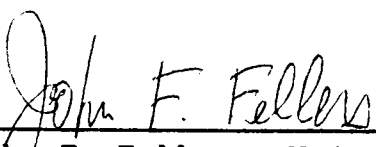


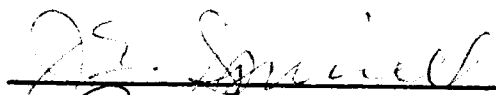
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A ROTATING ANNULAR DIE FOR CONTROL OF BIAXIAL ORIENTATION
IN MELT PROCESSED THERMOTROPIC LIQUID
CRYSTALLINE CELLULOSE DERIVATIVES

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

Gregory W. Farrell

June 1984

DEDICATION

This thesis is dedicated to my parents, Jack and Barbara Farell, for all their support and encouragement.

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The author wishes to thank professor John F. Fellers for the opportunity to work under him and for his guidance throughout this project.

The author is indebted to Proctor and Gamble for their financial support in this research.

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ABSTRACT

A rotating annular die was used to control the molecular orientation in melt processed thermotropic liquid crystalline cellulose ethers. The annular die consists of a rotating inner core and a simultaneously counter-rotating outer cylinder. The inner core and outer cylinder rotation speed was used to vary the velocity profile. Nitrogen gas could be fed through the inner core of the die to inflate the tubes and produce thin films.

Mechanical testing, birefringence measurements, and wide angle x-ray diffraction techniques using pole figures in conjunction with orientation functions show that the molecular orientation can be controlled by the rotating annular die. Tubes and films were characterized at various die rotation speeds. White-Spruiell biaxial orientation factors were $f_1^B = 0.80$ and $f_2^B = 0.021$ for an extrudate without die rotation. The rotating annular die is capable of changing the biaxial orientation factors to $f_1^B = 0.17$ and $f_2^B = 0.71$. The rotating annular die can change the mechanical properties of the hydroxypropyl cellulose films from highly biased in the machine direction to biased in the transverse direction. It is believed that the long relaxation times associated with thermotropic liquid crystalline material are responsible for the high degree to

which the orientation can be controlled through the use of a rotating annular die.

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CHAPTER I

INTRODUCTION

Over the past ten years, much work has been done in the area of liquid crystalline polymer materials. Liquid crystalline behavior has been found in many polypeptides [71,74,59], p-linked aromatic polyamides [51,40,58,10,62,97], aromatic polyesters [97,68,45], and other polycondensates. Werbowyj and Gray [90,91] found that liquid crystalline structures exist in hydroxypropyl cellulose-water solutions. Liquid crystalline characteristics were later reported in a wide range of cellulose derivatives by Panar and Wilcox [61]. These observations were extended to other cellulose derivatives by Aharoni [2] and Bheda, Fellers, and White [8,9].

The great interest in polymer liquid crystals has been partially associated with their ability to form high modulus and tensile strength fibers. These properties are believed to result from the orientation of the polymer chains attained by preparing and processing these anisotropic fluids. DuPont's fiber KevlarTM has drawn much attention in the area of liquid crystal processing [51]. KevlarTM is a p-linked aromatic polyamide formed by the wet spinning of a liquid crystalline solution of the polymer. This high modulus and tensile strength fiber is used for tire cord,

bullet-proof vests, composites for airplanes and automobile parts to reduce weight and add strength [33]. Films with these desirable mechanical properties have not yet been successfully developed for commercial use.

Shimamura, White, and Fellers and Suto, White, and Fellers have shown hydroxypropyl cellulose and ethyl cellulose to be thermotropic liquid crystals [79,85]. Liang, White, and Fellers [34] have produced fibers with very high degrees of uniaxial orientation from the liquid crystalline cellulose ethers.

The primary aim of this research was to create a process that can take advantage of the thermotropic liquid crystalline behavior of the cellulose ethers to control polymer chain orientation. A rotating annular die was used to obtain various chain orientations. The annular die consists of a rotating inner core and a simultaneously counter-rotating outer cylinder. The inner core and outer cylinder rotation speed was used to vary the flow profile. Nitrogen gas was fed through the inner core of the die to inflate the tubes and produce thin films.

Tubes and films with various die rotation speeds were produced from hydroxypropyl cellulose (HPC), ethyl cellulose (EC), polyethylene (PE), and polystyrene (PS). Hydroxypropyl cellulose and ethyl cellulose are ethers which have exhibited thermotropic liquid crystalline behavior.

Polyethylene and polystyrene are crystalline and amorphous reference materials used in the study. Optical birefringence, wide angle x-ray diffraction, mechanical property measurements, scanning electron microscopy, and pole figure analysis used in conjunction with White-Spruiell biaxial orientation factors were used to evaluate the tubes and films produced.

CHAPTER II

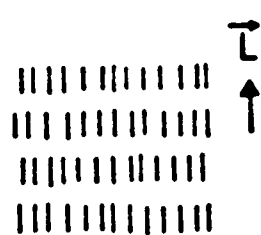
BACKGROUND

A. Polymer Liquid Crystals

Basic Types of Liquid Crystals

There are three basic types of liquid crystals following the proposed classification of Friedel [34] in 1922. These three categories are nematic, smectic, and cholesteric. A liquid crystal system may fit into more than one category. For example, some may appear as a smectic type just above its melting point and change to nematic or cholesteric at higher temperatures [57] (see figure II-1).

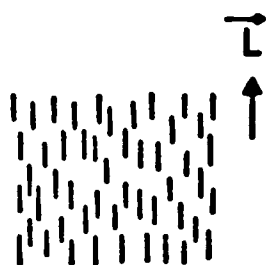
Since there are various types of smectic liquid crystals, Friedel's classification was extended to differentiate among them. Smectic phases are now referred to as smectic A, smectic B, etc. All smectic liquid crystals are layered with two dimensional order. The centers of gravity of the elongated molecule are arranged in equidistant planes. The arrangement of the centers of gravity within the planes may be at random or regular. Smectic A molecules have their long axes perpendicular to the planes, whereas smectic C has its axis tilted with respect to the planes by a certain angle [57]. In nematic liquid crystals, the long molecular axes of the molecule are aligned parallel. These differ from smectic crystals in



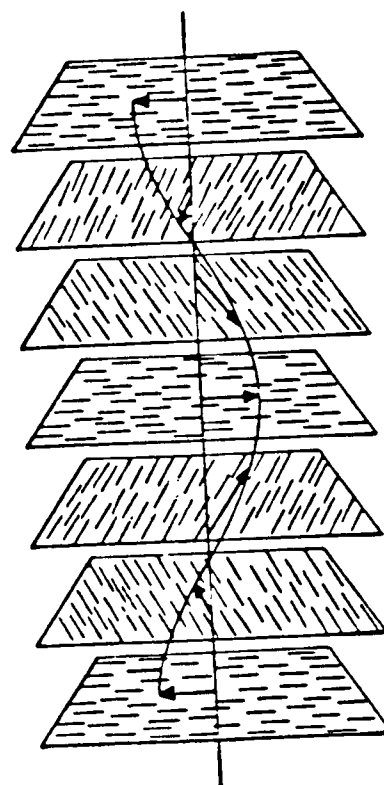
Smectic A



Smectic C



Nematic



Cholesteric

Figure II-1. Classifications of Liquid Crystals.

that their centers of gravity are distributed at random. The molecules are allowed to rotate freely about their long axis. Nematic liquid crystals are uniaxial with respect to all physical properties [57]. Cholesteric liquid crystals were named after cholesterol since many cholesterol esters form this type of liquid crystal. This type is formed by compounds which are chiralic, that is they are nonsuperimposable with their mirror image. The structure can be described as a twisted nematic structure. The direction of the long axis rotates continuously forming a helical structure. The pitch of this structure is the distance required for the helix to make a turn of 360 degrees. The direction of rotation may be left-handed (laevo) or right-handed (dextro) . Polymer liquid crystals would seem to be either nematic or cholesteric

Liquid crystal systems may be classified as thermotropic or lyotropic depending upon how the transition to the liquid crystalline state occurs. Thermotropic liquid crystals are brought about by purely thermal processes. The liquid crystals form from the action of heat alone. Lyotropic liquid crystals rely on the influence of solvents for liquid crystals to form. The two component system exhibits liquid crystalline behavior over a certain temperature range. The vast majority of known polymer liquid crystals are in this group.

Thermotropic Liquid Crystalline Polymers

Melt processing is the more desirable method as often times the solvent systems are expensive and/or toxic and lead to very difficult problems on an industrial scale. Thermotropic polymers have strong intermolecular bonding forces. Thus when they can be melted, it is at a high temperature to get enough thermo-kinetic energy to overcome these bonding forces.

Thermotropic liquid crystalline behavior is often found in polymers having rigid mesogenic units interconnected through flexible spacers along the main chain. The aromatic polyesters have become one of the most widely studied class of thermotropic polymers since the publication of Jackson and Kuhfuss [45] and their preparation of a copolymer of p-hydroxybenzoic acid and polyethylene terephthalate. The aromatic polyesters have very high melting points, and generally degrade before melting. By copolymerization, one can introduce bends, side groups, or flexible spacers into the chain, thereby reducing the melting point.

Shimamura, White, and Fellers [79] using hot-stage polarizing light microscopy have shown HPC to be a thermotropic liquid crystal. Figure II-2 shows the fractional transmission of light with the sample between crossed polars as a function of temperature. An isotropic liquid would pass no light. Figure II-2 shows that there exists

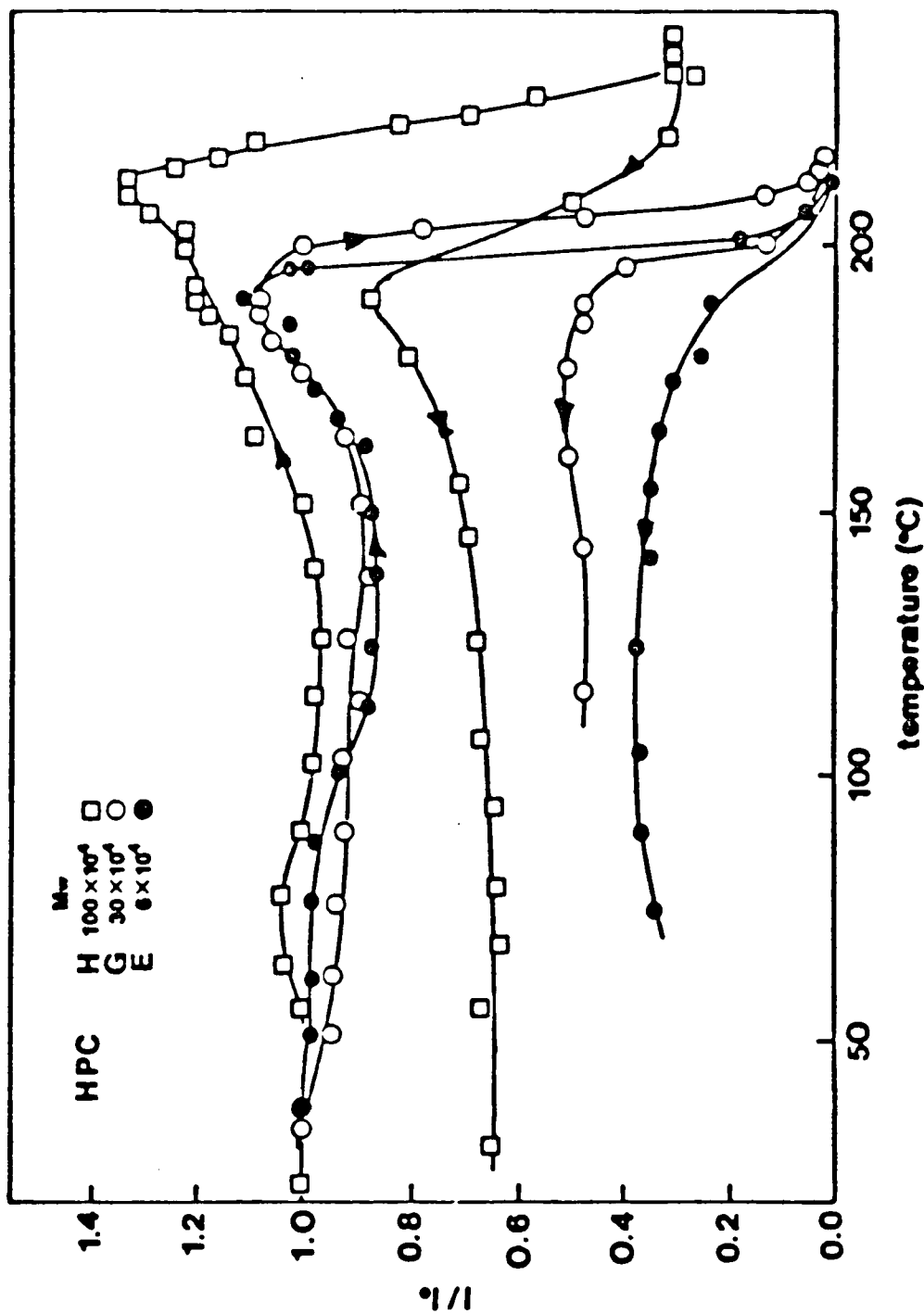


Figure II-2. Light intensity I/I_0 due to HPC between crossed polars as a function of temperature.

From Shimamura, K., White, J.L., and Fellers, J.F., J. Appl. Polym. Sci., **26**, 2165 (1981).

structure up to 200 degrees celsius. The material will flow at around 160 degrees celsius. As the molecular weight of HPC increases from E to G to H, there seems to be a tendency for the transition region to shift to higher temperatures. Suto, White, and Fellers [85] later found gradual and less remarkable behavior in EC.

Liang, White, and Fellers [52] compared DSC thermograms with their results from fractional light transmission. Figures II-3, II-4, II-5, and II-6 show a broad endothermic transitions in the ranges 165 to 200, 160 to 210, and 185 to 230 degrees celsius respectively for HPC type E, J, and G. The peak transition temperatures correspond to the region in the I/I_0 plot which shows a rapid decrease in fractional light transmission.

Molecular Geometry and the Formation of Thermotropic Liquid Crystals

When considering low molecular weight compounds which exhibit thermotropic liquid crystalline behavior, one generally finds molecules that are anisometric in configuration and bonding characteristics. Rigid, elongated molecules are prominent. The significance of rigidity is apparent when one examines the evolution of a substance with rising temperature from the crystalline to the smectic to the nematic to the isotropic states. Anisotropic intermolecular forces seem to be necessary to keep the

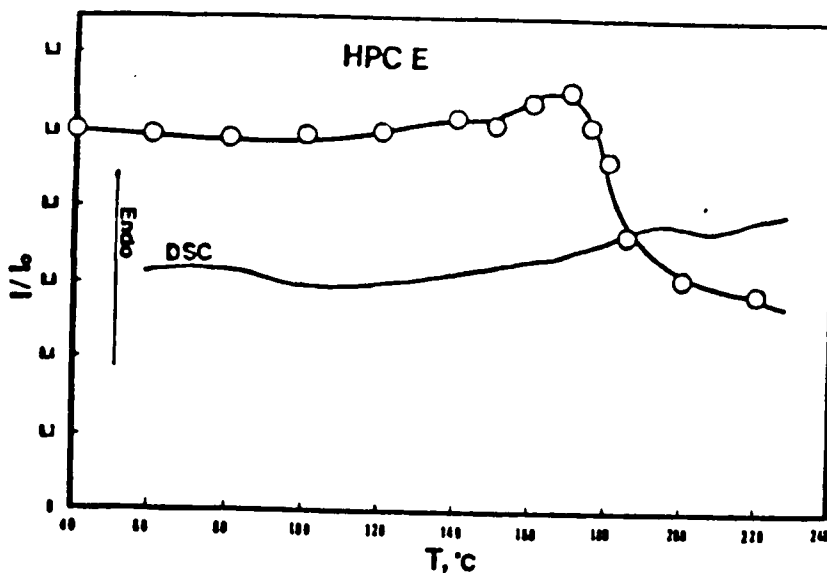


Figure II-3. Fractional transmission of light and DSC trace of HPC E.

From Liang, B., Fellers, J.F., and White, J.L., "A Basic Study of Ribboncast Film Extrusion of Liquid Crystalline Cellulose Ethers," report to Proctor and Gamble (1983).

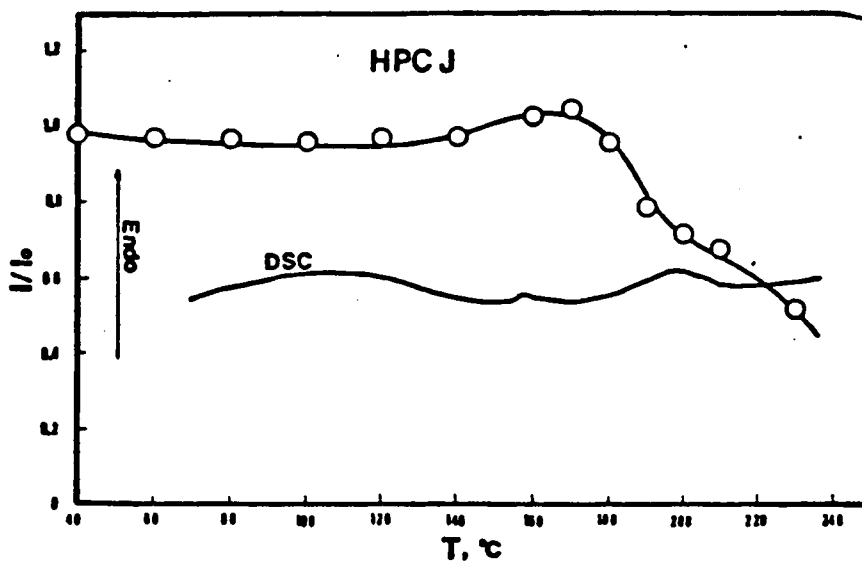


Figure II-4. Fractional transmission of light and DSC trace of HPC J.

From Liang, B., Fellers, J.F., and White, J.L., "A Basic Study of Ribboncast Film Extrusion of Liquid Crystalline Cellulose Ethers," report to Proctor and Gamble (1983).

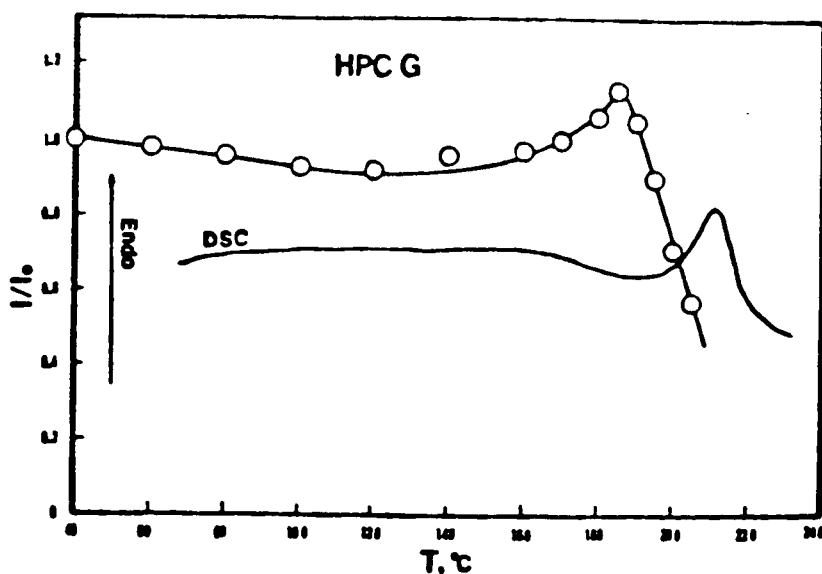


Figure II-5. Fractional transmission of light and DSC trace of HPC G.

From Liang, B., Fellers, J.F., and White, J.L., "A Basic Study of Ribboncast Film Extrusion of Liquid Crystalline Cellulose Ethers," report to Proctor and Gamble (1983).

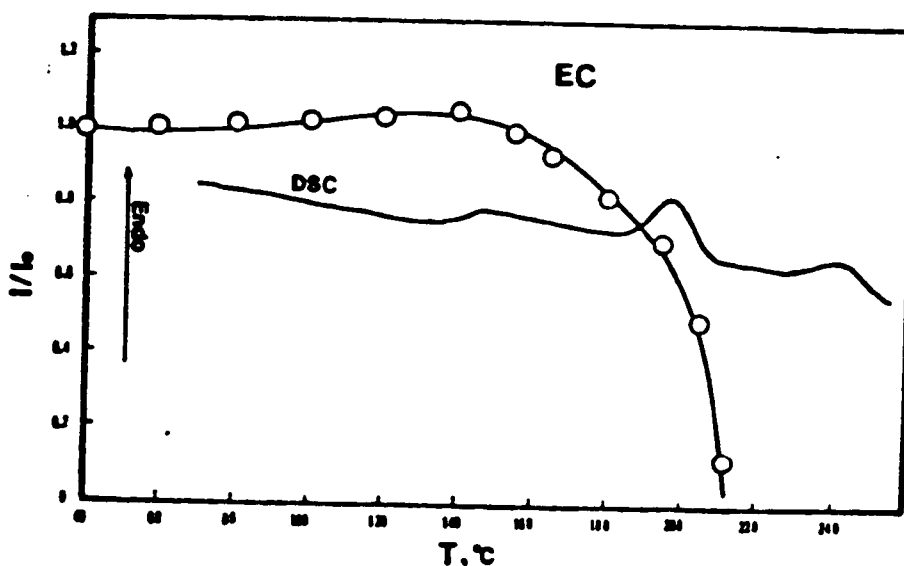


Figure II-6. Fractional transmission of light and DSC trace of EC.

From Liang, B., Fellers, J.F., and White, J.L., "A Basic Study of Ribboncast Film Extrusion of Liquid Crystalline Cellulose Ethers," report to Proctor and Gamble (1983).

longitudinal aggregates from breaking up at the melting point. High intermolecular forces are associated with the higher melting points. At these higher melting temperatures, the aggregates would vibrate so rapidly that liquid crystals could not exist. Thus, translational bonds should be weaker than lateral ones for liquid crystals to form [97].

The kinds of molecules which form thermotropic liquid crystals generally have features of common geometry. The molecules are usually elongated and rectilinear. Planar segments in the molecule will enhance crystallinity, e.g. benzene rings. Thermotropic liquid crystals tend to be rigid along its major axis. Double bonds are common along the axis of the molecules. Steric hinderences may also be a factor in limiting the rotation of the molecules. The coexistence of strong dipoles and easily polarizable groups in the molecule seems important. Liquid crystallinity is most likely to be enhanced if the strong dipole is on the molecular axis. Weak dipolar groups at the extremities of the molecule are of lesser importance [14].

These dipole effects observed in the low molecular weight liquid crystals do not apply to polymer liquid crystals. Thermotropic polymer liquid crystals are generally composed of rigid, planar molecules. Predominately these are aromatic groups linked together by

groups that limit the rotation of the molecule, such as amide or ester groups [7].

Phase Transitions

The conversions from the crystalline or isotropic liquid phases to the liquid crystalline state are true phase changes, as are the interconversions of the smectic and cholesteric mesophases. These transitions are all completely thermally reversible. However, the differences between the textures exhibited by some mesophases are subtle and some transitions may go undetected. In the case of the mesophase to crystal transition, supercooling is possible and is usually observed. Generally, the transitions between other phases (smectic, cholesteric, isotropic liquid) cannot be supercooled.

One would expect that crystallization in these materials to be similar to crystallization in oriented flexible polymer melts. In both cases the entropy of the melt is so low that the entropy change upon crystallization is small. Work can be considerably simplified by the use of liquid crystalline polymers because quiescent conditions may be used to obtain information on crystallization from oriented melts.

B. Cellulose and Cellulose Derivatives

Cellulose

Cellulose is very difficult to chemically define. The term "cellulose" is a broad classification with many uses and therefore not exact enough for neat classification. Cellulose always occurs in nature in association with other substances of which, the removal requires severe chemical treatment [29]. Growing plants synthesize carbohydrates. The carbohydrates are built from simple monosaccharides, predominately glucose. Some of the saccharide units may be chemically bonded to other compounds also present. Others may have been oxidized or chemically altered, so that the functional groups are not that of pure carbohydrates. The resulting mixture may be fractionated, but never separated into pure components. The term cellulose is often given to specific fractions isolated from the plants [60]. Sources of cellulose for commercial use are wood, cotton fibers, bast fibers, flax, jute, grasses, and straws. Cotton contains a maximum cellulose content of 94 per cent, while other sources range from 40 to 75 per cent in cellulose content [11] (figure II-7).

An idealized chemical entity called cellulose can be defined, although it can never be isolated. The "ideal" cellulose is a linear molecule composed of anhydroglucose units linked at the 1 and 4 positions through glucosidic

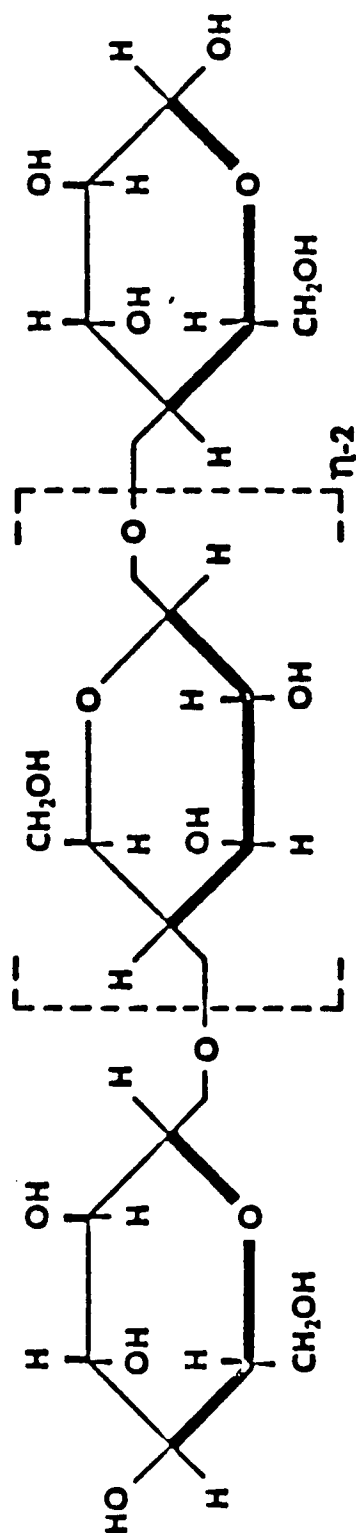


Figure II-7. Structure of Cellulose.

bonds with the beta configuration (see figure II-7). The number of chemical units may range from 50 to 5000 or more [60].

Cellulose shows a distinct tendency for crystallization. This is probably caused by the stiffness of the glucosidic chains and the hydrogen bonding with its frequent hydroxyl groups. The planar rings and the spatial distribution of the hydroxyl groups appear to favor the formation of laterally ordered sheets. These sheets exhibit a threefold anisotropy in relation to bonding strength [60]. In order to dissolve cellulose it is necessary to disrupt its crystallinity. This can be done by altering its hydrogen bonding by chemical or physical means. Cellulose is a two-phase system of amorphous and crystalline regions. The fringed micelle was the first used to explain the morphology of cellulose [15]. This model regards the cellulose microfibrils as assemblies of crystalline and amorphous regions, with each chain molecule extending through several crystalline and amorphous domains. Figure II-8 contrasts high and low crystallinity polymers using this model [55]. A chain folded model has been presented by Manly [54]. Manly believes that a protofibril of cellulose is a pure crystal of the polymer, represented by the pleated model (see figure II-9). The unpleated model represents a flat crystal of cellulose assuming zig-zag packing of the

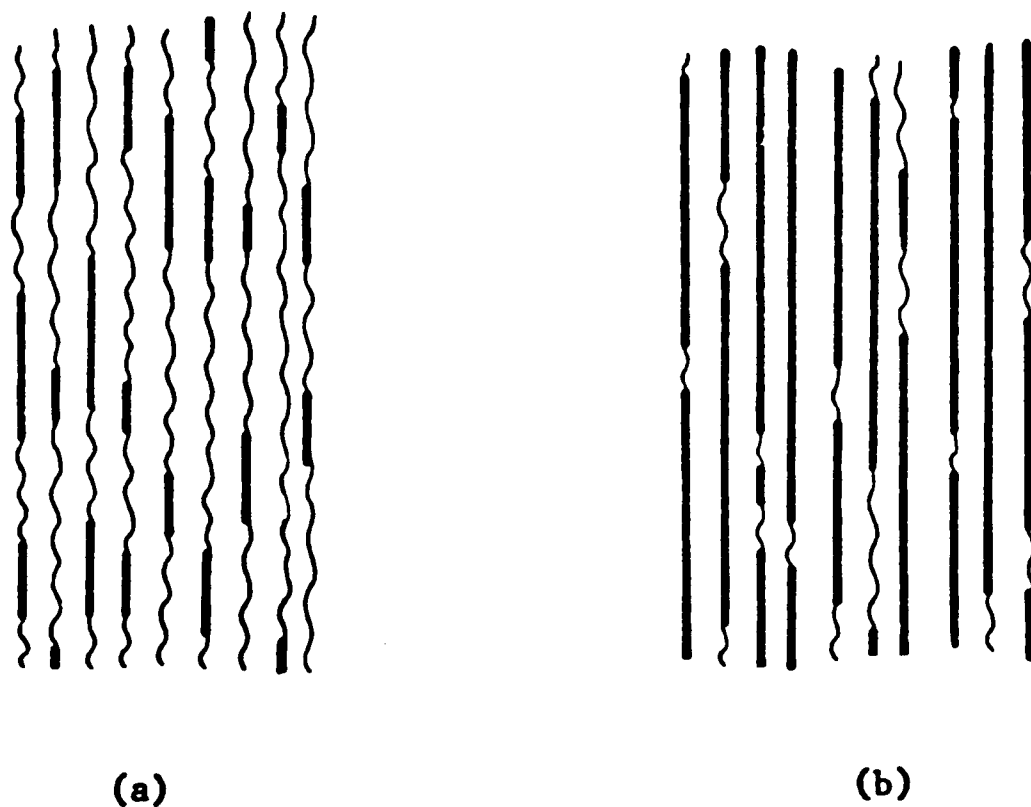


Figure II-8. Fringed-Micelle theory model of (a) low crystallinity polymer and (b) high crystallinity polymer.

From Bolker, H.I., "Natural and Synthetic Polymers," Marcell Dekker, New York (1974), Chapter 2.

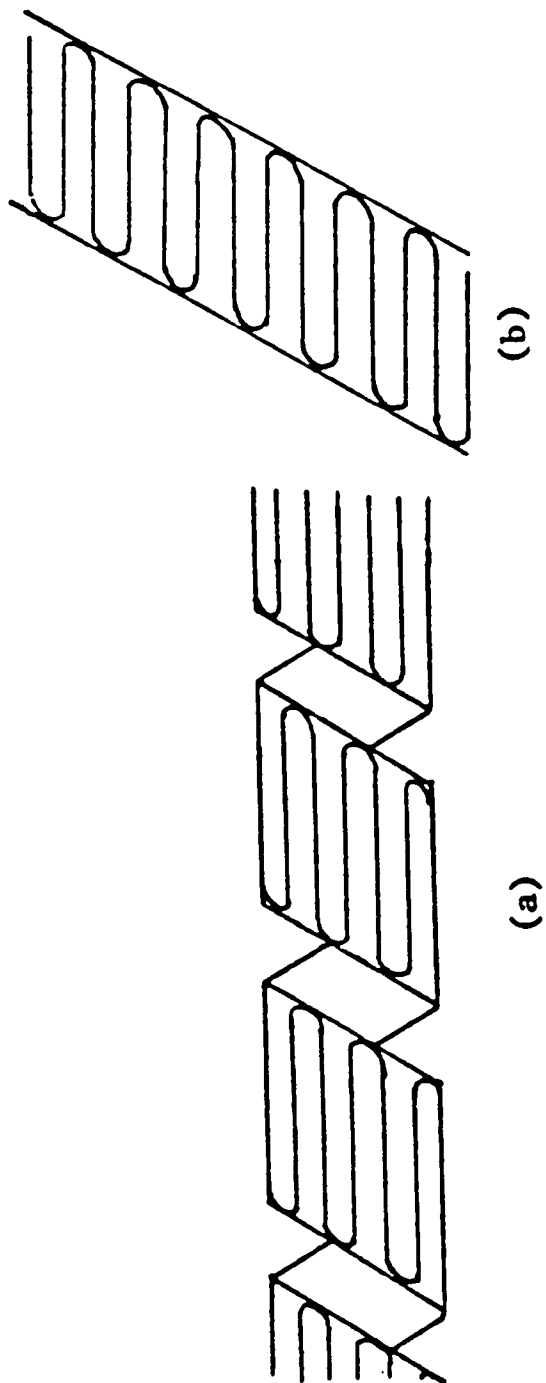


Figure II-9. Chain-folded model of native cellulose according to Manly: (a) pleated protofibril (b) unpleated protofibril.
 From Manly, R.ST.J., J. Polym. Sci., A-2, 9, 1025 (1971).

chain. A stretched out chain loses its crystallinity and acquires the morphology of regenerated cellulose.

Mechanical Properties of Cellulose and Cellulose Derivatives

The high degree of polymerization and the linear nature of cellulose molecules lead to the formation of a fibrous structure with excellent mechanical properties. The network structure formed by the bundles of chain molecules in the noncrystalline regions control the mechanical properties. The network can be considered to consist of chains of bonds joining one point to another. The crystalline regions can be considered as "spot welds" which do not deform appreciably. The crystallites, which are linked together by the noncrystalline regions, do not have a great effect on the mechanical properties. The mechanical properties are determined mainly by bond stretching and chain straightening in the noncrystalline regions of the cellulose [43].

Cellulose Derivatives

Almost all of the commercially important cellulose derivatives are either esters or ethers. It is apparent from figure II-7 that each unit of glucose has three hydroxyl groups at C-2, C-3, and C-6. Cellulose esters and ethers can be obtained by reacting the appropriate chlorides and acids with these free hydroxyls. Most of the technical problems of cellulose reactions center on the question of

availability of the hydroxyl groups. Problems are sometimes encountered when the cellulose hydroxyls are not available for reaction because of the crystallinity or due to the insolubility of the cellulose which hinders the access of the reagent to the hydroxyl group [81]. Reaction rate studies have shown that the C-6 hydroxyl group is esterified ten times as fast as the C-2 hydroxyls and C-3 hydroxyls. Whereas in etherification, the C-2 group is etherified twice as fast as the C-6, and the C-6 twice as fast as the C-3 [25]. Differences in accessibility of different hydroxyls result in very nonuniform products. Much of the research in cellulose derivative chemistry is dedicated to developing methods which hold this nonuniformity within acceptable bounds [81].

The degree of substitution (DS) is the number of hydroxyl groups that have been substituted. By controlling the average DS, a variety of derivatives can be obtained using the same substituent. In principle, it is possible to chemically modify cellulose through the three hydroxyl groups to give derivatives with a DS of three. The average DS affects the extent of the hydrogen bonding in cellulose, thus the solubility. In a reaction where more than one molecule can react with a hydroxyl group, the molecular substitution (MS) differs from the DS. The molecular substitution is the average number of reactant molecules

per anhydroglucose unit. In figure II-10, the DS is 2.5 and the MS is 4 .

Etherfication of the cellulose hydroxyls yields useful products. Cellulose ethers are organosoluble and thermoplastic, water soluble or aqueous alkali soluble depending on the kind and degree of structural change effected [75]. The principle cellulose ethers are the methyl, ethyl, hydroxyethyl, hydroxypropyl, and carboxymethyl celluloses. For water-soluble ethers, it is generally necessary to use a concentration of at least 40 per cent caustic soda and to have at least three hydroxyls per anhydroglucose unit. The introduction of the alkyl groups push apart the cellulose chains and opens them to penetration and solution by hydrolytic solvents [43]. Observations seem to indicate that the bulkier the substituent, the lower the degree of substitution required for water solubility. Cellulose esters are among the toughest thermoplastics and their combination of toughness, clarity, and moldability is very good. Cellulose esters are insoluble in water, but the lower substituted ones are sensitive to it. The sensitivity gradually decreases up to the laurate (C-12) , which with the higher esters is indifferent to water [29].

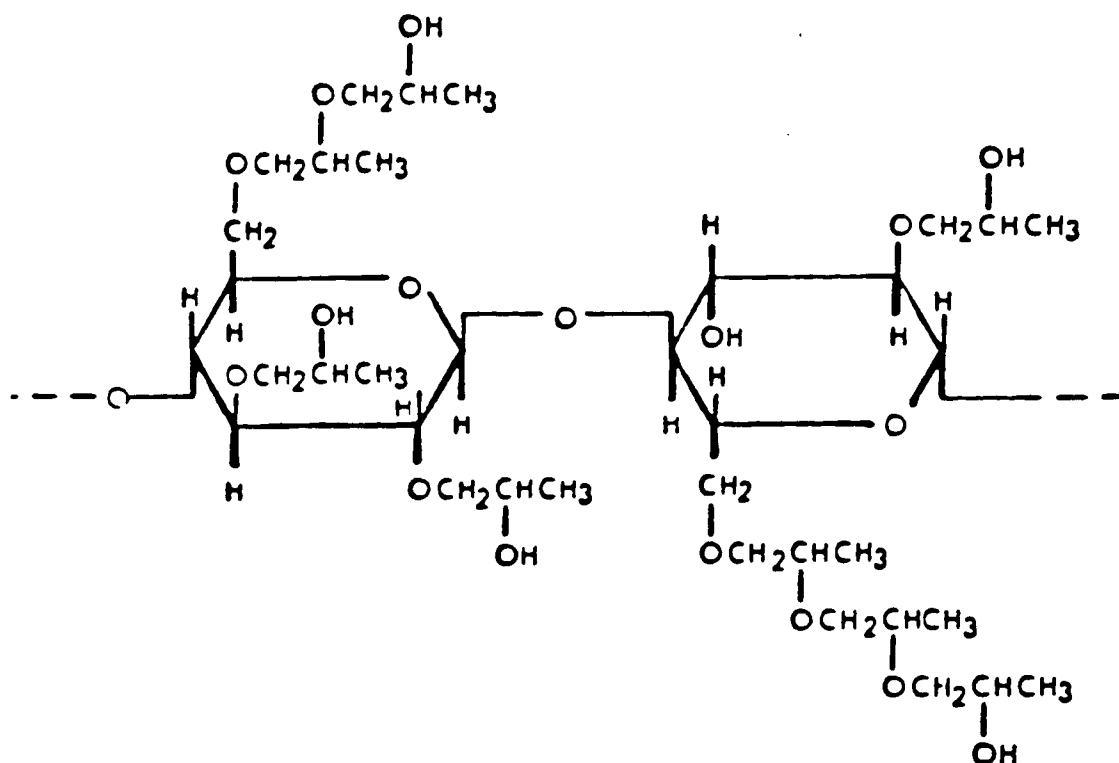


Figure II-10. Idealized structure of hydroxypropyl cellulose of MS 4.0.

From Elliot, J.H., J. Appl. Polym. Sci., 13, 755 (1969).

Hydroxypropyl Cellulose

Hydroxypropyl cellulose (HPC) is a cellulose ether. HPC is most commonly manufactured by reacting alkali cellulose with propylene oxide at elevated temperatures and pressures. Etherification takes place in such a way that hydroxypropyl substituent groups contain almost entirely secondary hydroxyls. The secondary hydroxyl present in the side chain is available for further reaction with the oxide, resulting in side chains containing more than one mole of combined propylene oxide. It is probable that most of the primary hydroxyls on the cellulose have been substituted and the reactive groups remaining are secondary hydroxyls (see figure II-10).

Samuels has extensively studied this polymer in the solid state using WAXS, birefringence, sonic modulus, SALS, and electron microscopy [72]. The intramolecular hydrogen bonding of the polypropylene oxide chains lead to a stiff, rodlike molecule. The HPC molecules were observed by Samuels to be packed into crystallites of 470 Å long and 34 Å in diameter.

Elliot [30] has investigated the rheological properties of HPC.

Ethyl Cellulose

Ethyl cellulose is made by the reaction of ethyl chloride with alkali cellulose. Ethyl cellulose is tough, flexible, and soluble in a wide range of solvents. Complete substitution of all three hydroxyl groups would give the triethyl ether a substitution of three. The completely substituted triethyl ether of cellulose has no commercial significance, however, because it lacks strength and flexibility, is not thermoplastic, and shows limited compatibility and solubility. Commercial products normally have a DS between 2.2 and 2.6. These are soluble in common organic solvents and are thermoplastic. Nearly completely substituted ethyl cellulose ranges in DS from 2.6 to 2.8. These are soluble in hydrocarbons but not in common oxygenated solvents. These melts are very viscous and melt processing is limited because of the absence of suitable plasticizers. Lower-substituted ethyl cellulose, with DS ranging from 0.8 to 1.7, is water soluble. The control of ethylation to obtain water solubility is difficult [60] (figure II-11).

Cellulose Acetate-Butyrate

Cellulose acetate-butyrate is generally manufactured by esterifying cellulose in a mixture containing both acetyl and butyryl radicals, containing enough anhydride to eliminate water produced during esterification. The desired

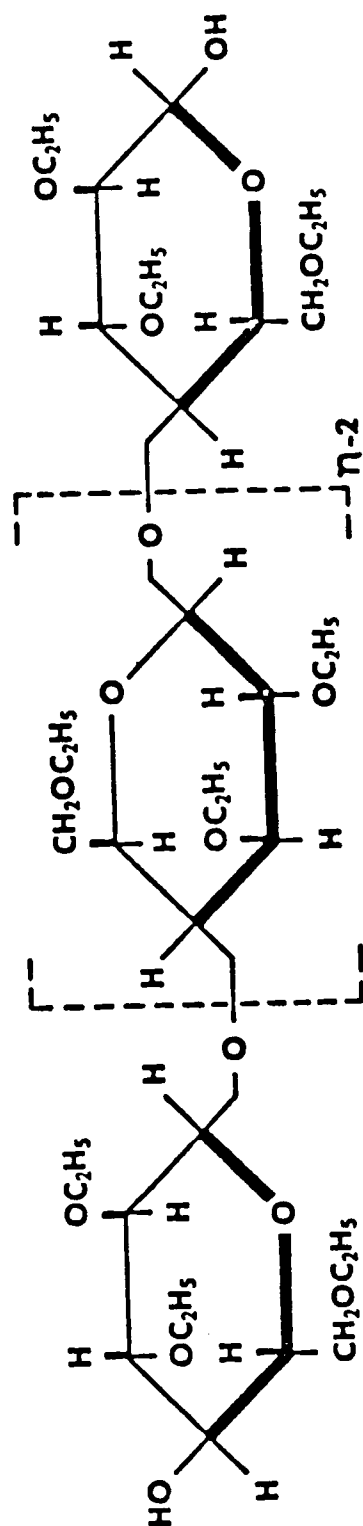


Figure II-11. Structure of ethyl cellulose.

proportion of acetyl to butyryl in the resulting ester is controlled by the composition in the esterfying bath [43].

Cellulose acetate-butyrate are available commercially with a range of butyric acid contents, the most common ranging from 17 to 37 per cent. In all cases, the esters are partially hydrolysed so as to contain 0.3 to 0.5 hydroxyl groups per unit. The higher the butyryl content, the greater the range of solvents and compatibility with plasticizers. For an equivalent degree of substitution esterification, the higher the butyryl content, the greater the moisture resistance and dimensional stability [43].

Boy, Schulken, and Tamblyn [13] have studied the crystallinity in secondary cellulose esters. They compared WAXS diffraction patterns with DSC thermograms. Cellulose esters which have a high degree of esterification are readily crystallizable by simple heat treatments. Such esters include cellulose triacetate, cellulose tripropionate, and mixed cellulose esters. X-ray diffraction analysis of esters having a substantially lower degree of substitution show very diffuse diffraction patterns which are only slightly crystalline in structure. Differential thermal analysis, however, shows strong endothermic peaks which appear to indicate melting of crystalline material. Once melted, these esters cannot be crystallized easily by heat treatments, but it was found that treatment with certain solvents will induce crystallization.

C. Tubular Blown Film Process

The tubular blown film process is used to produce thin films from thermoplastic materials. In this process the molten polymer is extruded from an annular die (usually upward). It is then drawn onto nip rolls which produce an airtight seal (see figure II-12). Air is blown through the die to generate an internal pressure which expands the annular film. The pressure difference across the bubble is very small, typically about 0.1 per cent of atmospheric pressure. Usually an air cooling ring is installed around the bubble to help shape and stabilize it. This also controls the frost line height. The blow-up ratio is the ratio of the final film diameter to the die diameter. Commercial blow-up ratios seem to range from 2 to 4 [65].

The literature cites many variations of producing tubular blown film [21,35,47,49,50,53,67,77,78,31,89]. However, the basic principles are the same.

Kinematics

The kinematics of the flow in the region between the die and the freeze line have been studied by Pearson and Petrie [63,64,66], Han [39], and White [96] using the theory of thin shells. In this theory it is assumed that the film thickness, h , is much smaller than the radius of curvature (i.e. $h \ll r$). This allows the curved film to be

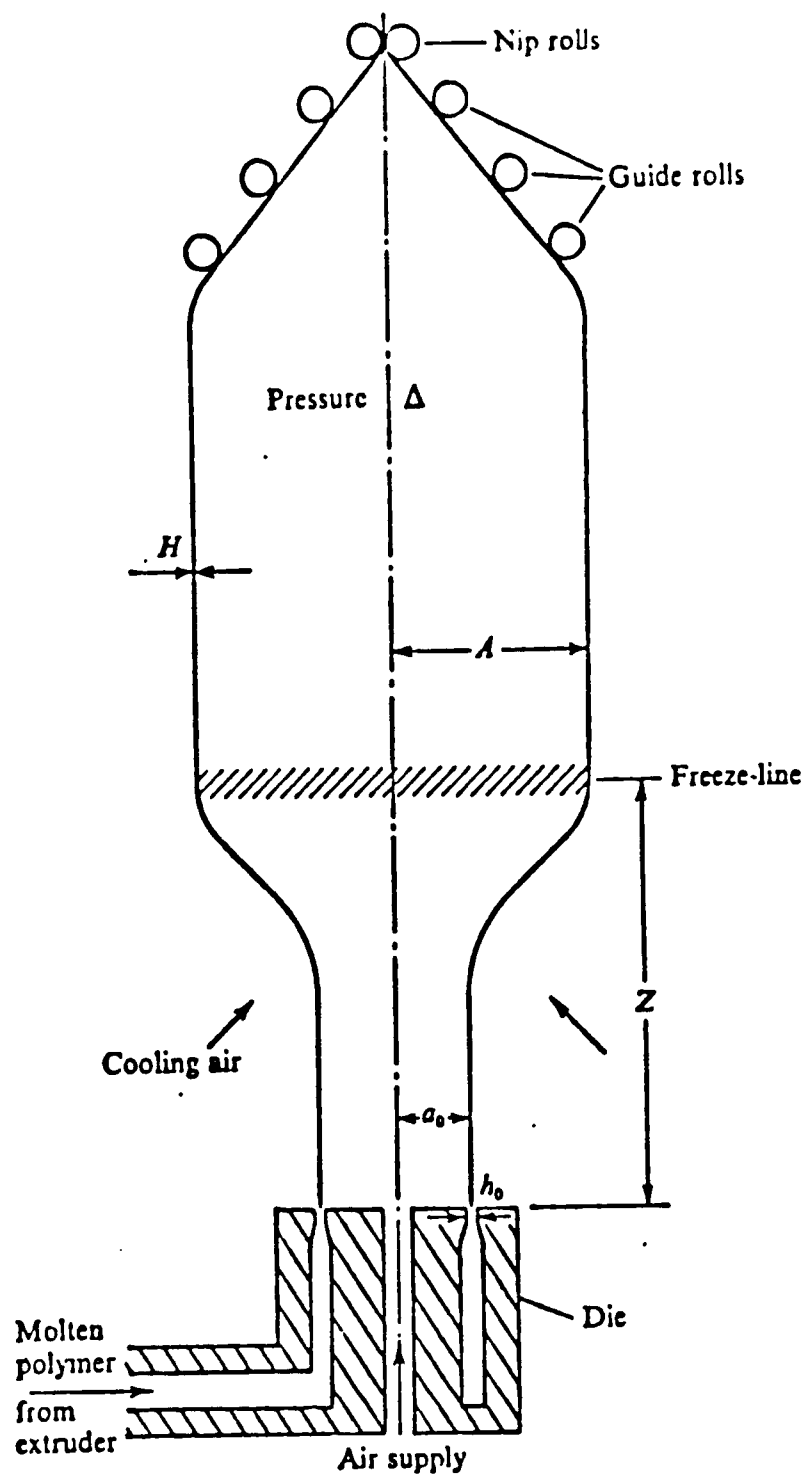


Figure II-12. Diagram of film blowing process.

From Pearson, J.R.A. and Petrie, C.J.S., J. Fluid Mech., 42, 609 (1970).

approximated by a plane film. The velocities are expressed in terms of h , r , and z , where z is the distance along the machine direction (figure II-13).

The rate of deformation tensor ($\underline{d}$) may be written as

$$\underline{d} = \frac{1}{2} [\underline{\nabla} \underline{V} + (\underline{\nabla} \underline{V})^T] = \begin{vmatrix} d_{11} & 0 & 0 \\ 0 & d_{22} & 0 \\ 0 & 0 & d_{33} \end{vmatrix} \quad (1)$$

where $\underline{\nabla} \underline{V}$ is the velocity gradient tensor, $d_{11} = \partial v_1 / \partial \xi_1$, $d_{22} = \partial v_2 / \partial \xi_2$, and $d_{33} = \partial v_3 / \partial \xi_3$.

The velocity gradients are that of a plane film being extended biaxially, and the shear components were neglected. The components of the deformation tensor ($\underline{d}$) in terms of r and h as a function of z are:

$$d_{11} = -V_1 \cos \theta \left(\frac{1}{h} \frac{dh}{dz} + \frac{1}{r} \frac{dr}{dz} \right) \quad (2)$$

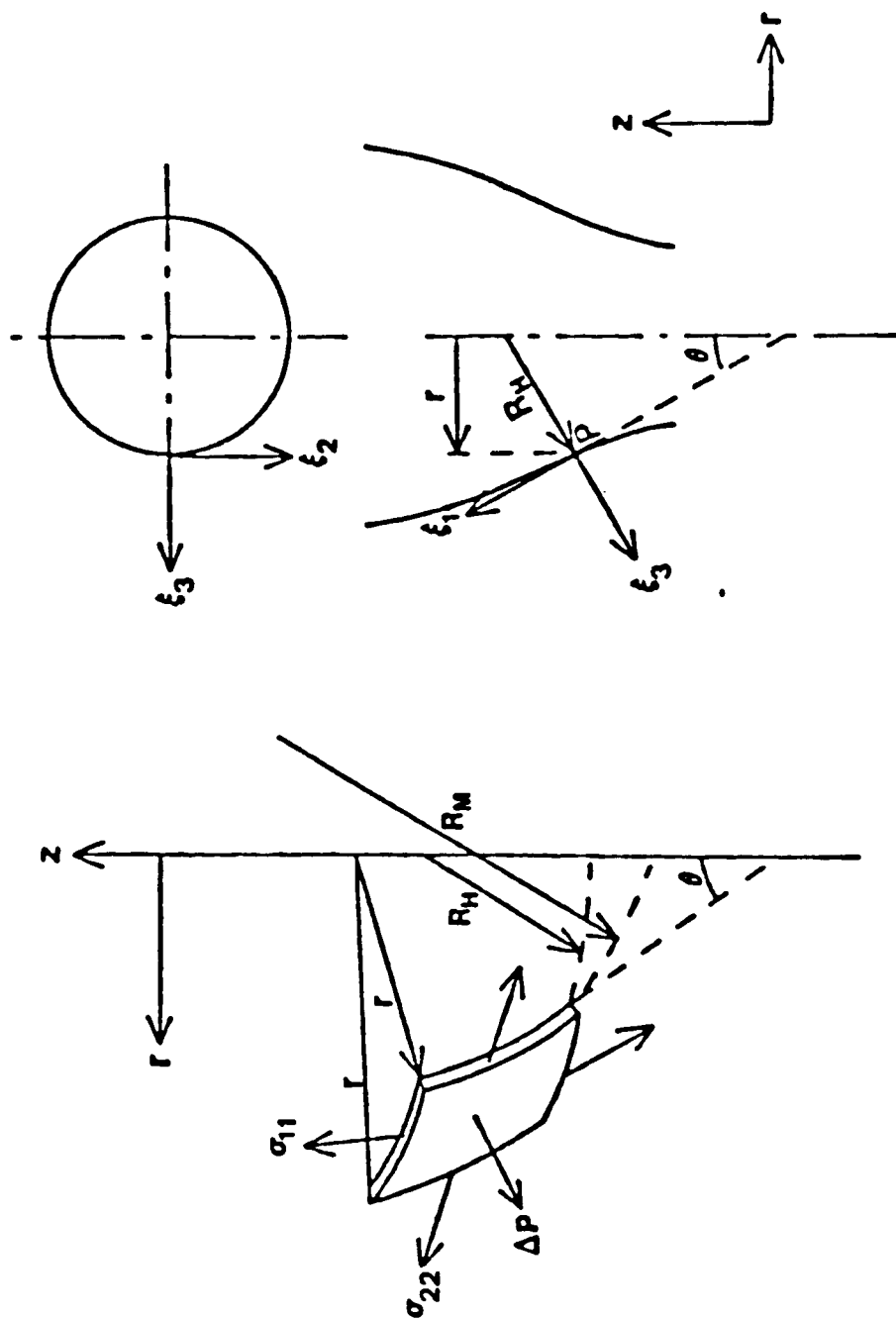


Figure II-13. Coordinate system for thin shell.

From Choi, K.J., PhD Dissertation, University of Tennessee, 1983.

$$d_{22} = V_1 \cos \theta \frac{1}{h} \frac{dh}{dz} \quad (3)$$

$$d_{33} = V_1 \cos \theta \frac{1}{r} \frac{dr}{dz} \quad (4)$$

where θ is the angle between the films meridional direction and the z direction.

For uniaxial extension, $d_{22} = d_{33} = -0.5d_{11}$ and for equal biaxial extension $d_{11} = d_{22} = -2d_{33}$. Han and Park [38] have shown that both types of deformation may be carried out in the film blowing process.

For a uniaxial extension it can be shown that

$$\frac{V_1}{V_0} = \frac{h_0^2}{h_1^2} = \frac{R_0^2}{R_1^2} = \frac{1}{B^2} \quad (5)$$

where V is the velocity, h is the film thickness, R is the film radius, and B is the blow-up ratio. Thus for V_1/V_0 greater than unity, the blow-up ratio B , R_1/R_0 , is less than unity. An equal biaxial extension leads us to

$$\frac{V_1}{V_0} = \left[\frac{h_1^2}{h_0^2} \right]^{1/2} = \frac{R_1}{R_0} = B \quad (6)$$

Here the drawdown ratio is equal to the blow-up ratio.

Pearson and Gutteridge [66] later developed new boundary conditions for the derived Pearson and Petrie [63] mechanical equations for the film blowing process and discussed numerical solution. Experimental studies of the kinematics of the blown film process have been reported by Ast [4,5], Farber and Dealy [32], Han and Park [38], and Kanai and White [48]. Farber and Dealy [32] and Kanai and White [48] discuss motion picture techniques to follow deformation history. Han and Park [38] used photographic techniques to study the effects of varying air pressure.

It is, of course, possible to produce multilayer film through coextrusion. Polymer melts may be combined from two or more extruders. This is sometimes desirable in order to combine characteristics of one or more materials. Motivation may result from the desired physical properties and/or economical considerations.

D. Rotating Annular Dies

Molecular orientation is usually a factor that must be considered when fabricating plastic objects. Often for films and synthetic fibers, molecular orientation is frequently used to optimize the physical properties. At other times efforts are made to reduce molecular orientation, especially in injection molding.

Cleereman [17,18,19,20] designed an injection molding process in which high degrees of multiaxial orientation are produced to enhance the mechanical properties of polystyrene cups. In this process the inner core of an annular die is rotated to create a helical flow in the die. The transverse rotational component of the flow results in improvements in the resistance to environmental stress cracking and other mechanical properties. Alfrey [1] has discussed the properties of multiaxially oriented material.

The process of generating helical flow has also been applied to the extrusion of tubing where the outer mandrel or inner core or both rotate [36]. Shepard et al. [80] and Debereev et al. [26] reported using a rotating mandrel to produce improved mechanical properties of the resultant pipe. Donald [27,28] has reported similar results using a counter-rotating mandrel and die.

Choi [23] used a counter-rotating mandrel and die to produce parisons for blow molding HDPE and PS bottles.

Molecular orientation studies showed that the orientation developed in the tubes carried over to the blown bottles. Choi found the level of orientation toward biaxiality increased as the die rotation increased.

The use of rotating die systems for the modification of weld lines in the extruded thermoplastic pipe and the effect on power consumption during extrusion have also been discussed [93,94]. Rotating annular dies have also been used to generate multilayer sheets and films [1].

The theory of the results of helical flow was discussed by Rivlin [70] and in more detail by Savins and Wallich [76] and Coleman and Noll [24]. Tanner [86,87] has theoretically analysed the helical flow of liquids and used an Oldroyd model to calculate theoretical velocities profiles. These predictions were compared with experimental results.

Alfrey [1] has examined a rotating die system where the inner and outer die members counter-rotate at the same angular velocity. If the polymer is Newtonian, the rotational velocity (V_θ) as a function of radial position would be

$$v_\theta(r) = \frac{T}{4\pi L\eta} \left[\frac{r}{r_0} - \frac{1}{r} \right] \quad (7)$$

where r is the radius, T is the torque, L is the annulus

length, η is the viscosity, and r_0 is the radius of the outer wall.

The axial velocity (V_z) would be given by

$$V_z(r) = \frac{\Delta P}{4\eta L} \left[\frac{(R^2 - R_2^2)}{\ln(R_2 / R_1)} \ln r + r^2 + \frac{(R^2 \ln R_1 - R_2^2 \ln R_2)}{\ln(R_2 / R_1)} \right] \quad (8)$$

where ΔP is the pressure drop through the annulus.

The helical path of a moving particle would be

$$\phi(r) = \cot^{-1} \frac{v_\theta(r)}{v_z(r)} \quad (9)$$

and the total angle Θ developed at a downstream position L would be

$$\Theta(r) = \frac{v_\theta(r)}{v_z(r)} \cdot \frac{L}{r} \quad (10)$$

E. Characterization of Orientation

When most polymers are subjected to extensive mechanical deformation, the molecular chains usually align in the direction of deformation. Molecular orientation is well known to have a major effect on the mechanical properties of both glassy [18,87] and crystalline [73,37] polymers and their fabricated products. The importance of orientation stems from the large difference in strength between the covalent bonds within the chain molecule and the van der Waals forces binding adjacent molecules. This difference in bonding strengths leads to differences in mechanical properties in differently oriented species.

In fiber spinning, large drawdown ratios are used to align the polymer molecules parallel to the fiber axis. This maximizes the tensile strength of the fiber. In films, any preferred orientation in the machine or transverse direction results in the deterioration of the properties in the other direction. In general, a balance of orientation between the machine and transverse direction is desired. Biaxial orientation results when a film is stretched in two directions at right angles to each other. The chain segments tends to line up parallel to the plane of the sheet but in a random direction in this plane.

There are many methods of detecting the overall

orientation of polymers. Among these are birefringence, sonic modulus, infrared dichroism, and various other property measurements that become anisotropic as a result of orientation. These physical property measurements can only give us some average (or moment) of the orientation distribution function.

Optical birefringence is one of the easiest and most often used techniques for determining the overall preferred orientation. Oriented polymer chains possess different refractive indices along and perpendicular to the chain backbone. The birefringence of a polymer sample is the difference between the refractive indices in any two selected directions.

$$\Delta n_{ij} = n_i - n_j \quad (11)$$

Birefringence measurements can be made by direct measurements of the refractive indices, using a compensator, or intensity measurements of emitting light.

The most direct method for studying the orientation of crystalline polymers is x-ray diffraction. This technique can give a complete orientation distribution function for the unit cells of the crystals. When an x-ray beam impinges on a specimen the diffracted rays can be recorded on photographic film. If there is no preferred crystalline

orientation a Debye ring of uniform intensity is found for each reflection. If preferred orientation exists, the ring breaks into arcs. The sharper the arcs, the higher the preferred orientation. This type of analysis is adequate for two dimensional structure (such as fibers); however, for specimens with three dimensional order a more complicated measure of orientation is required.

"Pole Figures" are a means of representing three-dimensional orientation of the molecules in a crystalline polymer from x-ray diffraction data. The orientation of a plane can be described by a vector perpendicular to a plane called a "pole". Probably the easiest way to define the distribution of poles in three dimensions is to consider a sphere with a vector having an origin at the center and intersecting the surface. This intersection on the surface will occur at a certain longitude and latitude. Since a sphere does not lend itself to publication, a circular plot is used for convenience. For polycrystalline materials, there would be many different crystals whose poles must be plotted. This produces a scatter of points for each pole represented on the circular plot. In order to easily interpret the orientation of the sample, only one pole distribution is plotted per graph (see figures II-14, II-15, II-16) [16].

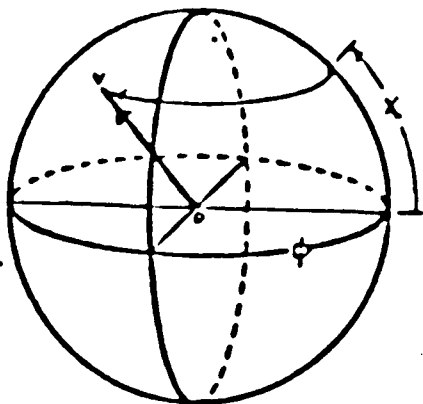


Figure II-14. Illustration of polar coordinates for pole vector.

From Clark, E.S., J. Ed. Modules Mat. Sci. Engr., 1, 568 (1979).

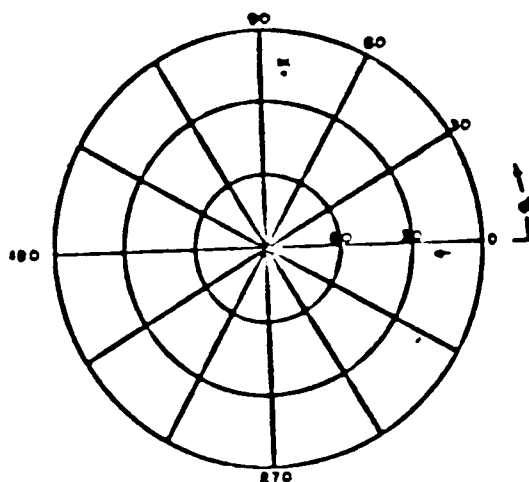


Figure II-15. Illustration of polar plot in planar form.

From Clark, E.S., J. Ed. Modules Mat. Sci. Engr., 1, 568 (1979).

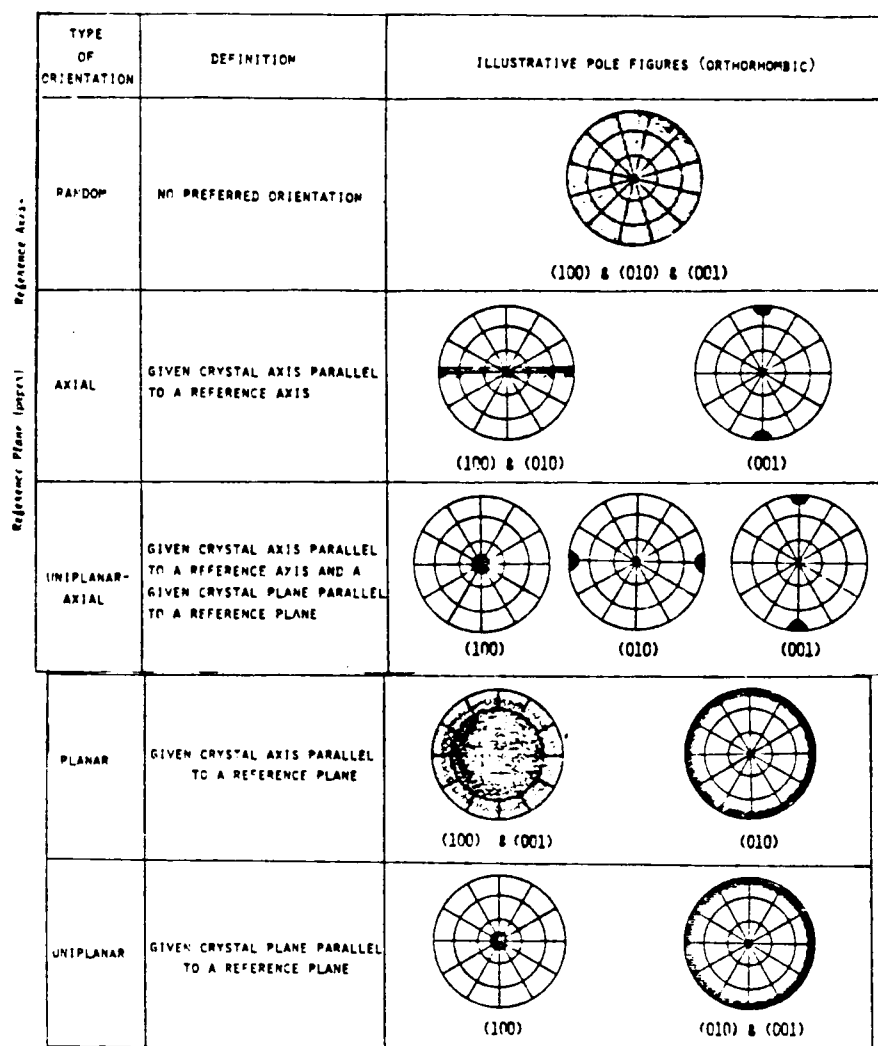


Figure II-16. Illustration of pole figure for various orientations (orthorhombic unit cell).

From Clark, E.S., J. Ed. Modules Mat. Sci. Engr., 1, 568 (1979).

Representation of Orientation

Thus far, molecular orientation has been treated qualitatively on the scale of the unit cell. However, the usefulness of the orientation data lies in the relationship between orientation and the mechanical properties. An orientation distribution function is necessary to give a complete and unbiased specification of the molecular orientation in a material. The properties of a material depend on certain orientation averages or moments of the distribution function [98]. Hermans [41,42] specified the orientation in terms of the anisotropy of the polarization tensor in a system with cylindrical fiber symmetry. He suggested that the orientation be specified in terms of the following distribution function:

$$f^H = \frac{3 \langle \cos^2 \phi \rangle - 1}{2} \quad (12)$$

For a homogeneous material

$$f^H = \frac{\Delta n}{\Delta^0} \quad (13)$$

where Δn is the birefringence and Δ^0 is the maximum or intrinsic birefringence of the system. Stein [7,8] later

extended Hermans' work and developed orientation factors for specifying the average orientation of a biaxially oriented sample with orthorhombic symmetry. His orientation factors are as follows:

$$f_{a,l} = 1/2 \left(3 \langle \cos^2 \phi_{a,l} \rangle - 1 \right) \quad (14)$$

$$f_{b,l} = 1/2 \left(3 \langle \cos^2 \phi_{b,l} \rangle - 1 \right) \quad (15)$$

$$f_{c,l} = 1/2 \left(3 \langle \cos^2 \phi_{c,l} \rangle - 1 \right) \quad (16)$$

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

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

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

For crystals with orthogonal axes

$$\langle \cos^2 \phi_{c,l} \rangle + \langle \cos^2 \phi_{b,l} \rangle + \langle \cos^2 \phi_{a,l} \rangle = 1$$

and

$$f_c + f_b + f_a = 0 \quad (21)$$

The Hermans-Stein orientation factors refer only to the crystalline phase. The birefringence of semicrystalline polymers is related to the orientation in the crystalline

and amorphous regions by

$$\Delta n = X \Delta^{oc} f_c + (1 - X) \Delta^{oa} f_{am} + \Delta n_{form} \quad (22)$$

where X is the crystalline fraction, f_c and f_{am} are Hermans orientation factors of the crystalline and amorphous phase, and Δ^{oc} and Δ^{oa} are the intrinsic birefringences of the crystalline and amorphous phases.

The problem with the Stein biaxial orientation factors is that they are based on Eulerian angles. Generally, they favor the machine direction and do not adequately describe the transverse direction. White and Spruiell [97] have proposed biaxial orientation factors based upon the anisotropy of the polarizability or attenuation tensors and the angles used by Stein. Two equations were developed for general analysis.

$$f_1^B = 2 \langle \cos^2 \phi_{c,1} \rangle + \langle \cos^2 \phi_{c,2} \rangle - 1 \quad (23)$$

$$f_2^B = 2 \langle \cos^2 \phi_{c,2} \rangle + \langle \cos^2 \phi_{c,1} \rangle - 1 \quad (24)$$

The subscript c refers to the chain direction and subscripts 1 and 2 refer to the reference directions (i.e. machine and transverse directions).

The above equations may be generalized for orthorhombic crystals to include all three crystallographic axes.

$$f_{a,1} = 2 \langle \cos^2 \phi_{a,1} \rangle + \langle \cos^2 \phi_{a,2} \rangle - 1 \quad (25)$$

$$f_{a,2} = 2 \langle \cos^2 \phi_{a,2} \rangle + \langle \cos^2 \phi_{a,1} \rangle - 1 \quad (26)$$

$$f_{b,1} = 2 \langle \cos^2 \phi_{b,1} \rangle + \langle \cos^2 \phi_{b,2} \rangle - 1 \quad (27)$$

$$f_{b,2} = 2 \langle \cos^2 \phi_{b,2} \rangle + \langle \cos^2 \phi_{b,1} \rangle - 1 \quad (28)$$

$$f_{c,1} = 2 \langle \cos^2 \phi_{c,1} \rangle + \langle \cos^2 \phi_{c,2} \rangle - 1 \quad (29)$$

$$f_{c,2} = 2 \langle \cos^2 \phi_{c,2} \rangle + \langle \cos^2 \phi_{c,1} \rangle - 1 \quad (30)$$

These orientation functions are not independent, but are related through

$$\langle \cos^2 \phi_{a,1} \rangle + \langle \cos^2 \phi_{b,1} \rangle + \langle \cos^2 \phi_{c,1} \rangle = 1 \quad (31)$$

$$\langle \cos^2 \phi_{a,1} \rangle + \langle \cos^2 \phi_{a,2} \rangle + \langle \cos^2 \phi_{a,3} \rangle = 1 \quad (32)$$

Thus four of the six orientation functions are independent.

The above definitions may be applied to tetragonal and hexagonal crystals with the restriction

$$f_{ay}^B = f_{by}^B \quad (33)$$

The biaxial orientation factors for amorphous polymers are defined as

$$f_1^B = \frac{\Delta n_{13}}{\Delta^{ca}} \quad (34)$$

$$f_2^B = \frac{\Delta n_{23}}{\Delta^{ca}} \quad (35)$$

For two phase semicrystalline polymers

$$\Delta n_{13} = X \left[\Delta_{ca}^{oc} f_{c1}^B + \Delta_{ba}^{oc} f_{b1}^B \right] + (1 - X) \left[\Delta^{oa} f_1^B \right] + \Delta n_{form} \quad (36)$$

$$\Delta n_{23} = X \left[\Delta_{ca}^{oc} f_{c2}^B + \Delta_{ba}^{oc} f_{b2}^B \right] + (1 - X) \left[\Delta^{oa} f_1^B \right] + \Delta n_{form} \quad (37)$$

For uniaxial orientation, one of the above orientation factors is zero, while the other reduces to the Hermans orientation factor. White and Spruiell [97] also describe their biaxial orientation factors in terms of an orientation function triangle (see figures II-17, 18, 19, 20). These orientation factors have been applied by Matsumoto, Fellers, and White [56] and Choi, Spruiell, and White [22] to express orientation in polystyrene films.

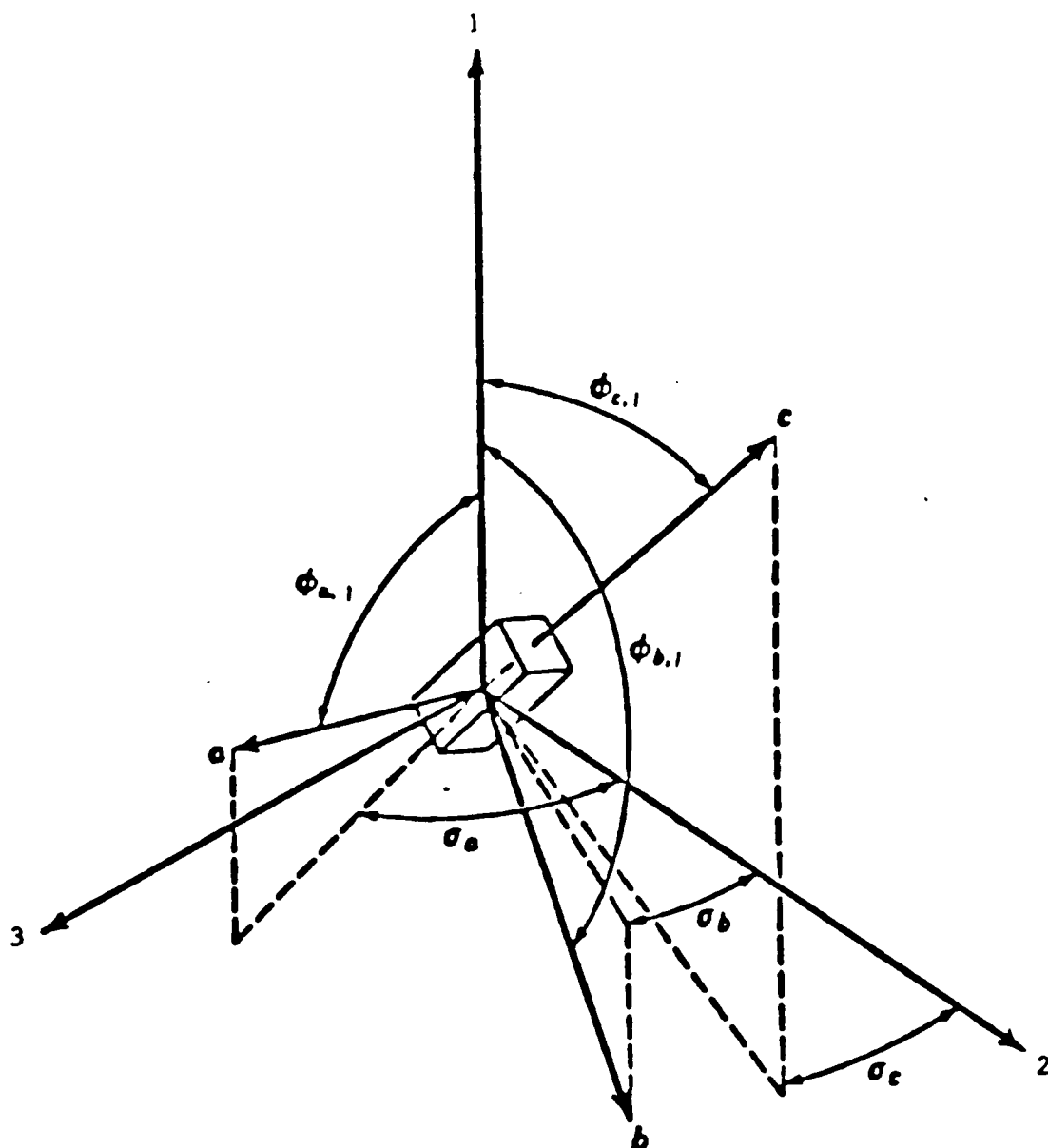


Figure II-17. Stein's coordinate system.

From White, J.L. and Spruiell, J.E., Polym. Engr. Sci., 21, 859 (1981).

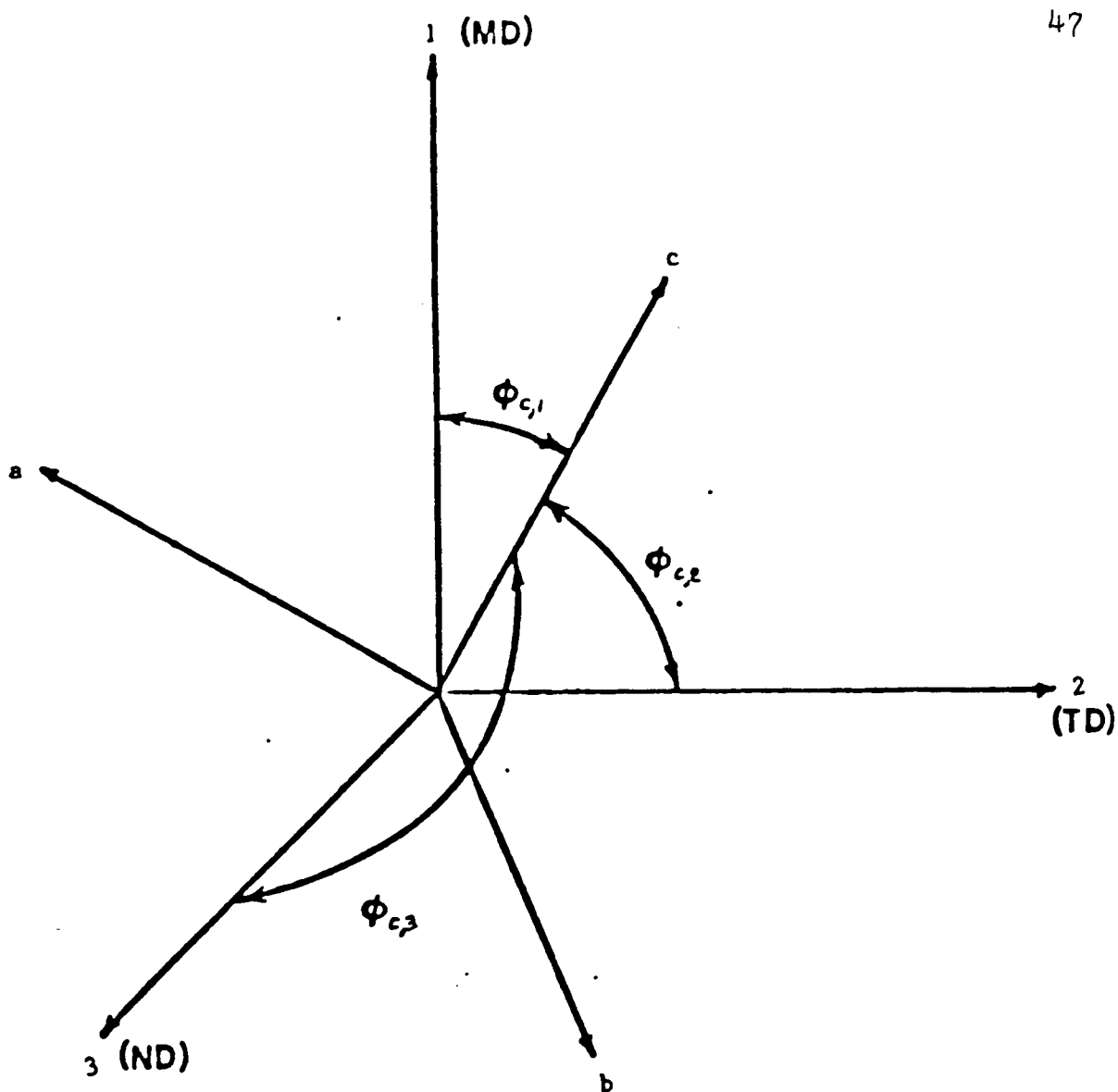


Figure II-18. White and Spruiell's coordinate system.

From White, J.L. and Spruiell, J.E., Polym. Engr. Sci., 21, 859 (1981).

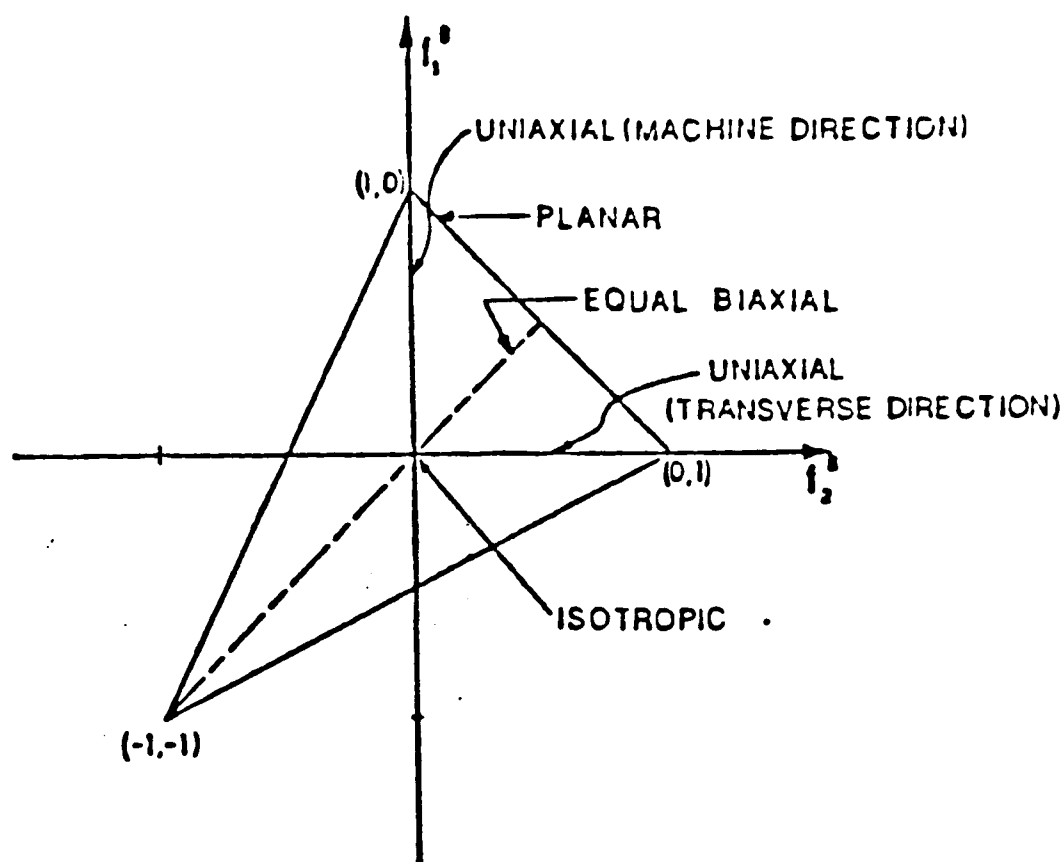
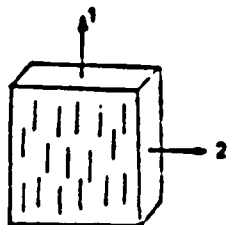


Figure II-19. Graphical representation of orientation, the orientation triangle diagram.

From White, J.L. and Spruiell, J.E., Polym. Engr. Sci., 21, 859 (1981).

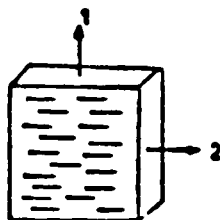
CHAINS || to 1



$$f_1^0 = 1$$

$$f_2^0 = 0$$

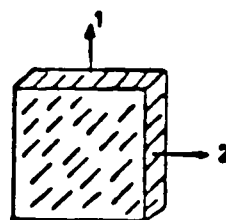
CHAINS || to 2



$$f_1^0 = 0$$

$$f_2^0 = 1$$

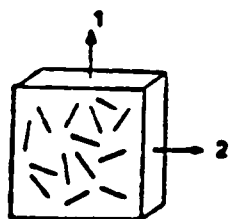
CHAINS || to 3



$$f_1^0 = -1$$

$$f_2^0 = -1$$

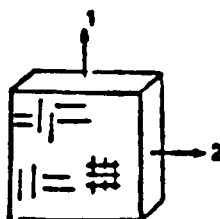
ISOTROPIC



$$f_1^0 = 0$$

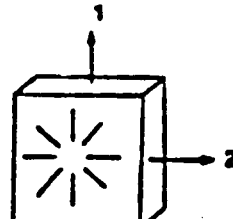
$$f_2^0 = 0$$

PLANAR EQUAL BIAxIAL



$$f_1^0 = \frac{1}{2}$$

$$f_2^0 = \frac{1}{2}$$



$$f_1^0 = \frac{1}{2}$$

$$f_2^0 = \frac{1}{2}$$

Figure II-20. Different states of orientation in films and White and Spruiell's biaxial orientation factors.

From White, J.L. and Spruiell, J.E., Polym. Engr. Sci., 21, 859 (1981).

Crystal Structure

The crystal structure of hydroxypropyl cellulose has been investigated by Samuels [72]. On the basis of wide angle x-ray diffraction, Samuels indicates that the unit cell may be considered to be pseudotetragonal with dimensions

$$a = b = 11.33 \text{ \AA}$$

$$c = 15.0 \text{ \AA}$$

where c is the chain axis repeat distance. The HPC molecule has a backbone of anhydroglucose units twisted into an irregular 3 to 1 helix.

Samuels [72] has indexed the WAXS patterns of HPC. The strongest reflection is the (100) which corresponds to the a and b axes. This is the equatorial reflection in a uniaxial film and has a Bragg's law d spacing of 11.33 Å. The next weaker reflections were the (002) and the (003) observed at d spacings of 7.49 and 4.98 Å.

Samuels estimated the degree of crystallinity to be between 15-20 per cent using density, calorimetry, and infrared measurements.

Ethyl cellulose is a polycrystalline material whose structure has not yet been explained.

Bunn [15] found polyethylene to have an orthorhombic unit cell with

$$a = 7.40 \text{ \AA} \quad b = 4.93 \text{ \AA} \quad c = 2.53 \text{ \AA}$$

The strongest reflections being the (110) and the (200).
The (020) and the (310) are the next strongers reflections
although they are much weaker than the (110) and (200).

CHAPTER III

EXPERIMENTAL

A. Materials

The materials used in this research were Klucel Type E (hydroxypropyl cellulose), Dow Ethocel Standard 20 (ethyl cellulose), Eastman CAB 171-2 (cellulose acetate butyrate), Dow Styron 685D (polystyrene), and Dowlex 2047 (linear low density polyethylene). See table III-1.

B. Fabrication

The materials were extruded through a 3/4 inch Rainville screw extruder with an L/D of 15. A feed hopper with a nitrogen purge was used in order to minimize water absorption and oxidative degradation of the cellulose derivatives.

The cellulosic powders were dried under vacuum at 80 degrees celsius for 12 hours prior to extrusion. After drying, 0.2 per cent erythorbic acid (stereoisomer of ascorbic acid) and 0.2 per cent mono-stearyl citrate were added to control degradation. This antioxidant-scavenger blend was obtained courtesy of Pfizer Chemical Company. The polymer was then blended in a planary mixer to assure a good distribution of the antioxidant.

The materials were extruded through a rotating annular

Table III-1. Materials

Polymer	Source	Commercial Name	DS	MS
Hydroxypropyl Cellulose	Hercules	Klucel Type E (MW = 60,000)	3	4
Ethyl Cellulose	Dow	Ethocel Standard 20 (Ethoxy content 48 - 49.5 %)	2.41 - 2.51	
Cellulose Acetate Butyrate	Eastman	CAB 171 - 2 acetyl content 17 % butyryl content 29.5 %	--	--
Polystyrene	Dow	Dow Styron 685 D (Melt index = 1.6)	NA	NA
Polyethylene	Dow	Dowlex 2047 (Melt index = 2.3)	NA	NA

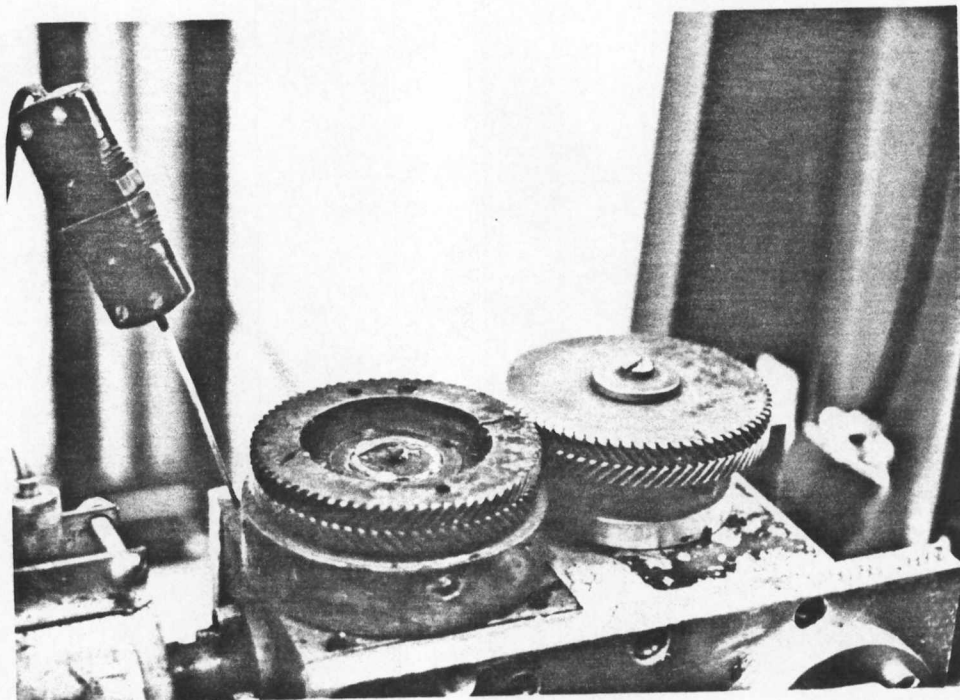
die (see figures III-1, III-2, III-3). The annular die consists of a rotating inner core and a simultaneously counter-rotating outer cylinder. A 43 rpm motor is connected through a gear box next to the rotating parts. The inner and outer walls are rotated at the same angular velocity. Rotational speeds of the outer cylinder and inner core were varied from 0 to 17.2 rpm. The outer cylinder has an inside diameter of 2.46 cm and an inner core outside diameter of 2.17 cm, giving a gap of 0.145 cm.

Four cartridge heaters in the die block were used to control the temperature. The extrusion temperatures were 150 for polyethylene, 175 for polystyrene, 170 for HPC, and 180 degrees celsius for EC and CAB.

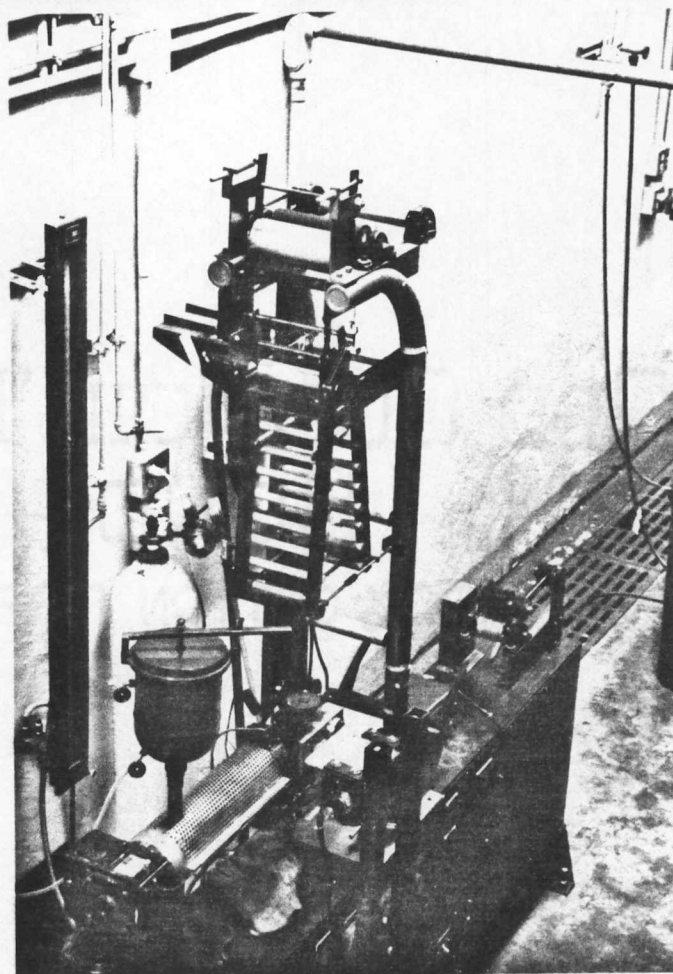
Nitrogen gas could be fed through the inner core to inflate the tubes and produce thin films. The conditions under which the tubes and films were fabricated from the process were characterized by the parameter R . R represents the ratio of the tangential wall shear rate ($\dot{\gamma}_t^w$) to the axial wall shear rate ($\dot{\gamma}_a^w$). This parameter combines the two process variables of linear extrusion rate and die rotation speed into one process variable.

$$\dot{\gamma}_t(r) = 2\Omega_0 R^2 (1/r^2) (k^2/(1-k^2)) \quad (38)$$

where Ω_0 is the angular velocity of the rotating surfaces,



(a)



(b)

Figure III-1. Experimental Apparatus (a) rotating die (b) film blowing process.

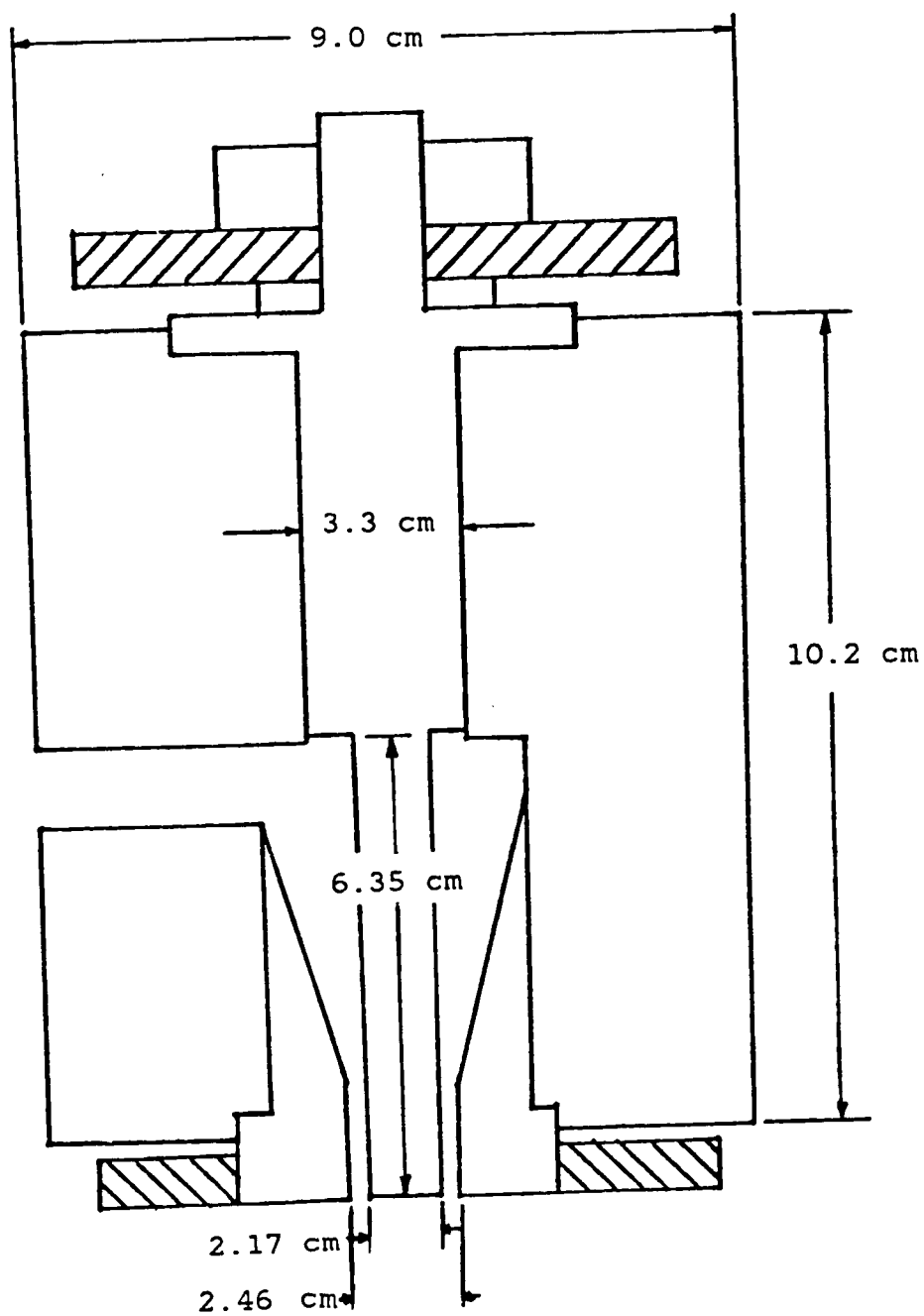


Figure III-2. Diagram of rotating annular die.

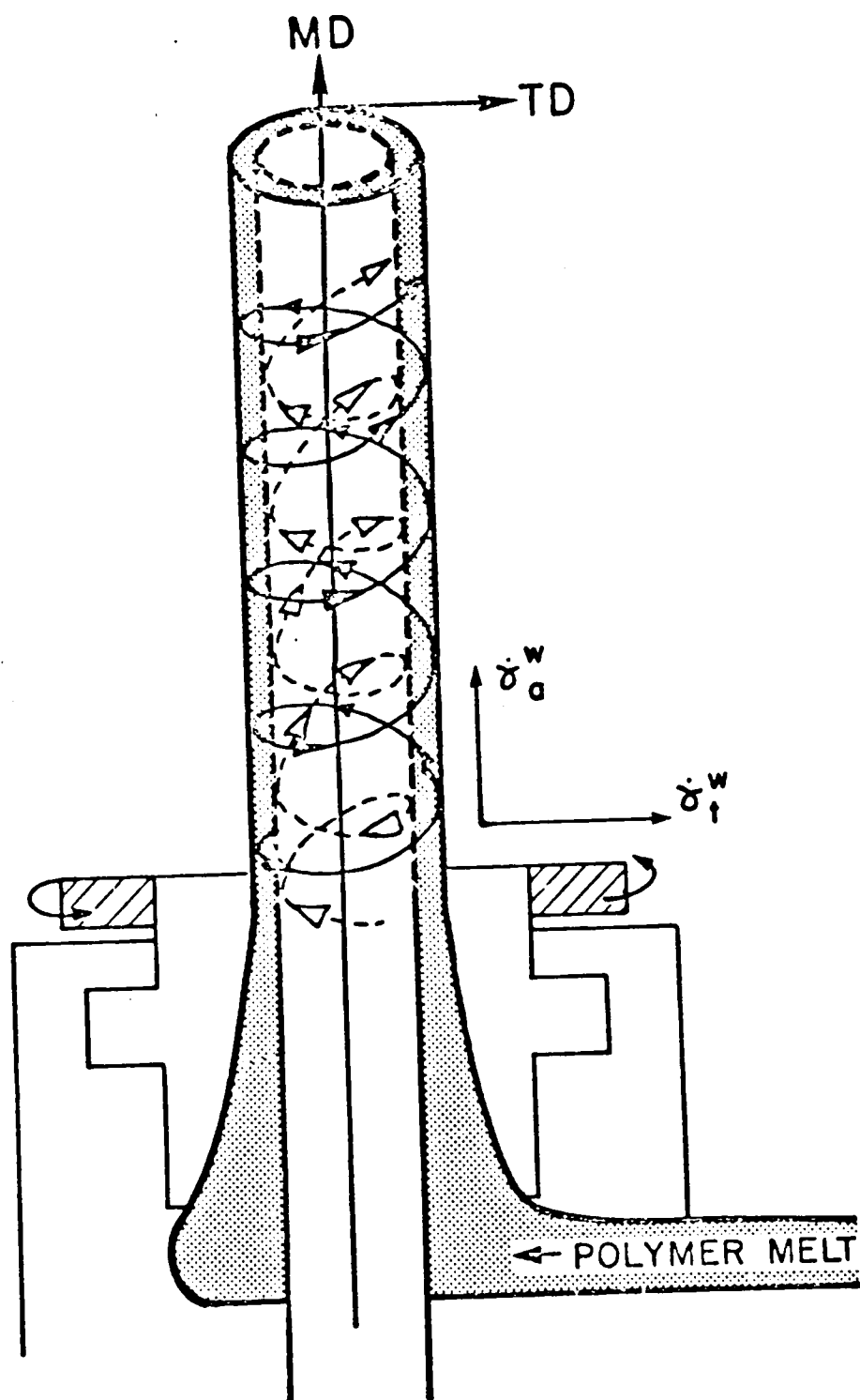


Figure III-3. Rotating annular die.

R is the outer radius, r is the radius, and K is the ratio of the inner radius to the outer radius. For the described system, this reduces to

$$\dot{\gamma}_i^w = 15 \Omega_0 \quad (39)$$

The axial wall shear rate ($\dot{\gamma}_s^w$) is calculated through

$$Q = \frac{\pi \Delta P R^4}{8\eta L} \left(\frac{(1 - k^4) - (1 - k^2)^2}{\ln(1/k)} \right) \quad (40)$$

where ΔP is the pressure drop, η is the viscosity, and L is the length. This reduces to

$$Q = 8.05 \times 10^{-4} \frac{\Delta P R^4}{\eta L} \quad (41)$$

We can measure Q and solve for $\Delta P/\eta L$ and find $\dot{\gamma}_s^w$ through

$$\dot{\gamma}_s^w = \frac{\Delta P R}{2\eta L} \left[1 - \frac{1 - k}{2 \ln(1/k)} \right] \quad (42)$$

C. Characterization

Optical Birefringence

The "in-plane" and "out of plane" birefringences of the samples were measured using a 7-order Babinet compensator and a Lietz Polarizing Polariscopes. The sample is placed in the goniometer with the desired sample axis for rotation parallel to the axis of the goniometer. The "in-plane" birefringence represents the difference in the refractive index between the machine and transverse directions, Δn_{12} . This measurement can be taken directly with the machine and transverse directions perpendicular to the light source.

The "out of plane" birefringence represents the difference in the index of refraction between the machine and normal (thickness) directions, Δn_{13} . This was measured using the procedure developed by Stein [82]. The "out of plane" birefringence was calculated through Stein's equation

$$\Delta n_{13} = \frac{\lambda_0}{d_0} \left[\frac{R_\phi (1 - \sin^2 \phi / n^2) - R_0}{\sin \phi / n^2} \right] \quad (44)$$

where λ_0 is the wave length of the light source, d_0 is the thickness of the film, n is the average refractive index of the media, ϕ is the angle of tilt, R_0 is the retardation of the film for normal incidence expressed in units of number of waves, and R_ϕ is the retardation of the film tilted through the angle ϕ .

The axis of the goniometer is rotated from 20 to 45 degrees at 5 degree intervals and readings taken at each point. The average value of n calculated for the different angles of tilt was taken as the "out of plane" birefringence.

Wide Angle X-ray Diffraction Analysis

Film Patterns

Wide angle x-ray diffraction patterns were made using a Philips x-ray generator with a copper target tube and a nickel filter. CuK x-ray radiation has a wavelength of 1.542 Å. The unit was operated at 30 KV and 20 mA. X-ray film patterns were taken through the normal direction by taping the sample directly to the sample holder. Since WAXS is limited to crystalline or semicrystalline polymers, this analysis was limited to HPC and PE. A good x-ray pattern required about 8 hours for HPC and 4 hours for PE tubes. Blown films required at least 12 hours for HPC and 7 hours for PE.

Pole Figure Analysis

A General Electric x-ray diffractometer equipped with a single crystal orienter was used for pole figure analysis. Monochromatic CuK radiation was emitted with a wavelength of 1.542 Å. The unit was operated at 40 KV and 15 mA.

Figure III-4 is a schematic of a goniometer that can be used for orienting a sample in the x-ray beam for a pole figure.

The diffraction data were recorded automatically by a Digital Equipment Corporation PDP-15 computer. Pole figure programs were developed by Prof. J.E. Spruiell. The sample was placed in the single crystal orienter and the diffraction angle, θ , was set for the desired pole. Pole figure data acquisition involved a circular scan in which the radial direction (ϕ) was set and the circumferential angle (χ) was changed in ten degree increments from 0 to 360. This process was repeated for radial angles (ϕ) between 0 and 90 in five degree increments. The intensity data were then transferred to the disc of the DEC-10 of the university computer system for computer plotting.

Evaluation of Orientation Functions

Average cosine values from equations for the White-Spruiell biaxial orientation functions may be calculated from pole figure analysis data. Figure III-5 shows the spherical coordinate system used to represent the plane normal. If ϕ is the angle between a chosen crystallographic direction and a reference direction, the average $\cos \phi$ squared ($\langle \cos^2 \phi \rangle$) over the entire sphere may be expressed as

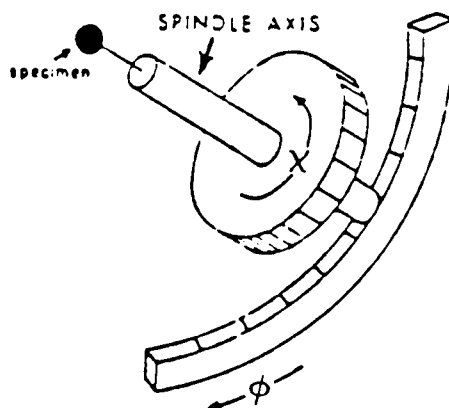


Figure III-4. Experimental schematic of a goniometer for orienting a sample in the x-ray beam.

From Clark, E.S., J. Ed. Modules Mat. Sci. Engr., 1, 568 (1979).

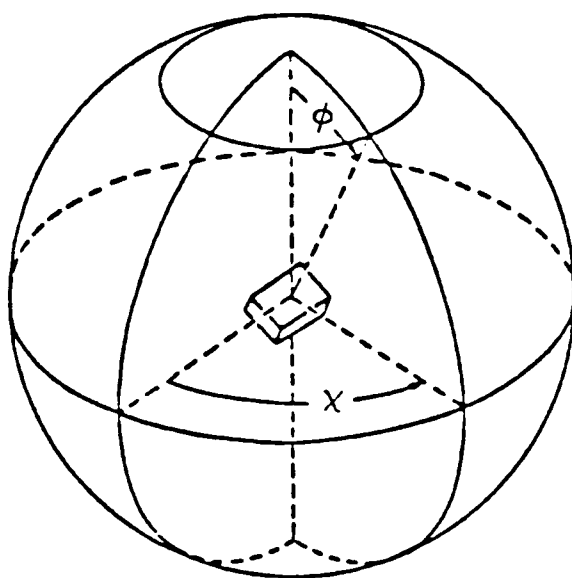


Figure III-5. Position of plane normal by spherical coordinates.

From Clark, E.S., J. Ed. Modules Mat. Sci. Engr., 1, 568 (1979).

$$\langle \cos^2 \phi \rangle = \frac{\int_0^\pi \int_0^{2\pi} I(\phi, X) \cos^2 \phi \sin \phi \, dX \, d\phi}{\int_0^\pi \int_0^{2\pi} I(\phi, X) \sin \phi \, dX \, d\phi} \quad (45)$$

where $I(\phi, X)$ is the diffracted x-ray intensity from planes perpendicular to the chosen crystallographic direction. This intensity is directly proportional to the pole concentration representing the relative amount of crystalline material having plane normals in the direction ϕ, X . We may write

$$I(\phi) = \int_0^{2\pi} I(\phi, X) \, dX \quad (46)$$

therefore

$$\langle \cos^2 \phi \rangle = \frac{\int_0^\pi I(\phi) \cos^2 \phi \sin \phi \, d\phi}{\int_0^\pi I(\phi) \sin \phi \, d\phi} \quad (47)$$

HPC has a tetragonal unit cell with the strongest reflection being the (100). The stronger c-axis reflections are hidden by the amorphous halo. Since the unit cell is tetragonal,

$$f_a = f_b$$

and

$$f_c = -2 f_a$$

so the c-axis orientation function can easily be determined.

As mentioned earlier, four of the six cosine squared values must be measured in order to specify the orientation. Since the diffracted intensity from the (020) is much weaker than that of the (200) or (110), diffraction data were taken from the (110) instead of the (020). Using the treatment discussed by Stein [84], we can calculate $\langle \cos^2 \phi_{020,1} \rangle$ and $\langle \cos^2 \phi_{020,2} \rangle$:

$$\langle \cos^2 \phi_{020,1} \rangle = 1.445 \langle \cos^2 \phi_{110,1} \rangle - 0.455 \langle \cos^2 \phi_{200,1} \rangle \quad (48)$$

$$\langle \cos^2 \phi_{020,2} \rangle = 1.445 \langle \cos^2 \phi_{110,1} \rangle - 0.445 \langle \cos^2 \phi_{200,1} \rangle \quad (49)$$

Sample Preparation

The pole figure samples were made by gluing tubes and films together using Duco cement in order to obtain cubic samples of around 1.5 cm. The thickness was usually slightly larger due to the presence of the glue. The samples edges were trimmed with razor blade and glue was applied to the edges to hold the sample together. The samples were then glued to the tip of a polystyrene rod and placed in the single crystal orienter.

Scanning Electron Microscopy

SEM photographs of the film cross sections and surfaces using an AMR High Resolution Electron Microscope model number 900. Samples were mounted on holders with epoxy and coated with gold-palladium alloy in a vacuum chamber to give them a conductive surface. The cellulose samples observed in cross-section were prepared by breaking at room temperature. fig 1 Mechanical Properties

The mechanical properties of the films produced were measured on an Instron Tensile Tester model number 1122. Samples of 0.635 cm by 3.0 cm were cut with a razor blade. The gauge length was 2.54 cm and the cross head speed was 2 mm/min. The mechanical properties of strips cut 0, 30, 45, 60, and 90 degrees off the machine direction were tested. The modulus, tensile strength, and elongation to break were determined.

CHAPTER IV

PROCESSING

A. Processing Conditions

In the fabrication of HPC, EC, CAB, PE, and PS tubes the extruder barrel was raised and the rotating annular die pointed downward. The polymer was extruded down out of the die at a linear extrusion rate of approximately 8.25 cm per minute. The die rotation speed was varied to produce tubes with R values ranging from 0 to 410. Samples of twenty five centimeters in length were collected and allowed to cool at room temperature.

Films were fabricated at conditions close to the tubes except nitrogen gas was used to inflate the tubes into thin films. Polyethylene film could be produced continuously using the blown film apparatus. HPC, EC, CAB, and PS formed stiff, brittle films that could not be taken up in the conventional manner. These films were taken up by hand.

The HPC and EC extrudates were blown to a blow-up ratio of 2.8 - 3.0 to give films 0.0152 - 0.0254 cm (6 - 10 mils) thick. The PS and PE films had blow up ratios of 4.8 - 5.0 to yield films of 0.00530 - 0.00318 cm (see table IV-1). The cellulose ethers were limited to a blow up ratio of 3.0 due to the die design. These polymers were extremely tough to inflate and had to be blown immediately upon exiting the

Table IV-1. Processing conditions

MATERIAL	THICKNESS (CM)	B	V/V	METHOD
HPC	0.0203	2.8	2.6	HAND
EC	0.0203	2.8	2.6	HAND
PE	0.0051	4.8	5.9	CONT.
PS	0.0038	5.0	7.5	HAND

die. The gears at the die exit limited the blow up at the die exit. The PE and PS films were not limited by the die design.

B. Rotating Annular Die Extrudate Behavior

The tubes extruded through the rotating die were characterized by thickness and outer diameter at room temperature. Table IV-2 shows the relationship between the tube thickness (T) and die rotation (R) for HPC, EC, CAB, PE, and PS. The PE extrudates appeared to undergo elongational flow after exiting the annular die. This was probably a result of the relatively high melt temperature (150 degrees celsius). As the die rotation increased, shear thinning increased this tendency for flow. The thickness of the EC, PS, and CAB tubes were observed to increase with R (see figure IV-1). The HPC behaved differently. The thickness of the HPC extrudates were independent of die rotation.

The tube diameter for CAB, PE, PS, and EC decreased with R. This could be due to elastic recovery in the tangential direction. However, HPC exhibited the inverse behavior. The HPC tube diameter was proportional to R. The die swell was defined as the ratio of the extrudate diameter (D_{EX}) to the die annulus diameter (D_0) measured at room temperature. That is

Table IV-2. Rotating die extrudate behavior

HPC			
R	T (CM)	D (CM)	D/D ₀
0	0.188	2.159	0.878
123	0.180	2.197	0.894
246	0.168	2.235	0.909
328	0.183	2.426	0.987
410	0.180	2.459	1.000
EC			
0	0.142	*	*
82	0.178	2.654	1.080
205	0.200	2.596	1.056
410	0.206	2.428	0.988
CAB			
0	0.262	2.858	1.162
82	0.259	2.773	1.128
246	0.305	2.718	1.105
328	0.302	2.527	1.028
410	0.386	2.477	1.007
PE			
0	0.163	2.233	0.908
82	0.152	2.032	0.826
205	0.137	1.433	0.583
328	0.132	1.250	0.508
410	0.132	1.143	0.465
PS			
0	0.292	3.175	1.291
82	0.381	2.530	1.029
205	0.409	2.418	0.983
328	0.429	2.154	0.876
410	0.447	2.052	0.835

* SAMPLE WAS NOT ROUND

T = 0.145

D = 2.459

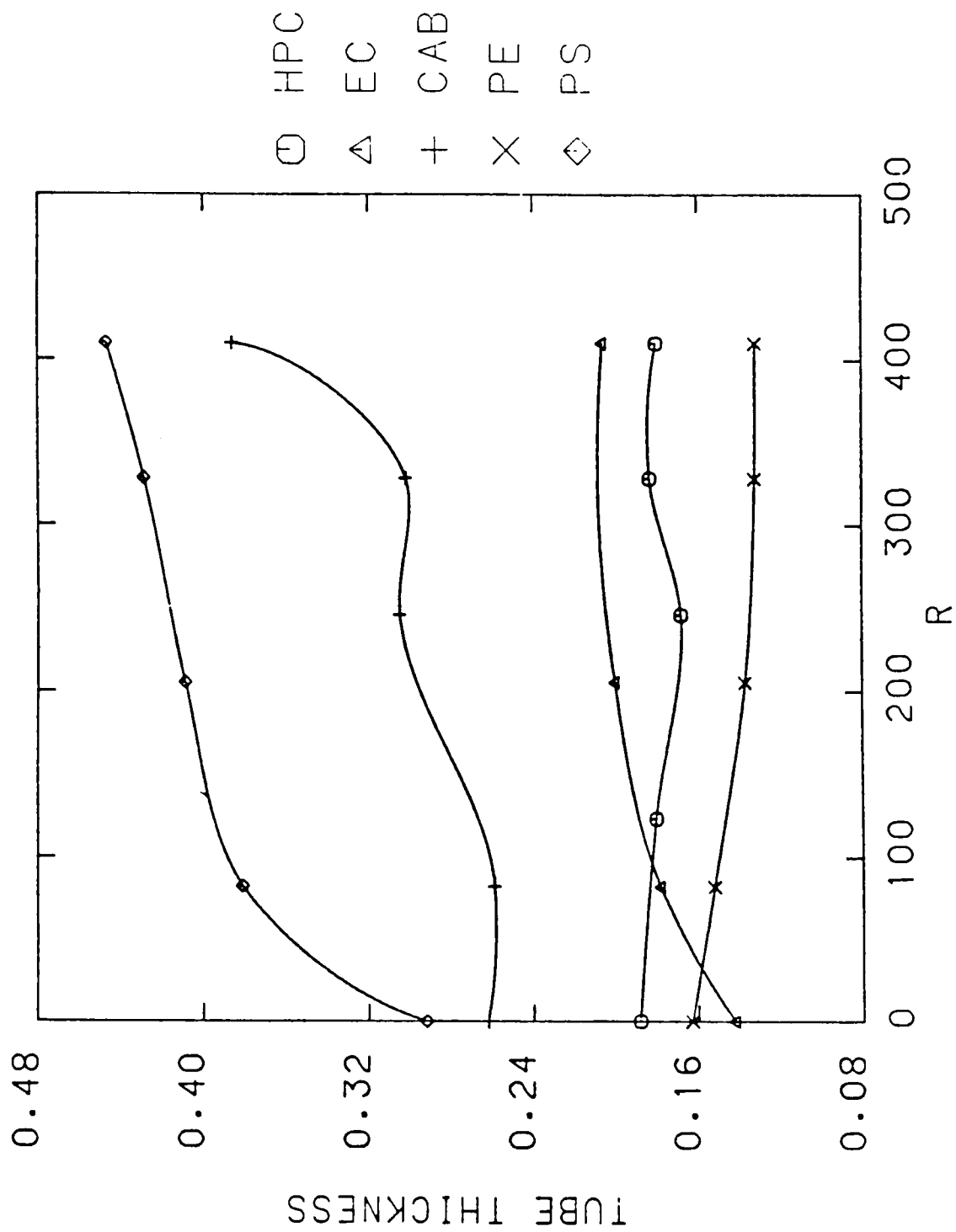


Figure IV-1. Tube thickness as a function of R.

$$\text{Die Swell} = \frac{D_{ex}}{D_o} \quad (50)$$

The tube diameter and die swell behavior are shown in figures IV-2 and IV-3.

Die swell is normally attributed to elastic recovery. As the polymer melt flows through the die entrance, the chains are slightly extended in the direction of flow. Upon exiting the die, the polymer chains tend to return to a random coil to increase its conformational entropy. This relaxation results in die swell.

CAB and PS extrudates without die rotation had die swells of 1.16 and 1.29, respectively. As R increased, the die swell decreased. EC exhibited similar behavior. It seems logical that the die rotation induces stress in the tangential direction which elongates the polymer chains in the direction of stress. Thus as the extrudate exits the die, the tube diameter would tend to decrease. For PS, the die swell ranged from 1.29 at $R = 0$ to 0.835 at $R = 410$.

The behavior of the HPC extrudates was dramatically different. HPC extrudates without die rotation exhibited die swells considerably less than unity (0.878). As R increased, the die swell increased to unity at $R = 410$.

Die swell does not occur in the HPC extrudates because the polymer chains behave as rigid rods with long relaxation

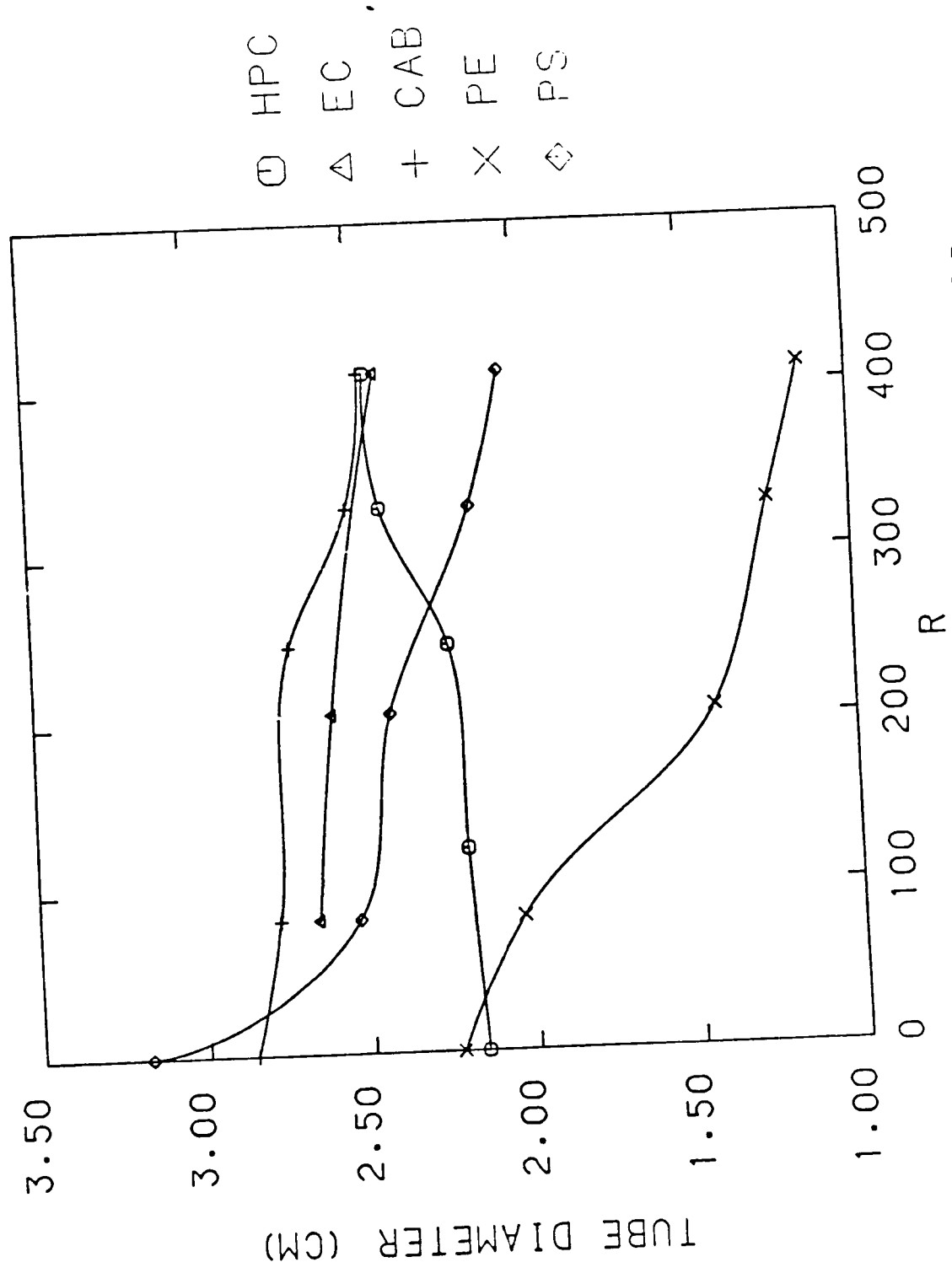


Figure IV-2. Tube diameter as a function of R.

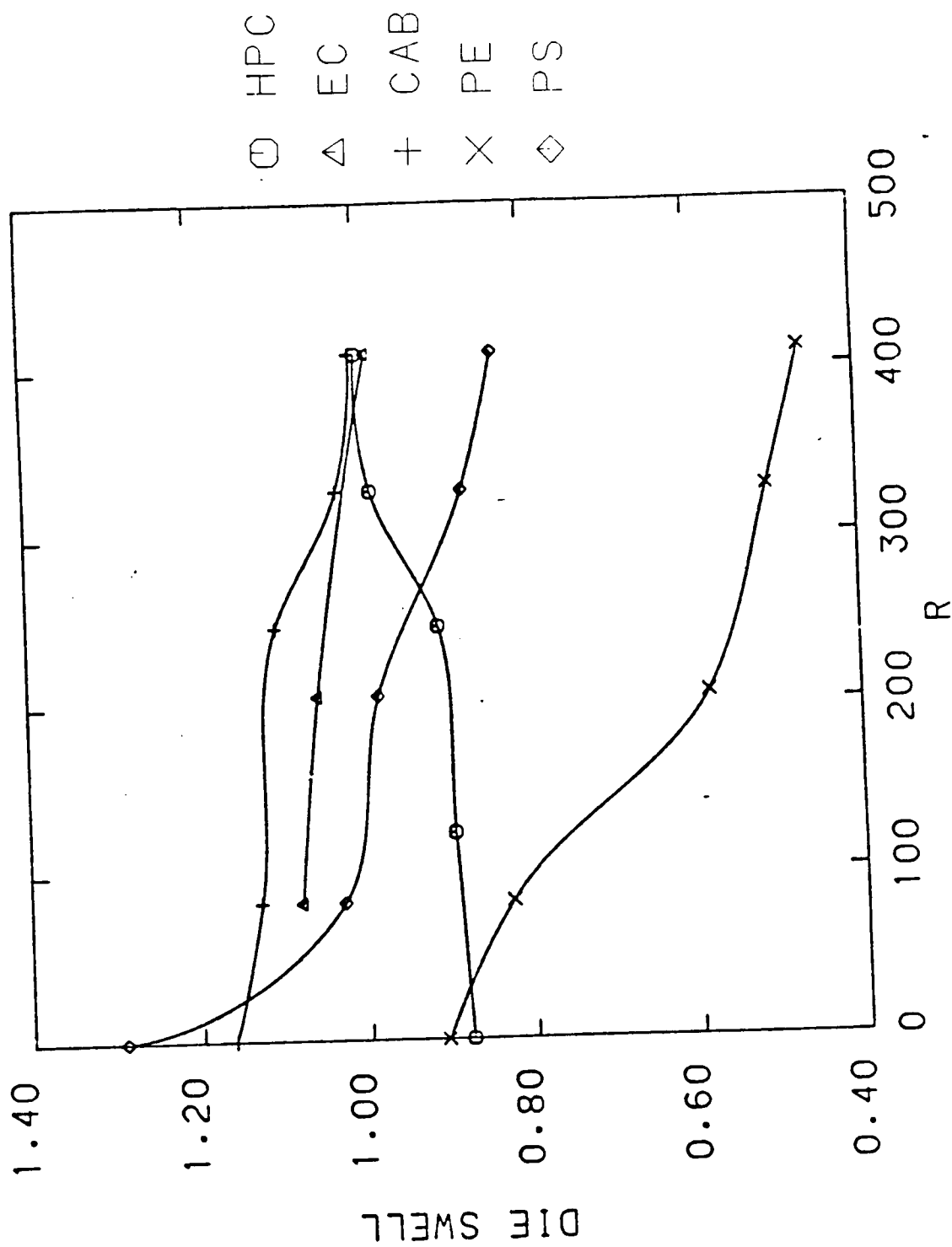


Figure IV-3. Die swell as a function of R.

times. Shear flow in the die orients the molecules in the machine direction. This orientation does not relax when the polymer melt exits the die.

CHAPTER V

CHARACTERIZATION OF MOLECULAR ORIENTATION

A. Introduction

The purpose of the following sections of this chapter is to characterize the molecular orientation of the tubes and films fabricated through the described process. Optical birefringence studies are presented in order to understand the overall orientation. Wide angle x-ray scattering (WAXS) was used to evaluate the crystalline regions of HPC and PE.

B. Optical Birefringence

The birefringences Δn_{12} , Δn_{13} , and Δn_{23} were determined for the tubes and films as a function of die rotation (R). The "1", "2", and "3" directions refer to the machine, transverse, and normal (or thickness) directions, respectively.

Table V-1 lists the values of Δn_{12} , Δn_{13} , and Δn_{23} as a function of R for the PS extrudates (see also figure V-1). The biaxial orientation factors listed in table V-2 and illustrated in figure V-2 were calculated using an intrinsic birefringence of - 0.125 [23]. In the PS tubes extruded without die rotation (R = 0), Δn_{12} was - 2.4×10^{-5} and Δn_{13} was - 2.0×10^{-3} . Δn_{13} indicates that the PS c-axis is preferentially oriented in the plane of the tube. The small

Table V-1. Birefringences of PS extrudates.

R	$\Delta n_{12} \times 10^3$	$\Delta n_{13} \times 10^3$	$\Delta n_{32} \times 10^3$
0	-2.4	-2.0	2.0
123	-1.5	-1.7	1.7
205	-1.0	-1.6	1.6
287	-0.81	-1.5	1.5
410	-0.44	-1.4	1.4

Table V-2. Orientation factors of PS extrudates.

R	F_1^B	F_2^B
0	0.016	0.016
123	0.014	0.014
205	0.013	0.012
287	0.012	0.012
410	0.011	0.011

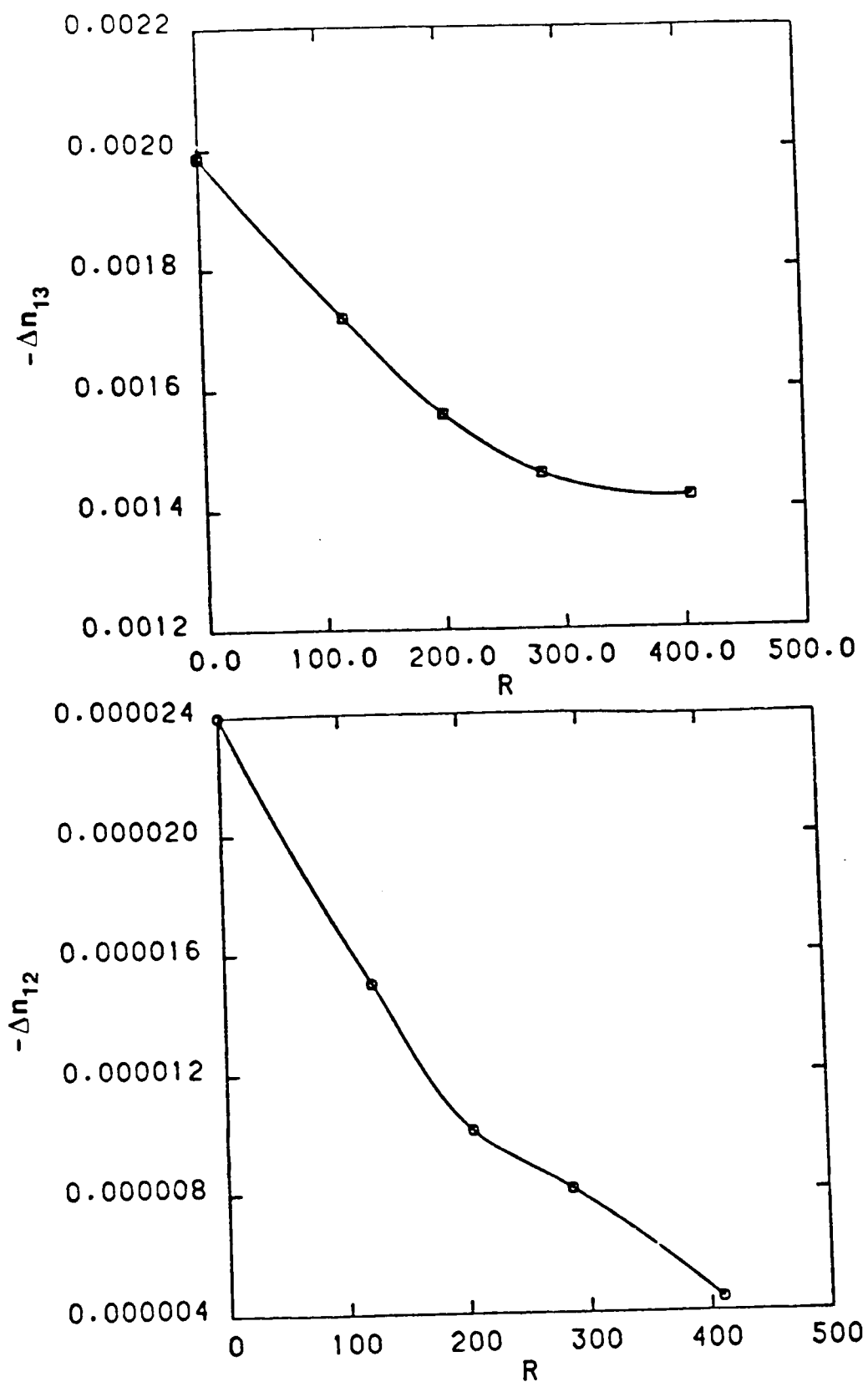


Figure V-1. Birefringences of PS extrudates.

value of Δn_{12} indicates that the c-axis is only slightly more oriented in the machine direction than in the transverse direction.

As R is increased from 0 to 410, Δn_{12} decreases from -2.4×10^{-5} to -0.44×10^{-5} . The die rotation decreases the slight preferential orientation in the machine direction. Δn_{13} also decreases with R. The die rotation decreased the preferential orientation in the plane of the tubes. The biaxial orientation factors f_1^B and f_2^B decreased from 0.016 and 0.016 to 0.011 and 0.011 as the die rotation was increased. Although the preferential orientation was very low, the die rotation would seem to drive away any preferential orientation.

The PS blown films were more biaxially oriented than the PS tubes as would be expected (table V-3 and V-4). Δn_{13} at $R = 0$ was -3.3×10^{-3} for the blown film compared to -2.0×10^{-3} for the extruded tube. With respect to die rotation, the PS film exhibited different behavior than the PS tubes. The die rotation increased Δn_{13} from -3.3×10^{-3} at $R = 0$, to -5.7×10^{-3} at $R = 410$. Thus as R increased, the tendency for the PS chains to lie in the film plane increases (figure V-3). Δn_{12} for the blown films were much higher than for the tubes (1.8×10^{-3} compared to 2.4×10^{-5}). This indicates an increased tendency for the c-axes to align in the machine direction. Die rotation did not have much

Table V-3. Firefringences of PS films.

R	$\Delta n \times 10^3$	$\Delta n \times 10^3$	$\Delta n \times 10^3$
0	-1.4	-3.3	4.7
82	-1.8	-3.3	5.2
205	-1.8	-3.5	5.3
287	-1.8	-4.3	6.1
410	-1.8	-5.7	7.4

Table V-4. Orientation factors of PS films.

R	F_1^B	F_1^B
0	0.026	0.037
82	0.027	0.041
205	0.028	0.043
287	0.034	0.049
410	0.045	0.059

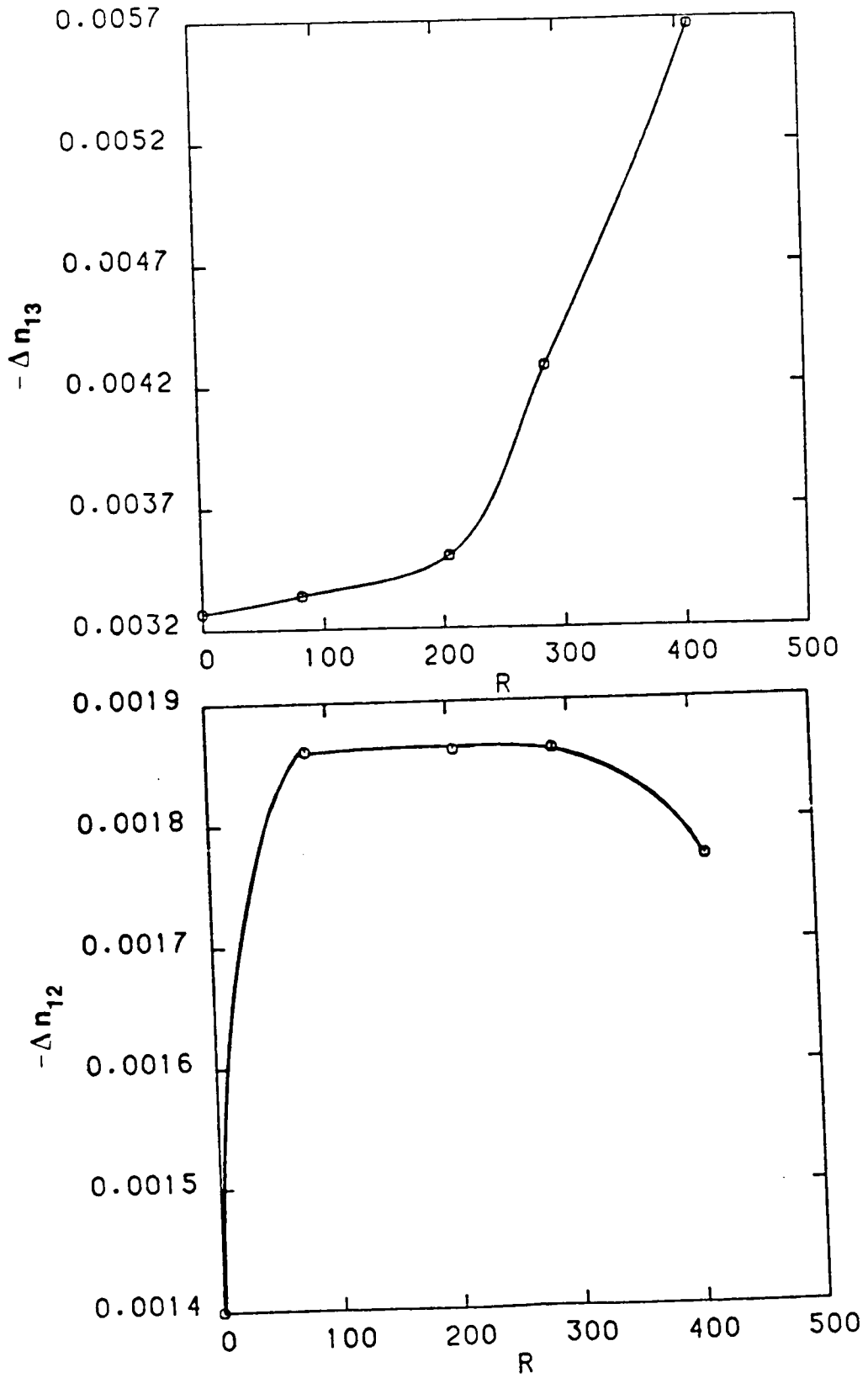


Figure V-3. Birefringences of PS films.

effect on Δn_{12} . At $R = 0$, Δn_{12} was equal to 1.4×10^{-3} . At $R = 82$, Δn_{12} increased to 1.8×10^{-3} . Any further increase in R did not have much effect (figure V-4). The biaxial orientation factors for the PS film, f_1^B and f_2^B increased from 0.026 and 0.037 at $R = 0$, to 0.045 and 0.059 at $R = 410$. Die rotation increases the biaxiality of the films.

Die rotation was observed to have the same effect on the PE extrudates as the PS extrudates (table V-5). All birefringences and thus the biaxial character decreased as R increased. Figure V-5 illustrates this effect. Die rotation reduced the preferential c-axis orientation in the machine direction. Δn_{12} decreased from 7.3×10^{-5} at $R = 0$ to 3.1×10^{-5} at $R = 410$. Δn_{13} was much larger than Δn_{12} . Δn_{13} at $R = 0$ was 5.6×10^{-3} . There is a slight tendency for the c-axis to lie in the plane of the tube. The c-axis orientation was only slightly greater in the machine than the transverse direction. Thus as with the PS tubes, the PE c-axis tends to lie in the plane of the tube and randomly within the plane.

The PE film was very similar to the PE extrudates. As shown in table V-6, Δn_{12} , Δn_{13} , and Δn_{23} are about the same as the PE tubes (table V-5). The further deformation of the extrudate did not lead to and increase in biaxiality. The PE film exhibited the same behavior with die rotation as the PE extrudates. Δn_{13} and Δn_{32} decreased and thus the die

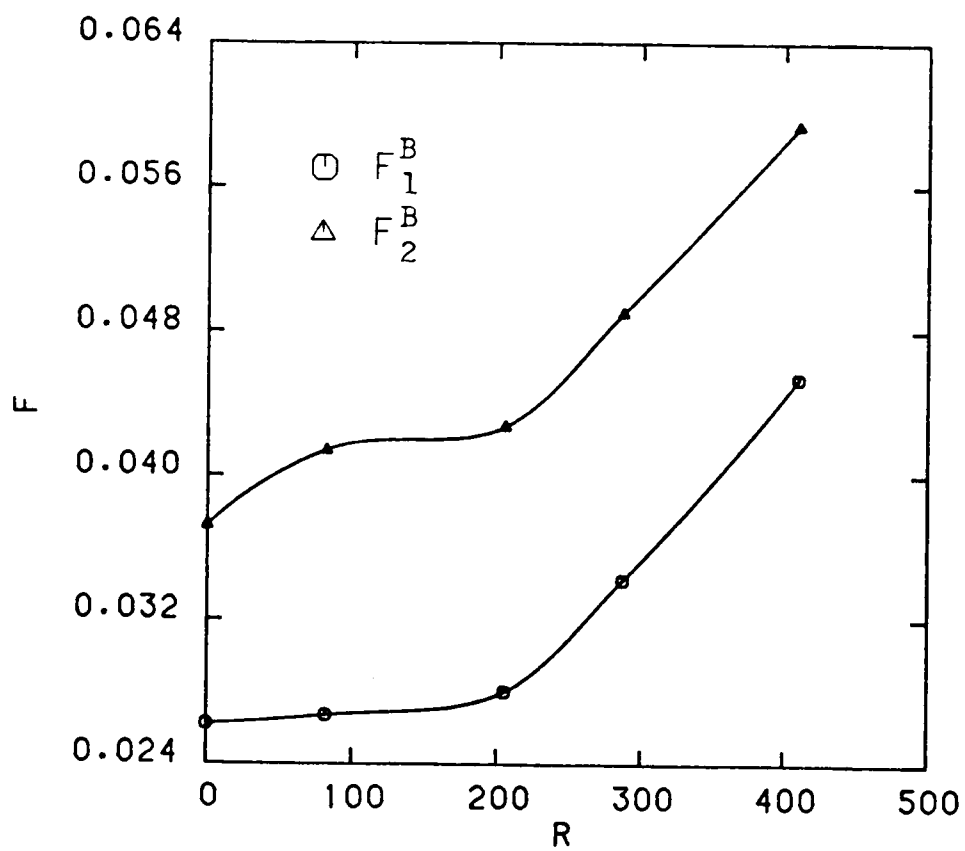


Figure V-4. Orientation factors of PS films.

Table V-5. Birefringences of PE extrudates.

R	$\Delta n_{12} \times 10^5$	$\Delta n_{13} \times 10^3$	$\Delta n_{32} \times 10^3$
0	7.3	5.6	-5.5
82	4.1	3.2	-3.2
205	3.3	2.6	-2.7
328	3.1	1.1	-1.1

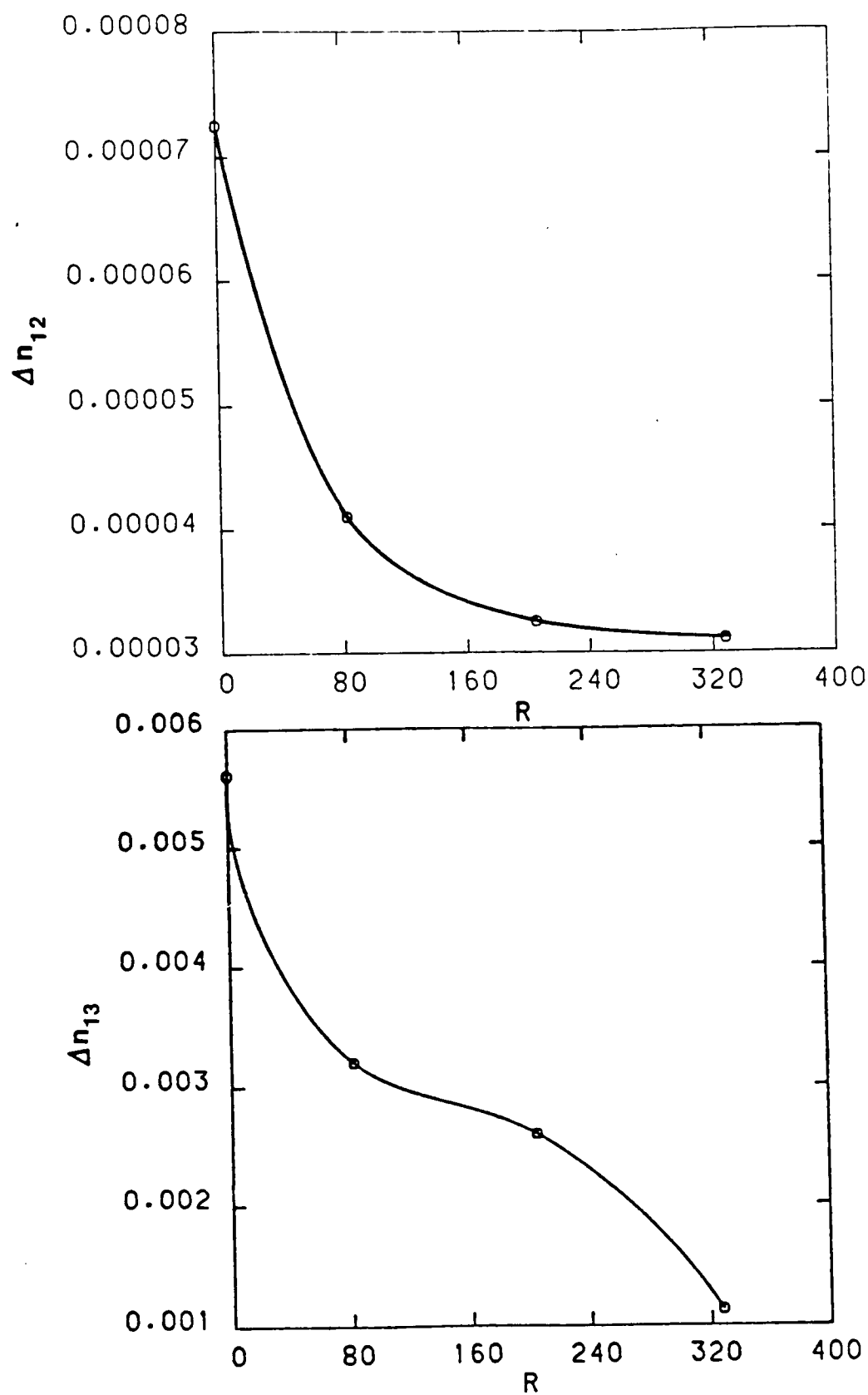


Figure V-5. Birefringences of PE extrudates.

Table V-6. Birefringences of PE film.

R	$\Delta n_{12} \times 10^5$	$\Delta n_{13} \times 10^3$	$\Delta n_{32} \times 10^3$
0	14.9	3.29	-3.14
82	4.00	2.71	-2.67
205	3.24	2.60	-2.57
328	3.11	1.13	-1.10
410	3.08	1.11	-1.08

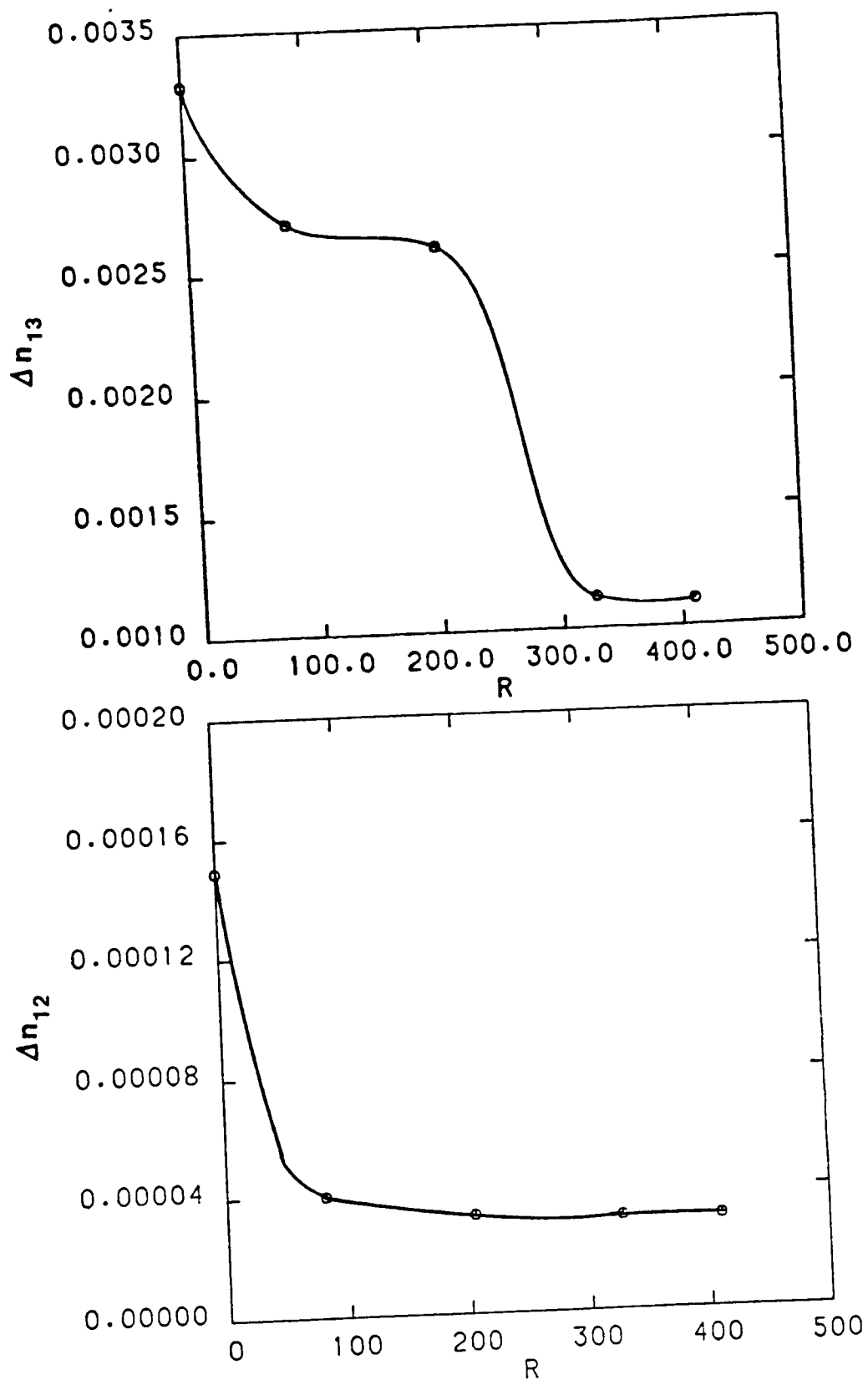


Figure V-6. Birefringences of PE film.

rotation appears to drive the film away from biaxiality.

The EC extrudates without die rotation had values of Δn_{12} of 4.7×10^{-5} and Δn_{13} of 2.4×10^{-3} (see table V-7). Thus, as with the PE and PS, there is a tendency for the chain axis to lie in the plane of the extrudate with only a slight preference for the machine over the transverse direction. However, the EC extrudates behaved quite differently than the PE and PS extrudates. Figure V-7 shows that Δn_{12} decreased with R while Δn_{13} and Δn_{23} increased dramatically. As shown in figure V-10, Δn_{12} decreased from 4.7×10^{-5} to 1.3×10^{-4} . Δn_{13} increased from 2.4×10^{-3} to a maximum of 8.6×10^{-3} . Thus die rotation increased the biaxial orientation of the tubes.

The inflation of the EC extrudates into films increased Δn_{12} from 4.7×10^{-5} to 4.8×10^{-4} , but did not have much effect on Δn_{13} . The effect seen in the EC extrudates was also observed in the EC blown films. Δn_{12} went from 4.8×10^{-4} to -8.6×10^{-5} as R went from 0 to 410. This indicates a change in preferential orientation from the machine to the transverse direction. The die rotation increased Δn_{13} from 2.0×10^{-3} at R = 0 to a maximum value of 8.1×10^{-3} at R = 82. Any further increase in R appears to be detrimental to the biaxiality of the film (table V-8; figure V-8).

The HPC tubes were highly birefringent and Δn_{12} could not be measured using a ten-order compensator. The c-axis

Table V-7. Birefringences of EC extrudates.

R	$\Delta n_{12} \times 10^5$	$\Delta n_{13} \times 10^3$	$\Delta n_{32} \times 10^3$
0	4.7	2.4	-2.4
82	4.4	2.3	-2.3
205	1.2	8.6	-8.6
328	0.13	4.8	-4.8

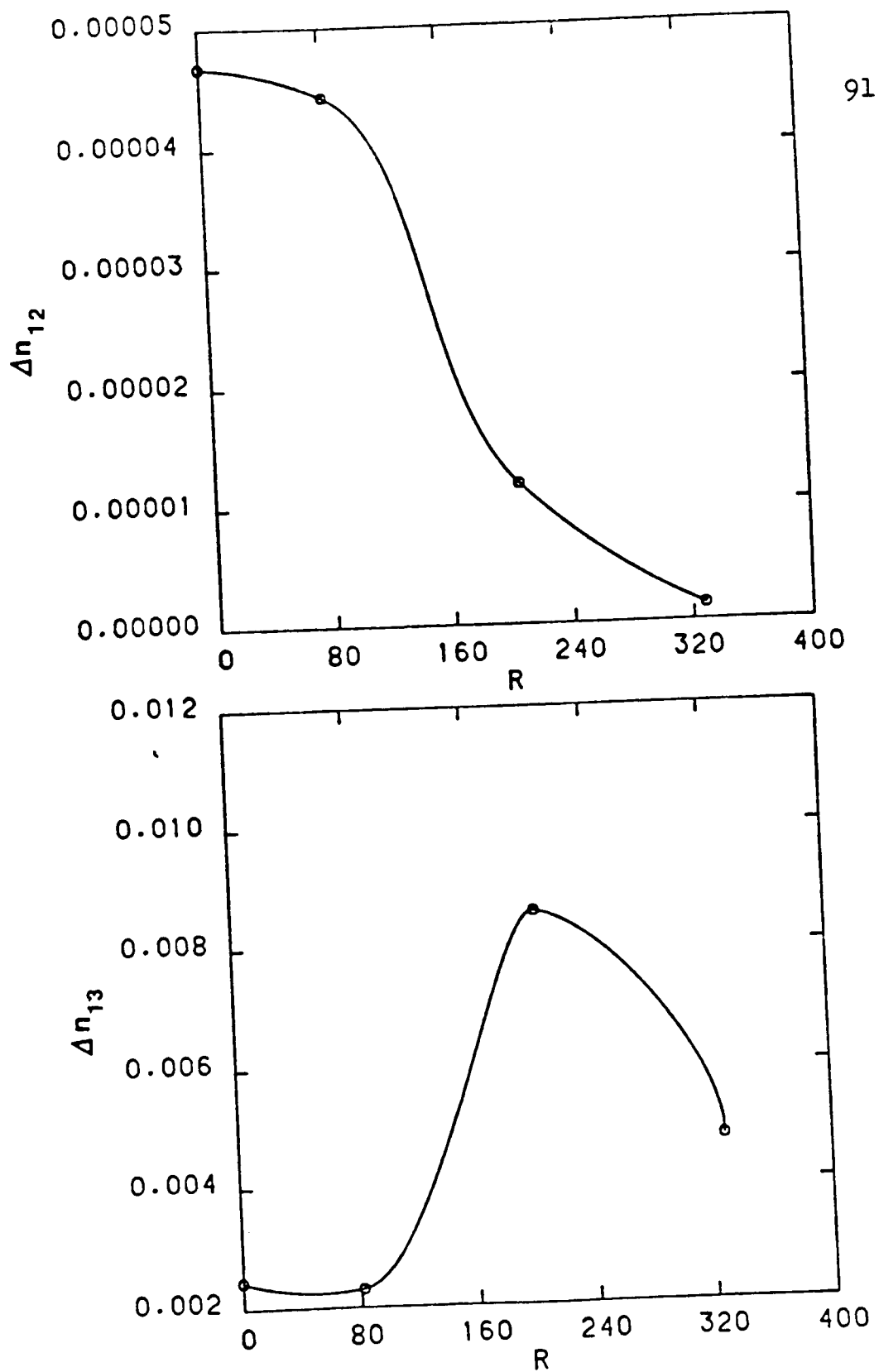


Figure V-7. Birefringences of EC extrudates.

Table V-8. Birefringences of EC films.

R	$\Delta n_{12} \times 10^4$	$\Delta n_{13} \times 10^3$	$\Delta n_{32} \times 10^3$
0	4.8	2.0	-1.5
82	4.7	8.1	-7.7
205	1.1	8.1	-8.0
410	-0.86	5.5	-6.4

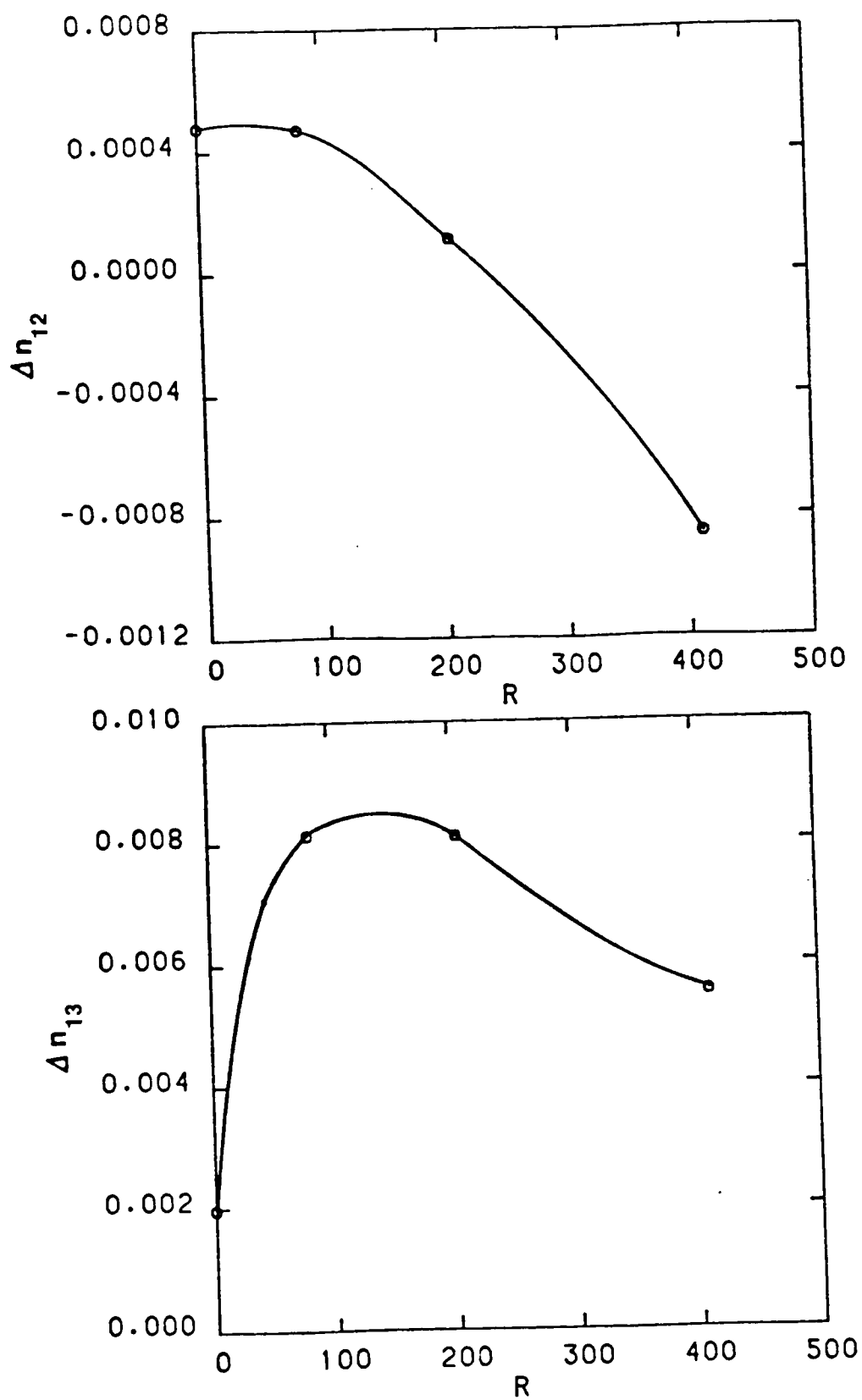


Figure V-8. Birefringences of EC films.

was highly oriented in the machine direction, orders of magnitude greater than the PE, PS, and EC extrudates. The HPC films were also highly birefringent, however the films were thin enough to allow birefringence measurements. Δn_{12} for a blown film with no die rotation was 8.2×10^{-3} indicating the film to be highly uniaxial. Die rotation can reduce Δn_{12} to 1.9×10^{-4} . The HPC appears to be highly planar. A small amount of die rotation increased Δn_{13} and Δn_{23} dramatically. Δn_{13} increased from 5.9×10^{-3} to 1.7×10^{-2} with $R = 82$. Any further die rotation would seem to have no effect on increasing the in and out of plane birefringence of the film. However, further increases in R would appear to shift the c-axis from the machine direction to the transverse direction (table V-9; figure V-9).

It is interesting to note that for the PS film, the tendency for the c-axis to lie in the plane of the film increased as R increased throughout the range studied. Whereas in the HPC and EC films, there appeared to be a limiting value of R , above which any further increase in die rotation no longer increases this tendency. Any further increase in R only changes the distribution of the c-axis between the machine and transverse directions.

Table V-9. Birefringences of HPC films.

R	$\Delta n_{12} \times 10^3$	$\Delta n_{13} \times 10^2$	$\Delta n_{32} \times 10^2$
0	8.2	0.59	0.23
82	6.6	1.7	-1.1
205	2.9	1.5	-1.2
287	0.62	1.6	-1.6
410	0.19	1.7	-1.7

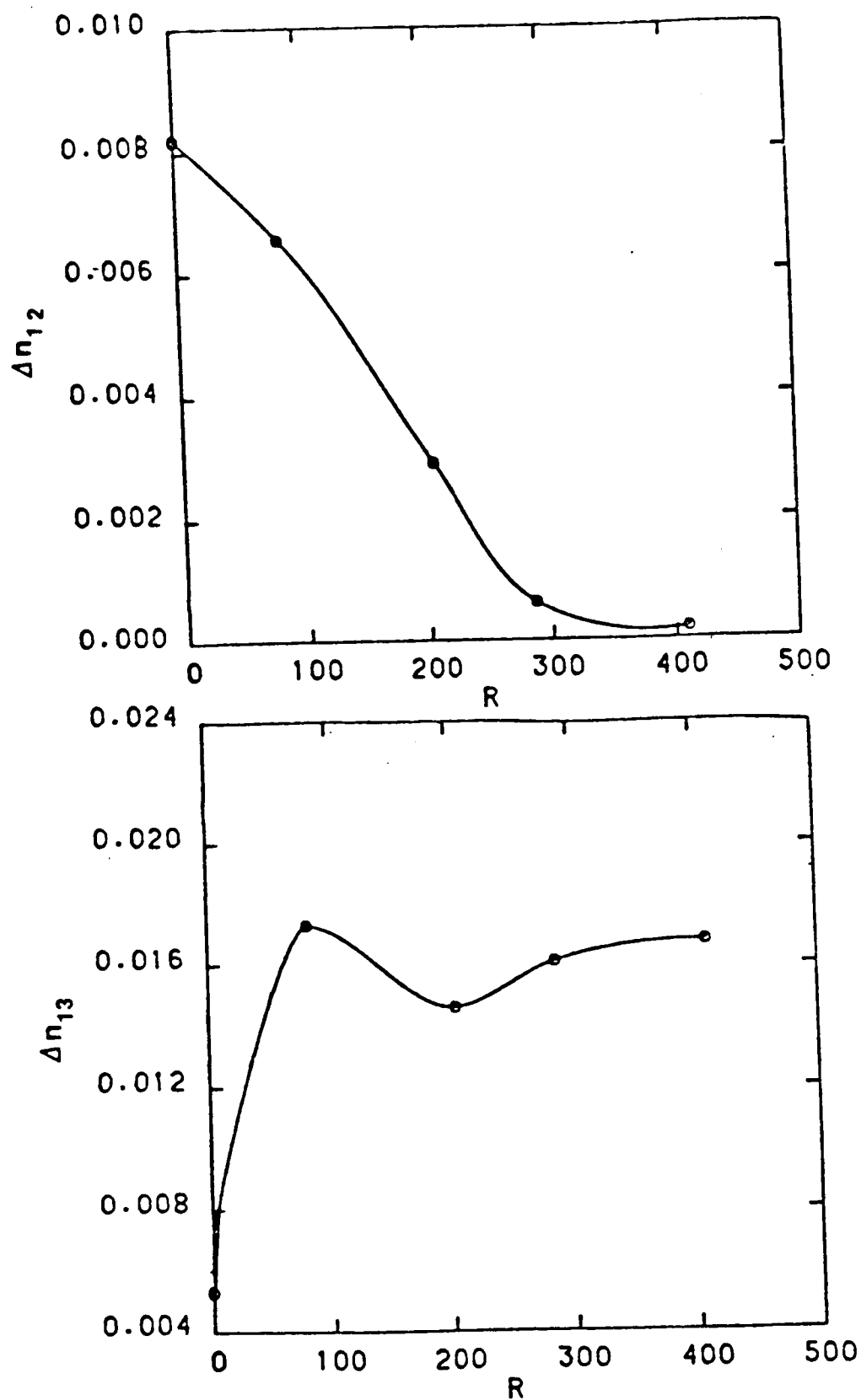


Figure V-9. Birefringences of HPC films.

Conclusions

Birefringence measurements show that the rotating annular die can greatly affect the overall polymer chain orientation. In the PS and PE extrudates, where the degree of preferential orientation was very low, the orientation decreased as R increased. It would seem that due to the short relaxation times and the slow cooling rates any preferential orientation induced by the die relaxed out.

The PE film exhibited behavior similar to the PE extrudates. Die rotation slightly decreased the preferential orientation in the films. Whereas the rotating annular die dramatically increased the biaxiality of the PS films. The blowing of the PS cooled the films at a rate which did not allow the preferential orientation produced in the die to relax completely.

The EC extrudates behaved quite differently than the PS and PE extrudates. The biaxiality of the EC tubes increased with R. The orientation generated in the die did not relax out as was the case for the PS and PE extrudates. This increased the biaxiality of the EC extrudates was also evident in the blown films.

The HPC tubes and films exhibited strikingly different behavior than that observed in PS, PE, or EC. The tubes and films were highly planar. A small amount of die rotation increased the tendency for the molecules to align in the

MD-TD plane. Any further increase in R had no effect on increasing this planar orientation, but redistributed the preferential orientation from the MD to the TD. The rotating annular die could change the orientation of the c-axis from highly biased in the machine direction to equal biaxial.

C. Wide Angle X-Ray Scattering Analysis

Polyethylene

The PE tubes and films did not possess enough preferential orientation to be easily evaluated through WAXS film patterns.

Figure V-10 shows the (200) and (110) pole figures for PE extrudates with $R = 0$. There is not a large amount of preferential orientation evident. These PE extrudates at $R = 0$ had biaxial orientation factors of $f_1^B = 0.086$ and $f_2^B = 0.026$. The (200) pole appears to be more concentrated in the MD-TD plane with an absence in the ND. The (110) is also concentrated in the MD-TD plane; more highly at some angle between the MD and TD planes. As one looks down the ND, there does not seem to be any preferential orientation of the (110). This suggests that the b-axis is preferentially oriented perpendicular to the plane of the film (ND) with the a and c-axes rotating randomly about the b-axis.

The pole figure for a PE extrudate with $R = 410$ (Figure V-11) is similar to that at $R = 0$. No conclusions could be drawn on the basis of the pole figures.

Table V-10 lists the White-Spruiell biaxial orientation factors at various values of R . The PE extrudates without die rotation had very low levels of preferential

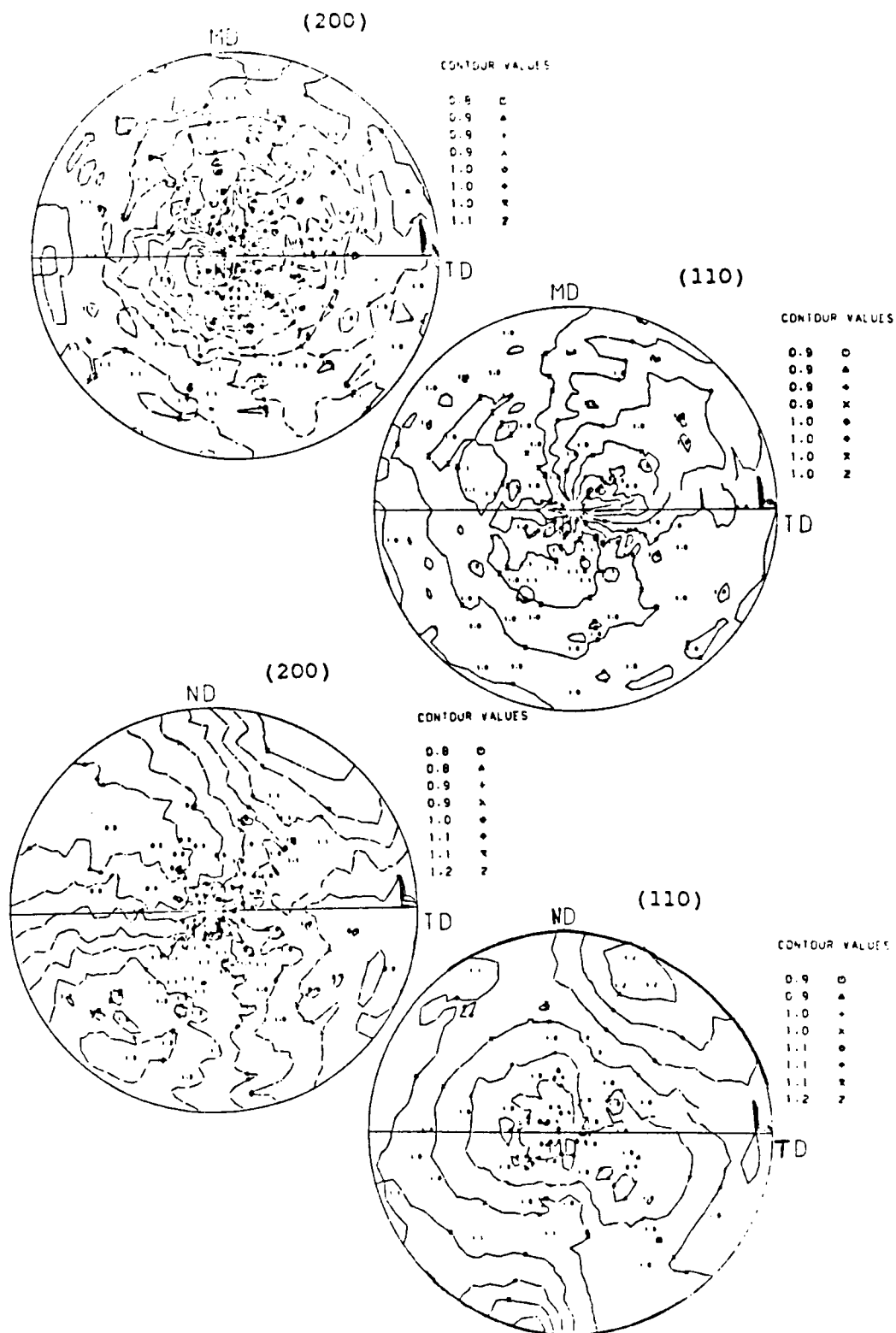


Figure V-10. (200) and (110) pole figures for PE extudates with $R = 0$.

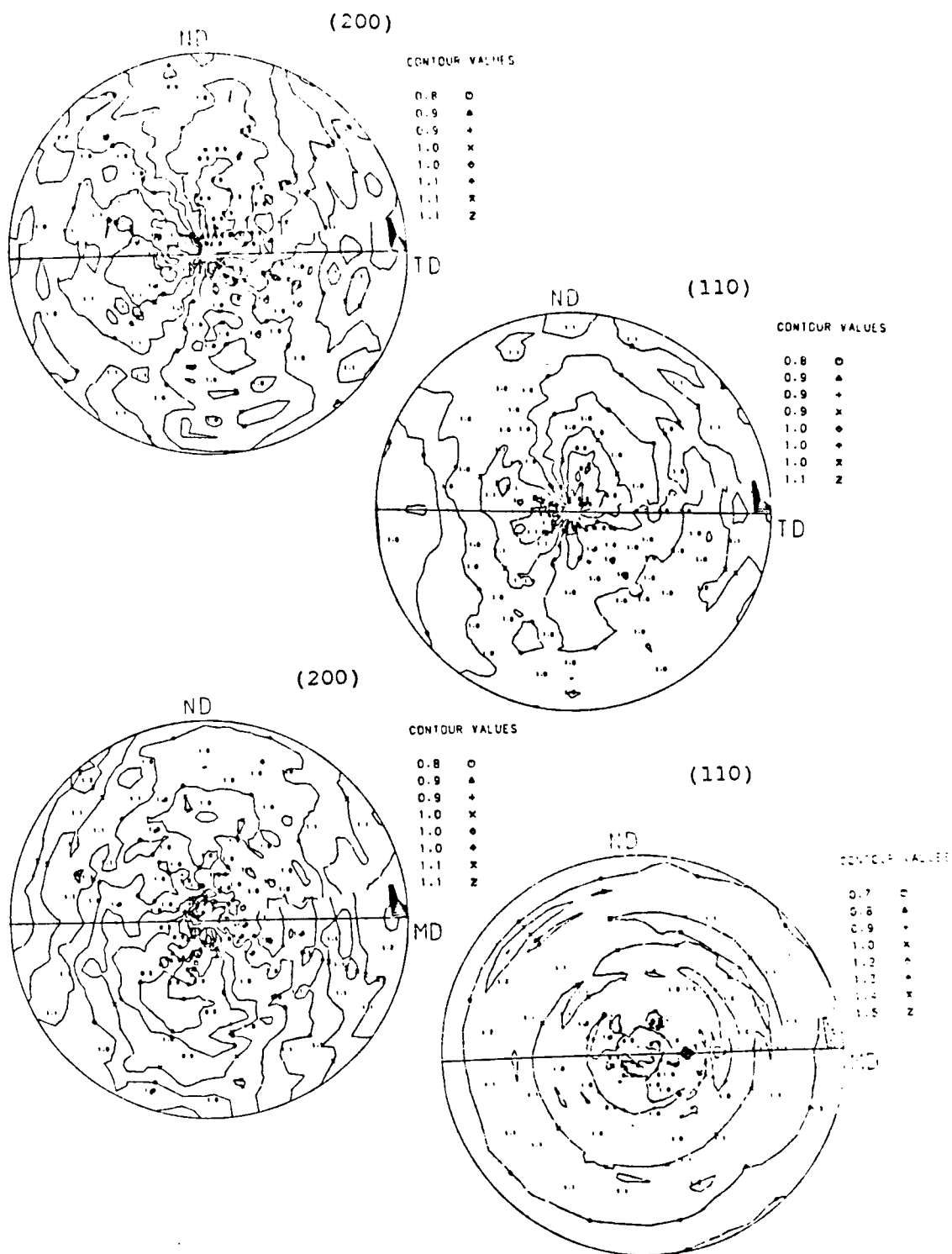


Figure V-11. (200) and (110) pole figures for PE extrudates with $R = 410$.

Table V-10. Orientation factors of PE extrudates.

R	$f_{1,c}$	$f_{2,c}$	$f_{1,a}$	$f_{2,a}$	$f_{1,b}$	$f_{2,b}$
0	0.086	0.026	-0.053	-0.055	-0.032	0.030
82	0.11	0.061	-0.060	-0.032	-0.047	-0.029
205	0.12	0.092	-0.055	-0.040	-0.068	-0.052
287	0.14	0.11	-0.073	-0.059	-0.066	-0.051
410	0.14	0.12	-0.055	-0.041	-0.087	-0.078

orientation. Die rotation increased the biaxiality of the PE extrudates. f_1^B increased from 0.086 at $R = 0$ to 0.14 at $R = 410$, while f_2^B increased from 0.026 to 0.12 at the same conditions. This effect is illustrated in figure V-12.

Figure V-13 pole figures show the PE blown films at $R = 0$ to be more highly oriented than the PE extrudates. The (200) pole is highly concentrated in the machine direction with an absence in the transverse direction. The (110) pole appears highly oriented at a slight angle between the MD and TD. The absence of reflections is much larger in the ND than the MD. Thus it would appear that the PE blown films have preferential orientation similar the extrudates but to a higher degree. The biaxial orientation factors f_1^B and f_2^B were 0.18 and 0.066, respectively. There was also an increased tendency for the b-axis to lie perpendicular to the thickness direction (ND).

There were subtle differences between the PE blown films at $R = 0$ and $R = 410$ (see figure V-14). The (200) plane is again concentrated in the MD and almost random about the ND-TD plane. The (110) was also randomly distributed about the ND-TD plane with an absence in the MD. There seems to be a slight decrease in the degree of preferential orientation.

Table V-11 lists the biaxial orientation factors of the PE blown films. The orientation factors were much higher

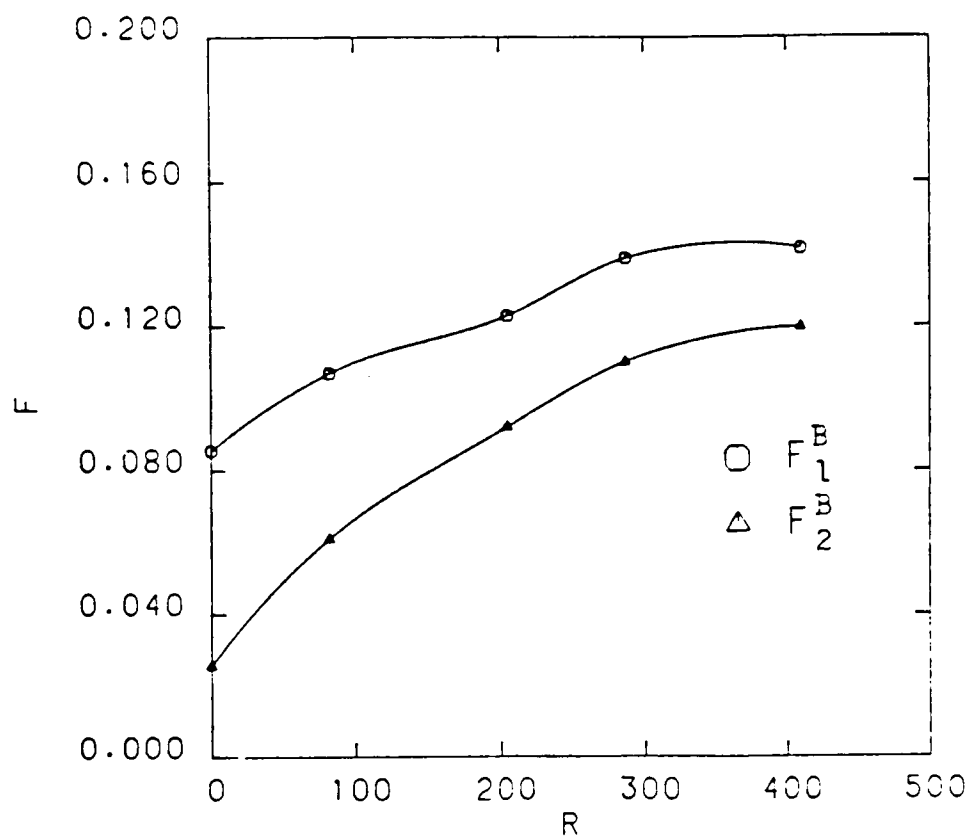


Figure V-12. Orientation factors of PE extrudates.

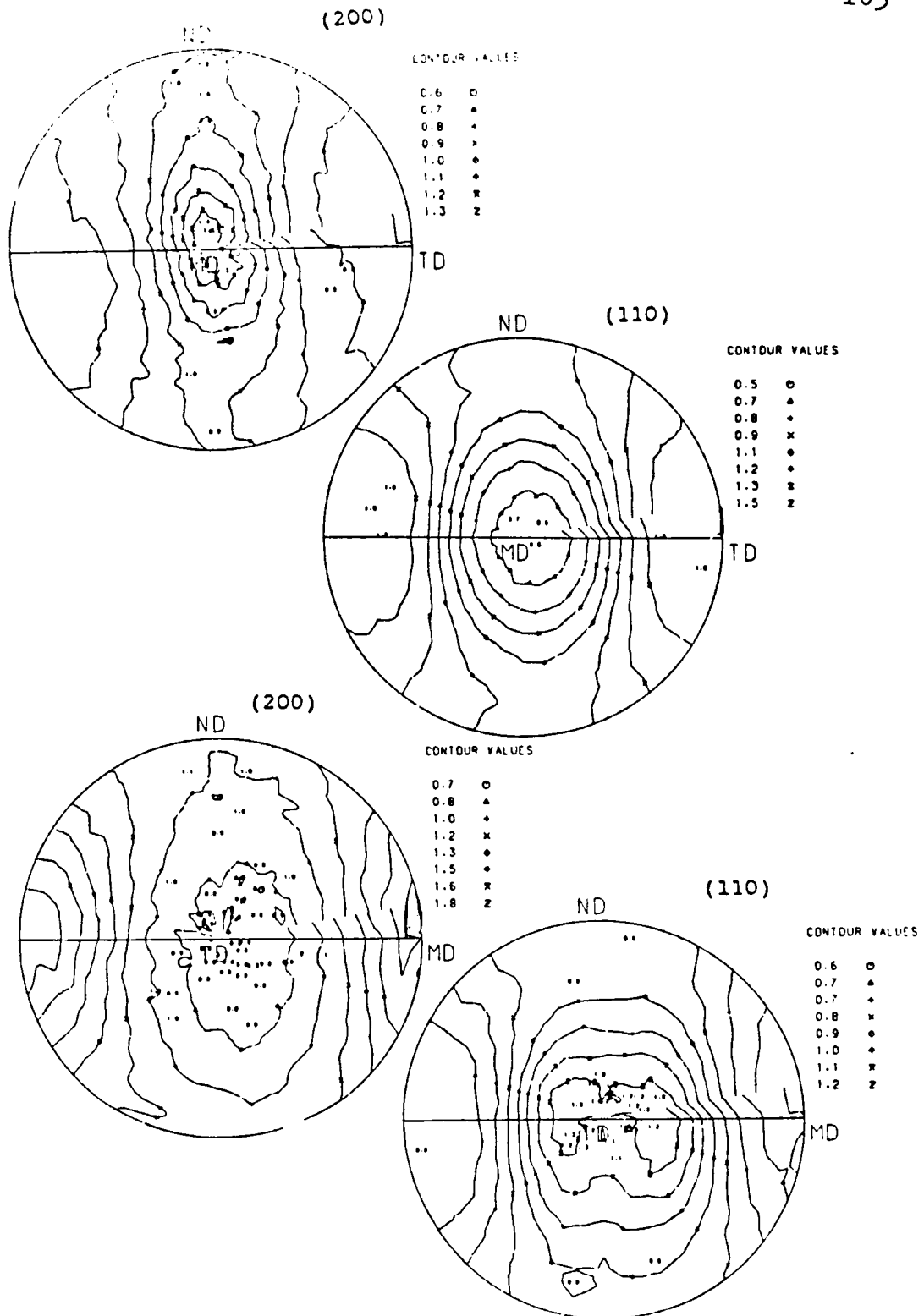


Figure V-13. (200) and (110) pole figures for PE blown film with $R = 0$.

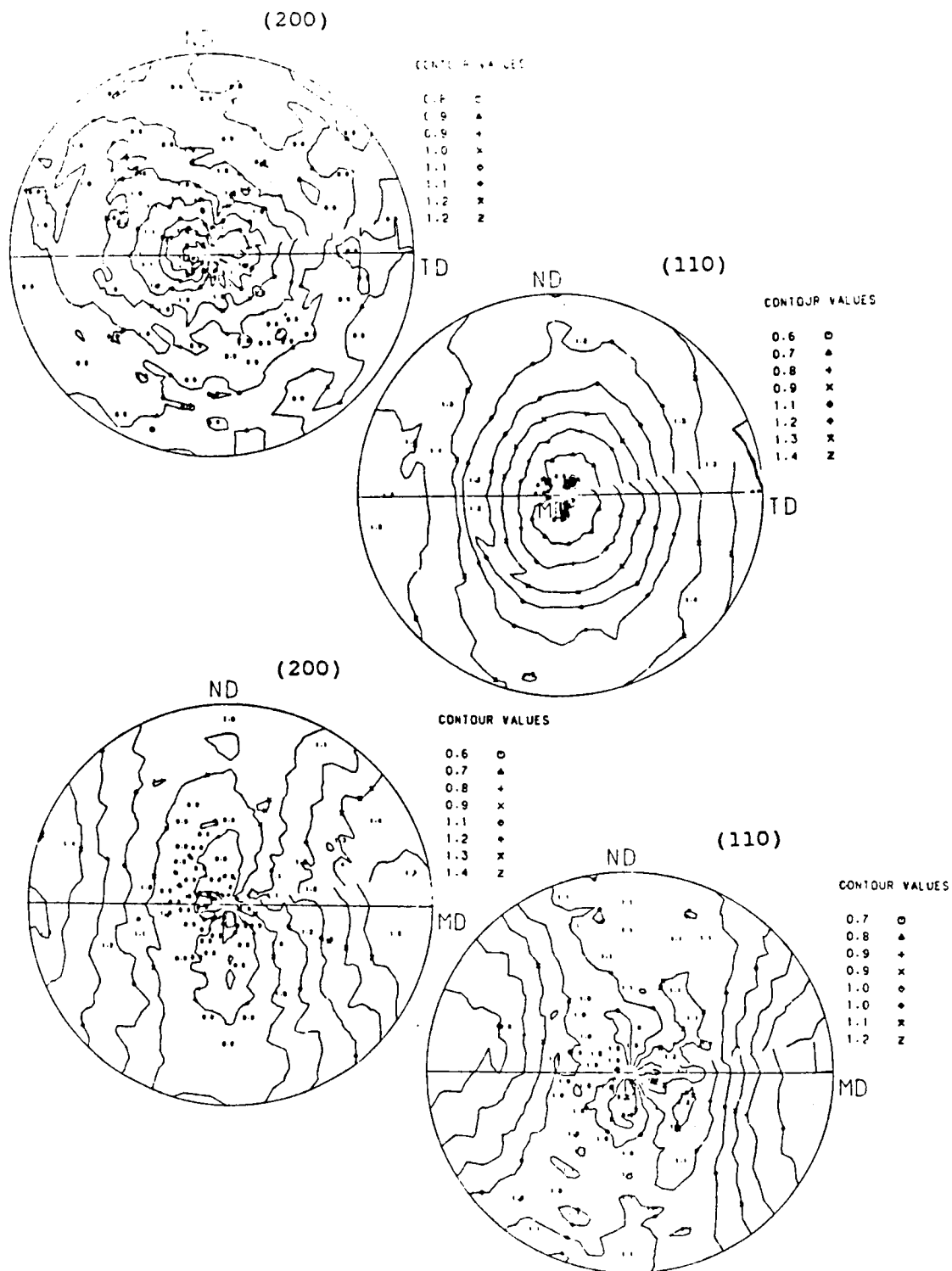


Figure V-14. (200) and (110) pole figures for PE blown films with $R = 410$.

Table V-11. Orientation factors of PE blown films.

R	$f_{1,c}$	$f_{2,c}$	$f_{1,a}$	$f_{2,a}$	$f_{1,b}$	$f_{2,b}$
0	0.18	0.066	-0.0017	-0.10	-0.18	0.034
82	0.16	0.13	0.0058	-0.024	-0.16	-0.11
205	0.15	0.15	-0.061	-0.057	-0.092	-0.093
287	0.17	0.14	-0.047	-0.077	-0.12	-0.060
410	0.14	0.17	-0.060	-0.068	-0.081	-0.11

for the PE films than the extrudates, indicating greater preferential orientation. There is a much greater tendency for the b-axis to lie perpendicular to the plane of the film. The c-axis distribution in the machine direction did not vary much with R, however the transverse direction biaxial orientation factor increased with die rotation (figure V-15). The tendency for the b-axis to lie perpendicular to the machine direction also increased with R. It would appear that a small amount of die rotation would be beneficial and that any more would not have much effect.

Hydroxypropyl cellulose

WAXS diffraction film patterns are a key qualitative indicator of molecular orientation for crystalline polymers. Figure V-16 shows how the molecular orientation of HPC extrudates respond to the various processing conditions available with the rotating annular die.

HPC has a tetragonal unit cell ($a = b$) with the strongest reflection being the (100) plane. The stronger c-axis reflections are hidden by the amorphous halo. The strong equatorial reflection in figure V-16 at $R = 0$ represents the (100) plane (a-axis). Since the a-axis reflection is highly concentrated in the transverse direction, we know that the c-axis is highly oriented in the

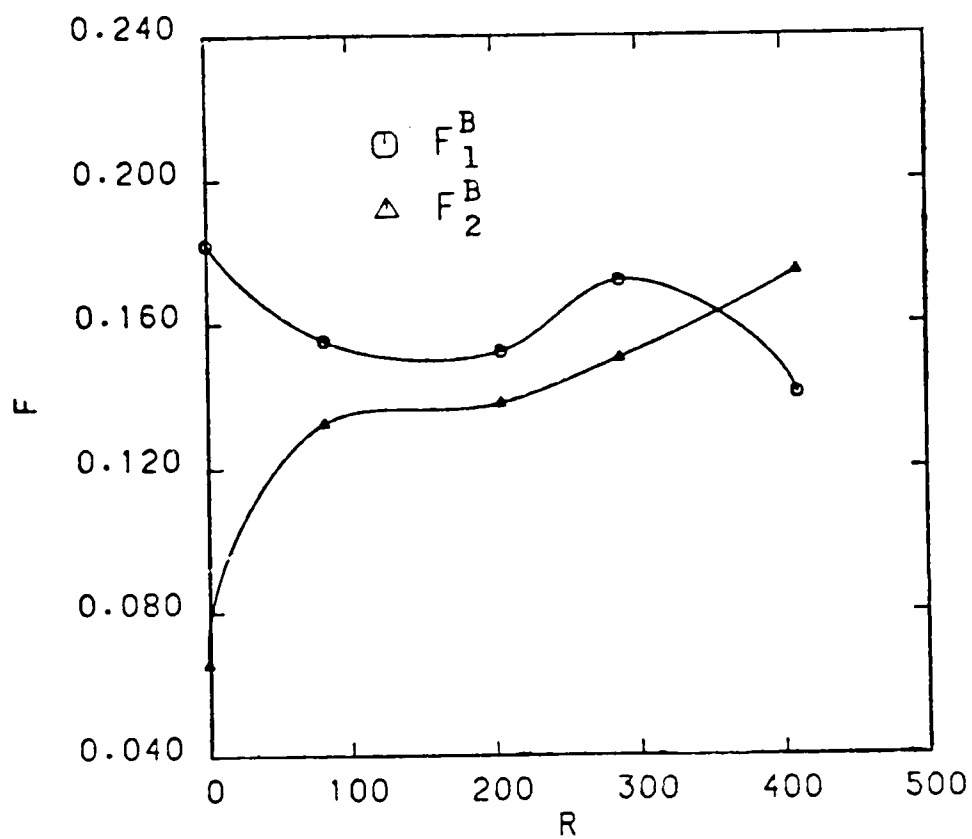


Figure V-15. Orientation factors of PE blown films.

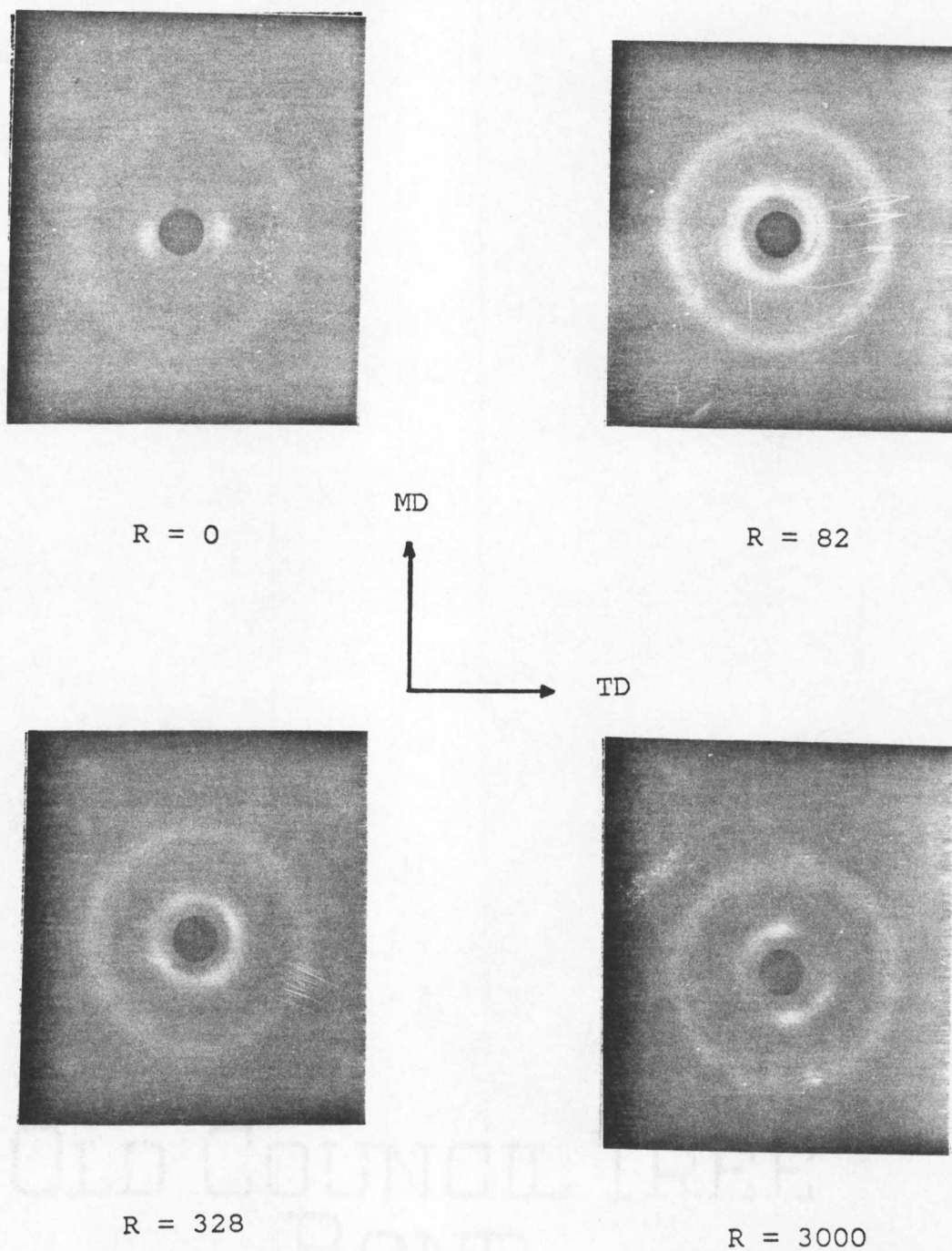


Figure V-16. WAXS patterns of HPC extrudates.

machine direction. Figure V-16 demonstrates the ability to rotate the polymer chain axis from the machine to transverse direction as R is increased. At $R = 82$ and $R = 328$, the strong equatorial reflection turns to a smear with a slightly higher intensity four-lobe pattern. This smear of intensity represents the variation in orientation with depth in the film due to varying shear rates. The four-lobe pattern is most likely a result of highly oriented tube walls with a different sense of twist.

$R = 3000$ represents an attempt to maximize the c-axis orientation by processing at a very slow extrusion rate and at the maximum die rotation speed. The film pattern shows that the shear occurring in the die has the ability to rotate the c-axis from the machine to predominately the transverse direction.

The WAXS patterns of the HPC films in figure V-17 are similar to the HPC extrudates in figure V-16. At $R = 0$, the c-axis is highly oriented in the machine direction. The blown film does not appear to be any more biaxial than the extrudate. The blown film at $R = 410$ shows the same character as the extrudates. The orientation established in the tubes is carried over to the films.

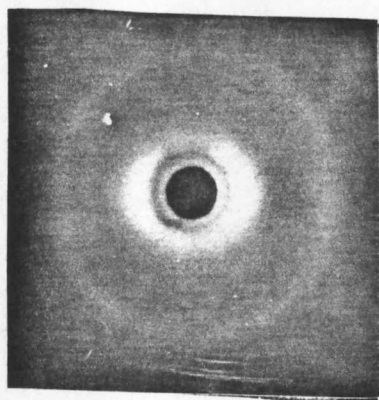
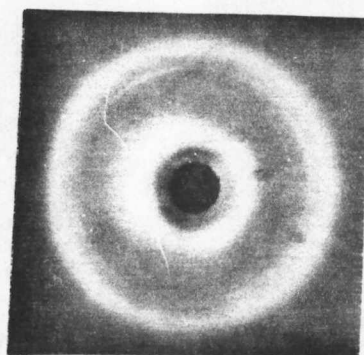
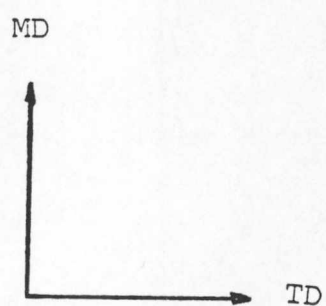
 $R = 0$  $R = 410$

Figure V-17. WAXS patterns of HPC films.

Pole figure analysis

Figure V-18 is the (100) pole figure for an HPC extrudate with $R = 0$. The a-axis is highly concentrated and symmetrically distributed in the ND-TD plane. There is also an absence of reflections in the machine direction. The biaxial orientation factors $f_1^B = 0.80$ and $f_2^B = 0.021$, again indicate the highly uniaxial orientation. The orientation is similar to that of a highly oriented fiber.

The (100) pole figure of an HPC extrudate with $R = 410$ is strikingly different than for $R = 0$. In figure V-19, one can see the concentration of a-axis reflections has shifted from the ND-TD plane toward the ND-MD plane. There is no longer an absence of (100) reflection in the machine direction. The machine direction biaxial orientation factor (f_1^B) has been changed from 0.80 to 0.39, while the transverse direction biaxial orientation factor (f_2^B) has increased from 0.021 to 0.61. The extrudate is still highly planar, however the c-axis orientation has changed from highly uniaxial in the machine direction to biased in the transverse direction.

We have shown that the rotating annular die can control the polymer chain orientation in HPC. Figure V-20 shows the (100) pole figure of an HPC extrudate with $R = 3000$. This represents an effort to maximize the c-axis transverse orientation and thus help determine the limitations of the

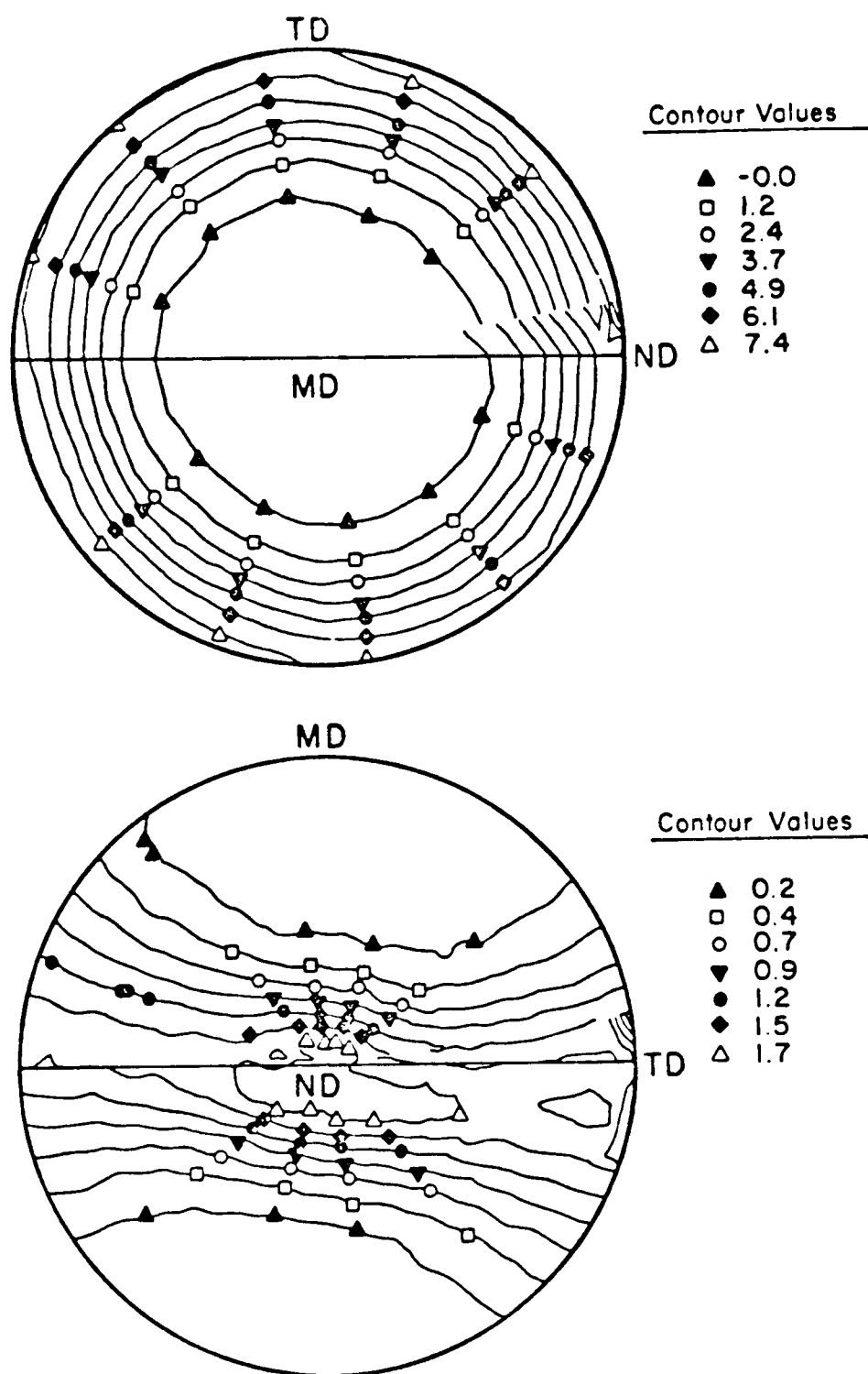


Figure V-18. (100) pole figures for HPC extrudates with $R = 0$.

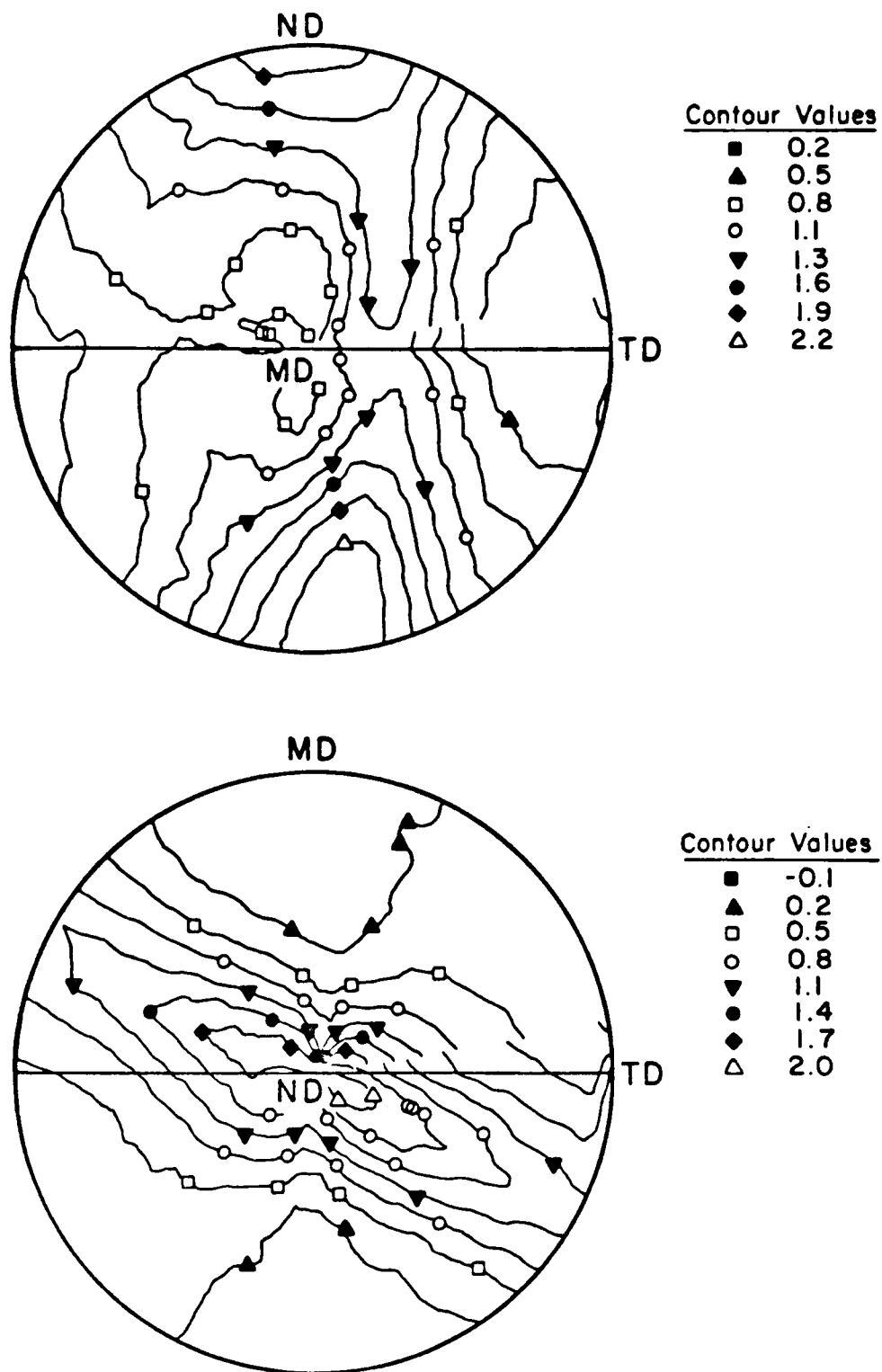


Figure IV-19. (100) pole figures for HPC extrudates with $R = 410$.

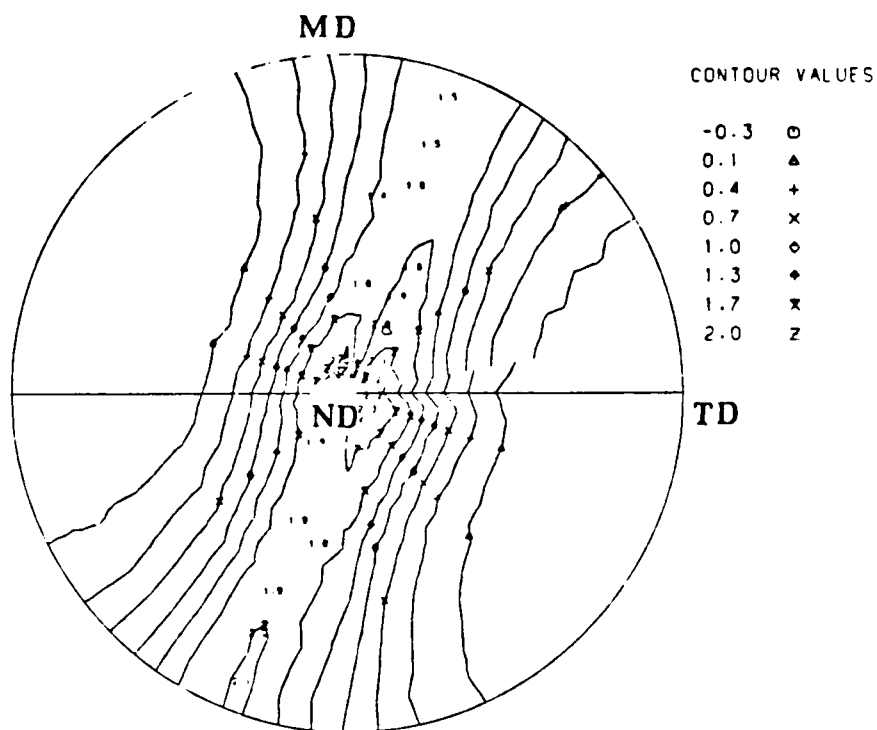
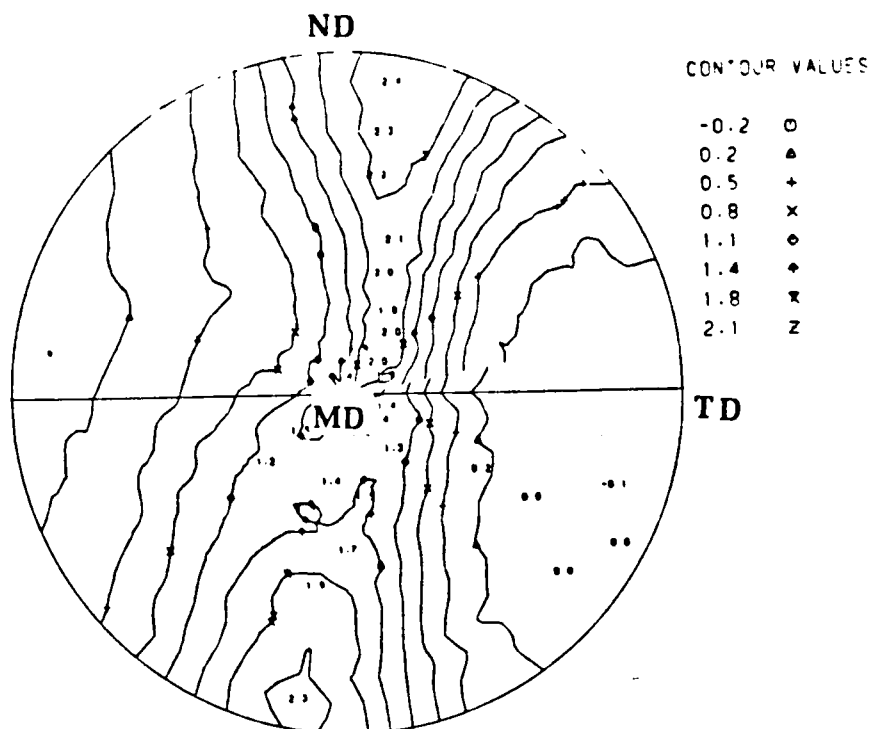


Figure V-20. (100) pole figures for HPC extrudates with
R = 3000.

process. The pole figure at $R = 3000$ is very similar to $R = 0$ (figure V-18) if the MD and TD directions are reversed. The White-Spruiell biaxial orientation factors for the sample are $f_1^B = 0.17$ and $f_2^B = 0.71$. The c-axis for $R = 3000$ is highly oriented in the transverse direction.

HPC blown films

The (100) pole figure for an HPC blown film is indistinguishable from an HPC extrudate at $R = 0$. Figure V-18 for an HPC extrudate would also be representative of an HPC blown film. The mechanical deformation of the film blowing process does not have much effect on increasing the polymer chain orientation in the transverse direction. The biaxial orientation factors change from $f_1^B = 0.80$ and $f_2^B = 0.021$ to $f_1^B = 0.71$ and $f_2^B = 0.059$ upon the expansion of the tubes. The HPC films are highly uniaxial in the machine direction.

Figure V-21 of the (100) pole figure of an HPC blown film with $R = 82$ shows the film to still be highly uniaxial. However, one can see that the closely spaced contour lines at $R = 0$ have spread further apart at $R = 82$. The rotating annular die has decreased the uniaxial character of the film. This observation is substantiated in that the biaxial orientation factors are now $f_1^B = 0.69$ and $f_2^B = 0.22$.

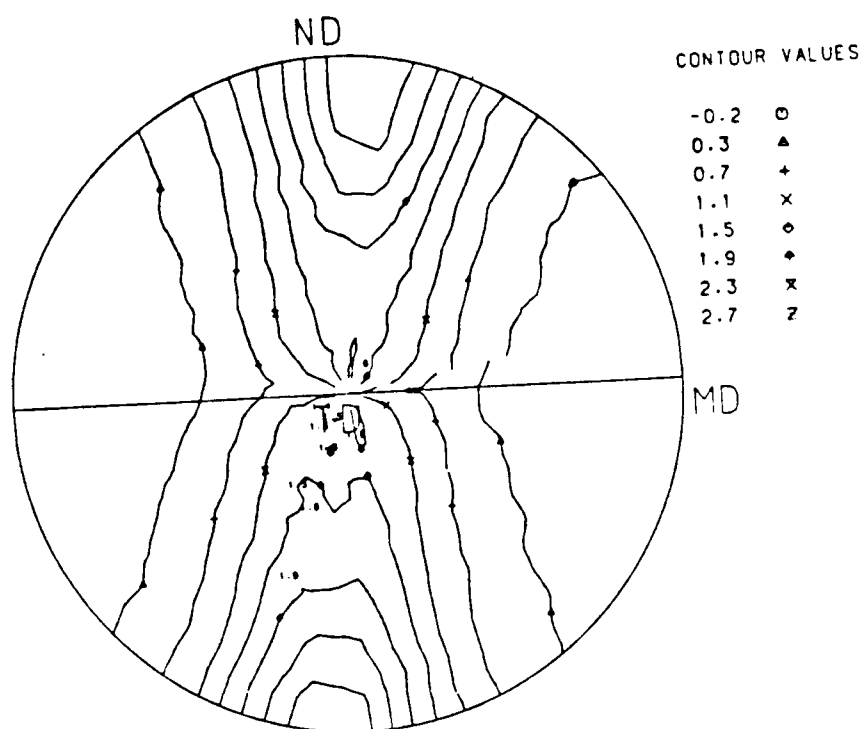
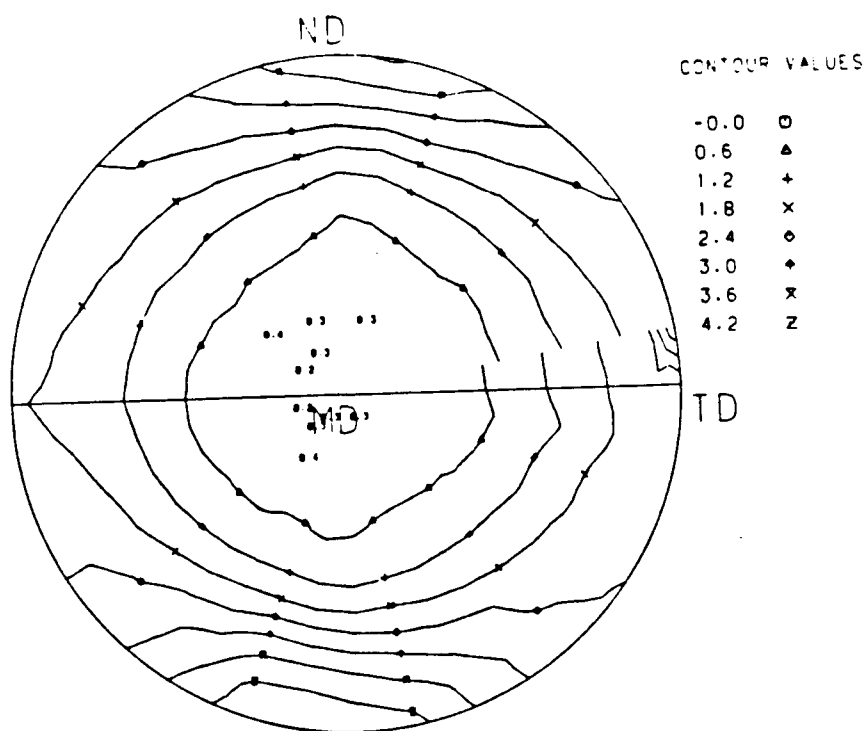


Figure V-21. (100) pole figures for HPC blown film with
R = 82.

At $R = 205$ (Figure V-22), the (100) pole figure shows further rotation of the a-axis from the transverse direction to the machine direction. The biaxial orientation factors for this sample are $f = 0.68$ and $f = 0.31$.

Figure V-23 is the (100) pole figure for an HPC blown film with $R = 287$. The a-axis appears to be only slightly more concentrated in the transverse direction than in the machine direction. The biaxial orientation factors for the sample are $f = 0.55$ and $f = 0.41$.

Table V-12 and table V-13 list the White-Spruiell biaxial orientation factors as a function of R for the HPC extrudates and blown films. Figure V-24 summarizes these results. The HPC extrudates and films were highly planar. As R is increased, the c-axis moves from highly uniaxial in the machine direction, past equibiaxial, to preferential orientation in the transverse direction.

An attempt was made to determine the amorphous orientation factors from the x-ray and birefringence data. However, due to the uncertainty of the intrinsic birefringences, these results are viewed as unreliable (see Appendix).

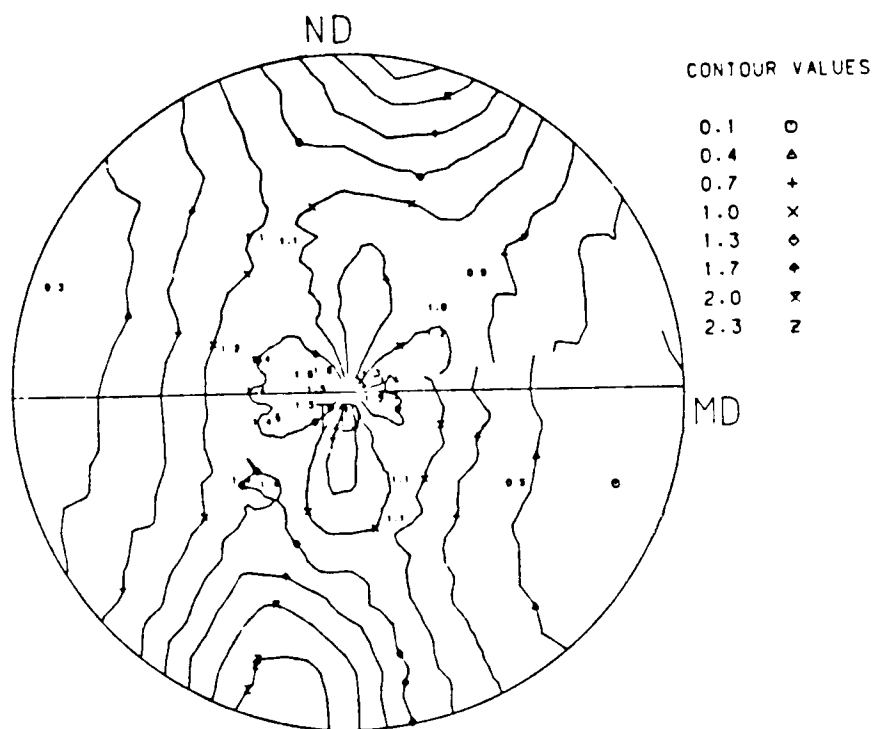
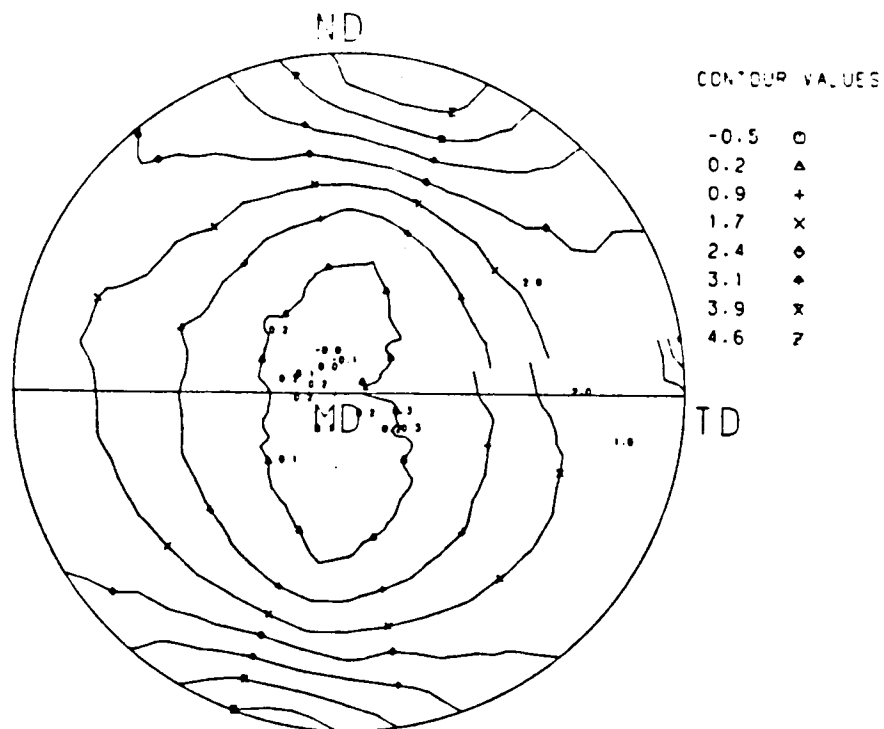


Figure V-22. (100) pole figures for HPC blown film with
R = 205.

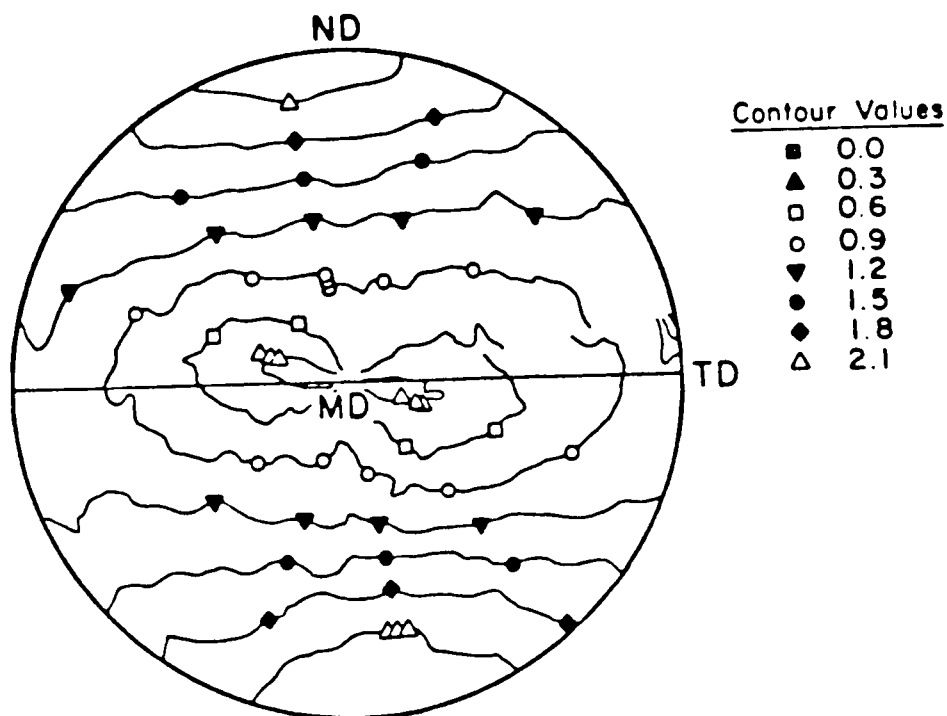
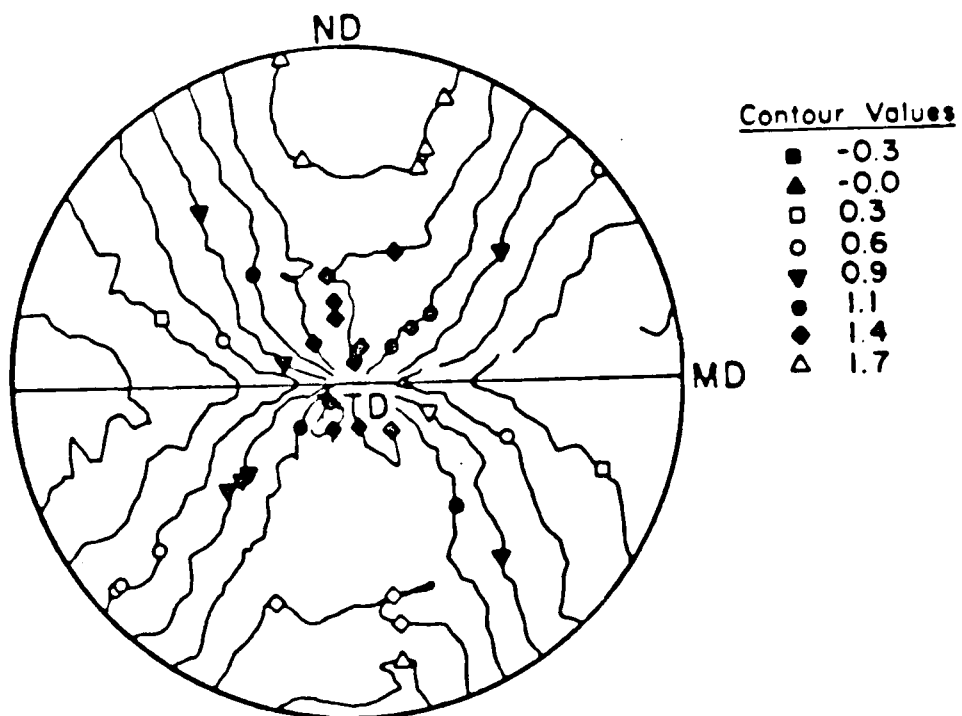


Figure V-23. (100) pole figures for HPC blown film with $R = 287$.

Table V-12. Orientation factors of HPC extrudates.

R	f_1^B	f_2^B
0	0.80	0.021
123	0.68	0.11
246	0.60	0.32
328	0.45	0.55
410	0.39	0.61
3000	0.17	0.71

Table V-13. Orientation factors of HPC blown film.

R	f_1^B	f_2^B
0	0.71	0.059
82	0.69	0.22
205	0.68	0.31
287	0.55	0.41
401	0.41	0.59

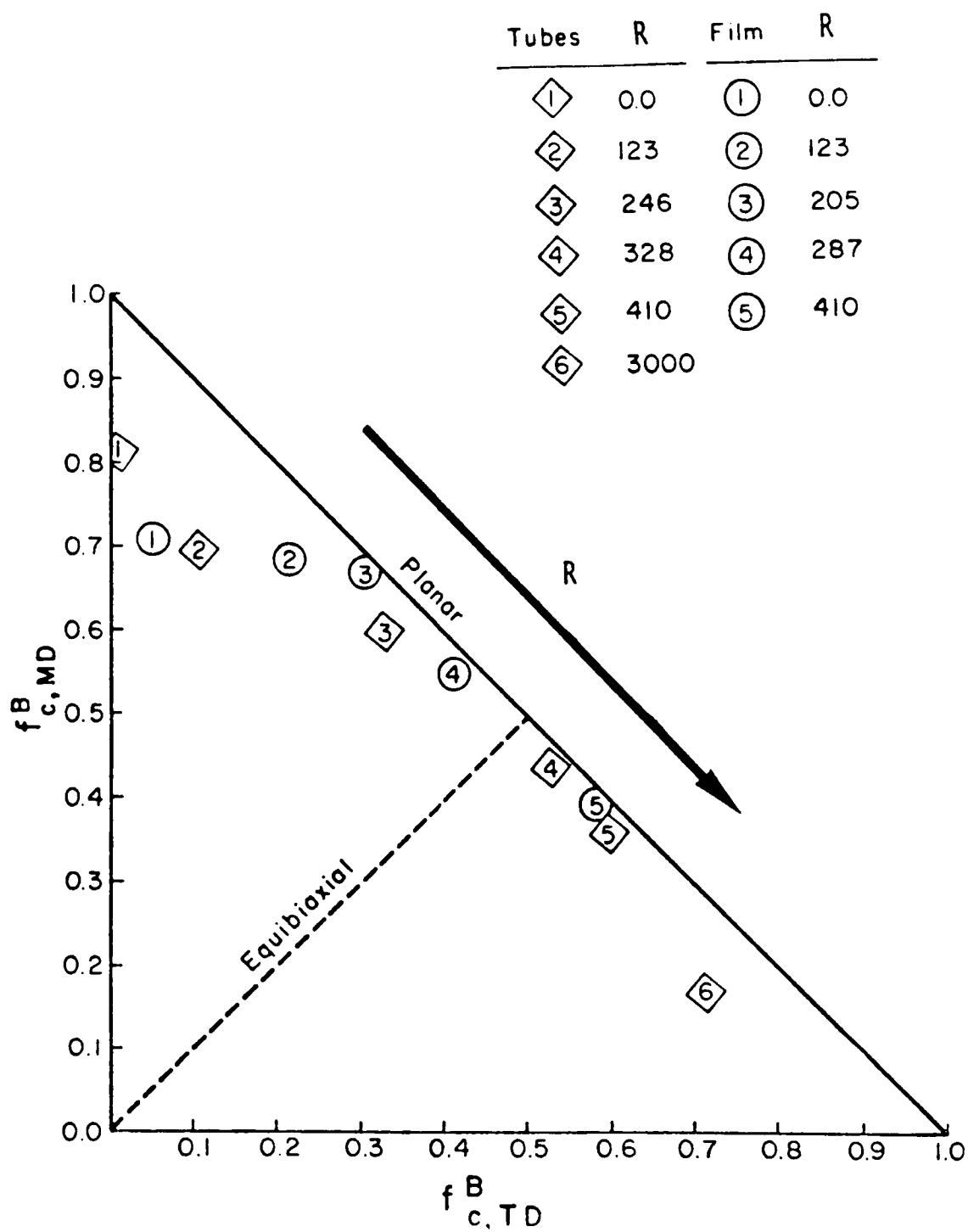


Figure V-24. Orientation factors of HPC extrudates and films.

Skin formation

The EC and HPC extrudates exhibited a skin formation. The skin of these extrudates could easily be delaminated from the bulk sample. Table V-14 summarizes the character of this outer layer for extrudates with $R = 0$. The skin of the EC extrudates was more highly birefringent than the core. Δn_{12} was 4.7×10^{-5} for the core and 5.9×10^{-5} for the skin. The in and out of plane birefringence (Δn_{13}) was 7.6×10^{-3} for the core and 2.4×10^{-2} for the skin. Thus the skin was much more highly oriented in the machine direction.

X-ray determination of the biaxial orientation factors in the HPC samples also revealed a highly oriented skin. The machine direction biaxial orientation factor (f_1^B) was 0.80 for the core and 0.90 for the skin.

This highly oriented skin is believed to result from the higher shear stresses developed at the die wall and the rapid cooling rate of the tube surface.

Delamination of tubes with die rotation

The HPC tubes extruded with die rotation delaminated upon fracture. Table V-15 describes a delaminated HPC tube with $R = 410$. The sample fractured into three layers. The outer layer was 0.021 cm thick. The birefringence between the machine and transverse directions was 9.2×10^{-5} . The maximum birefringence of the sample occurred between the

Table V-14. Skin-core structure of cellulose ethers

ETHYL CELLULOSE

NO ROTATION	$\Delta n_{12} \times 10^5$	$\Delta n_{13} \times 10^3$	$\Delta n_{32} \times 10^3$
CORE	4.7	7.6	-7.6
SKIN	5.9	24.0	-24.0

HPC

NO ROTATION	f_1^B	f_2^B
CORE	0.80	0.21
SKIN	0.90	0.02

Table V-15. Delaminated HPC tube with R = 410.

OUTER LAYER (THICKNESS = 0.021 CM)

DIE MARKS 45 DEGREES OFF MD

$$\Delta n_{12} = 9.2 \times 10^{-5}$$

$$\Delta n_{\text{Max}} = 4.4 \times 10^{-3} \quad 35^\circ$$

MIDDLE LAYER (THICKNESS = 0.020 CM)

NO DIE MARKS

$$\Delta n_{12} = -9.1 \times 10^{-5}$$

$$\Delta n_{\text{Max}} = 7.9 \times 10^{-3} \quad 45^\circ$$

INNER LAYER (THICKNESS = 0.104 CM)

$$\Delta n_{12} = -1.9 \times 10^{-5}$$

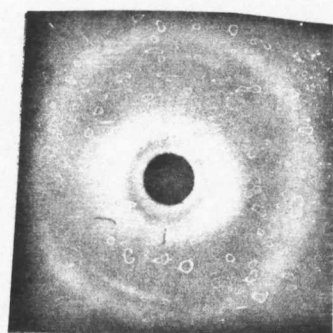
$$\Delta n_{\text{Max}} = 8.7 \times 10^{-4} \quad 45^\circ$$

directions parallel and perpendicular to the die marks. When the sample was rotated 35 degrees, the birefringence increased to 4.4×10^{-3} . Thus it appears that the outer layer is highly uniaxially oriented 35 degrees between the machine and transverse directions.

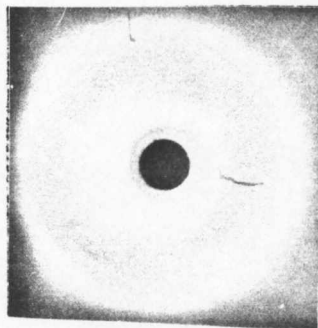
The middle layer was 0.0198 cm in thickness and was very similar to the outer layer. Δn_{12} was 7.9×10^{-3} . This indicates that the c-axes are more preferentially oriented in the transverse direction in this middle layer than in the outer layer. The maximum birefringence occurred when the sample was rotated about 45 degrees. Δn_{12} was 9.1×10^{-5} .

The inner layer of the extrudate was 0.104 cm thick, much thicker than the previous two layers. The birefringence between the machine and transverse directions was -1.9×10^{-5} . Thus there was a slight preferential orientation in the transverse direction.

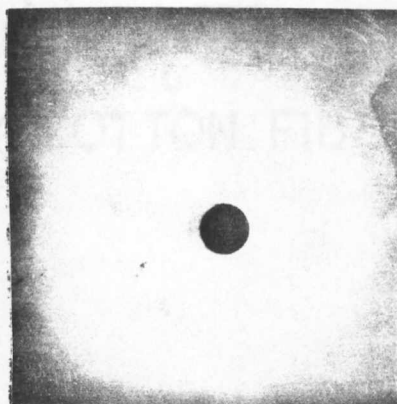
Figure V-25 shows the WAXS film patterns of the delaminated HPC extrudate with $R = 410$. The WAXS pattern of the outer layer shows the a-axis to be highly oriented 30 degrees off the transverse direction, thus the c-axis is highly oriented 30 degrees from the machine direction. The WAXS pattern of the middle layer of the delaminated tube show the a-axis to be highly oriented about 45 degrees from the machine and transverse directions. Thus the middle layer is more highly oriented toward the transverse



Outer layer



Middle layer



Inner layer

Figure V-25. WAXS film patterns of delaminated HPC extrudate with $R = 410$.

direction than the outer layer. The thicker inner layer shows the four lobed pattern observed for the bulk sample.

Figure V-26 shows the (100) pole of the outer layer of the HPC extrudate to be highly concentrated in a plane from the ND to a direction between the MD and TD. Thus the c-axis is highly uniaxial in a direction between the machine and transverse directions.

In figure V-27, one sees that the (100) pole has moved toward the machine direction. The c-axis in this layer is more highly oriented in the transverse direction.

Figure V-28 of the (100) pole of the thick inner layer of the tube is similar to the HPC extrudate at $R = 410$.

Table V-16 lists the biaxial orientation factors of the layers of the HPC extrudate. Again it is shown that the outer layer is not as highly oriented toward the transverse direction as the middle layer. This would indicate a complicated velocity profile. The outer layer of the extrudate would appear to be sticking to the die surface.

Conclusions

The effect of the rotating annular die on the molecular orientation of the PE tubes and films is unclear. The PE tubes and films produced by the process showed very low levels of preferential orientation. Birefringence studies

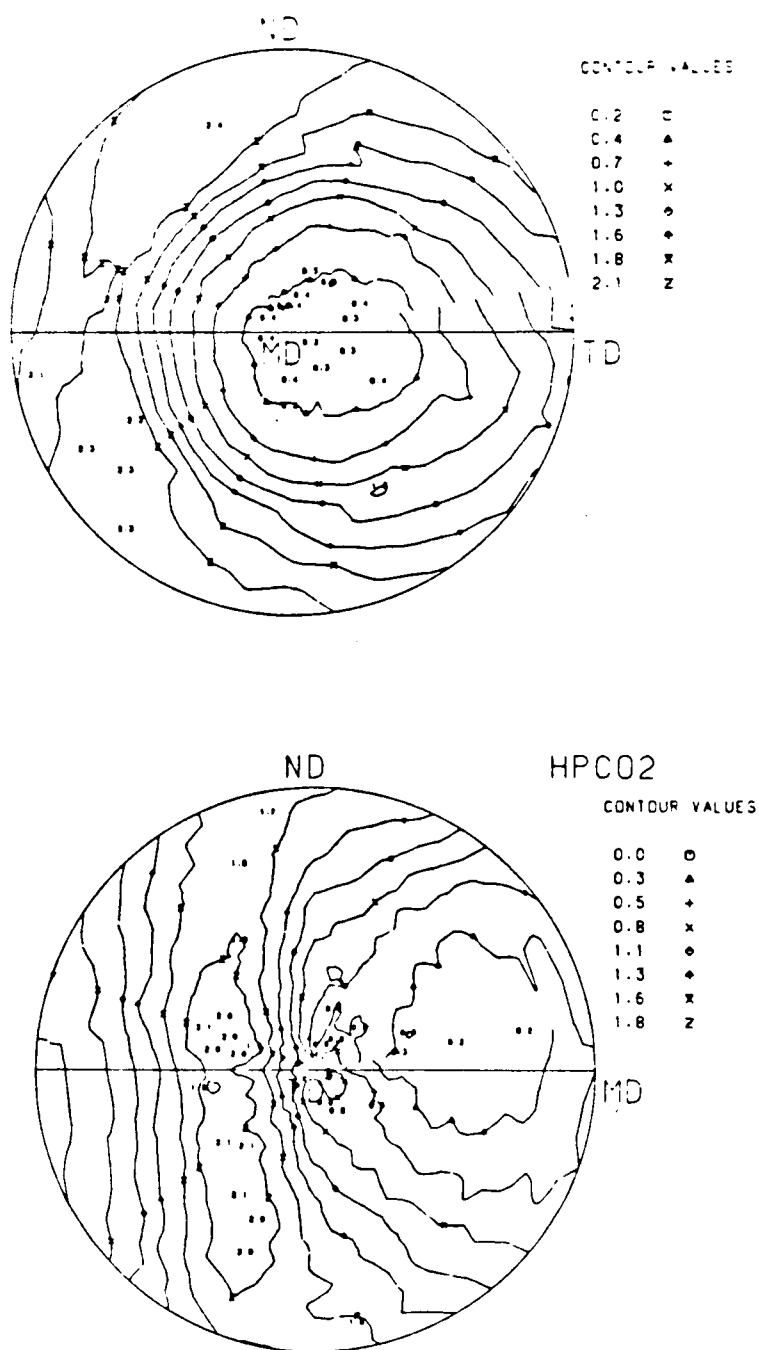


Figure V-26. (100) pole figures for the outer layer of HPC extrudate.

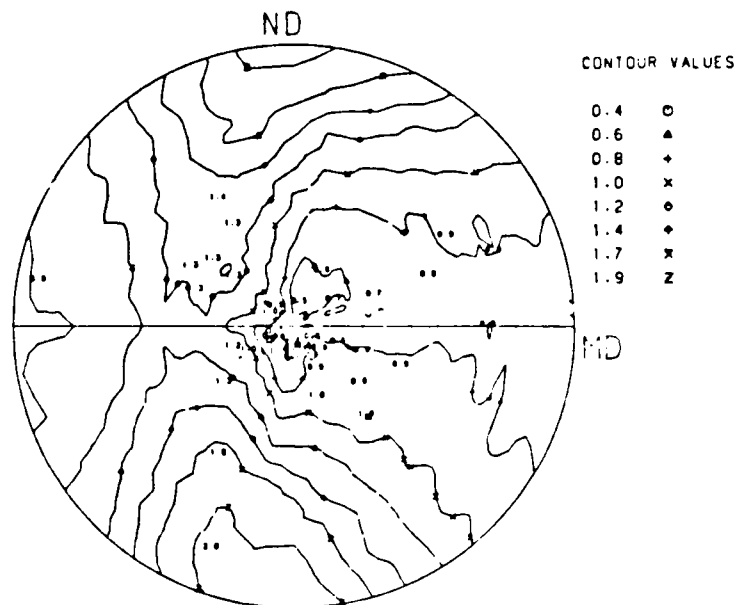
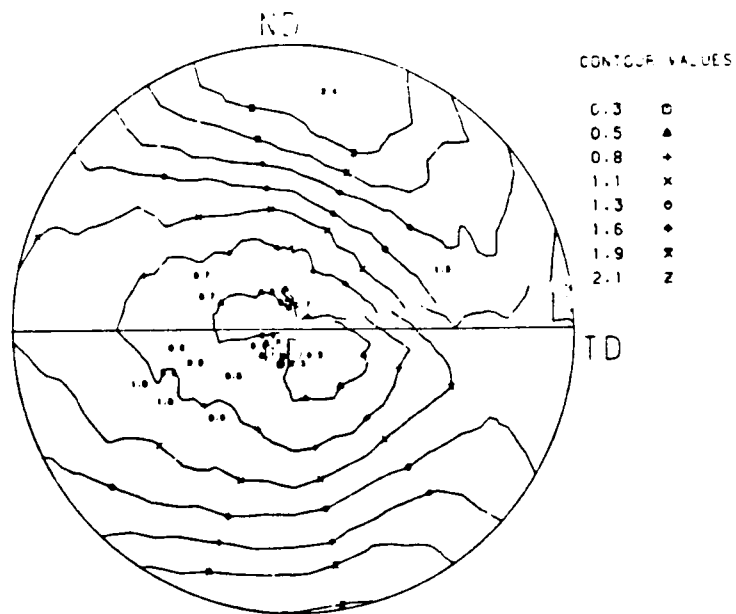


Figure V-27. (100) pole figures for the middle layer of HPC extrudate with $R = 410$.

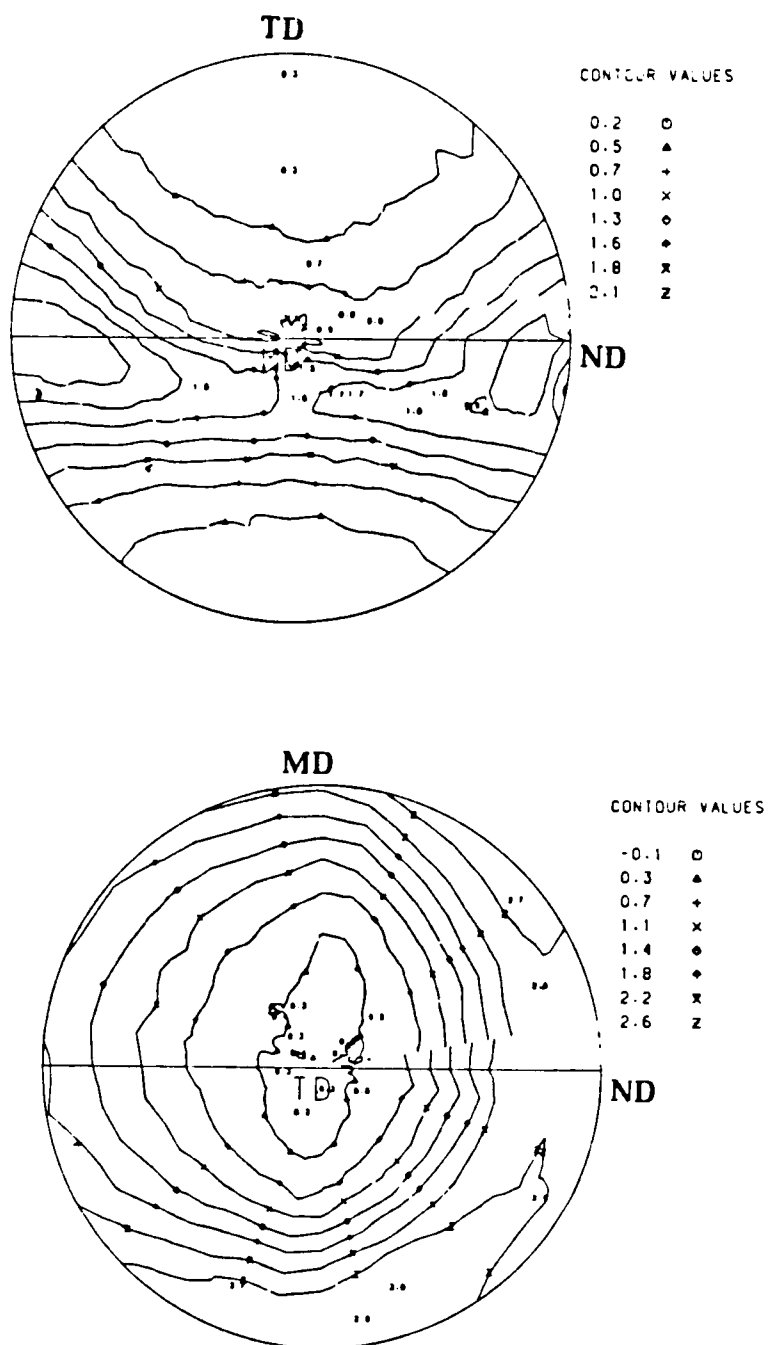


Figure V-28. (100) pole figures for the inner layer of HPC extrudate with $R = 410$.

Table IV-16. Orientation factors of delaminated HPC extrudate.

	f_1^B	f_2^B
Outer layer	0.59	0.33
Middle layer	0.53	0.42
Inner layer	0.30	0.68

indicate that the rotating annular die reduces the overall level of preferential orientation.

Wide angle x-ray scattering analysis of PE has shown that die rotation increases the tendency for the c-axis to lie in the transverse and machine directions. f_1^B and f_2^B increased with R for the PE extrudates, while for the PE blown films f_1^B was unchanged and f_2^B increased. The rotating annular die increases the biaxiality of the crystalline regions of the PE tubes and films. It appears that the increase in preferential crystalline orientation occurs at the expense of the amorphous phase.

The rotating annular die had a much greater effect on the orientation in HPC than was observed for PE. The extrudates and films produced without die rotation were highly uniaxial. WAXS film patterns, pole figure analysis, and biaxial orientation functions demonstrate the ability to rotate the c-axis from the machine direction to the transverse direction.

CHAPTER VI

MECHANICAL PROPERTIES OF BLOWN FILMS

A. Introduction

In this chapter the results of our investigations on the mechanical properties of the blown films are reported. Young's modulus, tensile strength, and elongation at break were measured for PE, PS, HPC, and EC blown films to study the effect of die rotation.

The mechanical properties were determined for samples 2.54 cm in length and 0.635 cm wide. The samples were tested at cross head speeds of 2 mm per minute for HPC, EC, and PS, while PE was tested at 50 mm per minute.

The HPC, EC, and PS films exhibited an elastic-brittle response with a small elongation to break. The PE films exhibited an elastic response to loading followed by yielding and ductile necking followed by a post-neck drawing regime.

B. Hydroxypropyl Cellulose

Table VI-1 shows the mechanical properties of the HPC blown films were significantly affected by the rotating annular die. An HPC blown film without die rotation is highly biased in the machine direction with respect to mechanical properties. For an HPC blown film with $R = 0$,

Table VI-1. Modulus of HPC blown films.

R=0	MODULUS (MPA)
MD	1370 $\pm$ 310
30 OFF MD	795 $\pm$ 163
45 OFF MD	708 $\pm$ 76
60 OFF MD	342 $\pm$ 94
TD	239 $\pm$ 27

R=205	MODULUS (MPA)
MD	1070 $\pm$ 156
30 OFF MD	952 $\pm$ 145
45 OFF MD	871 $\pm$ 142
60 OFF MD	559 $\pm$ 65
TD	491 $\pm$ 60

R=410	MODULUS (MPA)
MD	656 $\pm$ 82
30 OFF MD	744 $\pm$ 89
45 OFF MD	996 $\pm$ 162
60 OFF MD	1160 $\pm$ 148
TD	1000 $\pm$ 233

the modulus ranged from 1370 MPa in the machine direction to 239 MPa in the transverse direction. At $R = 205$, the modulus in the machine direction decreased to 1070 MPa, while the modulus in the transverse direction increased to 491 MPa. Further die rotation ($R = 410$) will decrease the modulus in the machine direction to 656 MPa. At $R = 410$, the transverse direction modulus increased from 239 to 1000 MPa. The effect of die rotation on the moduli is illustrated in figure VI-1.

As observed in table VI-2 and figure VI-2, the effect of die rotation on the stress to break of the HPC blown film is similar to that observed for the modulus. For a blown film without die rotation, the stress to break was relatively high in the machine direction (24.6 MPa) and much lower in the transverse direction (3.82 MPa). One can see that as R is changed from 0 to 410, the stress to break changes from highly biased in the machine direction to slightly biased in the transverse direction. The stress to break in the machine direction ranged from 24.6 MPa at $R = 0$, to 14.0 MPa at $R = 410$. While the stress to break in the transverse direction was increased from 3.82 MPa at $R = 0$ to 18.9 MPa at $R = 410$.

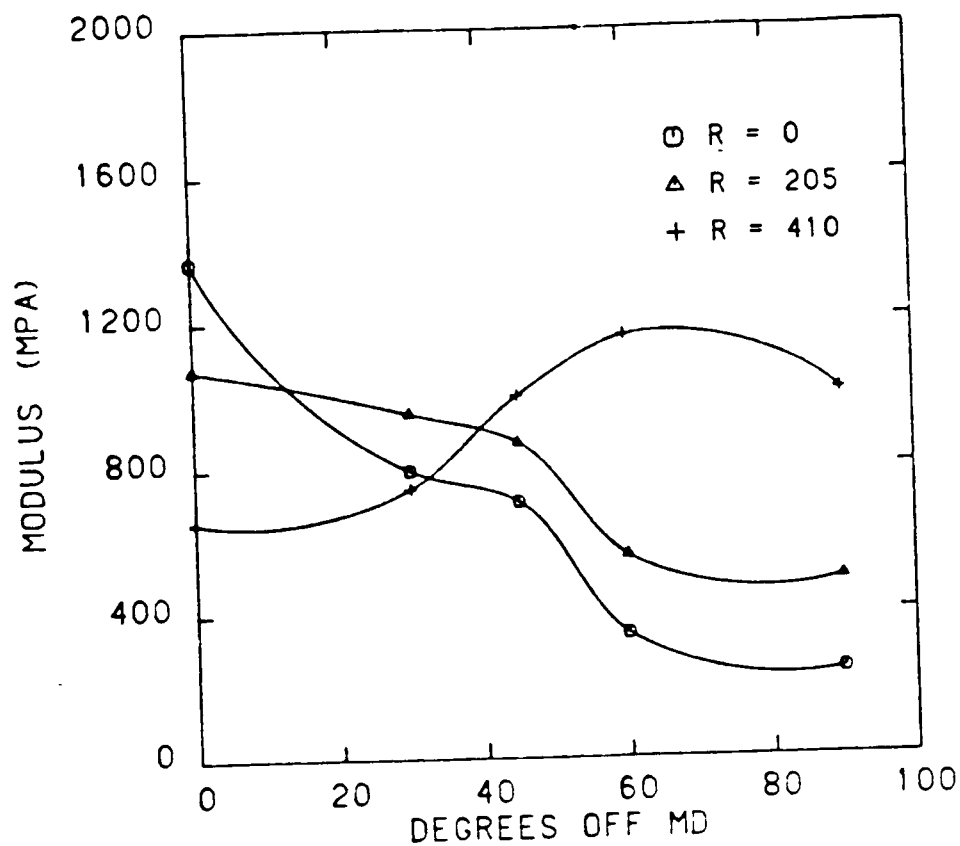


Figure VI-1. Modulus of HPC blown films.

Table VI-2. Stress to break of HPC blown films.

R=0	STRESS TO BREAK (MPA)
MD	24.6 ± 3.59
30 OFF MD	15.1 ± 3.58
45 OFF MD	11.5 ± 1.65
60 OFF MD	5.87 ± 1.93
TD	3.82 ± 0.81

R=410	STRESS TO BREAK (MPA)
MD	14.0 ± 3.2
30 OFF MD	17.4 ± 1.9
45 OFF MD	16.7 ± 1.2
60 OFF MD	22.5 ± 5.4
TD	18.9 ± 4.5

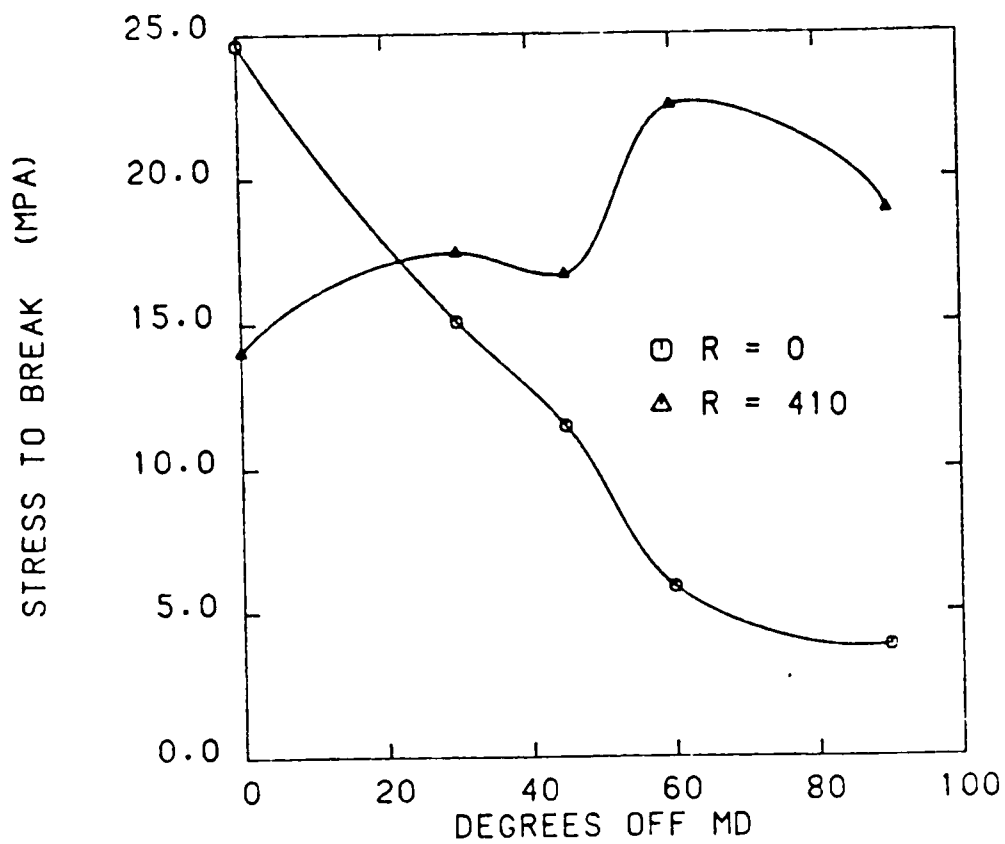


Figure VI-2. Stress to break of HPC blown films.

The elongation at break varied significantly, such that no conclusion as to the effect of die rotation could be made. The strain to break for the HPC films ranged from 0.011 to 0.061.

C. Ethyl Cellulose

The rotating annular die had a similar effect on the mechanical properties of EC as HPC, although this effect was not as marked. As was the case with HPC, the EC films at $R = 0$ were highly biased in the machine direction with respect to mechanical properties. For a blown film without die rotation, the modulus ranged from 1760 MPa in the machine direction to 1040 MPa in the transverse direction. At $R = 410$ these moduli changed to 1140 MPa in the machine direction and 1350 MPa in the transverse direction (table VI-3; figure VI-3).

Figure VI-4 shows the stress to break was influenced by the rotating annular die to a greater extent than the modulus. At $R = 0$, the stress to break was 32.5 MPa in the machine direction and 10.5 MPa in the transverse direction. At $R = 410$, the stress to break in the machine direction decreased to 9.91 MPa and increased to 16.0 MPa in the transverse direction. As was the case for the HPC films, the elongations at break were not consistent enough for any evaluation as to the effect of die rotation. The elongations at break ranged from 0.011 to 0.042.

Table VI-3. Mechanical properties of EC blown films.

R=0	MODULUS (MPA)	STRESS TO BREAK (MPA)
MD	1760 $\pm$ 528	32.5 $\pm$ 4.5
30 OFF MD	1430 $\pm$ 205	12.4 $\pm$ 3.0
45 OFF MD	1430 $\pm$ 165	12.5 $\pm$ 5.3
60 OFF MD	1320 $\pm$ 680	12.5 $\pm$ 3.3
TD	1040 $\pm$ 169	10.5 $\pm$ 6.3
R=410		
MD	1140 $\pm$ 167	9.91 $\pm$ 2.4
30 OFF MD	1300 $\pm$ 188	11.7 $\pm$ 1.8
45 OFF MD	1440 $\pm$ 152	16.1 $\pm$ 2.6
60 OFF MD	1210 $\pm$ 81	19.0 $\pm$ 5.3
TD	1350 $\pm$ 263	16.1 $\pm$ 5.2

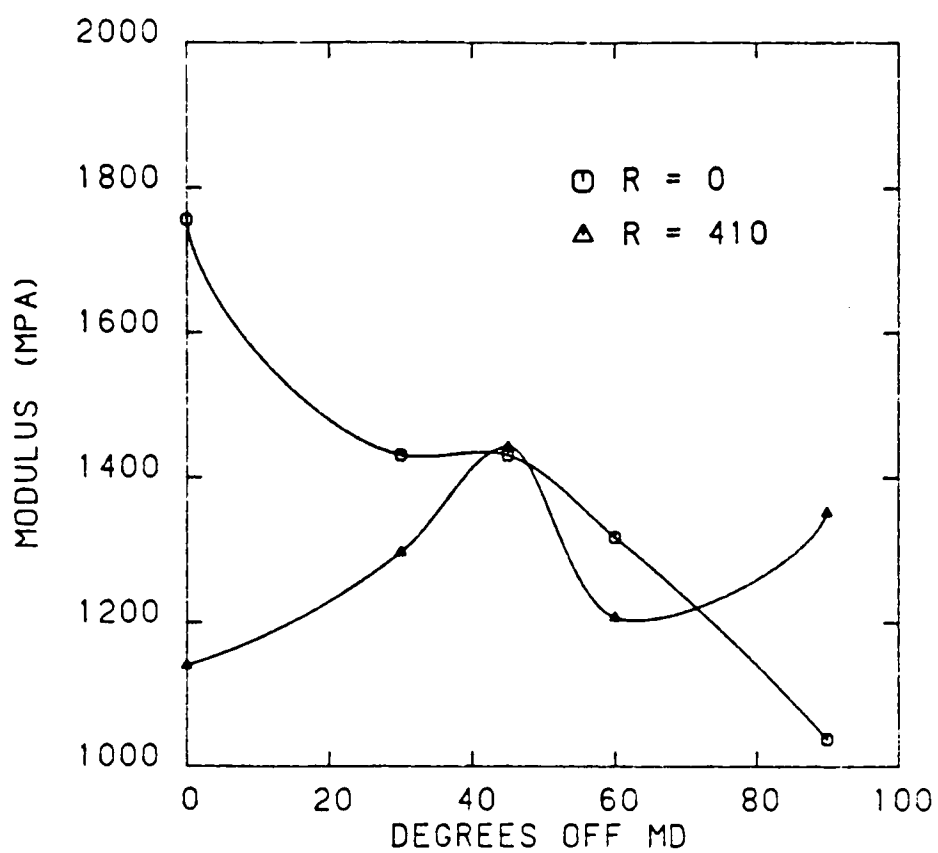


Figure VI-3. Modulus of EC blown films.

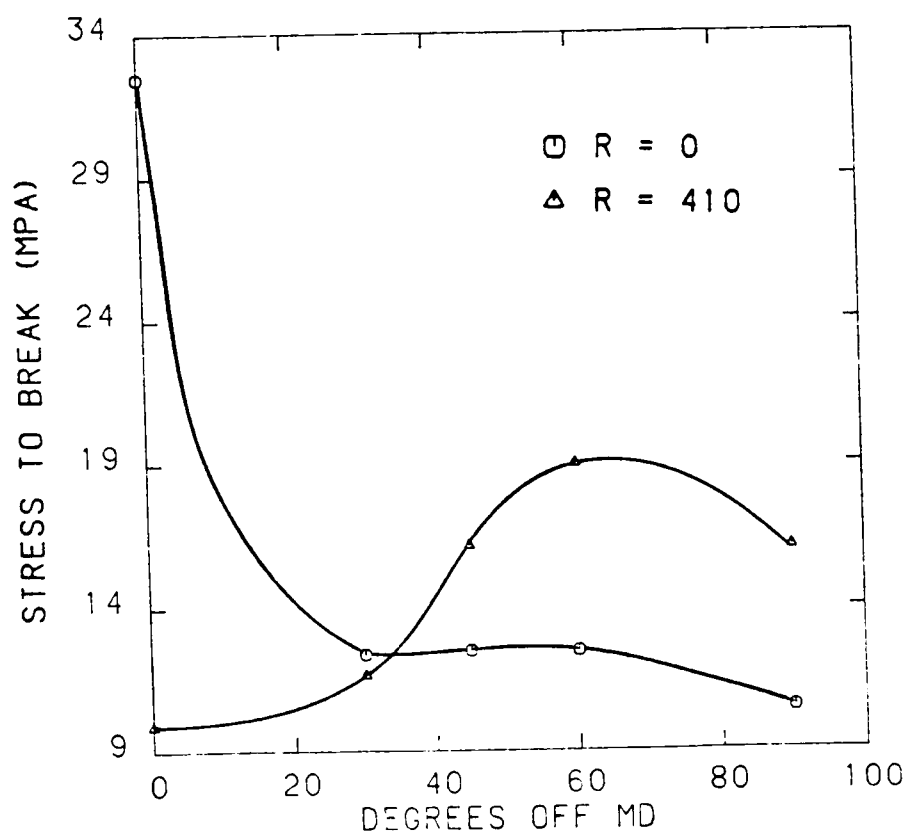


Figure VI-4. Stress to break of EC blown films.

D. Polystyrene

Table VI-4 shows that the mechanical properties of the PS film exhibited different behavior than the HPC and EC films. The modulus of the PS films at $R = 0$ was only slightly greater in the machine direction (2420 MPa) than in the transverse direction (2130 MPa). Die rotation increased these moduli to 3040 MPa and 3100 MPa in the machine and transverse directions respectively (figure VI-5). This represents an increase in modulus of over 25 per cent.

Figure VI-6 shows the stress to break behaved similar to the modulus with respect to die rotation. At $R = 0$, the stress to break was much greater in the machine direction (60.6 MPa) than in the transverse direction (44.4 MPa). At $R = 410$, the stress to break in the machine direction increased to 80.3 MPa and the transverse direction increased to 81.0 MPa.

These results are in agreement with Cleereman [17-21] who reported a substantial biaxial toughening of amorphous glassy polystyrene by rotating the core of an annular injection mold during the process. Choi [23] has reported an increase in biaxial orientation in blow molded bottles extruded from a rotating annular die. His samples could not be subjected to mechanical testing due to thickness variations, however, one would expect that the bottles

Table VI-4. Mechanical properties of PS blown films.

R=0	MODULUS (MPA)	STRESS TO BREAK (MPA)
MD	2420 $\pm$ 220	60.6 $\pm$ 17.2
45 OFF MD	2150 $\pm$ 524	49.2 $\pm$ 12.7
TD	2130 $\pm$ 157	44.4 $\pm$ 2.0
<u>R=410</u>		
MD	3040 $\pm$ 527	80.3 $\pm$ 10.5
45 OFF MD	3050 $\pm$ 507	72.6 $\pm$ 4.8
TD	3100 $\pm$ 271	81.0 $\pm$ 4.9

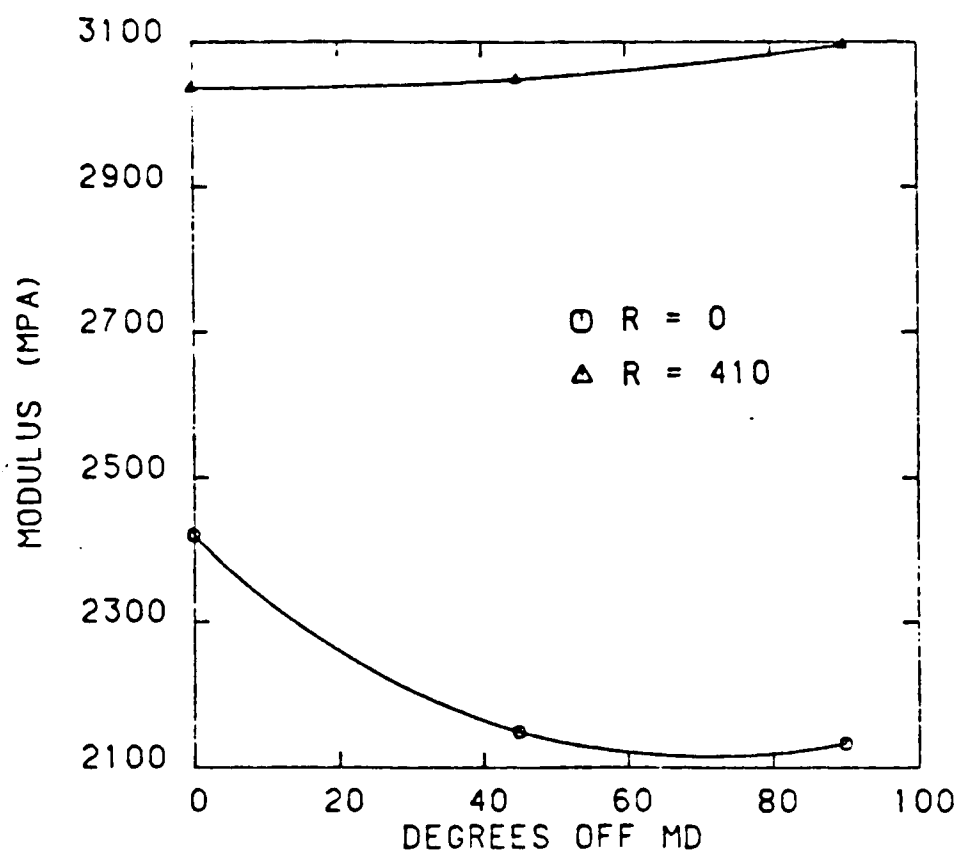


Figure VI-5. Modulus of PS blown films.

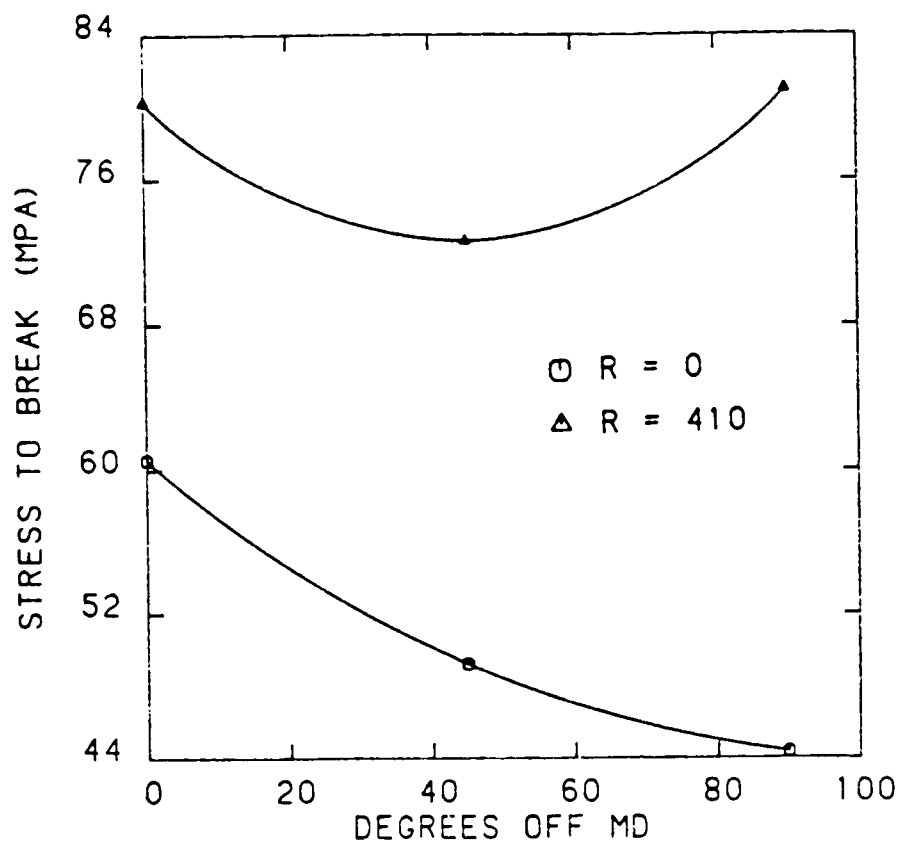


Figure VI-6. Stress to break of PS blown films.

extruded from the rotating die would have superior mechanical properties.

The elongations at break ranged from 0.035 to 0.040. Again these values were not consistent enough to reach any conclusions.

E. Polyethylene

Die rotation did not appear to have any effect on the mechanical properties of the PE blown films. The PE films had moduli of approximately 142 MPa, yield stresses around 10.5 MPa, and a stresses to break of 11.8 MPa. The elongation at break ranged from 7.8 to 9.5. The standard deviation for each test ranged from 8 to 15 per cent. This was larger than differences in the samples with and without die rotation.

The relatively large deviations in mechanical properties result from the inability to form a uniform film. The rotating annular die created instabilities in the film blowing process. Also, any large increases in the biaxiality of the PE films may have relaxed out. An air cooling ring would have been beneficial in both areas.

F. Degradation

An attempt was made to control polymer chain degradation by the addition of an antioxidant-free radical scavenger blend mixed in with the cellulosic powders and the

use of a nitrogen purge feed hopper. Table VI-5 shows the effect of extrusion on the intrinsic viscosities of the EC and HPC extrudates. The intrinsic viscosity of EC was measured in methanol at 25 degrees celsius and HPC was measured in ethanol at 25 degrees celsius. The standard samples refer to the polymer prior to extrusion and the extrudate refers to the polymer after extrusion. The intrinsic viscosity of the EC decreased from 1.12 to 1.05 and the HPC decreased from 1.56 to 1.45. Thus, there was some polymer chain degradation taking place. This undoubtedly decreased the mechanical properties of the films produced.

G. Effect of Water Absorption on HPC

As the HPC tubes and films were allowed to remain in the atmosphere and absorb water, they changed in character from very brittle to flexible. While the modulus of the HPC films did not show any effect to water absorption, the stress to break of the films increased significantly. This is shown in table VI-6 and figure VI-7. At $R = 0$, the stress to break in the machine direction increased from 24.7 MPa to 40.0 MPa. A more dramatic increase was noted in the transverse direction, where the stress to break increased from 3.82 to 13.1 MPa. At $R = 410$, the stress to break in the machine direction showed a similar increase as it

Table VI-5. Effect of extrusion on intrinsic viscosity.

EC STANDARD $[\eta]_{\text{MeOH}} = 1.12$

EC EXTRUDATE $[\eta]_{\text{MeOH}} = 1.05$

HPC STANDARD $[\eta]_{\text{EtOH}} = 1.56$

HPC EXTRUDATE $[\eta]_{\text{EtOH}} = 1.45$

Table VI-6. Effect of water absorption on stress to break in HPC blown films.

	STRESS TO BREAK (MPA)	
	INITIAL	AFTER THREE MONTHS
MD	24.7 $\pm$ 3.6	40.0 $\pm$ 9.3
30 OFF MD	15.1 $\pm$ 3.6	34.3 $\pm$ 5.2
45 OFF MD	11.5 $\pm$ 1.7	29.8 $\pm$ 2.4
60 OFF MD	5.87 $\pm$ 1.9	19.1 $\pm$ 2.8
TD	3.82 $\pm$ 0.8	13.1 $\pm$ 2.4

R=410

MD	14.0 $\pm$ 3.2	29.3 $\pm$ 2.4
30 OFF MD	17.4 $\pm$ 1.9	27.4 $\pm$ 3.2
45 OFF MD	16.7 $\pm$ 1.2	23.1 $\pm$ 3.0
60 OFF MD	22.5 $\pm$ 5.4	19.4 $\pm$ 3.0
TD	18.9 $\pm$ 4.5	17.2 $\pm$ 3.8

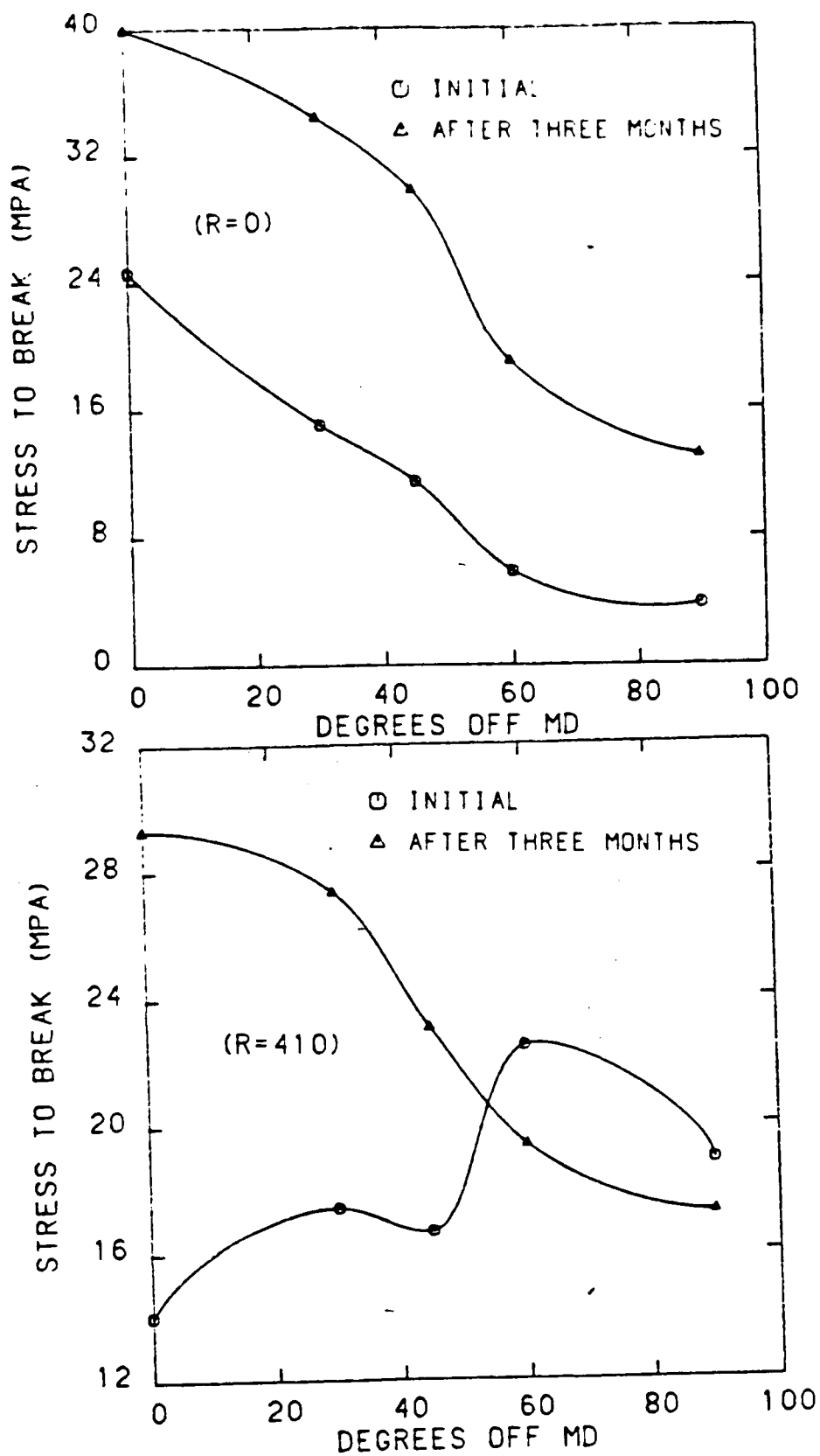


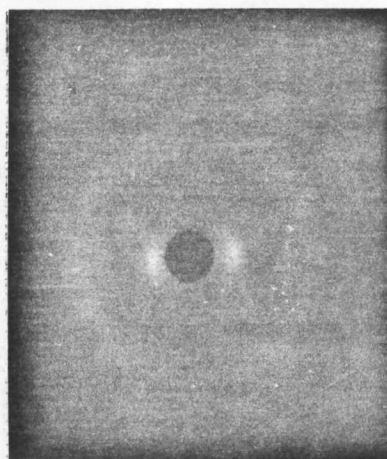
Figure VI-7. Effect of water absorption on stress to break in HPC blown films.

changed from 14.0 to 29.3 MPa. However, the stress to break in the transverse direction decreased from 18.9 to 17.2 MPa.

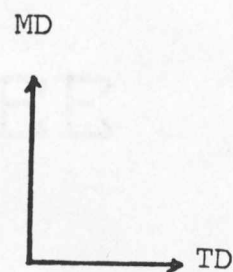
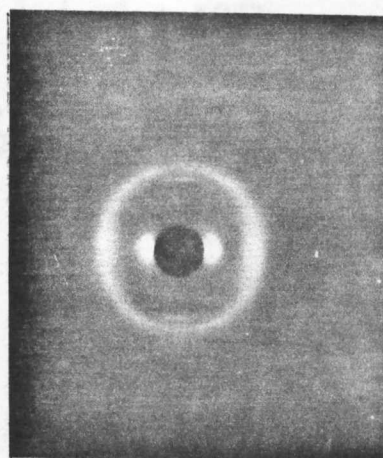
Figure VI-8 shows the effect of water absorption on the WAXS patterns of HPC film with $R = 0$. From observing the patterns of the extrudate stored in a dessicator and an extrudate stored in the atmosphere, it would appear that further crystallization is taking place. Since Young's modulus is determined at low strains, it would be predominately determined by the stretching in the amorphous regions. This could be why a change was not noted. Whereas the stress to break depends more on the crystalline regions, a dramatic increase was noted due to the increase in crystallinity.

H. Conclusions

The mechanical properties of the HPC and EC films at $R = 0$ were much greater in the machine direction than in the transverse direction. As the die rotation was increased, the mechanical properties decreased in the machine direction and increased in the transverse direction. This behavior was more dramatic for the HPC than EC. These materials are highly planar and it appears that the chain axis is being moved from the machine to the transverse direction. Thus the mechanical properties of the transverse direction increased at the expense of the machine direction.



Extrudate stored in desiccator.



Extrudate after three months in atmosphere.

Figure VI-8. Effect of water absorption on the WAXS patterns of HPC film.

The polystyrene behaved differently than the cellulose ethers. The mechanical properties of the blown films were only slightly biased in the machine direction. Die rotation significantly increased the modulus and tensile strength in all directions. As birefringence measurements indicate, die rotation increased the tendency of the chain axis to lie in the plane of the film. This leads to a biaxial toughening of the film. The increase in mechanical properties in the transverse direction is not achieved at the expense of the machine direction.

The PE film did not show any effect of die rotation on the mechanical properties. It would appear that any increased biaxial orientation relaxes out.

The die surfaces were very rough. When the HPC, EC, and PS films failed, they generally broke along the die marks. Smoothing the die surfaces would increase the stress to break of these films.

CHAPTER VII

EXAMINATION OF SUPERSTRUCTURE

A. Introduction

Scanning electron microscopy was used to study the superstructure of the tubes and films fabricated by the described process. Surfaces and cross sections were observed without die rotation ($R = 0$) and with die rotation ($R = 410$).

B. Results

Examination of the PE and PS tubes and films did not reveal any effect of die rotation in the products. Whereas, striking effects were noted in the HPC and EC samples.

SEM photomicrographs of an HPC extrudate without die rotation are shown in figure VII-1. Part (a) is a cross sectional view, that is one is looking down along the machine direction. The top of the figure represents the outside wall of the tube. Here we can observe the skin-core structure of the extrudate. The skin is approximately 150 μ m in thickness, compared to 800 μ m for the core. A "skin" is not observed on the inside wall of the tube. This is somewhat surprising when one considers that the inside wall has a similar shear history as the outside wall. It would appear that the absence of a skin formation is due to

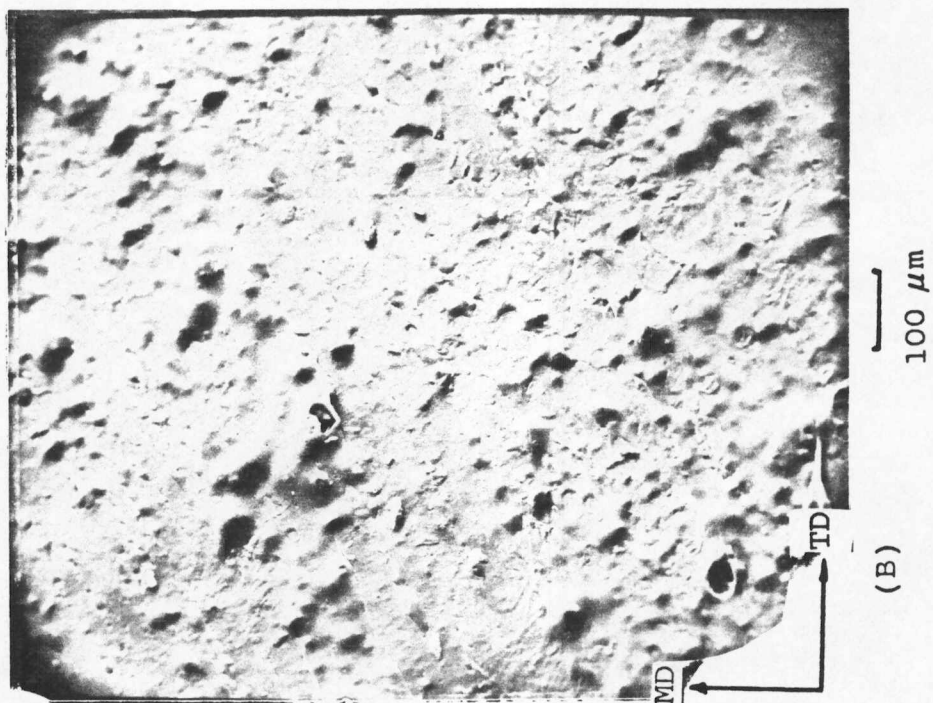
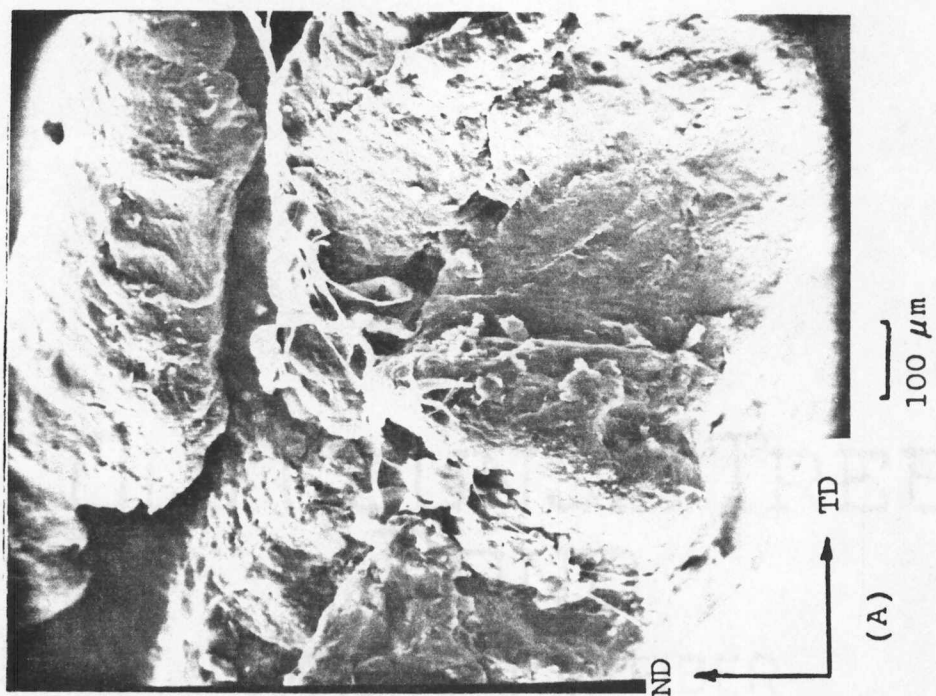


Figure VII-1. SEM photomicrographs of HPC extrudate without die rotation.

the difference in heat transfer. The higher orientation induced by shear stresses on the outside of the tube is cooled rapidly before it can relax out, leading to the skin-core structure. Whereas the highly oriented layer on the inside of the extrudate cools more slowly and some of this higher orientation relaxes out. This results in the inner wall orientation being approximately the same as the core. The tube surface appears very coarse as observed in part (b). Figure VII-2 shows that die rotation smooths the surface and eliminates the grainy texture.

When the tubes extruded with $R = 410$ were fractured to examine in cross section, the samples delaminated into three distinct layers. The thickness of the outer layer being around 500 μ m, the middle layer 475 μ m, and the inner wall 525 μ m. The morphology of these layers were quite different.

The outside layer displayed a very "fine" texture in cross section as observed in figure VII-3. These small fibrils appear to be aligned in the transverse direction. The outer portion of this layer broke in the neutral direction in a staircase manner. A minimum of four different levels can easily be detected. This can be attributed to the variation in the tangential shear rate through the thickness of the film. As the viewer moves down this staircase away from the outer wall, the steps become

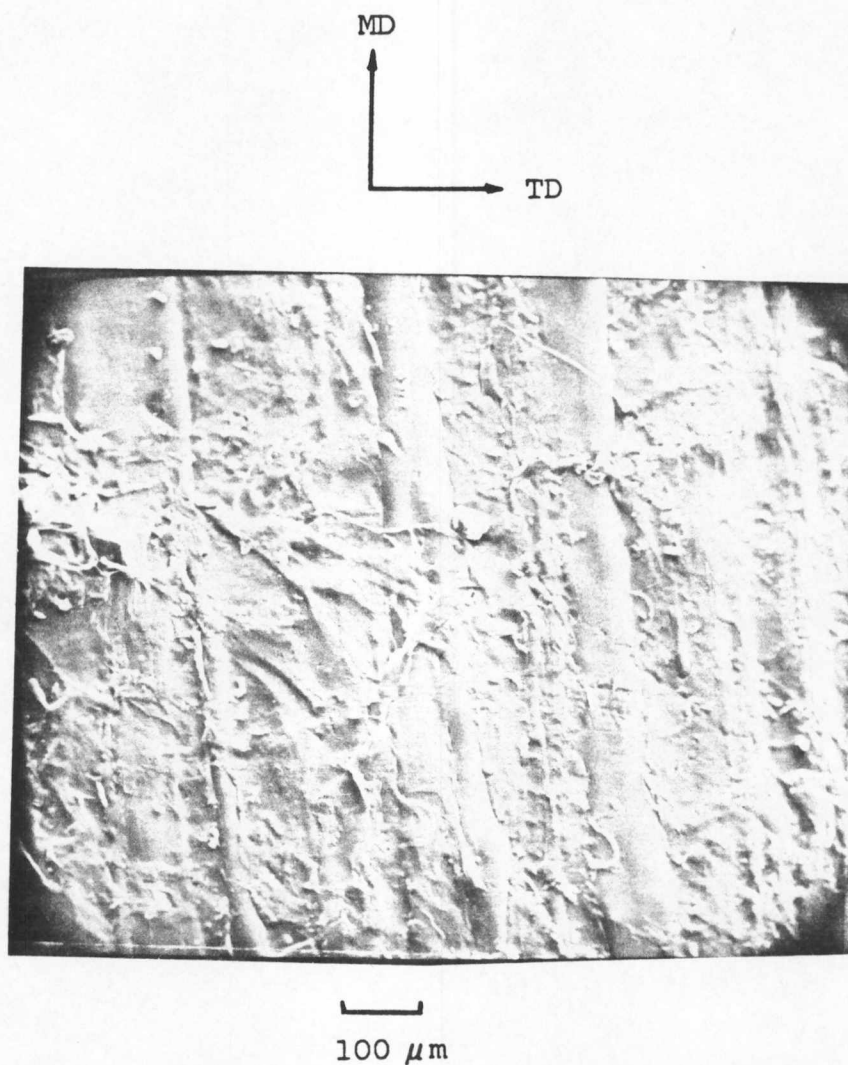
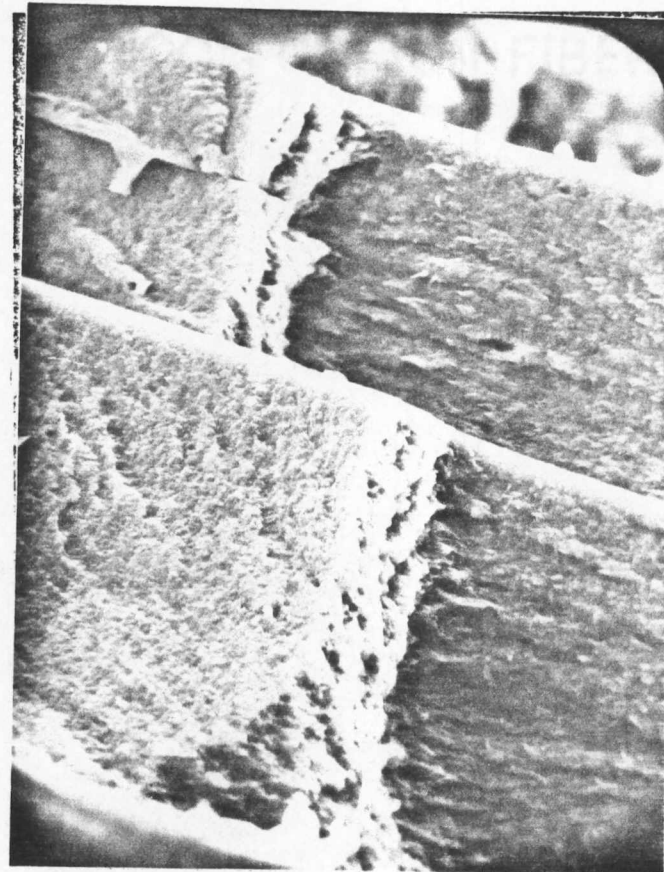
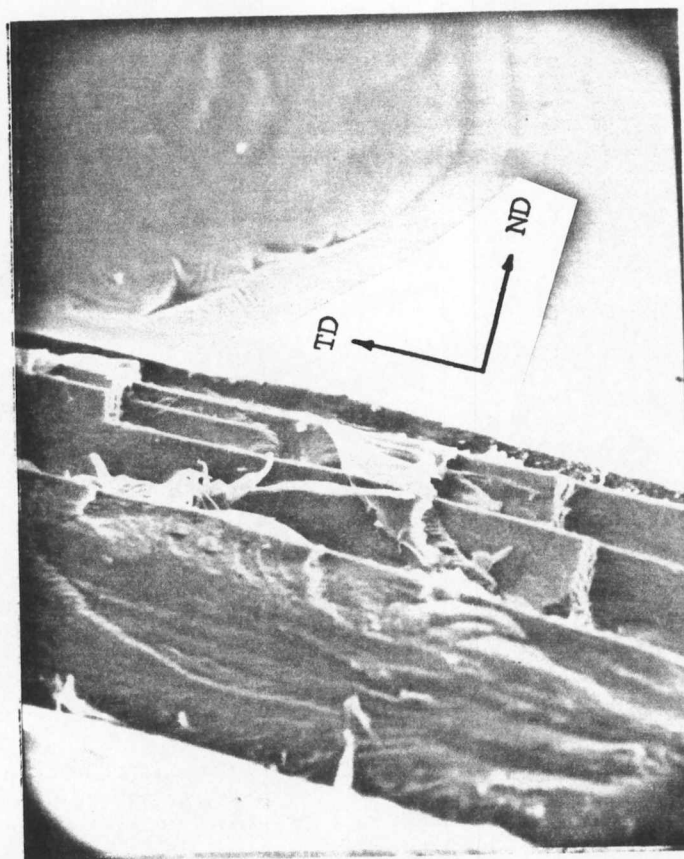


Figure VII-2. SEM photomicrograph of HPC extrudate surface with $R = 410$.



(B) 20 μm



(A) 100 μm

Figure VII-3. SEM photomicrographs of the outer wall of an HPC extrudate with $R = 410$.

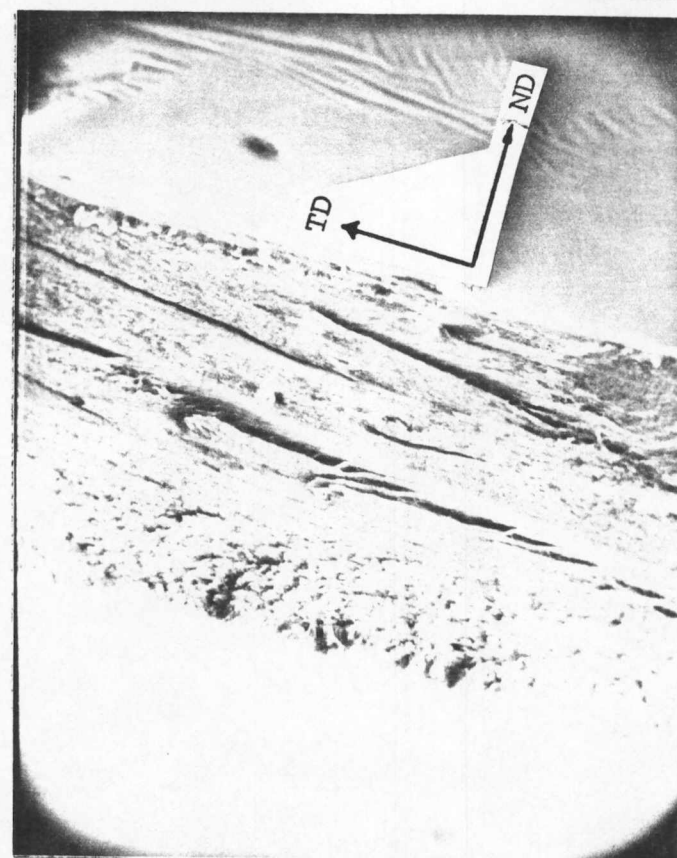
larger. The last level being much larger and coarser than the previous.

Figure VII-4 is of the inner layer of the delaminated extrudate. The inner layer of the delaminated extrudate was extremely coarse. Again the fibrous structures were observed to be aligned in the transverse direction. Large voids appeared as cracks which propagated in the same direction as the fibrous bundles (TD). The fibrous bundles can be observed transversing the cracks.

Figure VII-5 of the inner wall of the delaminated HPC extrudate with $R = 410$ was very different than the preceding two layers. This layer was not as fibrous as the middle layer. It was similar to the outer layer except its texture was uniform through its thickness. This region was absent of voids.

Figure VII-6 shows the SEM photomicrographs of the HPC blown film surfaces with $R = 0$ (a) and $R = 410$ (b). Both surfaces are fairly coarse. With $R = 0$, various bumps and holes were visible on the film's surface. When the die surfaces were rotated, most of these surface imperfections were eliminated.

SEM Photomicrographs of the HPC film cross sections were quite contrasting. One observes in figure VII-7 (a) that in the HPC blown film without die rotation, the fibrous bundles were quite large. These bundles are oriented in the



(A)



(B)

Figure VII-4. SEM photomicrographs of the middle layer of an HPC extrudate with $R = 410$.



(A)

100 μm



(B)

20 μm

Figure VII-5. SEM photomicrographs of the inner wall of an HPC extrudate with $R = 410$.

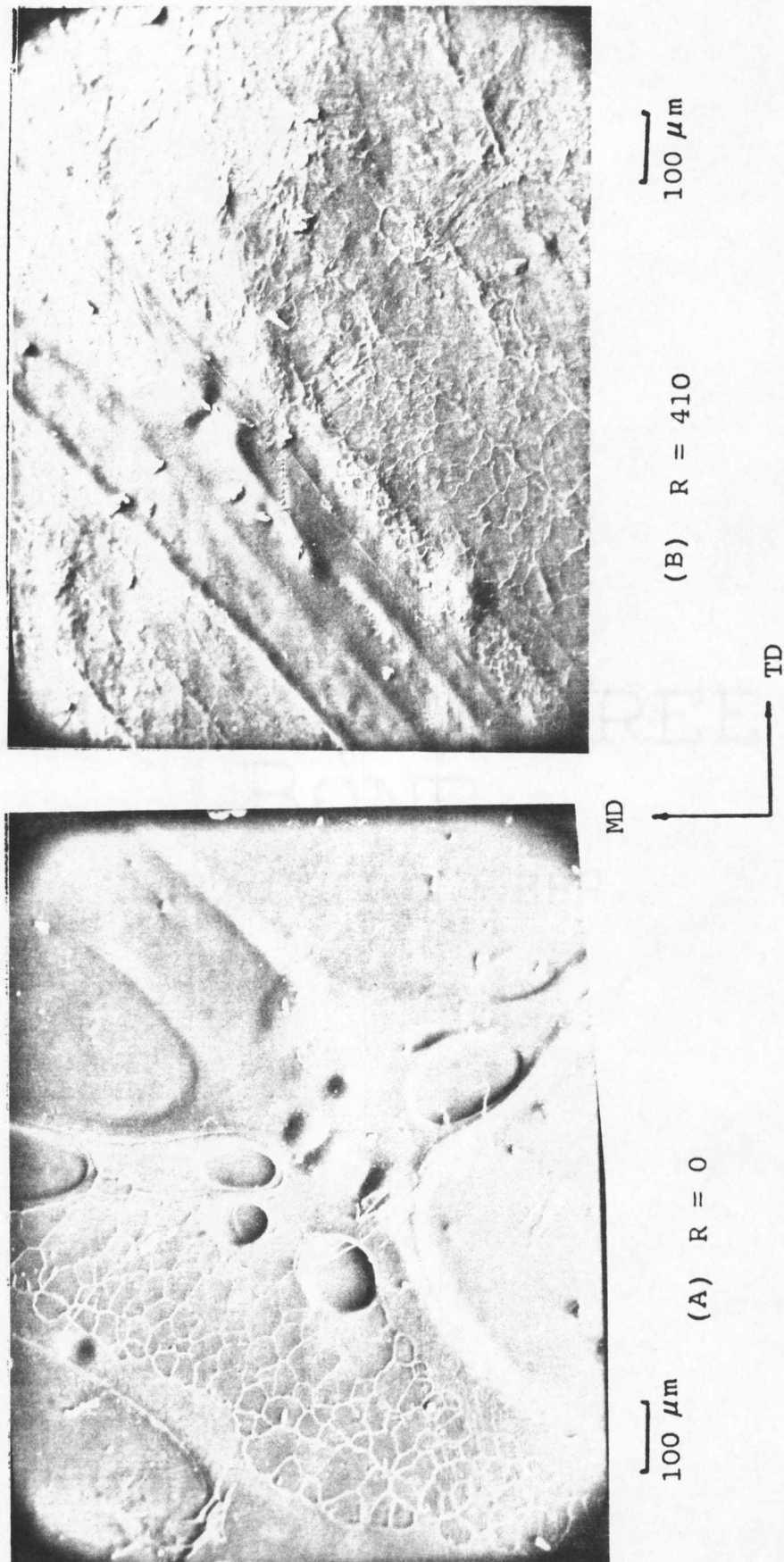


Figure VII-6. SEM photomicrographs of the surfaces of HPC blown films.

(A) $R = 0$ 
20 μm (B) $R = 410$

Figure VII-7. SEM photomicrographs of the cross section of HPC blown films.

machine direction. When the die is rotated, these large bundles of fibers disappear and a much finer structure is formed (see figure VII-7 (b)). These very thin fibers are oriented in the transverse direction. The properties observed were continuous across the thickness of the films.

Figure VII-8 displays the surfaces of EC extrudates. The surfaces were very coarse, much coarser than that observed in the HPC. At $R = 0$, the graininess in the lower right hand corner is representative of the sample. The surface in the upper left resulted when the surface was fractured. Die rotation did not improve the quality of the surface. At $R = 410$, the surface was rougher and nonuniform.

The EC extrudate cross sections were very similar for samples with and without die rotation as observed in figure VII-9. The fibrous structure is on a much smaller scale than that observed in HPC. The fibrous structure was predominately on the skin for $R = 0$. Whereas for $R = 410$, the fibrous layers were thinner and present through the thickness of the tube.

Die rotation had a drastic effect on the surfaces of the EC blown films. In figure VII-10 at $R = 0$ (part a), the surface is very grainy as was observed in the EC extrudates. Occasionally, smooth "holes" were observed. This is possibly due to the presence of PE. As observed in part b,

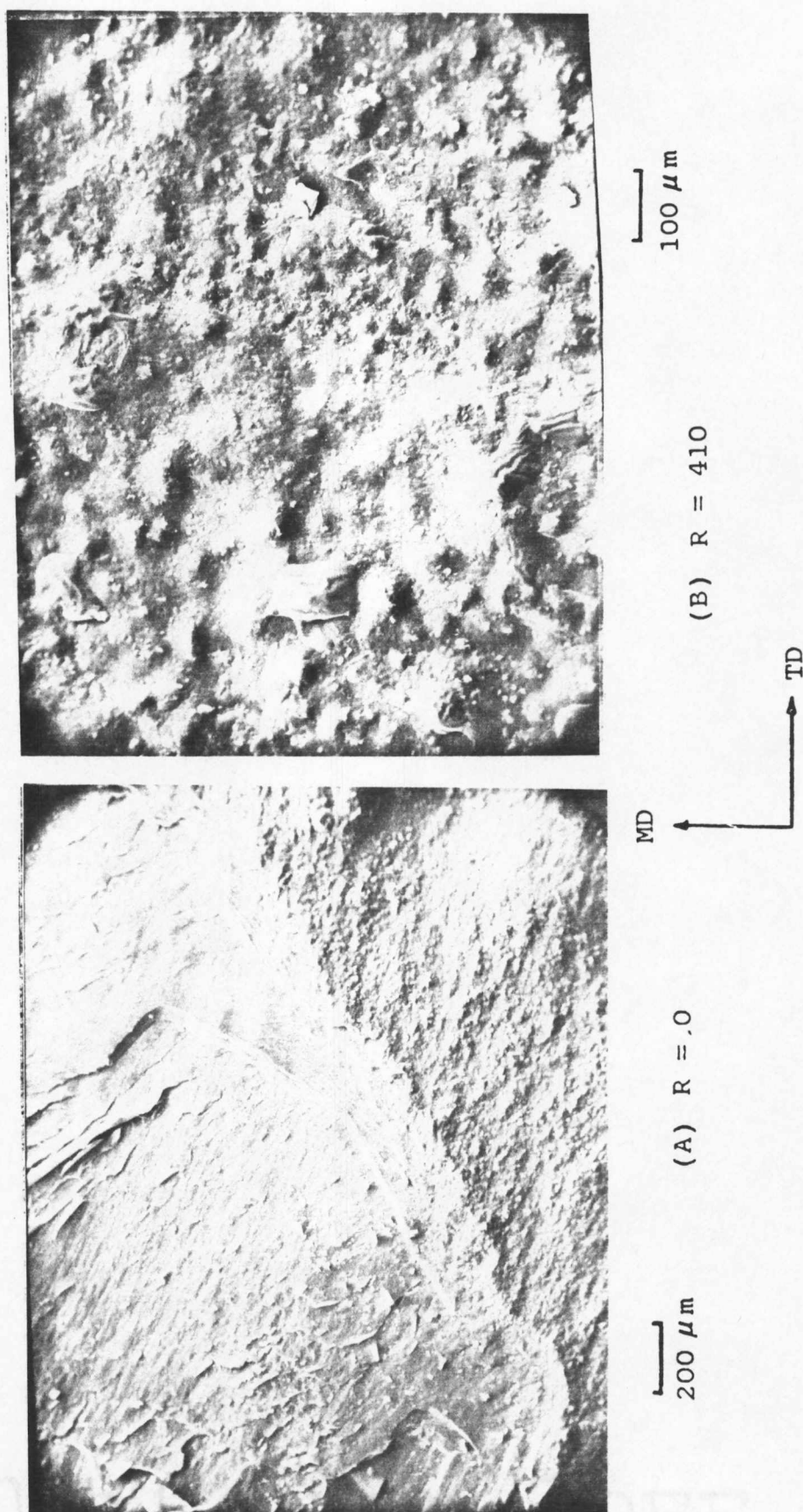
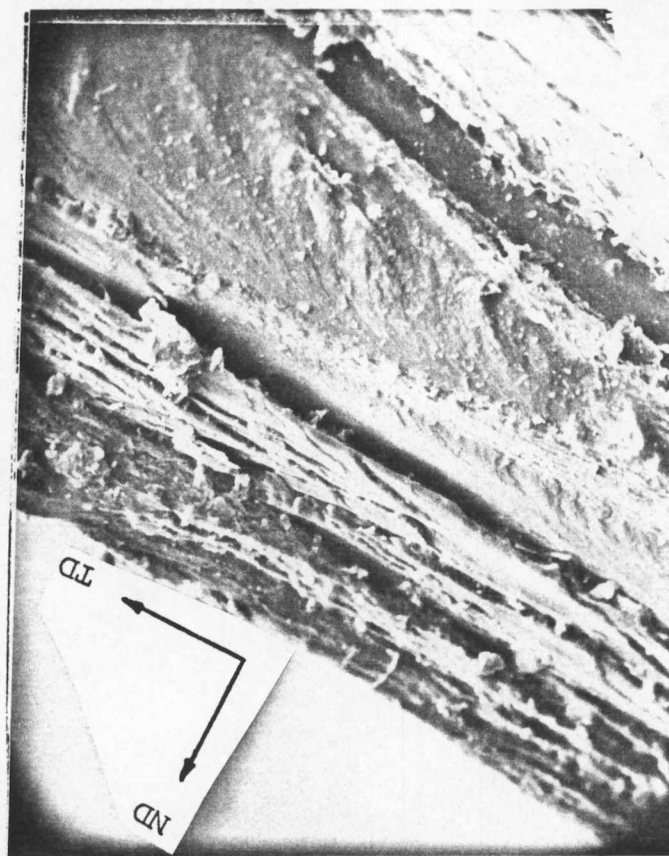
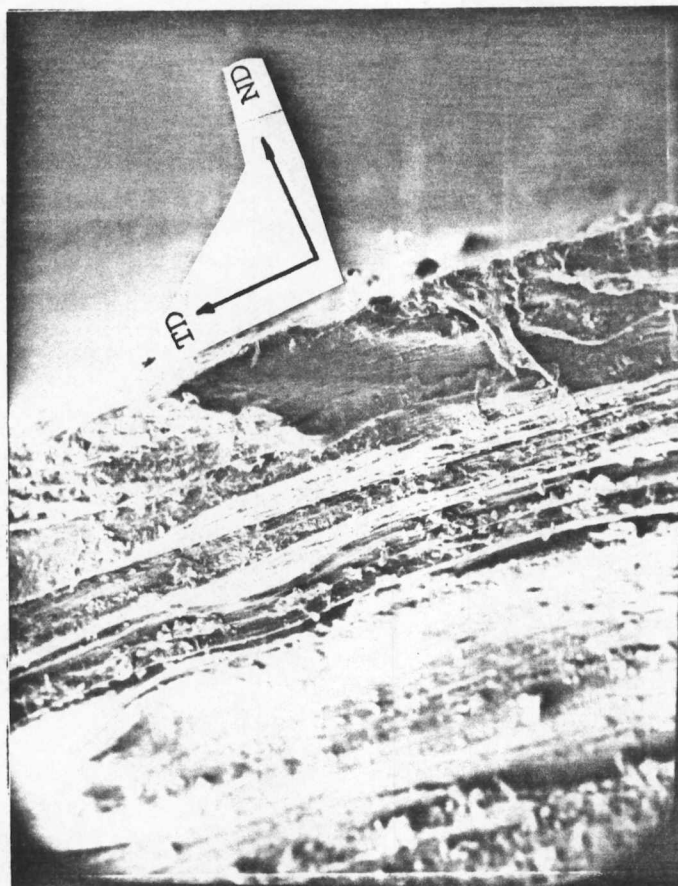


Figure VII-8. SEM photomicrographs of the surfaces of EC extrudates.



(A) $R = 0$

100 μm



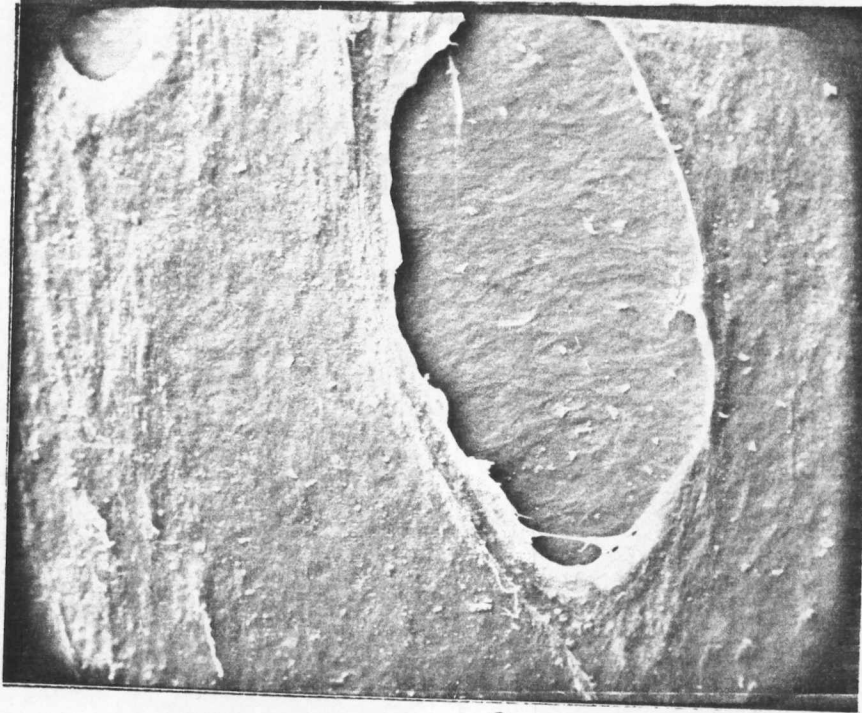
(B) $R = 410$

200 μm

Figure VII-9. SEM photomicrographs of the cross section of EC extrudates.



(A) $R = 0$



(B) $R = 410$

$\overline{\quad}$
200 μm

Figure VII-10. SEM photomicrographs of the surface of EC blown films.

die rotation changed the film surface to grainy to smooth. The "holes" observed in the films changed from ellipsoidal in the machine direction to ellipsoidal in the transverse direction.

Figures VII-11 and VII-12 show the cross sections of EC films with and without die rotation. The films blown without die rotation were very coarse, much coarser than the EC extrudates. A gradient in texture is present from the walls to the center of the film. As has been noted previously in other samples, die rotation generates a finer structure composed of many layers.

C. Conclusions

The rotating annular die has a drastic effect on the morphology of HPC and EC. The grainy surfaces formed with these materials are smoothed out by die rotation. The tubes and films produced without die rotation formed coarse fibrillar structures with the fiber bundles aligned in the machine direction. When the surfaces of the die were rotated, the large fibrils were broken down into very fine fibrils. The rotating surfaces moved the fiber bundles from the machine to the transverse direction.

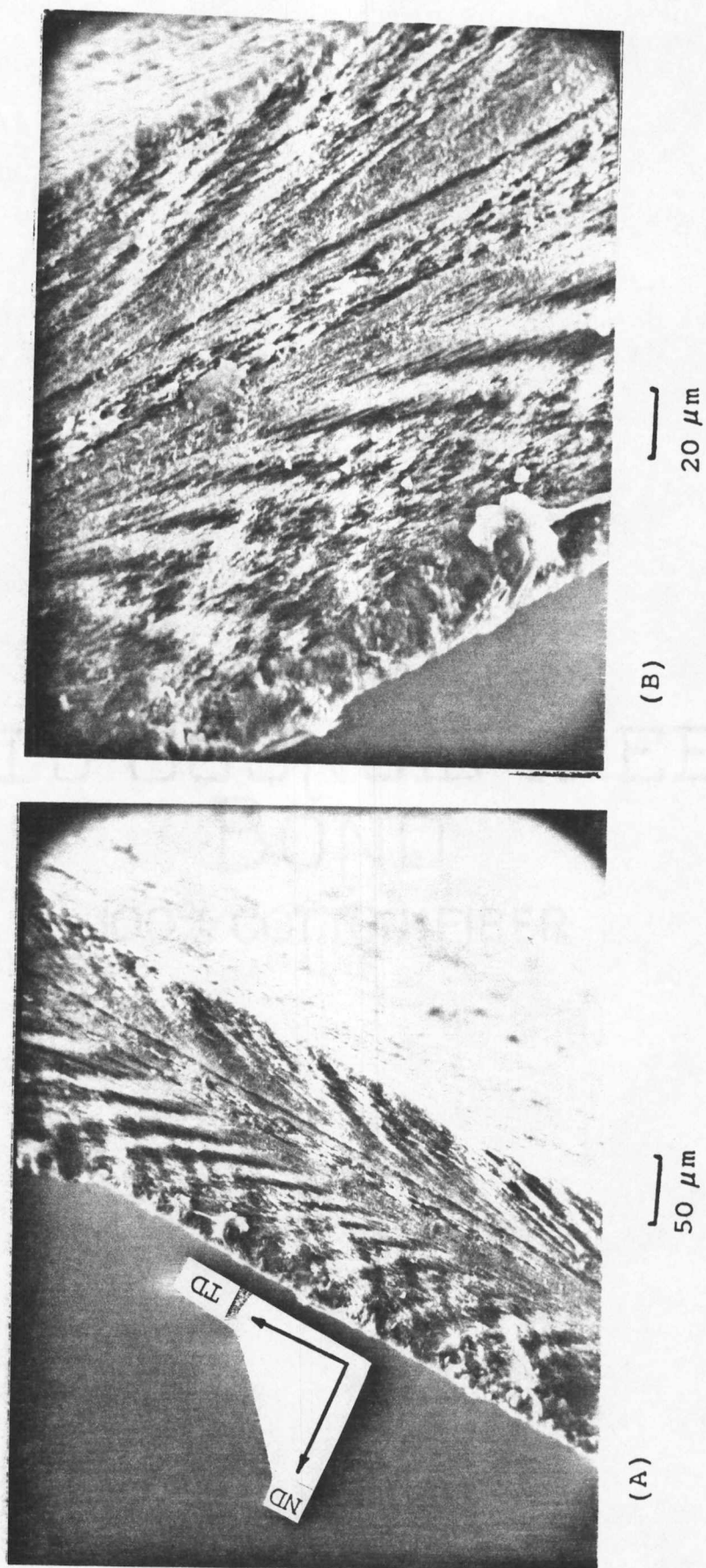
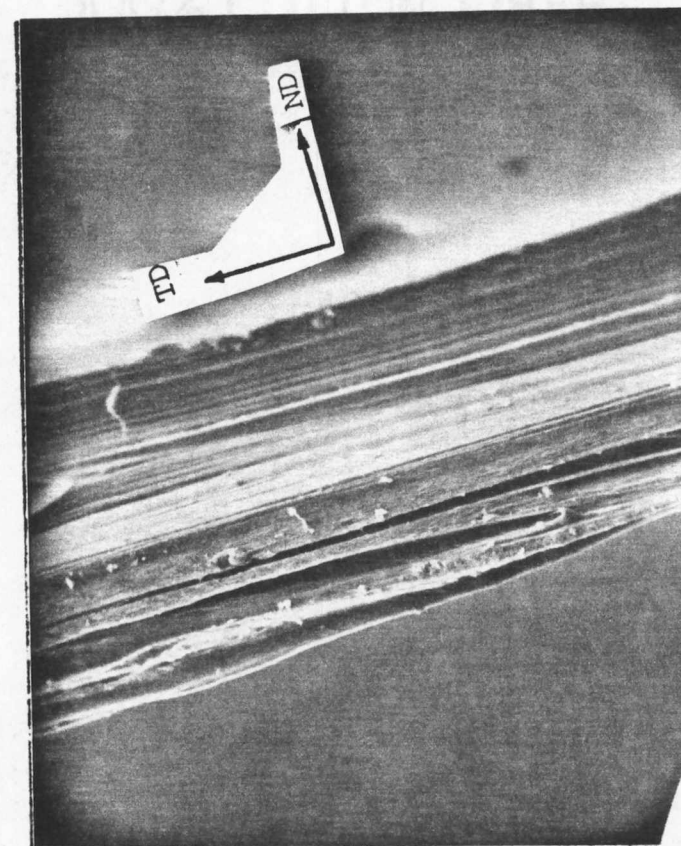
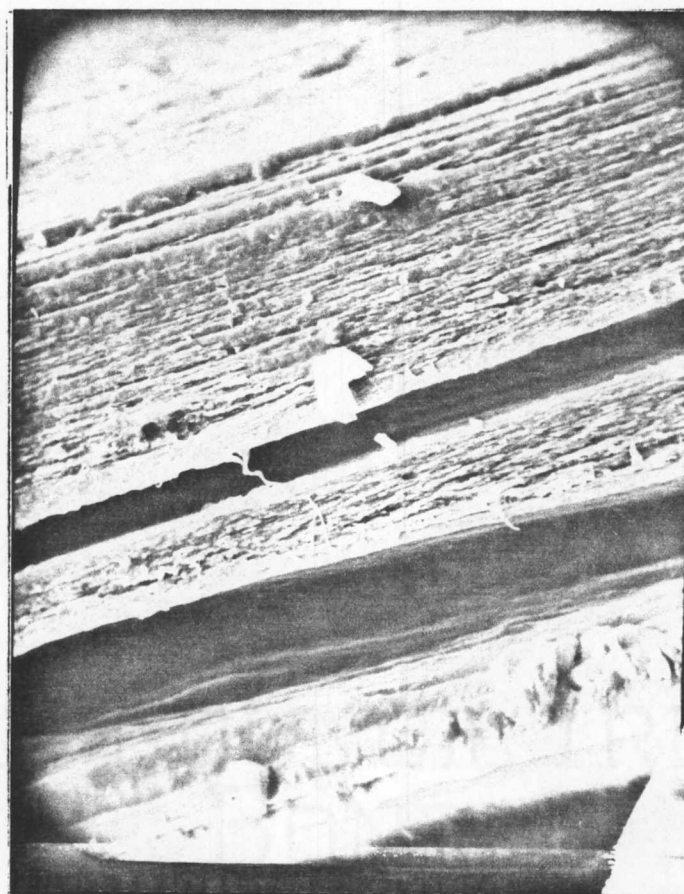


Figure VII-11. SEM photomicrographs of the cross section of EC films without die rotation.



(A)



(B)

Figure VII-12. SEM photomicrographs of the cross section of EC film with $R = 410$.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

The rotating annular die has been used successfully to control the molecular orientation in melt processed thermotropic liquid crystalline cellulose derivatives. Due to the long relaxation times of these materials, this process is much more effective than for the polyolefins. By controlling the angular velocities of the rotating surfaces, the polymer chain axis can be placed at any desired position between the machine and transverse directions. In HPC extrudates, the White-Spruiell biaxial orientation factors ranged from $f_1^B = 0.80$ and $f_2^B = 0.021$ to $f_1^B = 0.17$ and $f_2^B = 0.71$.

As the molecular orientation of the cellulose ethers can be controlled, so can the mechanical properties. For hydroxypropyl cellulose blown films the modulus and stress to break were highly biased in the machine direction. The modulus was 1370 MPa in the machine direction and 239 MPa in the transverse direction. Through the use of the rotating annular die, films were produced with moduli of 656 MPa in the machine direction and 1000 MPa in the transverse direction.

Not only did the rotating annular die control the molecular orientation and the mechanical properties, but it also changed the morphology of the HPC and EC tubes and films. Die rotation smoothed the surfaces and eliminated the graininess of the products. The die rotation also created a much finer superstructure as observed in cross section. The relatively large fibrous bundles of cellulose derivatives were eliminated through die rotation and a very fine structure was generated.

The ethyl cellulose studied in this research did not display the degree of liquid crystalline character observed in hydroxypropyl cellulose. This could be a result of the grade of ethyl cellulose selected for study. A more highly substituted ethyl cellulose would be more crystalline, however, its viscosity is greater and more difficult to work with.

B. Recommendations

As with any first generation process there were points which could be improved. In the PE blown film, the rotating die created instabilities and much of the orientation produced in the die is believed to relax out. An air cooling ring would be beneficial for both circumstances.

The die surfaces were not smooth. Die marks could be observed on the surfaces of the extrudates and blown films.

These imperfections served as failure sites. The stress to break of the films could be improved by smoothing the die surfaces. The mechanical properties of the cellulose ethers could also be improved by better controlling chain degradation. A screw more suitable for handling the cellulosic powders, reducing the residence time in the extruder would be beneficial.

The die design limited the blow up ratios of the cellulose ethers. The lip on the outer cylinder limited the expansion as they had to be blown immediately upon exiting the die. Increasing the blow up ratio would allow very thin films to be produced.

There are many aspects of this research which would be interesting for further study. In this research no emphasis was placed on studying the orientation distribution within the depth of the film. This would give insight into the complicated velocity profile.

Separate and variable speed controls for the inner core and outer cylinder could be used in order to assure equal biaxial orientation. The effect of the die gap on the orientation generated is also of interest.

In this research, the extrudates were allowed to cool at room temperature. No attempt was made to quench these materials and study the orientation. A study of this nature

could be beneficial in evaluating the relaxation times for the polyolefins and cellulose derivatives.

An isothermal chamber might also be useful in the blowing of the hydroxypropyl cellulose film. The orientation generated in the die carried over into the films. The blowing of the film in an isothermal chamber might lead to an increase in the transverse direction orientation.

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APPENDIX

The x-ray diffraction data was used in conjunction with the birefringence data in an attempt to evaluate the amorphous orientation in the HPC blown films. Equations 36 and 37 on page 44 show the relationship between the crystalline and amorphous orientation factors and the out of plane birefringences, Δn_{13} and Δn_{23} . The problem with this calculation lies in the uncertainty of the intrinsic birefringences. Onogi et. al. [59] suggested an intrinsic birefringence of 0.032 for HPC. This value was used for both Δ_{ca}^{oc} and Δ^{oa} . HPC has a tetragonal unit cell, therefore Δ_{ba}^{oc} is zero.

Table A-1 lists the x-ray determined crystalline orientation factors and the calculated amorphous orientation factors at the corresponding values of R. The amorphous orientation factors for HPC blown films without die rotation were very low ($f_1^B = 0.09$ and $f_2^B = 0.07$). However, die rotation had a drastic effect. Die rotation increased both amorphous orientation factors to about 0.5. This indicates that the amorphous regions lie in the plane of the film. These orientation factors appear to be extremely high.

Cellulose had an intrinsic birefringence of 0.07. If the intrinsic birefringence of HPC was twice that used in the calculation of the amorphous orientation factors

(0.064), the values listed in table A-1 would be reduced by about one half. Due to the uncertainty of the intrinsic birefringence, these values are viewed as unreliable.

Table A-1. Amorphous orientation factors

R	$f_{c,1}^B$	$f_{c,2}^B$	f_1^B	f_2^B
0	0.71	0.06	0.09	0.07
82	0.69	0.22	0.50	0.37
205	0.68	0.31	0.43	0.39
287	0.55	0.41	0.49	0.52
410	0.41	0.59	0.55	0.52

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