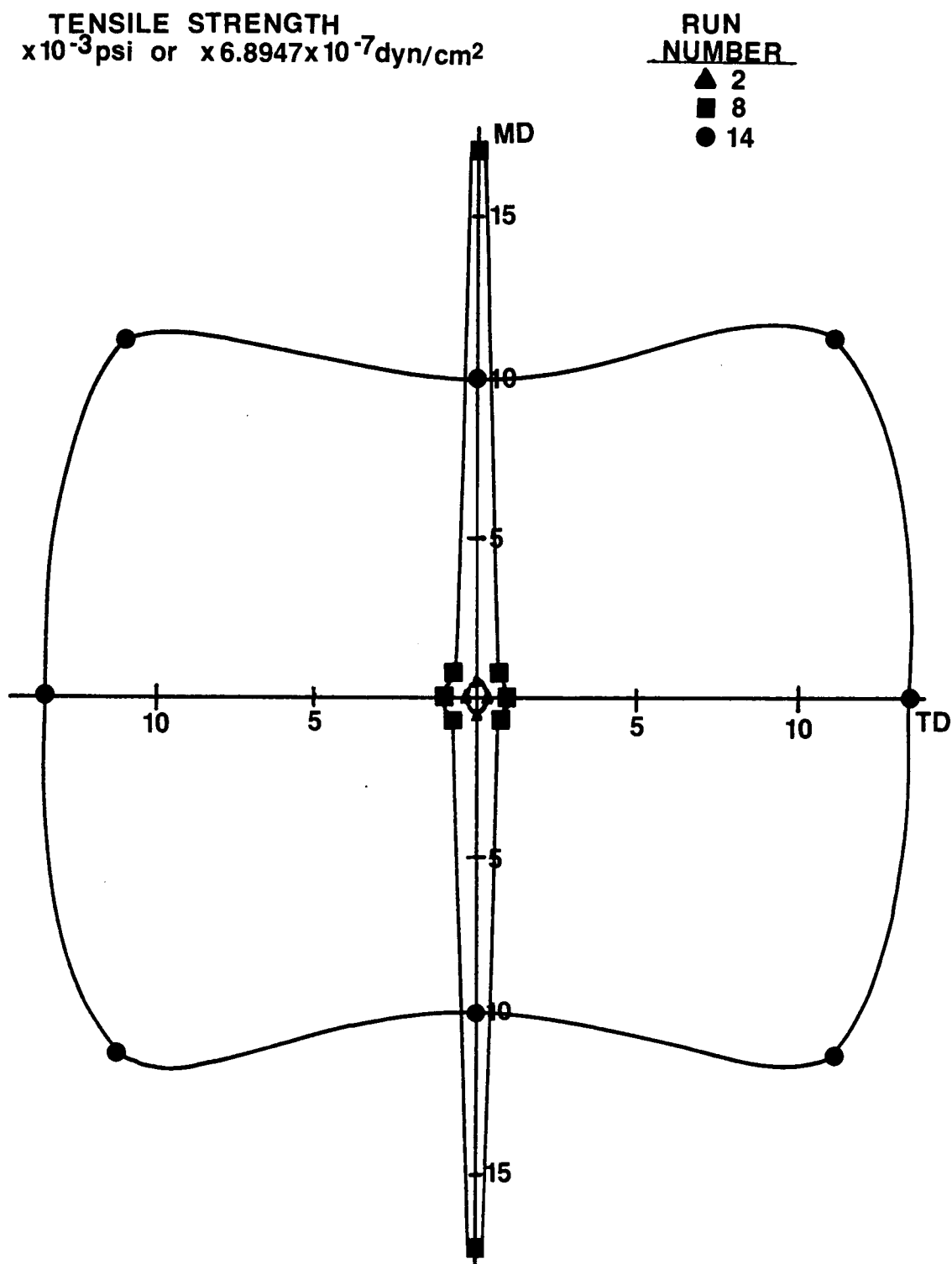


Figure 62. Radial Plots of Tensile Strength as a Function of Film Direction for Extruded, Uniaxially Drawn, and Mandrel Processed Films Coagulated in 25% Water and 75% Methanol.

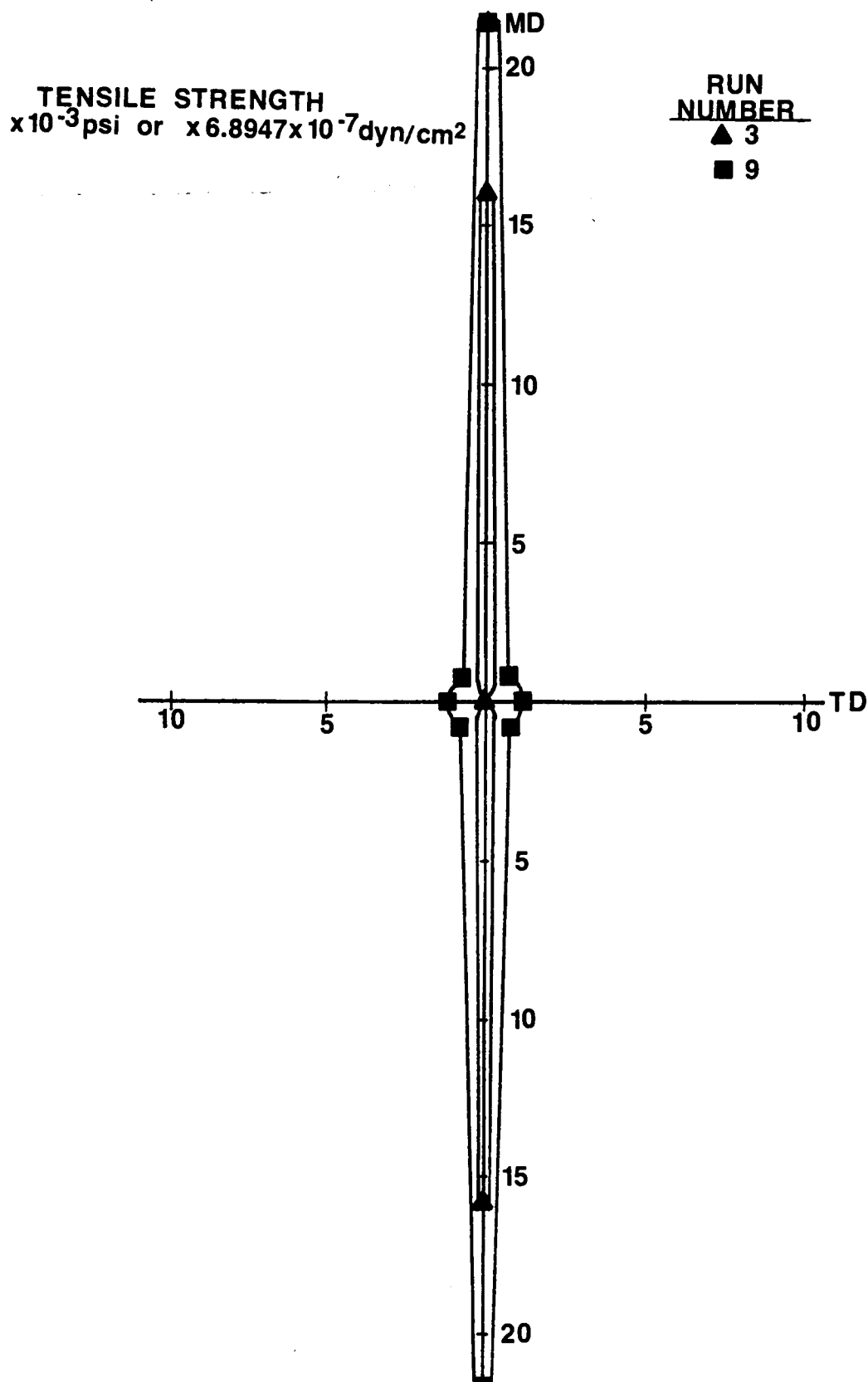


Figure 63. Radial Plots of Tensile Strength as a Function of Film Direction for Extruded and Uniaxially Drawn Films Coagulated in 45% Water and 55% Methanol.

TENSILE STRENGTH
 $\times 10^{-3}$ psi or $\times 6.8947 \times 10^{-7}$ dyn/cm²

RUN
 NUMBER
 ▲ 4
 □ 10
 ● 17
 --- 19

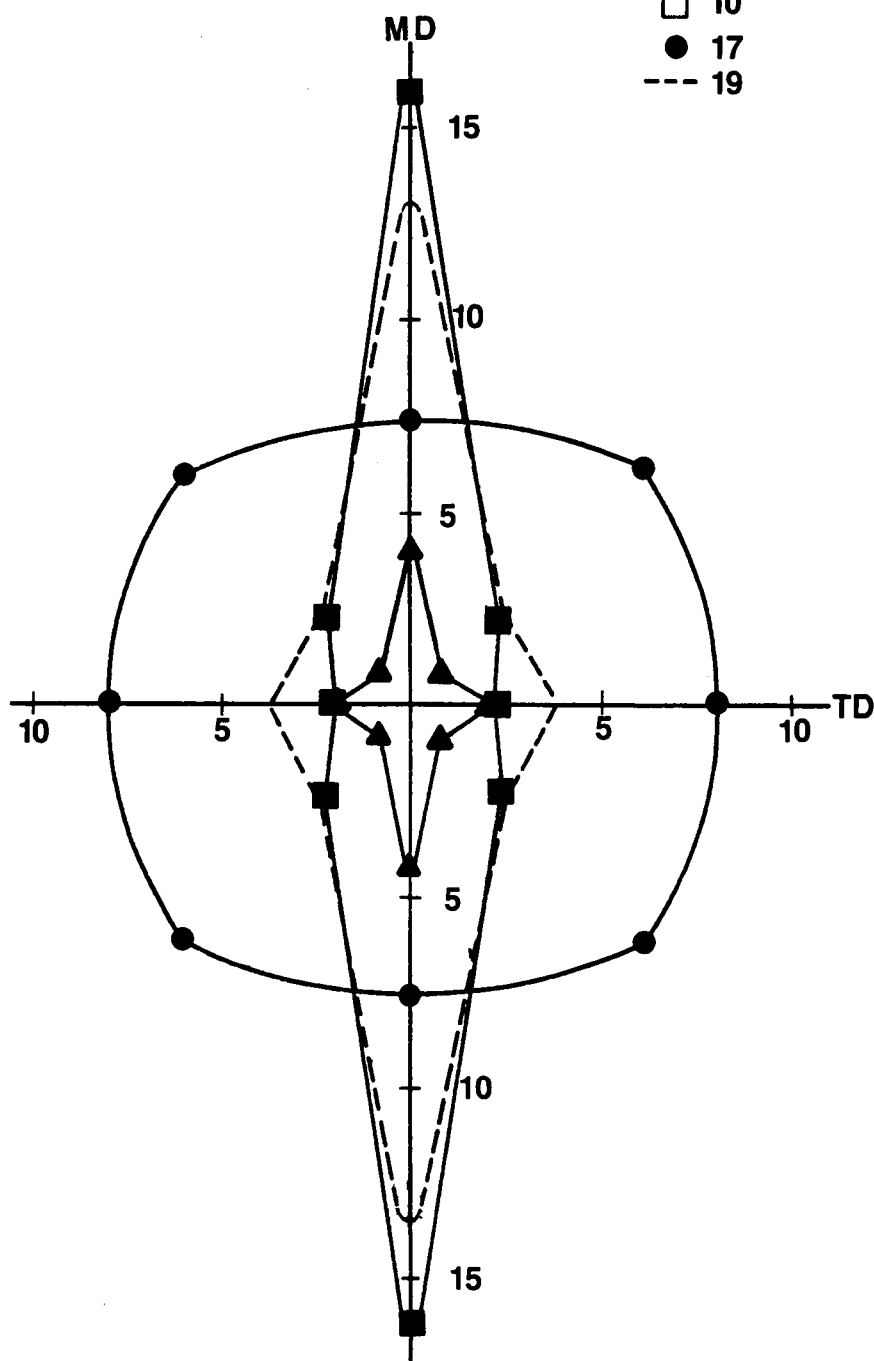


Figure 64. Radial Plots of Tensile Strength as a Function of Film Direction for Extruded, Uniaxially Drawn, and Mandrel Processed Films Coagulated in 50% Methanol and 50% Ethanol.

TENSILE STRENGTH
 $\times 10^{-3}$ psi or $\times 6.8947 \times 10^{-7}$ dyn/cm²

RUN
 NUMBER

▲ 5

■ 11

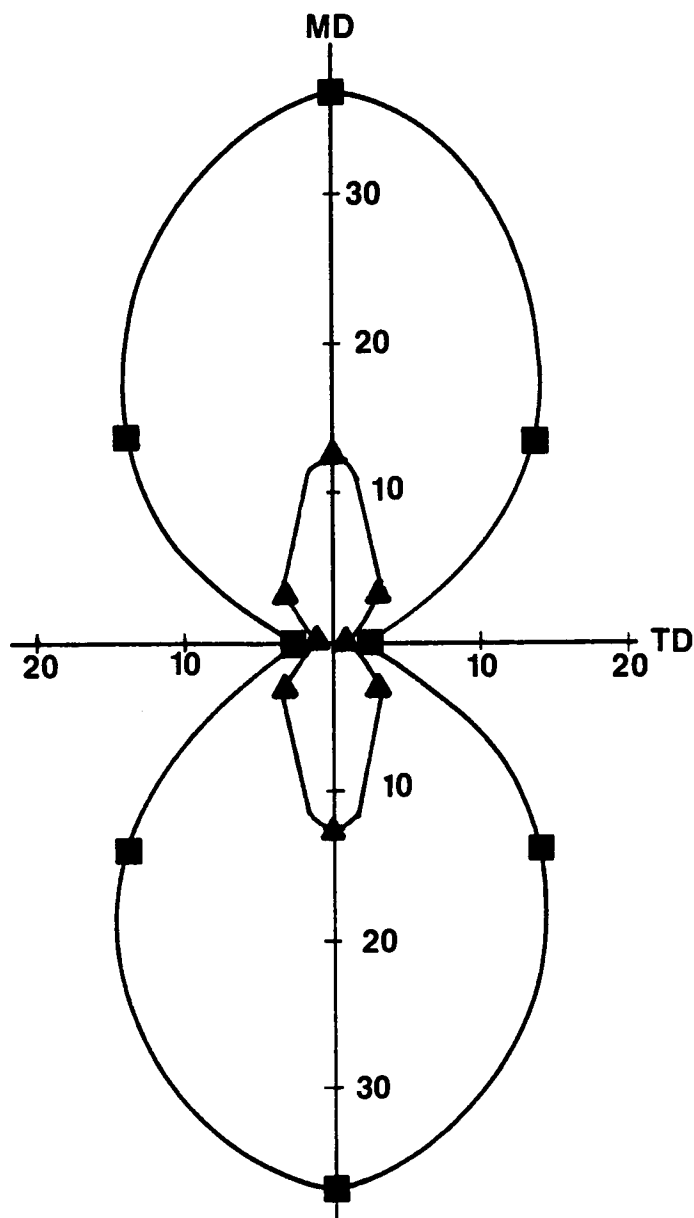


Figure 65. Radial Plots of Tensile Strength as a Function of Film Direction for Extruded and Uniaxially Drawn Films Coagulated in Water.

TENSILE STRENGTH
 $\times 10^{-3}$ psi or $\times 6.8947 \times 10^{-7}$ dyn/cm²

**RUN
 NUMBER**

▲ 6
 ■ 12
 ● 18

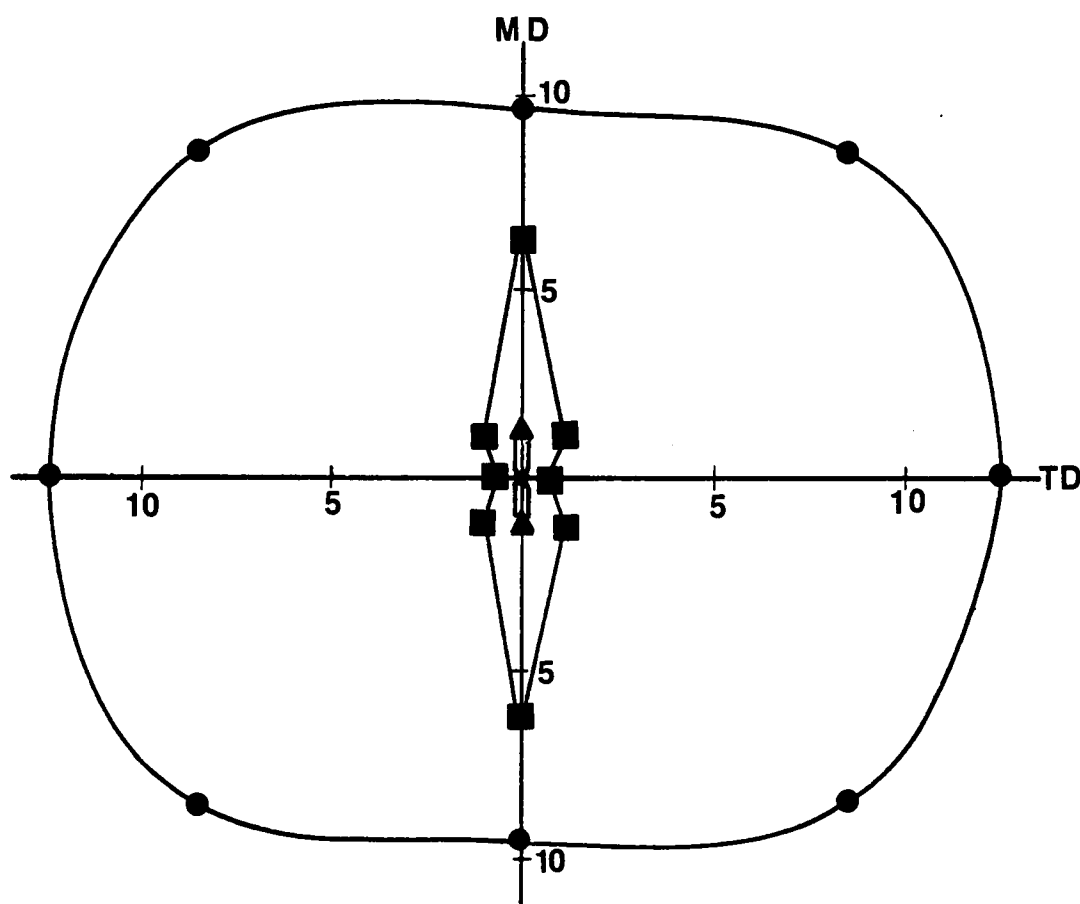


Figure 66. Radial Plots of Tensile Strength as a Function of Film Direction for Extruded, Uniaxially Drawn, and Mandrel Processed Films Coagulated in 25% Water and 75% Ethanol.

INITIAL MODULUS
 $\times 10^{-5}$ psi or $\times 6.8947 \times 10^{-9}$ dyn/cm²

RUN
NUMBER

▲ 1

■ 7

● 13

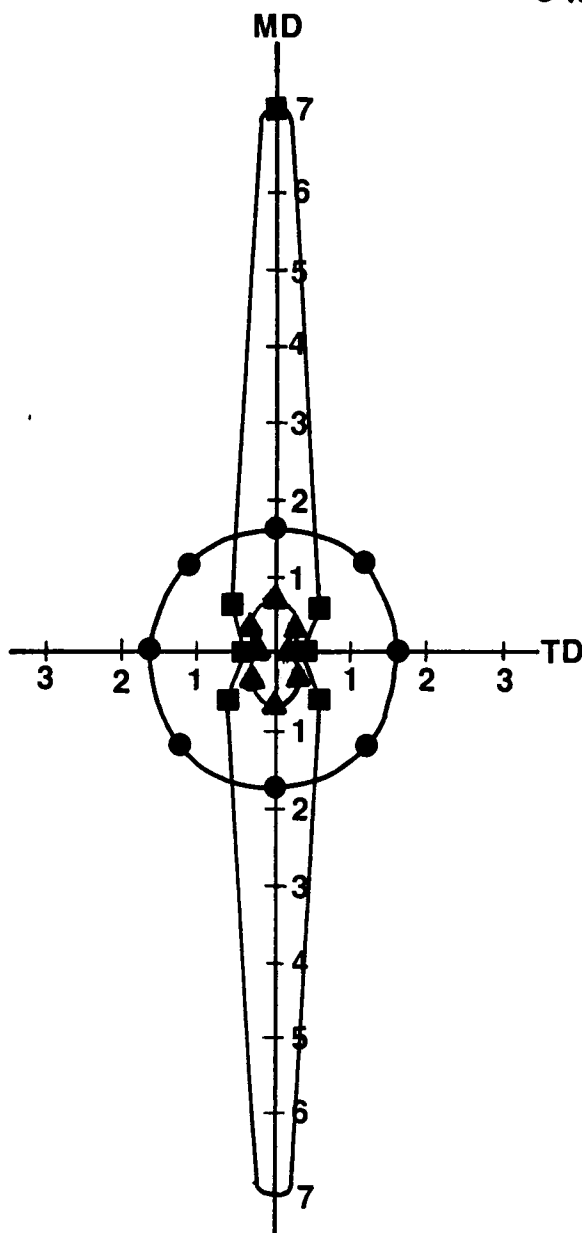


Figure 67. Radial Plots of Modulus as a Function of Film Direction for Extruded, Uniaxially Drawn, and Mandrel Processed Films Coagulated in 5% Water and 95% Methanol.

INITIAL MODULUS
 $\times 10^{-5}$ psi or $\times 6.8947 \times 10^{-9}$ dyn/cm²

RUN
 NUMBER
 ▲ 2
 ■ 8
 ● 14

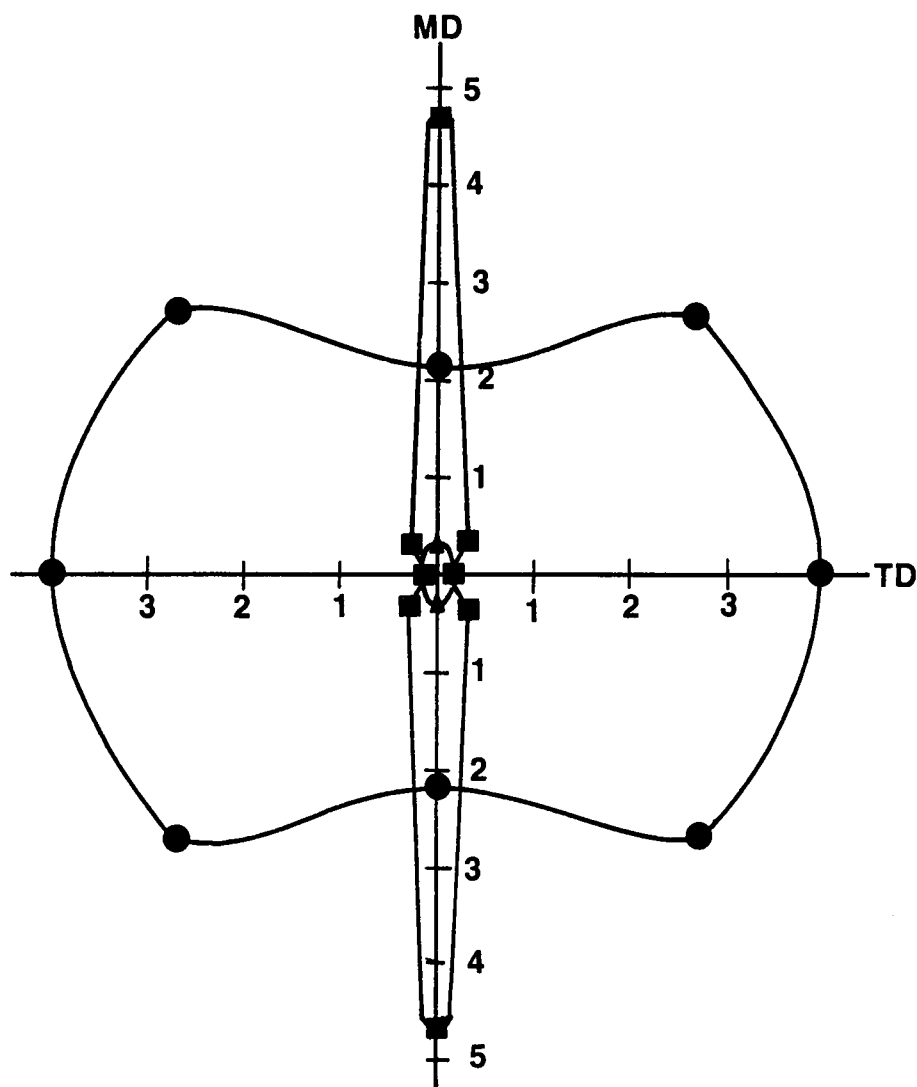


Figure 68. Radial Plots of Modulus as a Function of Film Direction for Extruded, Uniaxially Drawn, and Mandrel Processed Films Coagulated in 25% Water and 75% Methanol.

INITIAL MODULUS
 $\times 10^{-5}$ psi or $\times 6.8947 \times 10^{-9}$ dyn/cm²

RUN
NUMBER

▲ 3

■ 9

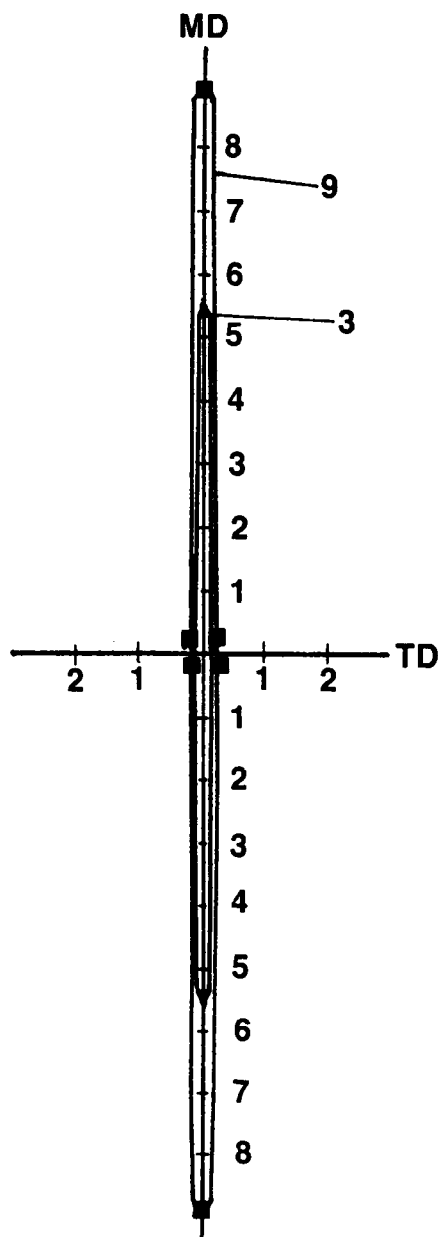


Figure 69. Radial Plots of Modulus as a Function of Film Direction for Extruded and Uniaxially Drawn Films Coagulated in 45% Water and 55% Methanol.

INITIAL MODULUS
 $\times 10^{-5}$ psi or $\times 6.8947 \times 10^{-9}$ dyn/cm²

RUN
NUMBER
 ▲ 4
 ■ 10
 ● 17
 ---19

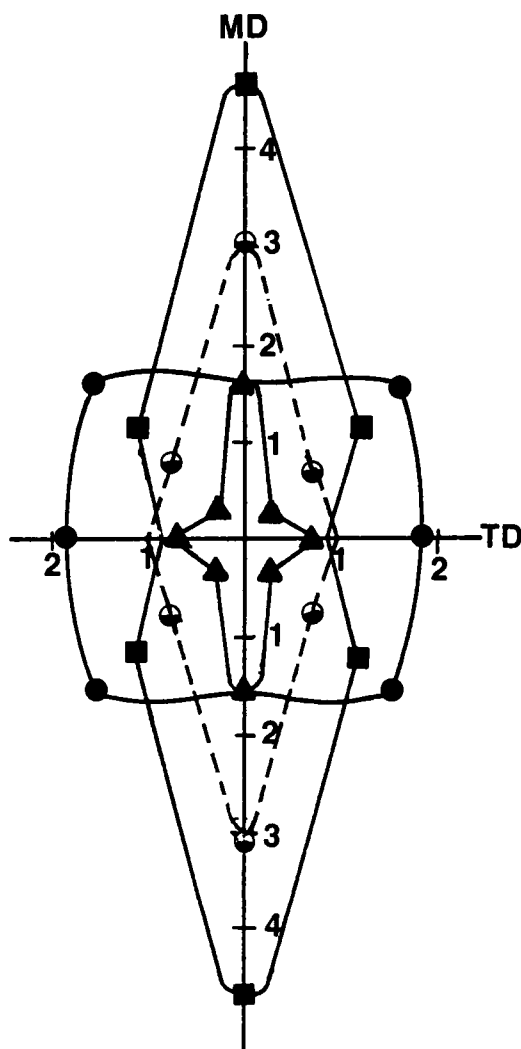


Figure 70. Radial Plots of Modulus as a Function of Film Direction for Extruded, Uniaxially Drawn, and Mandrel Processed Films Coagulated in 50% Methanol and 50% Ethanol.

INITIAL MODULUS
 $\times 10^{-5}$ psi or $\times 6.8947 \times 10^{-9}$ dyn/cm²

RUN
NUMBER

▲ 5

■ 11

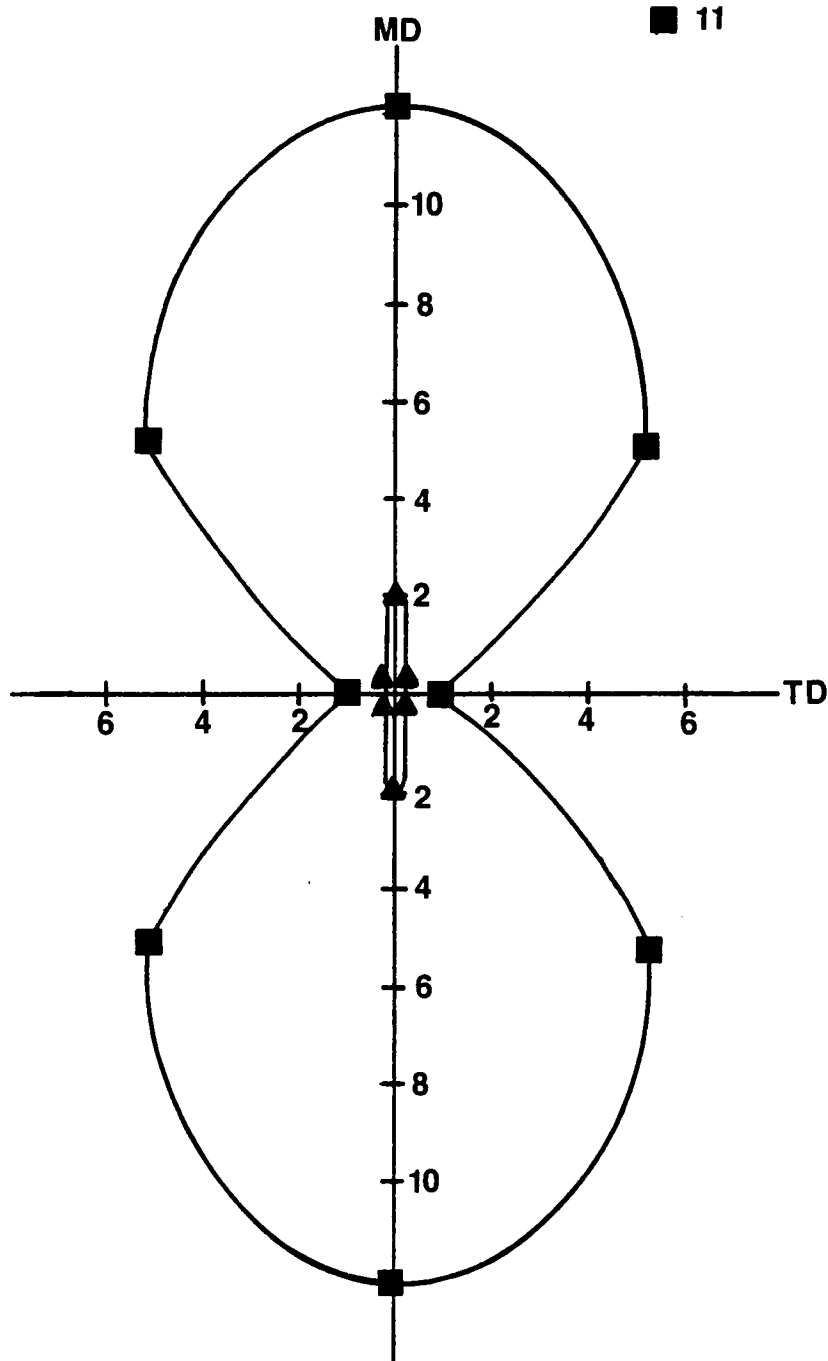


Figure 71. Radial Plots of Modulus as a Function of Film Direction for Extruded and Uniaxially Drawn Films Coagulated in Water.

INITIAL MODULUS
 $\times 10^{-5}$ psi or $\times 6.8947 \times 10^{-9}$ dyn/cm²

RUN
 NUMBER

△ 6

□ 12

● 18

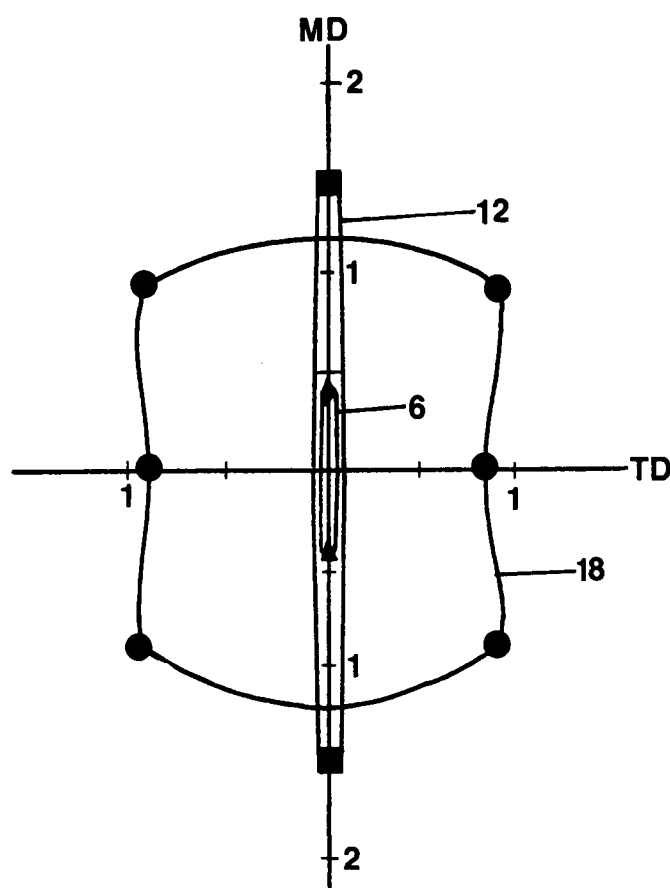


Figure 72. Radial Plots of Modulus as a Function of Film Direction for Extruded, Uniaxially Drawn, and Mandrel Processed Films Coagulated in 25% Water and 75% Ethanol.

average thickness difficult, therefore introducing some error into the modulus and stress data. It also makes any percent elongation data and, to some extent, initial modulus data subject to error due to the fact that wrinkles pull out slightly under load. Also the wrinkles act as defects in the film structure resulting in early failure. SEM photomicrographs in the next chapter will also demonstrate an extensive amount of voids present in undrawn films which also act as defects.

The effect of coagulant on film strength shows trends towards higher strengths resulting from higher water content in the coagulant; see Table 15, page 169.

Discussion

In most cases, the undrawn films are relatively weak compared to the other films; see Table 15. As was seen in the orientation functions, WAXS patterns, and pole figures, the degree of orientation is much lower than either the uniaxial films or biaxial films.

The two films which demonstrated fairly good strength were samples 3 and 5, both of which were made from coagulants with higher water content. Orientation functions didn't show a marked increase for these samples; see Table 13, page 142. This increase in strength could be due to the increased coagulating ability of water. That is, water probably removes more acid resulting in less degradation.

The modulus and tensile strength properties for sample 6, though low, aren't low enough to explain the low orientation functions for the same sample.

B. Uniaxially Drawn Films

Results

Figure 73 is a typical set of stress strain curves for uniaxially drawn films. There is a very large variation in modulus and tensile strength as a function of film direction. Modulus and tensile strength are much greater in the machine direction than the transverse direction. Percent elongation at break doesn't show a consistent pattern in terms of film direction, though it does indicate the relatively brittle nature of the film in all directions. The shape of the machine and 45° direction curves don't indicate well defined yield points, with both ending in a brittle failure. The curve in the transverse direction appears to flatten out immediately indicating some type of initial yield point, which could be due to film wrinkles pulling out.

Table 15 shows tensile strengths moduli and percent elongation at break for uniaxially drawn films as a function of film direction. Average tensile strengths for the machine and transverse directions are 2.0×10^4 psi and 1.1×10^3 psi respectively. Average modulus values for the machine and transverse directions are 6.5×10^5 psi

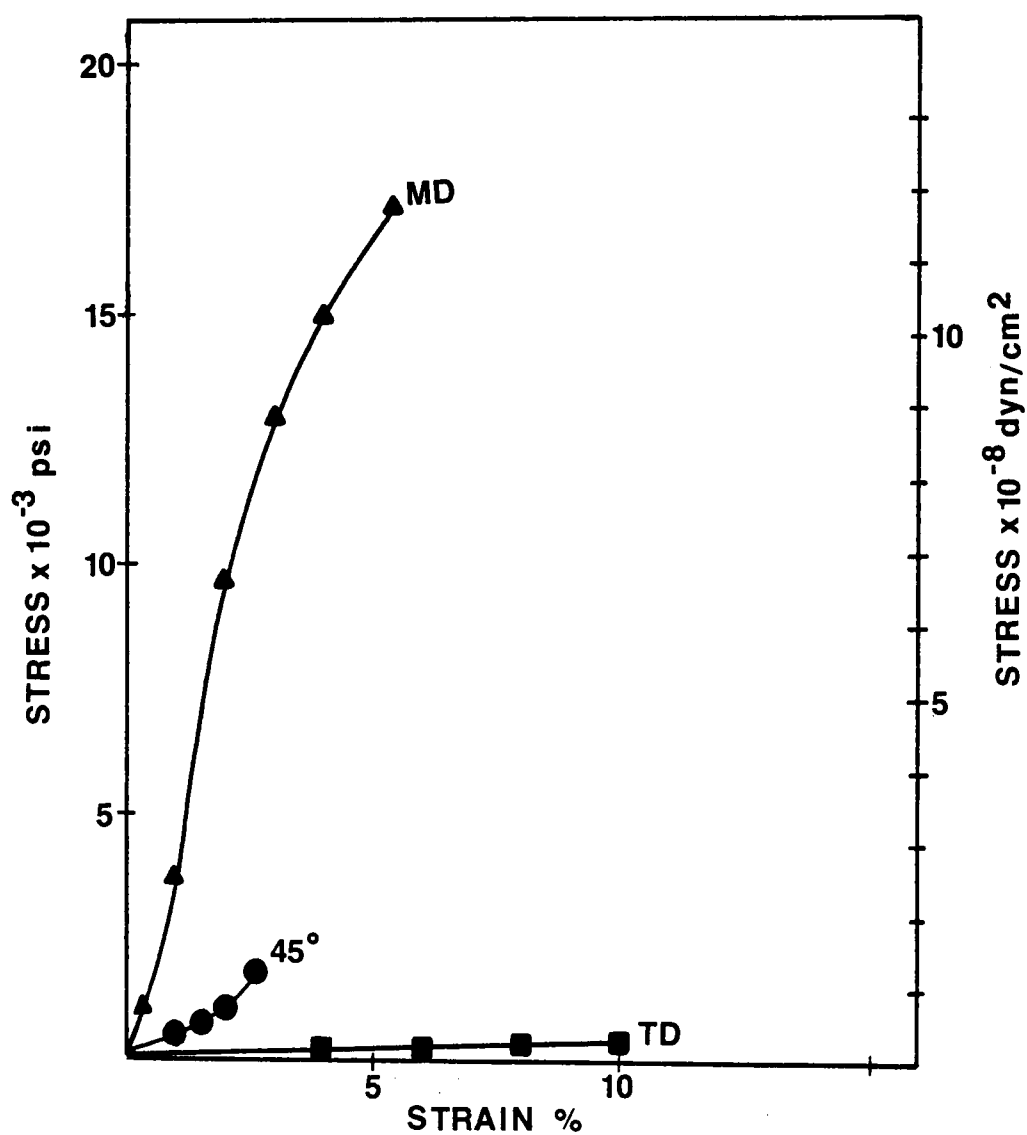


Figure 73. Typical Stress Strain Curves for Uniaxially Drawn Films as a Function of Film Direction.

and 4.0×10^4 psi respectively. Percent elongation at break ranged from 2.0 to 11.0 with no real consistency as a function of film direction.

Plots of breaking stress as a function of film direction are in Figures 61 - 66, pages 171- 176. It can be seen that the tensile strength in the machine direction for uniaxially drawn film is much higher than those of the undrawn films. Both types of films are very weak in the transverse direction. In other words, the plots are oval shaped with the long axis in the machine direction.

Plots of initial modulus as a function of film direction, as seen in Figures 67 through 72, pages 177-182 demonstrate the same situation as described above, high degrees of orientation in the machine direction as compared to the transverse direction, resulting in essentially oval shaped plots.

Experimental problems similar to the undrawn films resulted from the films wrinkling in the machine direction. In some cases the films were so brittle in the transverse direction that clamping them would create rips in the machine direction of the film sample.

Discussion

Kevlar 29^R in the fiber form has a tensile strength of 525,000 psi and a modulus of 12.0×10^6 psi. Percent elongation at break is 4.4%. Obviously, the uniaxially oriented films don't come close to these values with the

highest tensile strength being 37,000 psi and the highest modulus 1.2×10^6 psi. This is partially due to conditions that wouldn't allow the film to be drawn as highly as the fibers because no air gap was present as in the fiber process. Another reason could be due to degradation in the films before and after coagulation.

Using water as a coagulant usually gives higher values for breaking strength and modulus. Water may be the best coagulant for Kevlar^R films. The other coagulants may leave residual amounts of sulfuric acid in the films resulting in degradation.

The fact that Kevlar^R 29 fibers were annealed under tension at temperatures around 500°C and the films weren't may have a lot to do with differences in strength between the two. It is a known fact that annealing Kevlar^R fibers greatly enhances their strength.

Comparing the mechanical properties of machine direction samples of the uniaxially drawn films to the undrawn film gives a dramatic difference in strength and modulus. Tensile strength for the uniaxially drawn samples are an average value of 2.9×10^4 psi as compared to a 6.4×10^4 psi average for the undrawn samples. Average modulus values are 6.0×10^5 psi and 1.7×10^5 psi respectively for the uniaxial and undrawn films.

Transverse direction properties are very weak for both cases; see Table 15.

The uniaxial character of the film as demonstrated by the orientation functions is supported by the mechanical properties, that is, relatively high strength in the machine direction indicative of c-axis orientation in the machine direction and low strength in the transverse direction. Sample 12 is also consistent with the orientation function in that it is considerably weaker than other samples made under similar conditions. As was mentioned before, this was probably due to degradation and the resulting lower drawdown ratios.

C. Mandrel Processed Films

Results

Typical stress strain plots as a function of film direction may be seen in Figure 74. Breaking strengths range from 9,000 psi to 20,000 psi with no great loss of strength in any direction. Modulus values ranged from 2.1×10^5 psi to 7.3×10^5 psi indicating strength or stiffness at least of the same order in all directions. Percent elongation at break goes from 2.5 to 9% in the sample shown. Yield points, if any, aren't well defined and the shape of the curves are generally like that of the transverse direction plot. All of the failures were brittle fractures.

Table 15 on page 169 demonstrates tensile strengths, moduli, and elongation at break for mandrel processed

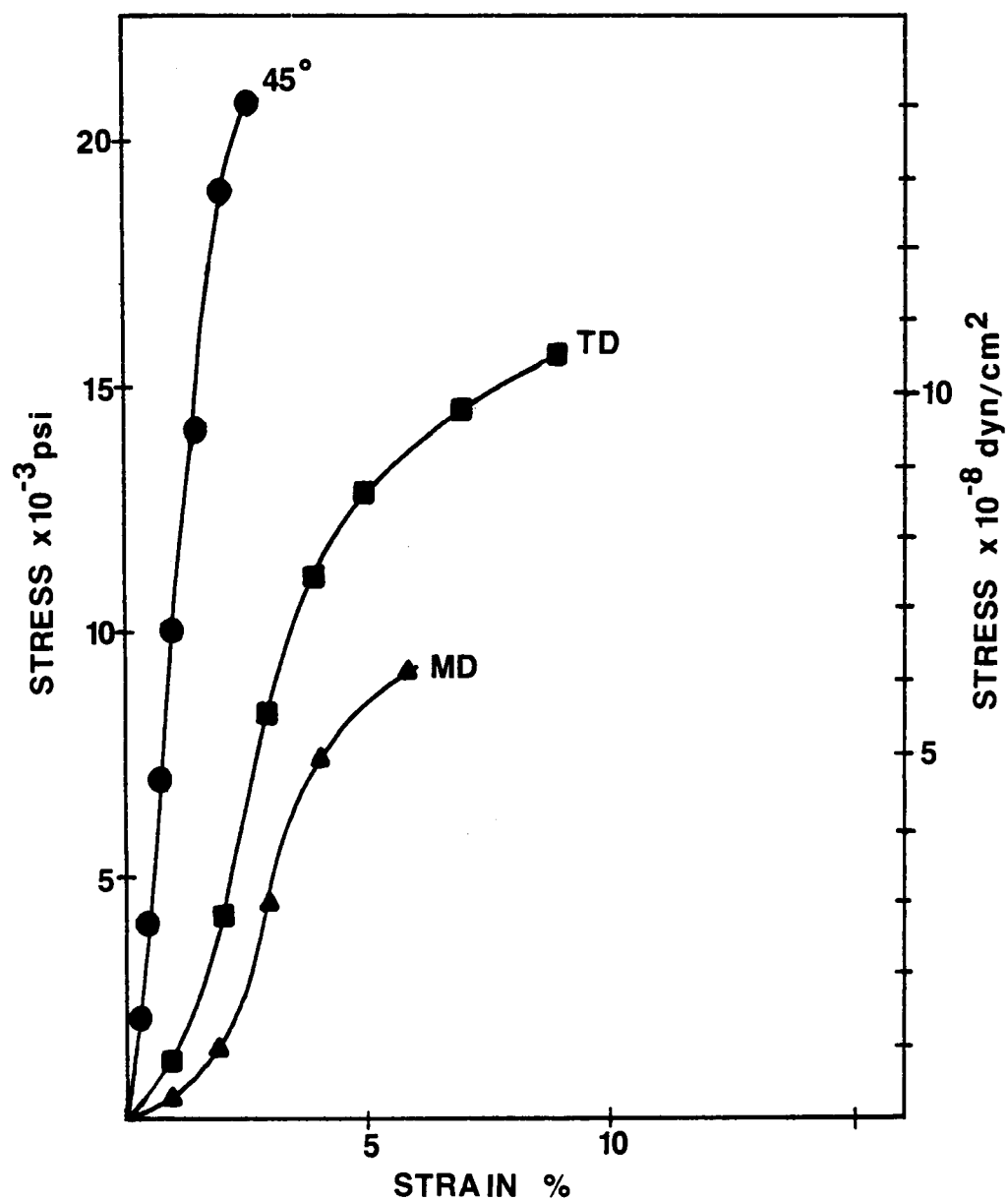


Figure 74. Typical Stress Strain Curves for Mandrel Processed Films as a Function of Film Direction.

films. Average values for tensile strengths in the machine and transverse directions were 8.2×10^3 and 9.7×10^3 psi respectively. The average modulus value for the machine direction was 1.6×10^5 psi and for the transverse direction 2.1×10^5 psi. Percent elongation at break ranged from 3.5 to 10% with no trends in terms of film direction, except that all the films were relatively brittle.

Plots of breaking stress as a function of film direction may be seen in Figures 61-66, pages 171-176. In all cases the tensile strength didn't vary greatly as it did in the uniaxially drawn films. Plots of modulus as a function of film direction indicates the same situation; see Figures 67-72, pages 177-182. The general shape for the above plots is round as compared to oval for the uniaxial films.

Wrinkling in these films wasn't as extensive as in the other processes. The wrinkles were very small and didn't follow in any particular direction. They did provide defect sites leading to early film failure.

Run number 19 is a film drawn down over the mandrel with a drawdown greater than one. Mechanical properties indicate an increase in strength and modulus as seen in Table 15. Figures 64 and 70 demonstrate the uniaxial nature of this film in terms of tensile strength and modulus.

Discussion

Tensile strength in the transverse direction for biaxially drawn films has increased by a factor of six to ten times over that of the uniaxially drawn films. The tensile strength in the machine direction has been reduced somewhat compared to uniaxial film, usually by a factor of 1.5 to 2 times.

A similar comparison can be made with modulus in the transverse direction. For biaxial films, an average of 2.0×10^5 psi was obtained. Modulus in the same direction for uniaxial films is an average of 4.0×10^4 psi. Modulus in the machine direction is on the order of 1.9×10^5 psi for the mandrel process and 6.45×10^5 psi for the uniaxial process.

Coagulants cannot be taken into account as a major factor affecting mechanical properties in biaxial film. This is due to the small range of coagulants used and the relatively similar nature of the chemicals making up the coagulants. As was explained in the processing chapter, large amounts of water, over 30% by volume, couldn't be used.

Mechanical properties compare fairly well with orientation functions, pole figures, and WAXS patterns. Tensile strength and modulus are relatively uniform in all directions indicative of biaxial orientation. The high values for the c-axis orientations of run number 18 aren't

consistent with higher mechanical properties, that is, mechanical properties are similar, within experimental error, to the other films. This could be a result of degradation which probably wouldn't effect orientation as much as it would mechanical properties.

Once again, it should be mentioned that none of the biaxially oriented films were annealed under tension. Attempts were made to anneal the films, at temperatures of 450°C, with the film being held in a rigid aluminum frame. The result was a very brittle, weak film. This could have been the result of residual amounts of sulfuric acid left in the film. Clearly further work is needed in this area.

CHAPTER VII

THE DETERMINATION OF SUPERSTRUCTURE IN UNDRAWN,
UNIAXIALLY DRAWN, AND MANDREL
PROCESSED PPD-T FILMS

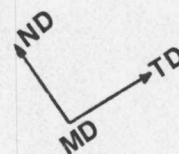
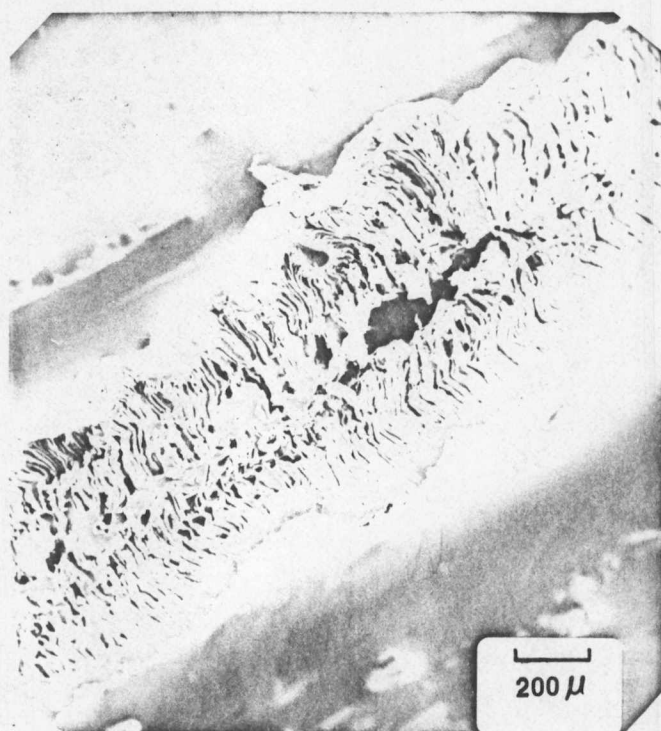
Scanning electron microscopy is used to determine the nature of the superstructure for PPD-T films in cross section and on the film surface. Cross sections are cut perpendicular to the machine direction, so one is looking through the machine direction. A comparison is made between the three film processes in terms of superstructure and its relationship to molecular orientation and mechanical properties.

A. Undrawn Films

Results

Undrawn or extruded films exhibit extensive voiding, with the voids being on the order of 200 μ in the normal direction, in all cases except for films coagulated in 45% water and 100% water. Figure 75 demonstrates some typical cross sections of undrawn films. Note that there appears to be a skin like structure on the outer boundaries of the film surface. In both examples, the voids start from the outer skin and proceed toward the center of the cross section. Large holes in the center of the cross sections can be seen. Apparently, these holes extend

a.



b.

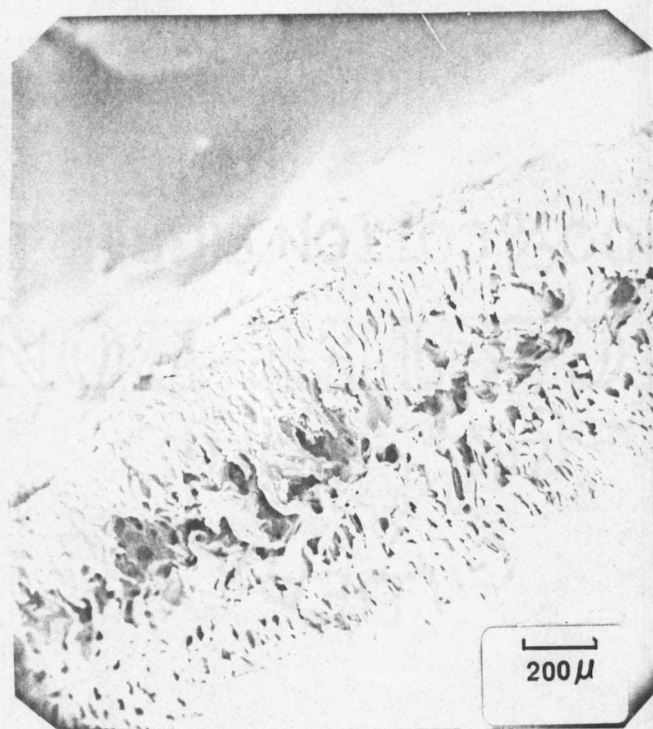


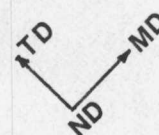
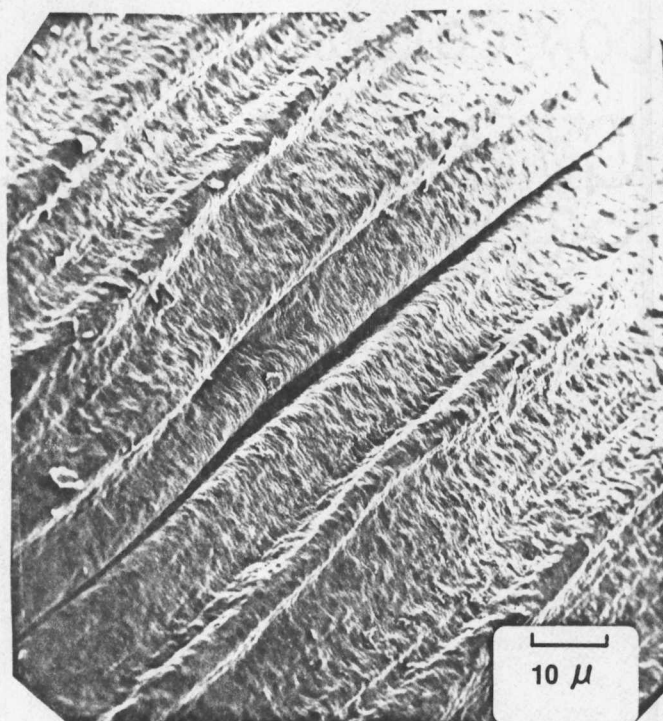
Figure 75. SEM Photomicrographs of Typical Cross Sections in Extruded Film, Coagulated in Alcohol Solutions of 0-25% Water.

throughout the length and width of the film, because the film can be split apart easily at these holes and pulled into two separate sections. Large wrinkles are present on the surface of both cross sections. Average film thickness for undrawn film with the above type of void system ranged from 0.5 mm to 1 mm.

Figure 76 presents a view normal to the film plane for films coagulated in solutions of water and alcohol with the water content ranging from 0% to 25% by volume. Wrinkles are present in all undrawn films. Sometimes, they are more pronounced in some films than in others, but they are always present and always travel in the machine direction. Some films, in addition to extensive wrinkling, exhibit holes in the film surface; see Figure 76.

Undrawn films coagulated in pure water or 40% water and 55% methanol exhibit a different cross section from other films coagulated with less water present. The pure water sample demonstrates two types of cross sections, a heavily voided section and a solid like section with much smaller voids on the order of 200 μ versus 5 to 15 μ respectively. The voids in both examples don't appear to be as extensive or as deep as the other films; see Figure 77. The skin structure on the outer surfaces of the cross section is still present. Film thickness is considerably less than other extruded films, in the range of 0.25 mm.

a.



b.

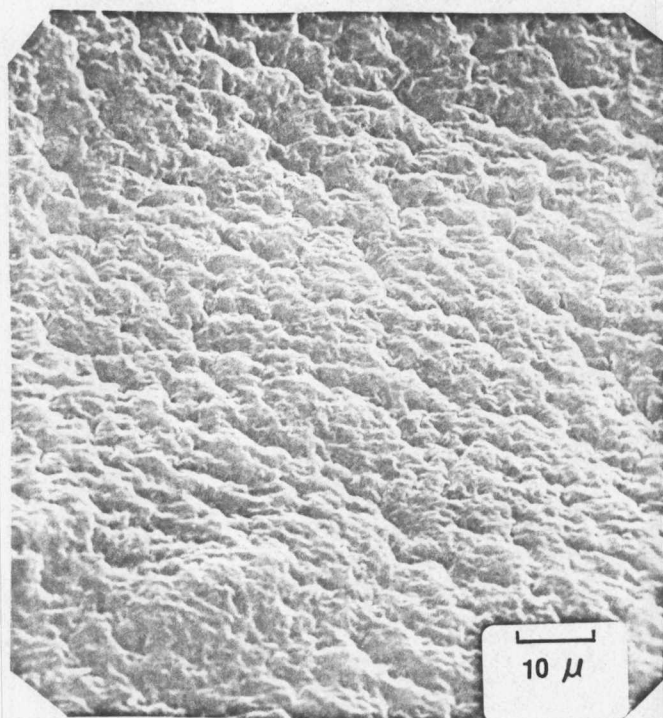
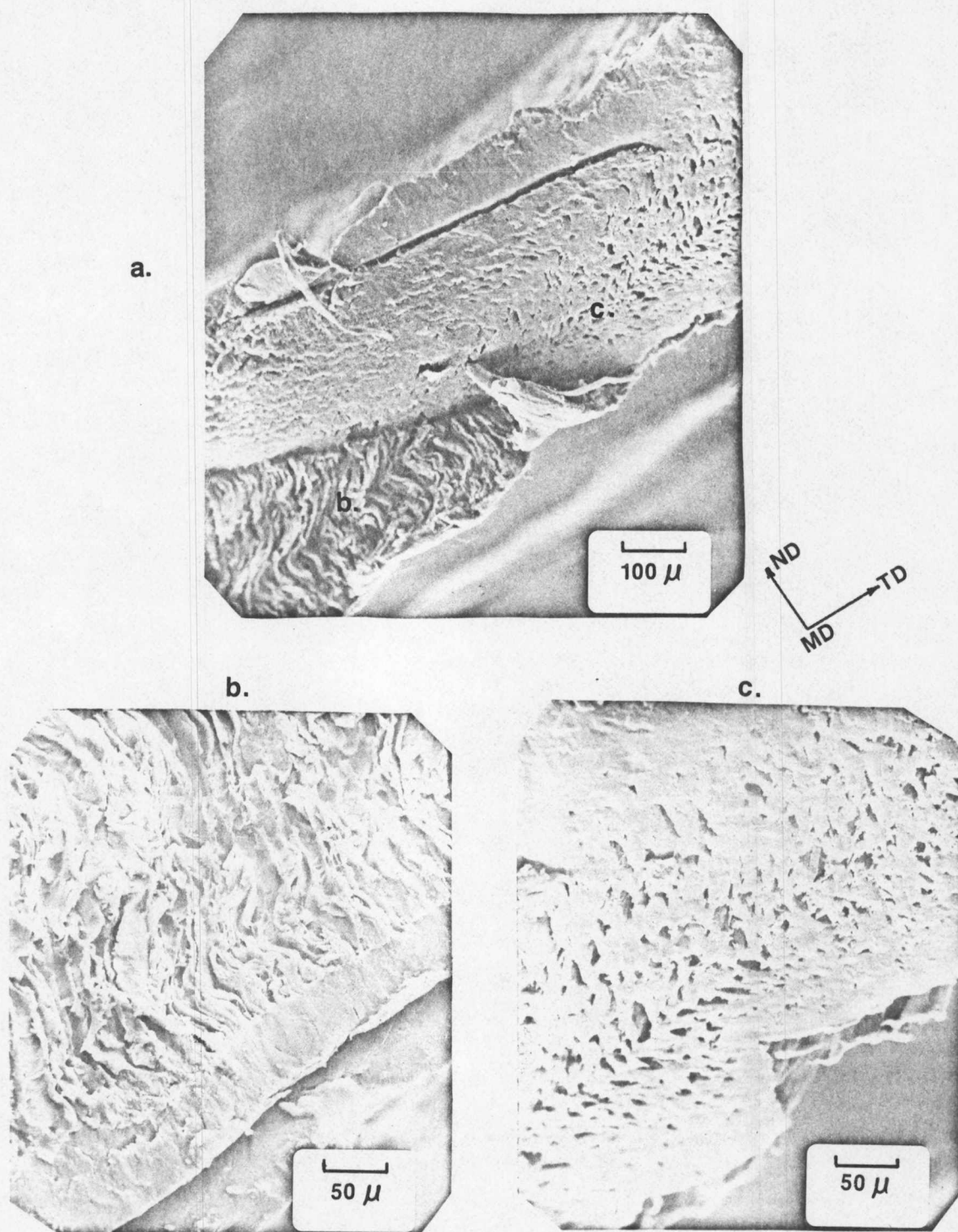


Figure 76. SEM Photomicrographs of Typical Film Surfaces of Extruded Film Coagulated in Alcohol Solutions of 0-25% Water.



(b) and (c) are enlargements of areas in (a).

Figure 77. SEM Photomicrographs of Cross Sections in Extruded Film Coagulated in 100% Water.

Figure 78 presents a view normal to the film plane. Note the wrinkling in the machine direction.

Undrawn films coagulated in 45% water and 55% methanol exhibited cross sections seen in Figure 79. There are relatively few visible voids present as compared to previous films. One feature worth noting was the line going through the center of the cross section. Film thickness ranged from 0.05 mm to 0.09 mm, substantially thinner than any of the other undrawn films.

Discussion

Figures 75a and 75b demonstrate a finger like void structure similar to the void structure identified by Hancock et al.(30) for wet spun Nomex^R fibers. Hancock et al.'s fibers had a diameter of 0.43 mm which is close to the thickness range of the undrawn films, 0.5 mm to 1 mm. The water coagulated films seemed to have an intermediate structure, with shallow finger like voids and solid section combined in the same film; in this case the film thickness was 0.25 mm. Hancock et al.'s Kevlar^R wet spun fibers exhibited a solid like cross section with fiber diameters ranging from 0.16 mm to 0.19 mm. The films coagulated in 45% water and 55% methanol exhibited a solid like cross section. Film thickness was between 0.05 mm to 0.09 mm. Clearly the presence of finger like voids is more a function of film thickness than any other factor. The film thickness which determines the presence of voids seems to

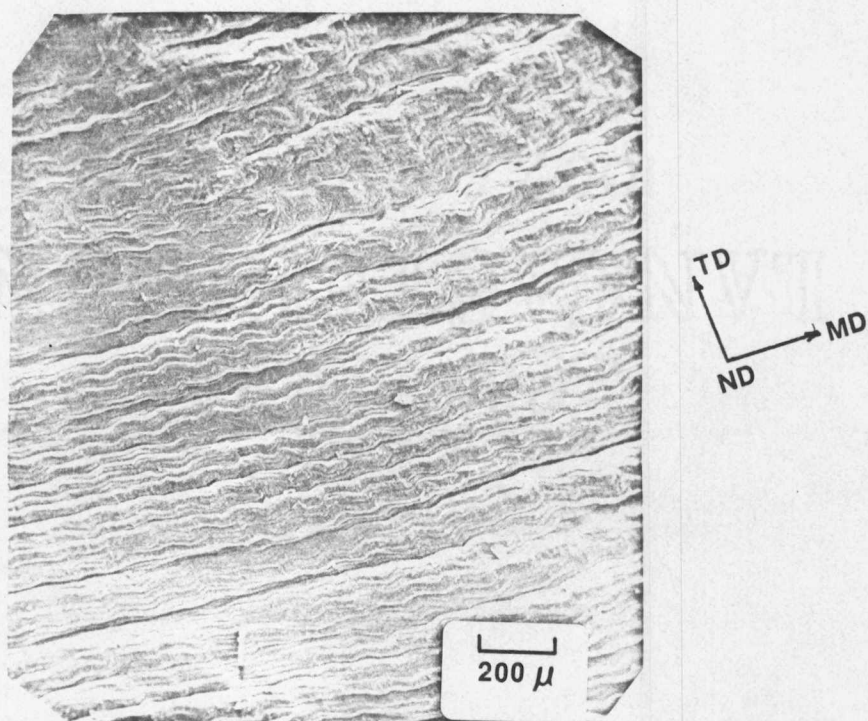


Figure 78. SEM Photomicrograph of the Film Surface of an Extruded Film Coagulated in 100% Water.

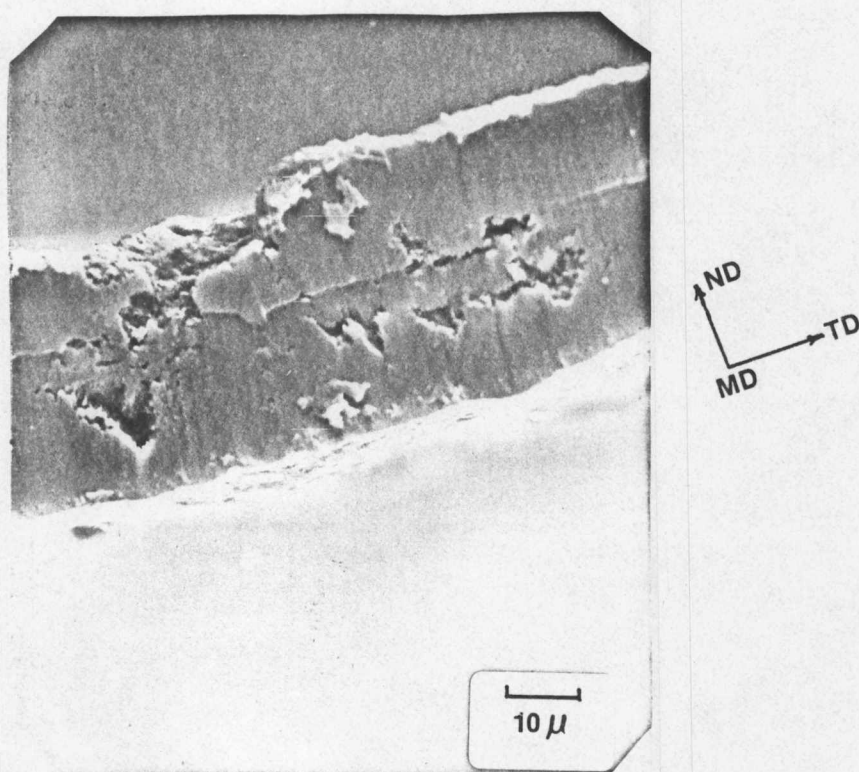


Figure 79. SEM Photomicrograph of a Cross Section in an Extruded Film Coagulated in 45% Water and 55% Methanol.

be between 0.09 mm and 0.25 mm. Films thicker than these values usually contain finger like voids. Since the degree of orientation decides film thickness, orientation history must also be a factor in determining the presences or absences of finger voids.

The effect of coagulants on void formation is unclear. Higher water content appears to reduce the amount of voids present; see Figures 77 and 79. Clearly more work needs to be done in this area, with a larger variety of coagulants and temperatures. It should also be understood that many of the experimental runs were done once and that more work is needed in repeating these experiments.

In almost all the films there appears to be a line going through the center of the cross section representing the point where the coagulant meets from both edges. The result is a void or hole where thickness depends mainly on the film thickness. The thicker the film, the wider the void; refer to Figures 76 and 79.

The skin like structure on the outer surfaces of the film is similar to the skin core effect observed by Shimamura et al.(81) for melt spun Hydroxypropyl cellulose fibers, which is believed to be a thermotropic liquid crystal. The outer skin was found to represent a higher degree of orientation than the material inside the skin. This orientation is believed due to the high shear rates at the wall of the die and is characteristic of liquid

crystal systems. This outer skin in PPD-T extruded films may account for most of the uniaxial orientation present in run numbers 1, 2, 4, and 6; see Table 13 on page 142. The films with more solid like cross sections didn't have higher orientation functions than those with voids present; see run numbers 3 and 5 in Table 13.

The voids, wrinkles, etc., all represent defect sights, which could result in premature failure during mechanical testing. They help to partially explain the low machine direction tensile strengths for run numbers 1, 2, 4, and 5, from 4.5×10^2 psi to 1.3×10^4 psi. It should be noted that the films with the least voids, run numbers 3 and 5, were also the strongest; see Table 15, page 169.

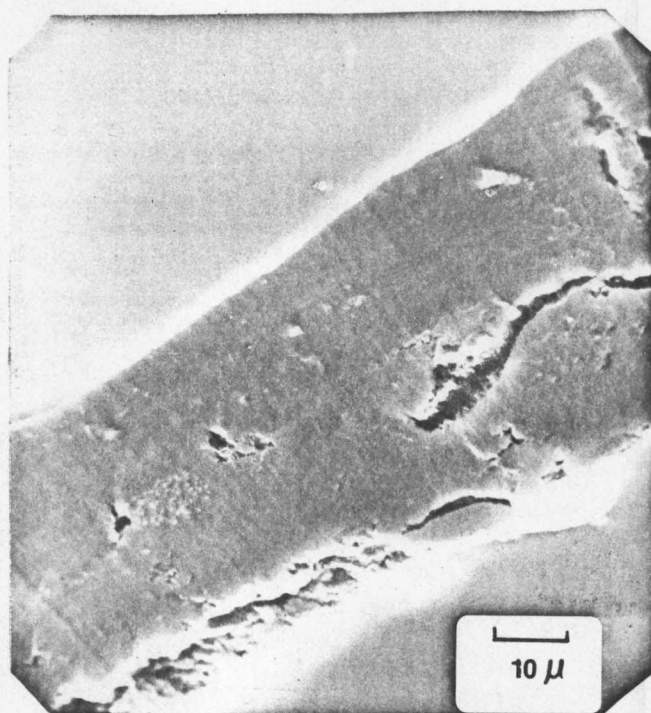
B. Uniaxially Drawn Films

Results

Most uniaxially drawn films exhibited very few voids, at magnifications as high as 1,000 x; see Figure 80. The voids present in Figure 80b appear to be a result of wrinkling during the coagulation process. Film thickness ranged from 0.025 mm to 0.19 mm.

Viewing the film normal to the film plane shows that extensive wrinkling is present in some films but not others; see Figure 81. Actually, when seen with the naked eye, all films exhibited some form of wrinkling with the wrinkles or folds traveling in the machine direction.

a.



b.

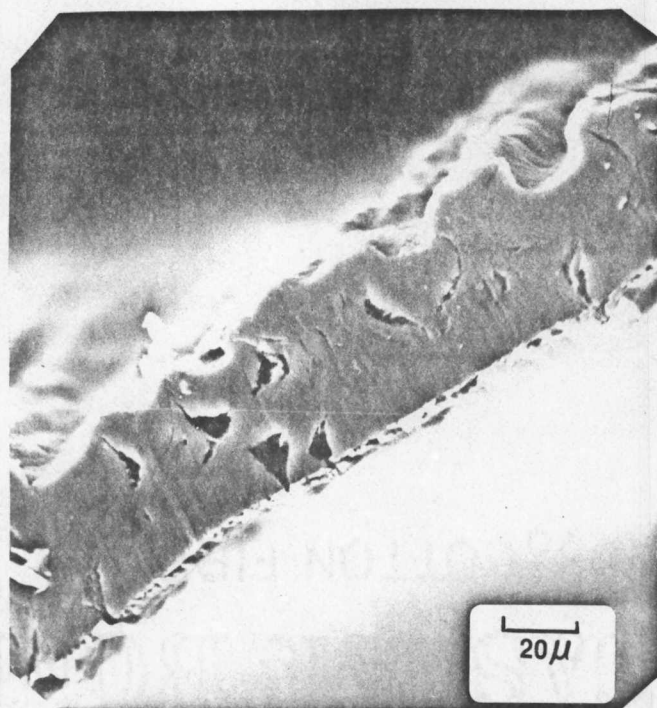
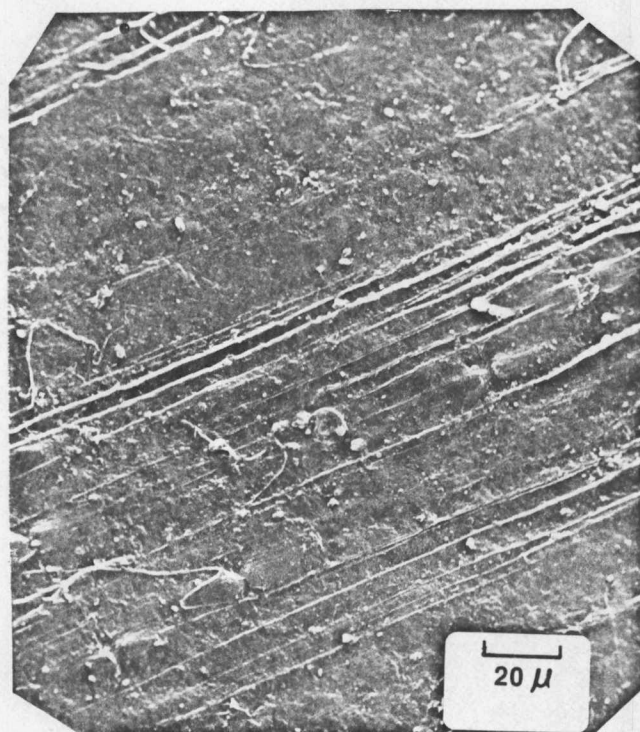


Figure 80. SEM Photomicrographs of Typical Cross Sections in Uniaxially Drawn Film.

a.



b.

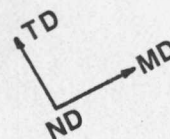


Figure 81. SEM Photomicrographs of Typical Film Surfaces of Uniaxially Drawn Film.

No skin core effects were observed and no distinct voids going through the center of the cross sections were seen as was the case in the extruded films.

The exception to the above situation was the cross section of run number 12. This film exhibited extensive voiding but in a manner different from the undrawn films; see Figure 82. In this case, the voids, on the order of $50\ \mu$ in the normal direction, seem to originate from a central solid like point in the cross section and radiate toward the outer surfaces. There also appears to be a skin on the outer surfaces as seen in extruded films. This film exhibited exceptionally poor mechanical properties and orientation functions which was attributed to degradation of the polymer; see Figure 82.

Discussion

In all of the examples except run number 11, the films present a solid like cross section, which is very similar to the cross section of Hancock et al.'s Kevlar^R fibers. Film thickness usually ranged from 0.025 mm to 0.1 mm, which is equal to or below Hancock's fiber thickness. Once again it must be said that the presence or absence of voids is probably more a function of film thickness and possibly orientation than any other factor.

Run number 12 resulted in a situation, in terms of void structure, different from any of the aforementioned situations. The very center of the film cross section is

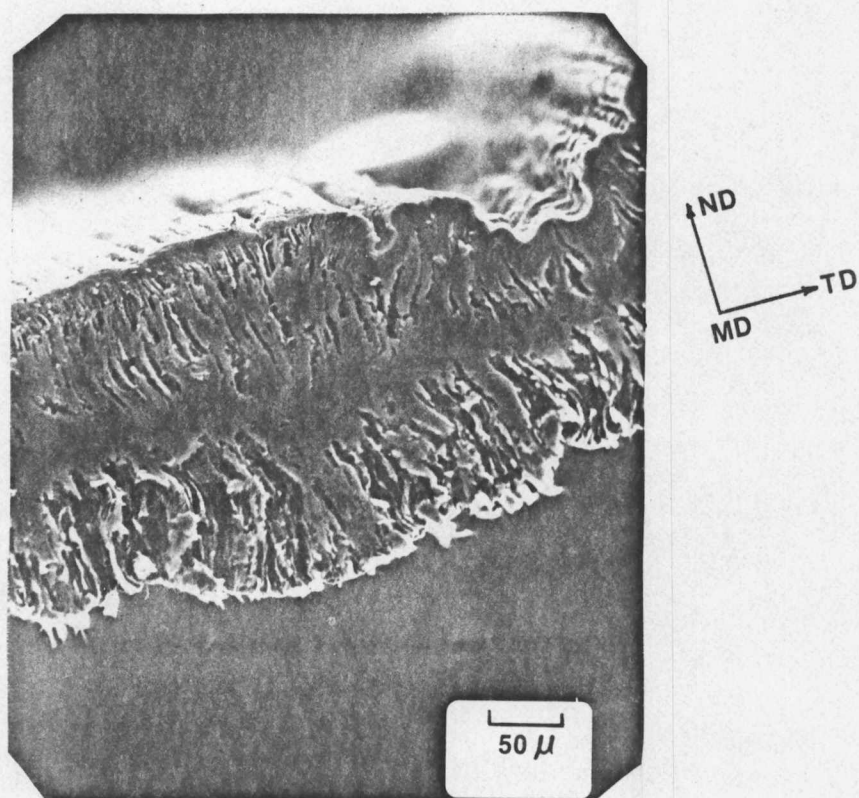


Figure 82. SEM Photomicrograph of a Cross Section in a Uniaxially Drawn Film that may Have Degraded.

solid with finger like voids projecting from it toward the film surface. This film could represent the transition stage between the solid like cross section and the finger void cross section.

All of the films except run number 12 have solid like cross sections and exhibited similar orientation functions in the range of 0.04 to 0.20 for f_{yc}^B and 0.40 to 0.52 for f_{zc}^B . Run 12 had orientation functions of 0.000 for f_{yc}^B and 0.16 for f_{zc}^B , lower values than the extruded films. These low values could be attributed to degradation and partially to the formation of finger like voids which might inhibit orientation of the molecules due to their formation.

Mechanical properties were relatively high with tensile strengths ranging from 1.6×10^4 psi to 3.7×10^4 psi in the machine direction. This can be attributed mostly to the high degree of orientation but it could also be due to the lack of large voids in the film.

Coagulant type didn't appear to have an effect on the presence or absence of voids for the magnifications attempted, usually no higher than 5,000 x. A larger variety of coagulants is needed to do further experiments along this line.

C. Biaxially Drawn Films

Results

Figure 83 is a typical cross section of a mandrel processed film. In every case, no voids can be seen up to magnifications of 5,000 x. In some cases, a line can be seen running through the center similar to the cross section of the undrawn film in Figure 79, page 200. Film thickness typically ranged from 0.005 mm to 0.1 mm.

Figure 84 presents a view normal to the film surface. In every case, the surface is relatively smooth.

Discussion

Since all mandrel process films were usually in the 0.005 mm to 0.1 mm thickness range, it was expected to find solid like cross sections regardless of coagulants. Some of the biaxial films exhibit the line going through the center of the cross section, probably representing a void formed by the meeting of coagulant from both film edges, and some did not.

Biaxial films also exhibit a relatively smooth surface as compared to the wrinkled surface of undrawn and uniaxially drawn films. It should also be noted that shrinkage in the biaxial films was almost nonexistent. Shrinkage for the uniaxial films was always relatively large in the direction perpendicular to the wrinkles or the transverse direction.

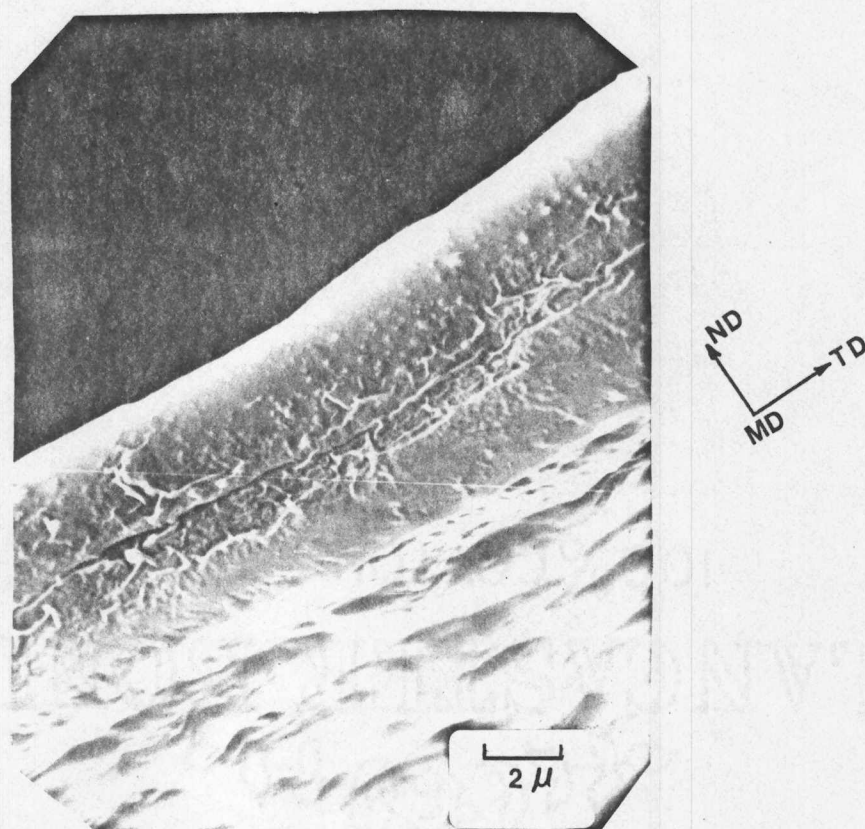


Figure 83. SEM Photomicrograph of a Typical Cross Section in a Mandrel Processed Film.

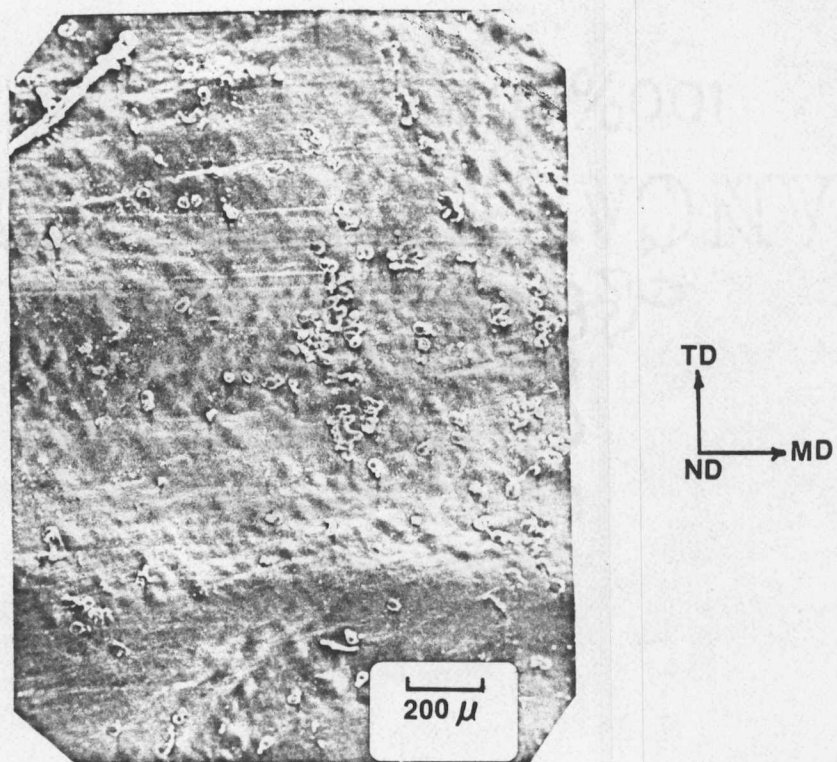


Figure 84. SEM Photomicrograph of a Typical Film Surface of a Mandrel Processed Film.

Orientation functions were similar as were pole figures for all of the biaxial films and no real correlation can be made between the superstructure and degree of orientation.

Mechanical properties were fairly consistent for all of the films (see Table 15, page 169) but not particularly high. This could be the result of microvoids causing defects in the film but more likely it is the result of degradation resulting from leftover H_2SO_4 .

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

There will be an attempt in this chapter to draw the previous chapters together and to present certain broad conclusions about the present film processes. Also, recommendations will be made as to what corrections are needed in the film processes and where the processes will be going in the near future.

A. Processing Conditions

It was determined in Chapter IV that one of the principle faults in all three film processes was the die design. Unequal distribution of the polymer throughout the die as a result of a pressure gradient existing in the die was considered to be the leading cause of uneven film thickness. In the near future, a new die will be built having the polymer entering from the top and a more equal pressure distribution.

Two additional problems that plague the present process are bubble removal from the polymer solution and the amount of polymer solution used. A new quicker method is needed to remove air bubbles to help reduce polymer degradation. Possibly some type of apparatus that spreads the solution thinly and then applies a vacuum could be developed. Also, much more polymer solution is needed to achieve

steady state conditions. To make larger amounts, a more efficient method is needed to mix the sulfuric acid and PPD-T. It would help greatly if the PPD-T could be obtained in a powdered form. A larger reservoir also would be needed to hold larger quantities.

Instead of using the present pump and piston system, a new delivery process such as a twin screw extruder could be used. This method could remove bubbles and extrude the polymer solution at the same time.

Take up rates need to be under more controlled conditions. Perhaps several nip rollers such as those used in blown film processes could be adapted to the present process.

Mandrel design needs further study. Some important variables would be mandrel shape, the angle if a cone shape is used, and the initial and final radii.

The coagulant makeup or content appears to be an important factor in controlling degradation in the polymer film. The better coagulants, such as water, are more effective at removing sulfuric acid. Another approach would be to neutralize the acid as well as remove it by using a buffered solution.

B. Molecular Orientation

Clearly, high degrees of molecular orientation can be achieved through the present process. The uniaxially

drawn films produced considerable molecular orientation in the machine direction and the mandrel processed films produce a high degree of biaxial orientation; refer to Chapter V beginning on page 130 . With improved film quality, using the previous suggestions, higher levels of orientation may be achieved. Another feature of these films which may be used to determine orientation in the future is that they contain microvoids. The shape of the microvoid as determined by small angle x-ray diffraction may be a very good indicator as to the level and type of orientation in the film.

C. Mechanical Properties

Tensile strengths and modulus values, though high for films, didn't reach the expected levels; see Chapter VI, page 167 . Of course, much more work needs to be done in reducing the level of degradation in the films. Also, experiments with high temperature annealing between 250°C and 500°C need to be carried out. At the moment, new designs are being developed to accomplish said experiments. Recently, biaxial films have been obtained with tensile strengths as high as 40,000 psi in all directions using the present apparatus, so the future looks very bright in terms of producing high strength biaxially oriented PPD-T films.

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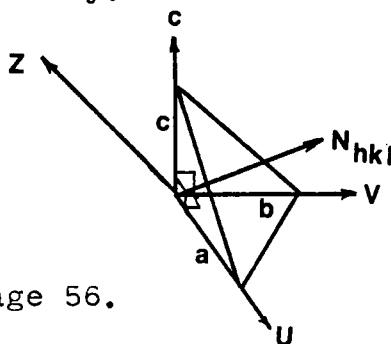
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APPENDICES

APPENDIX I

A METHOD FOR DETERMINING $\cos^2\theta_{bz}$ AND $\cos^2\theta_{cz}$
 FOR THE PPD-T ORTHORHOMBIC UNIT CELL USING
 THE (110) AND (200) PLANES (3)

The model used for this type of analysis may be seen below. The reference axis is the z direction. The coordinate system is cartesian with u, v, and c as the axes. The vector $N_{(hkl)}$ is normal to the reflecting plane. For an orthorhombic system, a and b are parallel to u and v respectively.



$\theta = \phi$
 From Figure 22, page 56.

A. Determining $\cos^2\theta_{bz}$

The vectors Z and N are expressed in the following manner:

$$Z = (\cos\theta_{v,z})i + (\cos\theta_{u,z})j + (\cos\theta_{c,z})k \quad (1)$$

$$N = ei + fj + gk \quad (2)$$

The scalar product of Z and N is:

$$N \cdot Z = \cos\theta_{hkl,z} = e \cos\theta_{u,z} + f \cos\theta_{v,z} + g \cos\theta_{c,z} \quad (3)$$

For a distribution of orientation, the mean-square cosine of $\theta_{hkl,z}$ is given by:

$$\begin{aligned}\overline{\cos^2 \theta_{hkl,z}} &= e^2 \overline{\cos^2 \theta_{u,z}} + f^2 \overline{\cos^2 \theta_{v,z}} + g^2 \overline{\cos^2 \theta_{c,z}} \\ &+ 2ef \overline{\cos \theta_{u,z} \cos \theta_{v,z}} \\ &+ 2fg \overline{\cos \theta_{v,z} \cos \theta_{c,z}} \\ &+ 2eg \overline{\cos \theta_{c,z} \cos \theta_{v,z}}\end{aligned}\quad (4)$$

Simplification conditions for an orthorhombic unit cell resulting from crystallographic symmetry are as follows:

- a. All cross product averages are zero
- b. If hko planes are present $g = 0$. Since $f^2 + e^2 + g^2 = 1$ then $f^2 = (1 - e^2)$. Equation 4 becomes

$$\overline{\cos^2 \theta_{hko,z}} = e^2 \overline{\cos^2 \theta_{u,z}} + (1 - e^2) \overline{\cos^2 \theta_{v,z}} \quad (5)$$

$$\text{In this case, } \overline{\cos^2 \theta_{u,z}} = \overline{\cos^2 \theta_{a,z}} \quad (6)$$

$$\overline{\cos^2 \theta_{v,z}} = \overline{\cos^2 \theta_{b,z}} \quad (7)$$

$$\text{and } \overline{\cos^2 \theta_{hko,z}} = \overline{\cos^2 \theta_{(110),z}} \quad (8)$$

Rearranging equation 5 and substituting 6, 7, and 8 gives the following equation:

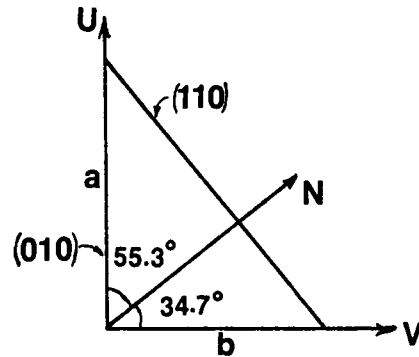
$$\frac{\overline{\cos^2 \theta_{(110),z}} - e^2 \overline{\cos^2 \theta_{a,z}}}{(1 - e^2)} = \overline{\cos^2 \theta_{b,z}} \quad (9)$$

B. Determining e and f

$$e = \cos \theta_{(110),a} = \cos 55.3^\circ = 0.5693$$

$$f = \cos \theta_{(110),b} = \cos 34.7^\circ = 0.8221$$

Refer to the figure below.

C. Determining $(\cos^2 \theta_{c,z})$

Using the value obtained from equation 6, $\cos^2 \theta_{b,z}$ and for $\cos^2 \theta_{a,z}$, substitute into equation II.30 page 55 to obtain $\cos^2 \theta_{c,z}$.

To determine orientation functions, one may use the same analysis as above to obtain values for $\cos^2 \theta_{b,y}$ and $\cos^2 \theta_{c,y}$ and also equation II.31, page 55.

APPENDIX II

ORIGINAL WAXS PATTERNS FOR FIGURES 43, 50, AND 54

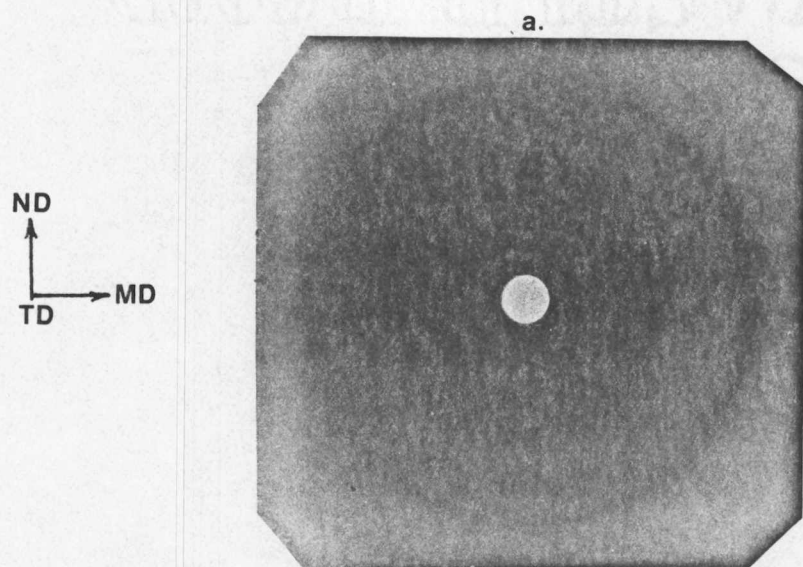
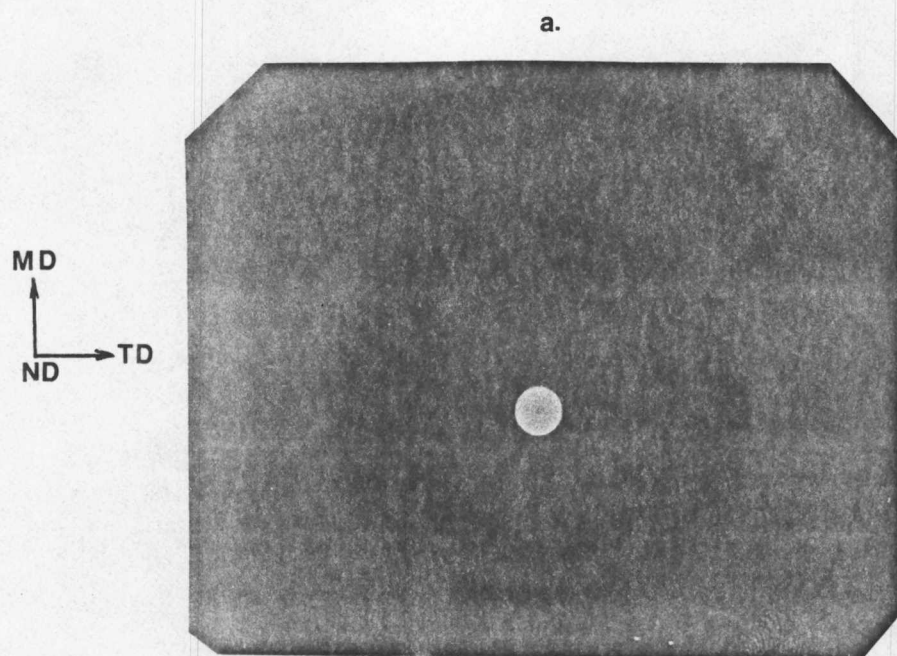
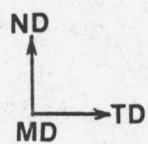
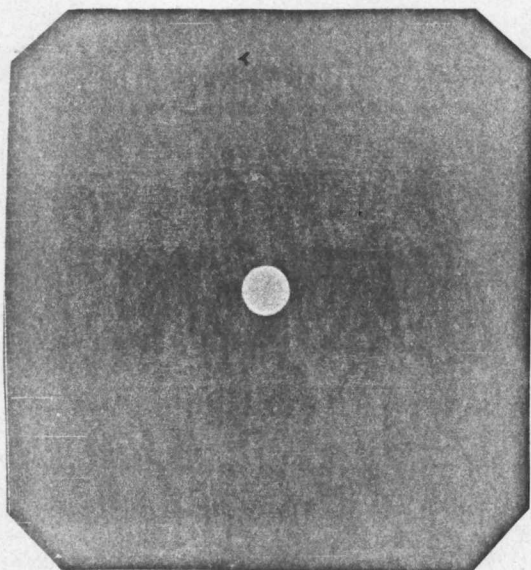


FIG. 43



a.



b.

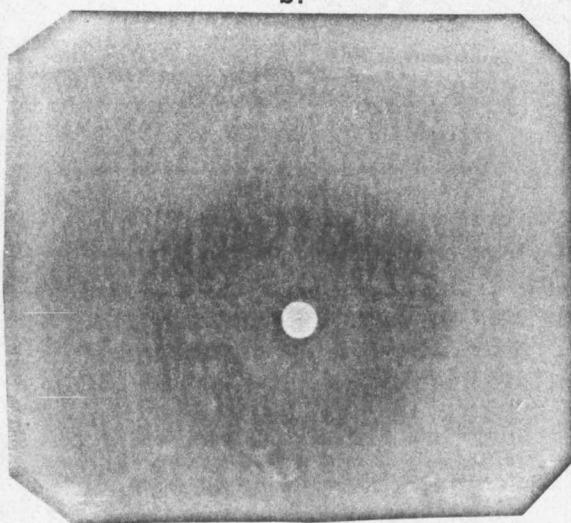
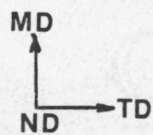


FIG. 43

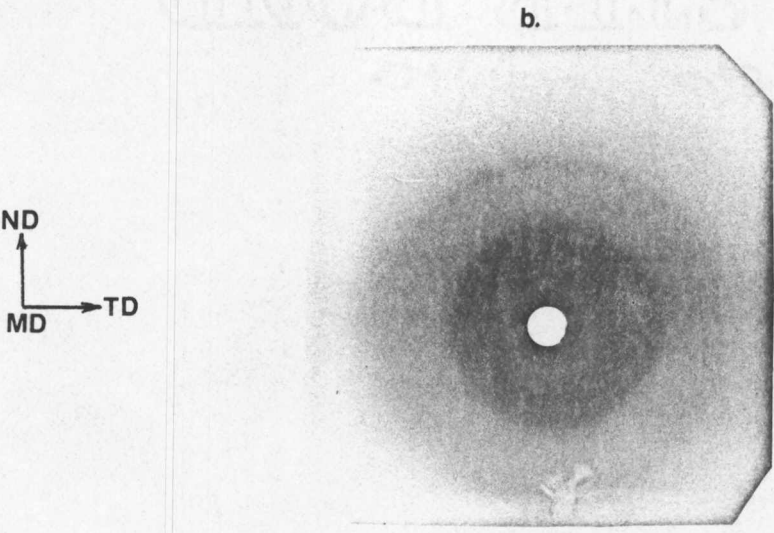
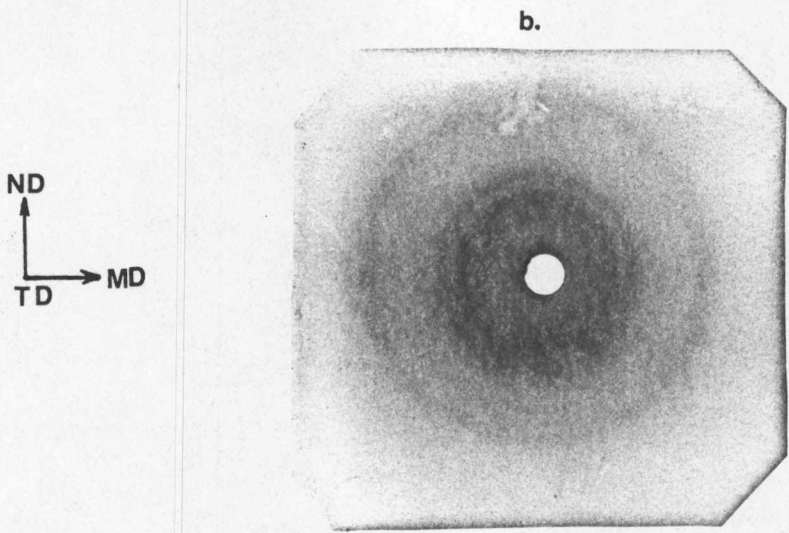


FIG. 43

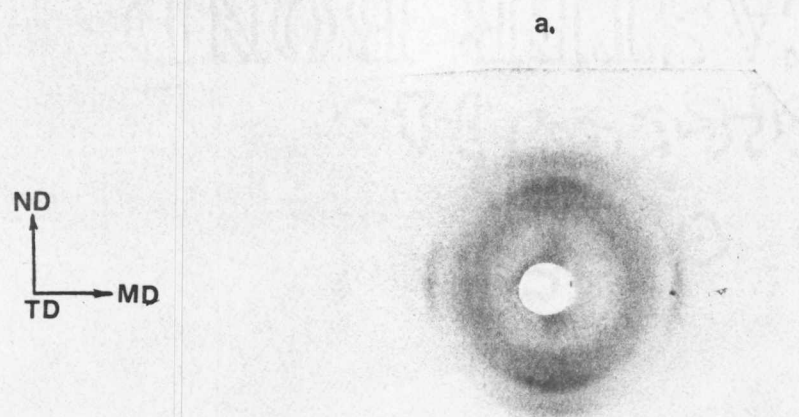
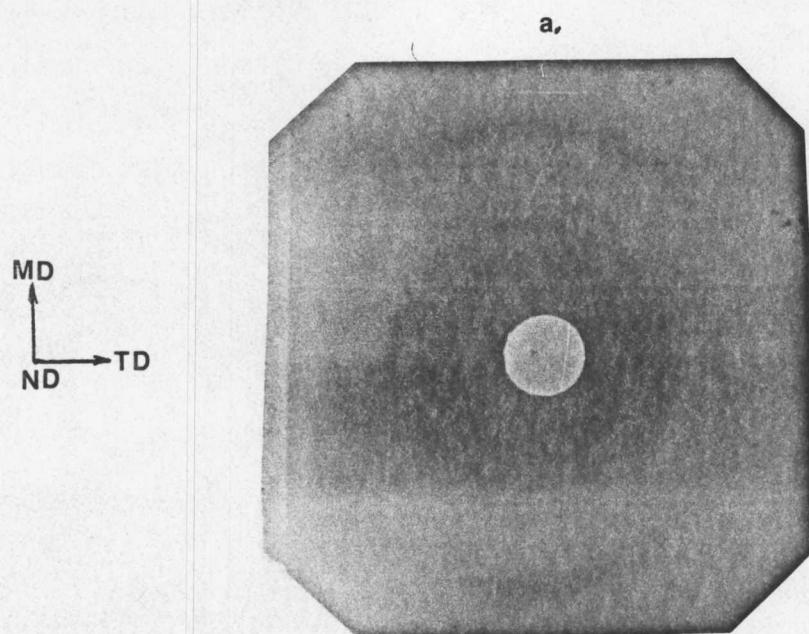
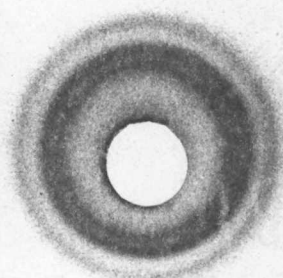
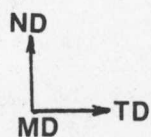


FIG. 50

a.



b.

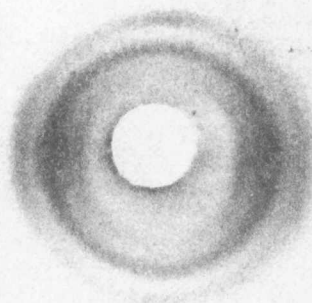
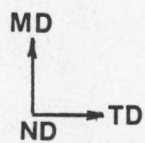
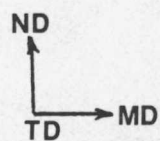
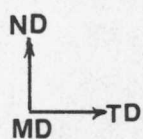
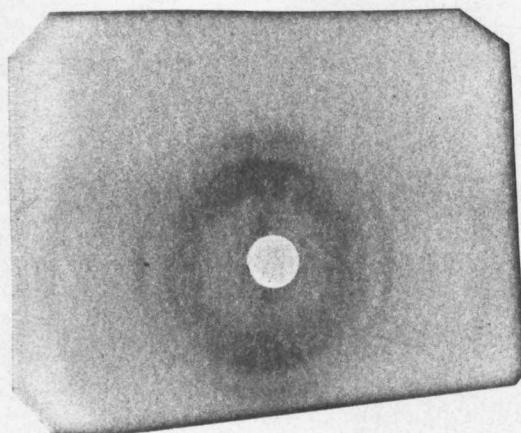


FIG. 50



b.



b.

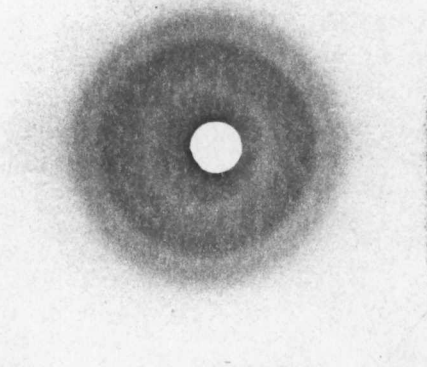


FIG.50

MD
ND → TD

ND
TD → MD

FIG. 54

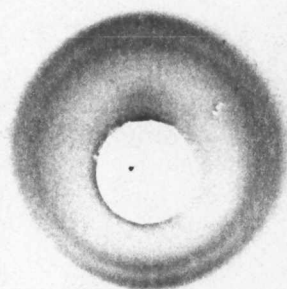
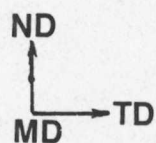


FIG. 54

VITA

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The author is a member of the National Honor Society, the National Athletic Honor Society, the Society of Outstanding American High School Students, Phi Kappa Phi, Sigma Chi Fraternity, and the Society of Plastics Engineers.