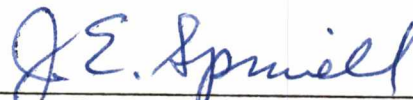


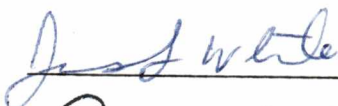
To the Graduate Council:

I am submitting herewith a thesis written by Hiroshi Ashizawa entitled "Clarity and Internal/External Structure of Blown Polyethylene Films." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.



Joseph E. Spruiell, Major Professor

We have read this thesis and
recommend its acceptance:



Accepted for the Council:



Vice Chancellor
Graduate Studies and Research

CLARITY AND INTERNAL/EXTERNAL STRUCTURE
OF BLOWN POLYETHYLENE FILMS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Hiroshi Ashizawa

December 1982

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DEDICATED TO SUSANNE

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ABSTRACT

The direct transmission factors of linear low density and low density polyethylene blown films were measured as a function of film preparation conditions. The contribution of scattering from the film surface was investigated by separating the overall direct transmission factor into components due to transmission through the bulk film phase and transmission through the surface phase. At lower polymer deformation rate and higher cooling rate the overall direct transmission factor had higher values. The surface phase direct transmission factor dominates the overall direct transmission factor. Surface irregularities of blown PE film are affected by crystallization mechanisms near or at the film surface and flow defects caused by deformations within the die and beyond the die exit. Direct transmission factor of HDPE/PP blend films were also studied as a function of composition. Each phase direct transmission factor showed a maximum near 50 weight percent polyethylene.

Profiles of surface irregularities of the blown films were obtained using a surface profiler and characterized statistically. Scanning electron microscopy was also used to help characterization of surface irregularities. HDPE showed the roughest surface irregularities and LDPE showed the smoothest surface irregularities. A good correlation was found between the standard variation of height deviation of the film surface irregularities and the film's surface phase direct transmission factor.

Orientation in L-LDPE and LDPE films were studied using both birefringence and wide angle X-ray pole figures. Both L-LDPE and LDPE showed a typical a-axis orientation along the machine direction with the b-axes concentrated towards the normal direction.

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CHAPTER 1

INTRODUCTION

The blown film process is the most important fabrication method for the production of thermoplastic films. This process is most commonly used for polymer film manufacturing operation because of its better economics and satisfactory mechanical properties.

Polyethylenes are probably the most widely used for this application. These films have a more or less milky white or hazy appearance caused by light scattering by the films. In spite of the importance of haze in end-use applications, there is little published information on the mechanisms and causes of haze development in films.

The purpose of this thesis is to acquire a better understanding of the causes of haze of polyethylene blown films. Improved understanding should provide a guide for film fabrication conditions to achieve lower haze levels. Molecular orientation of these polyethylene films will be also studied.

CHAPTER 2

BACKGROUND REVIEW AND LITERATURE SURVEY

2.1 Blown Film Process

For the past thirty years, the film blowing process has attracted great interest in the polymer processing industry for the production of thin thermoplastic films and is the source, today, of much of the polyolefin film, polyvinyl chloride film, and polyvinylidene chloride film sold.

The film blowing process may be considered to combine features of blow molding and flat film extrusion. An advantage of the film blowing process over the flat film process lies in that the former permits one to have biaxially oriented film, whereas the latter can produce only uniaxially oriented film.

As schematically shown in Fig. 2.1, in the blown film process, a thin film is produced by means of the extrusion of a polymer melt through an annular die. The molten polymer tube exiting from the die is drawn upward by a take-up device. At the bottom of the die, air is introduced, inflating the tube to form a bubble. An air ring which is located around the die is also used to cool the hot bubble rapidly and solidify it at some distance above the die exit. The inflated and solidified bubble is then flattened as it passes through the nip rolls. The nip rolls, driven by a variable speed motor, provide the axial tension needed to pull the film upward, and the form an airtight seal,

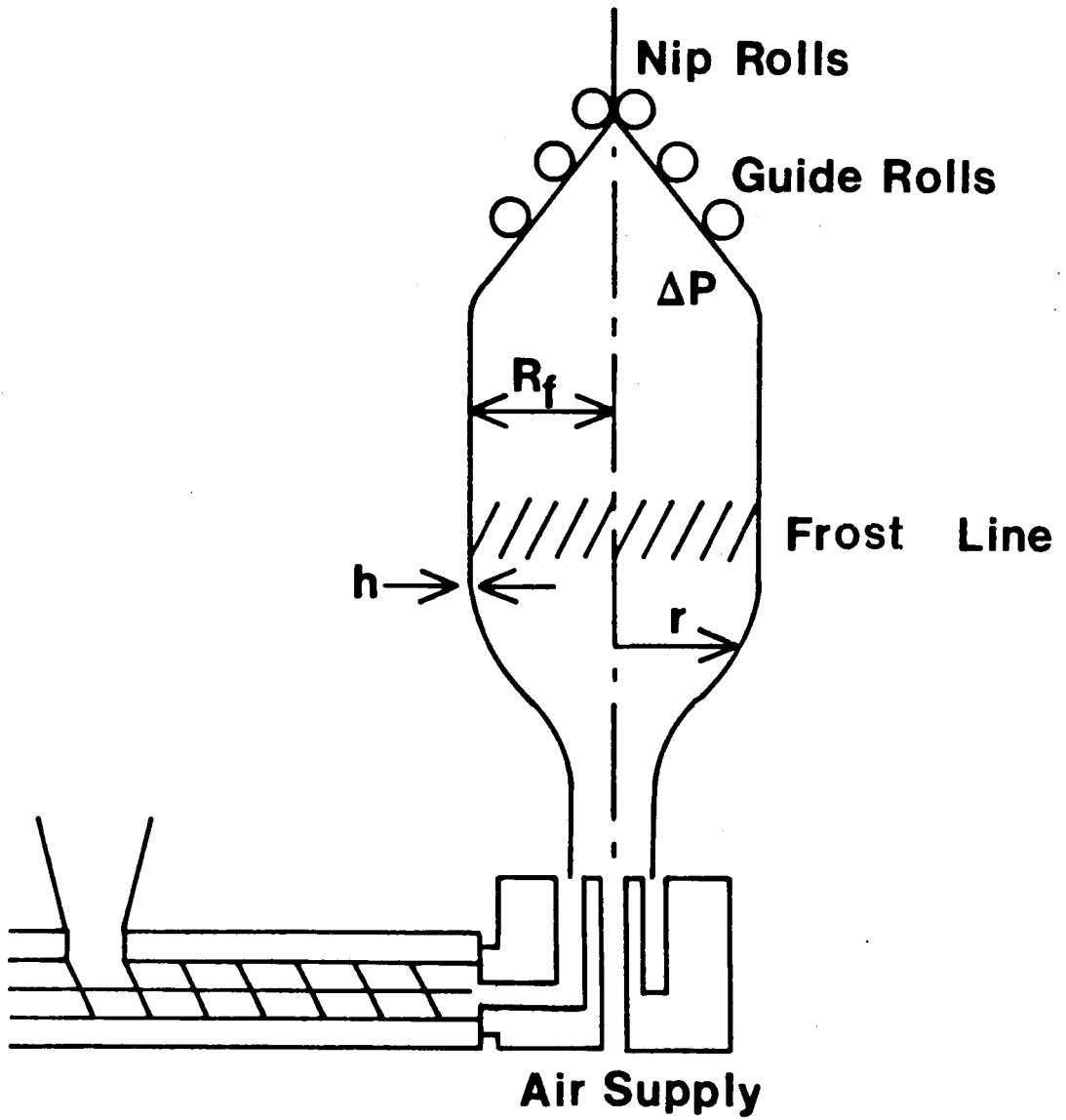


Figure 2.1. Blown film extrusion process.

so that a constant air pressure, slightly above atmospheric, is maintained in the inflated bubble. The pressure inside the bubble is controlled by adjusting the air supply to the bottom of the die.

There are several important processing variables that may affect the optical properties of finished products as well as that of the mechanical properties. These are the draw-down ratio, blow-up ratio, and the frost-line height. The draw-down ratio is the ratio of final product velocity to molten polymer velocity at the die exit along the machine direction. The blow-up ratio is the ratio of final bubble diameter to die diameter. The frost-line height is the distance between the die exit and the point where molten polymer solidifies.

The dynamics of the blown film process are rather complex due to the expansion of the bubble. It was only in 1965 that appropriate force balance equations were developed by Alfred (4) using the theory of mechanical equilibrium of membranes of rotational symmetry. In 1970, the dynamics of this process were developed in great detail in a series of papers by Pearson and Petrie (53, 54, 55) presuming the film is a thin shell. The assumptions made are the film thickness is small compared with other dimensions of the bubble including its radii of curvature, and that the velocity gradients can be approximated locally by those of plane film being extended biaxially. These developments are reviewed in monographs by Han (29) and Middleman (48).

2.2 Optical Properties of Polymer Films and Their Measurements

Optical properties of a material depend on its interaction with the electromagnetic field of the incident light. A great many optical

properties result from the fact that this interaction involves a whole series of molecular parameters. Two principal groups of optical properties can be distinguished. Those resulting from molecular property averages and those caused by local deviations from these averages. Refraction, absorption, and diffraction phenomena belong to the first group, and scattering effects belong to the second group (23). The characteristic optical properties for finished polymer film products such as haze, transmittance, gloss, etc., are considered to be scattering effects caused by a variation in refractive index or differences in the orientation of anisotropic volume elements within the polymer film and on its surfaces.

For example, polystyrene film, known as a typical noncrystalline polymer, has a very low haze value ($0.1 \sim 3.0\%$) and very high transmittance value ($92 \sim 87\%$), because of its homogeneous internal structure and its rather smooth surface. On the other hand, polyethylene film, known as a typical semicrystalline polymer, has higher haze value ($10 \sim 50\%$ for HDPE, $\sim 5\%$ for LDPE) and lower transmittance value ($40 \sim 0\%$ for HDPE, $57 \sim 35$ for LDPE), because of its inhomogeneous internal structure and its uneven surface (45).

The magnitudes of typical scattering properties of solid polymers have been discussed and reviewed by Ross and Birley (61).

When a quasi-monochromatic and parallel beam of light of flux ϕ , normally incident upon a slab of an inhomogeneous material, immersed (for simplicity) in a homogeneous medium having a refractive index equal to the average refractive index of inhomogeneous material, the following equation holds:

$$\phi = \phi_{\text{undev}} + \Delta\phi_A + \Delta\phi_{\text{SC}} \quad (2.1)$$

where ϕ_{undev} , $\Delta\phi_A$, $\Delta\phi_{\text{SC}}$ represent the amount of flux transmitted without deviation through the inhomogeneous medium, the amount of flux absorbed, and the amount of flux scattered, respectively.

For the vast majority of solid polymers, scattering is the predominant mechanism of attenuation in the visible region of the electromagnetic spectrum, and, in most cases

$$\Delta\phi_A \ll \Delta\phi_{\text{SC}} \quad (2.2)$$

So, equation (2.2) becomes

$$\phi \doteq \phi_{\text{undev}} + \Delta\phi_{\text{SC}} \quad (2.3)$$

The direct transmission factor (specular transmittance) T is defined by

$$T = \frac{\phi_{\text{undev}}}{\phi} = 1 - \frac{\Delta\phi_{\text{SC}}}{\phi} \quad (2.4)$$

If we take scattering to be proportional to the beam intensity

$$\Delta\phi_{\text{SC}} = \tau\phi\Delta l \quad (2.5)$$

where the factor of proportionality τ is the total scattering cross section or scattering coefficient (sometimes called turbidity) and Δl is the thickness of the layer investigated. τ is a quantity of fundamental importance, describing the overall scattering properties of a material. As $\Delta\phi_{SC} = -\Delta\phi$, in infinitesimal form equation (2.5) becomes

$$d\phi = -\tau\phi dl \quad (2.6)$$

which upon integration leads to

$$T = \exp(-\tau\Delta l) \quad (2.7)$$

τ has the dimension (length)⁻¹ and is usually expressed in cm⁻¹. The direct transmission factor T is often utilized in the plastic film industry as a criterion of film clarity (3, 5, 57) which is a measure of the capacity of the inhomogeneous material, i.e., the film, to allow observation of details in the image of an object when observed through the film. It is a dimensionless number, expressed as a percentage. The clarity usually depends on the distance between the object and the inhomogeneous optical system.

Several methods for determining clarity have been described (10, 13, 82, 83). Clampitt et al. (13) developed a technique which allows the determination of the direct transmission factors not only of the bulk but of each surface (air side and chill-roll side). By placing the same side of two identical films together with a liquid whose refractive index is similar to that of polyethylene in between, they could extract the scattering contribution of each surface phase of the film. The

schematic diagram of the instrument used for determination of the direct transmission factor is shown in Figure 2.2.

The total amount of scattered light $\Delta\phi_{SC}$ can be thought of as consisting of two component parts, the forward scattered part $\Delta\phi_{SC}^f$ and the backward scattered part $\Delta\phi_{SC}^b$ (see Figure 2.3)

$$\Delta\phi_{SC} = \Delta\phi_{SC}^f + \Delta\phi_{SC}^b \quad (2.8)$$

The total transmitted light flux through the inhomogeneous medium, ϕ_T , is given by

$$\phi_T = \phi_{undev} + \Delta\phi_{SC}^f \quad (2.9)$$

and the forward scattered fraction, χ_{SC}^f , which is a ratio of the forward scattered light flux to the total transmitted light flux is given by

$$\chi_{SC}^f = \frac{\Delta\phi_{SC}^f}{\phi_T} \quad (2.10)$$

The loss in contrast due to forward scattering is expressed by the forward scattered fraction χ_{SC}^f and is, sometimes, in the plastics industry, called haze. In commercial hazemeters, only the forward scattered light deviating more than 2.5 degrees from the directly transmitted light direction is considered haze (5). A schematic diagram of an instrument for measuring haze value is shown in Figure 2.4 (61).

The gloss is a property of the surface of a material. For practical purpose, the gloss is defined as the ratio between flux, ϕ_r^{Wr} ,

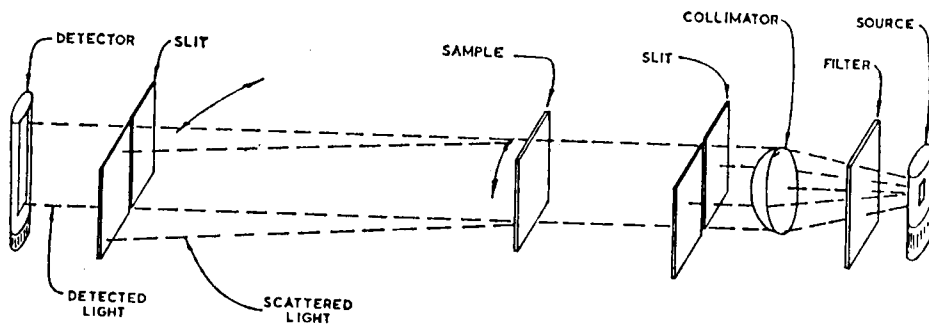


Figure 2.2. Direct transmission factor apparatus "Scattermaster".

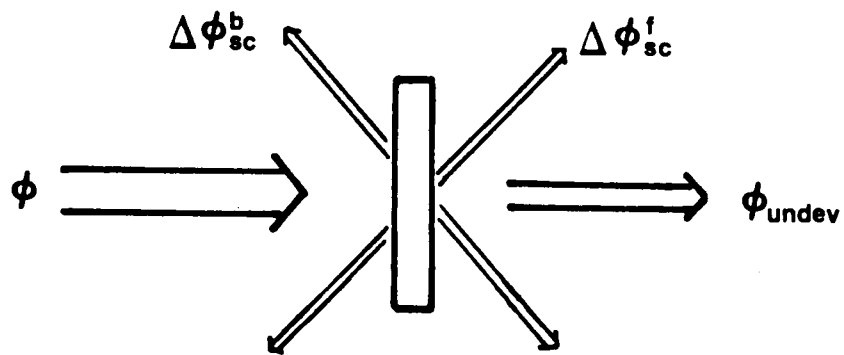
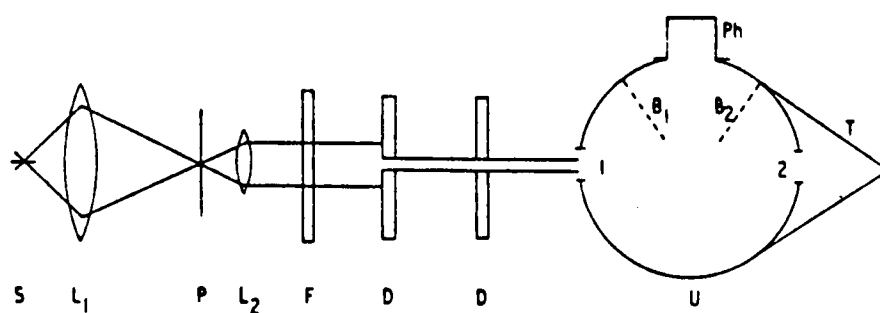


Figure 2.3. The components of scattered light.



S, light source; L_1 , condenser system; P , pinhole (secondary light source); L_2 , collimator (anastigmat lens); F , monochromatic filter; D , diaphragms for adjusting the beam diameter; U , integrating (Ulbricht) sphere, with a minimum diameter of 250 mm; T , light trap; Ph , photodetector; B_1 , baffle used in total transmission factor measurement; B_2 , baffle used in total reflection factor measurement; 1 and 2, apertures diametrically opposite in the integrating sphere.

Figure 2.4. Schematic diagram of commercial hazemeter (61).

scattered within an arbitrary solid angle W_r around the geometrical reflection direction and the incident flux, ϕ .

$$G = \frac{\phi_r^{W_r}}{\phi} \quad (2.11)$$

Its magnitude depends on the refractive index of the material, the smoothness of the surface, and the occurrence of any subsurface optical features.

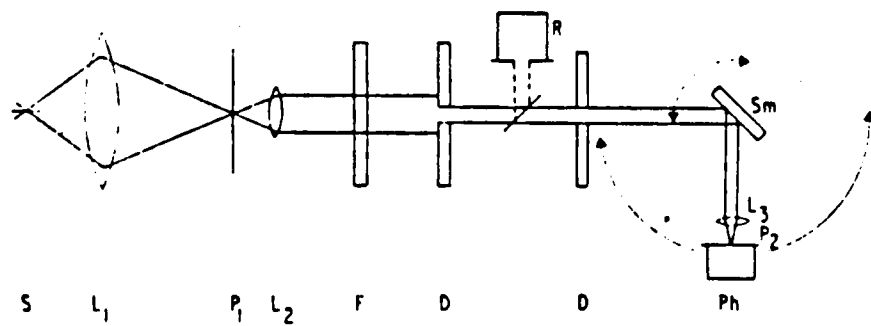
The usual procedure for assessing the scattering from the medium and from the surface individually consists of determining their combined contribution and then, using an immersion method, of measuring the effect due only to the medium.

The standard test method for gloss is presented by the ASTM (6), and schematic diagram of the instrument for measuring gloss value is shown in Figure 2.5 (61).

2.3 Light Scattering from the Internal Structure of Polymers

Light scattering from the internal structure of solid polymers was first considered by Debye and Bueche (18) and Goldstein and Michalik (28).

Stein and his coworkers (67, 68, 69, 70) have studied the scattering of light from crystalline polymers experimentally and theoretically. It was found that the scattering from polyethylene films at angles greater than 8 degrees probably results from refractive index



S, light source (mercury arc lamp); L₁, condenser system; P₁, pinhole (secondary light source); L₂ and L₃, identical anastigmat lenses, for collimating (L₂)

F, monochromatic filter; D, diaphragms to adjust the size of the beam; S_m, sample (usually immersed in a liquid having the same refractive index as the sample); Ph, photodetector (photomultiplier or photocell); R, monitor photodetector system.

Figure 2.5. Schematic diagram of glossmeter (61).

fluctuations occurring in regions smaller than spherulites. They also found out that the dimensions of this structure remain fairly constant during the melting of crystallites, but the refractive index differences between the structure and its surroundings decreases.

In the study of light scattering from oriented polymer films, it was found that the absolute scattering power of an oriented sample is considerably less than for unoriented samples. This would be a result of a decrease in both orientation and density fluctuation (69, 70, 71).

Stein and his coworkers (72, 73, 75, 76, 77) have also studied the small angle light scattering from polyethylene films using polarized light. Small angle photographic light scattering patterns from isotropic polyethylene films have been shown to depend on the size of the spherulites and the difference between its radial and tangential polarizabilities. From the experimental Hv scattering patterns which are obtained by placing a sample film between vertically polarized monochromatic incident light and an analyzer whose plane is horizontal, the average spherulite size can be obtained from the equation

$$\frac{4\pi a}{\lambda} \sin\left(\frac{\theta_m}{2}\right) = 4.09 \quad (2.12)$$

where a is the average radius of the spherulite, λ is the wave length of the incident light in the medium, θ_m is the scattering angle corresponding to maximum scattered intensity. It was concluded that fluctuations in orientation are the dominant cause of light scattering in crystalline polyethylene. But in most of these investigations, scattering from polymer surfaces has been reduced to negligibly low

levels by coating the polymer with a fluid with a refractive index equal to that of the polymer or by crystallizing the polymer between smooth glass microscope slides.

From the observations of small angle light scattering patterns of quenched, rolled HDPE film, Stein et al. (74) asserted that the transparency of such polyethylene films is not primarily related to crystallite size but rather to the type of morphology and to the size of superstructures much larger than the crystallites themselves.

Based on this result Desper (21) has accounted for the transparency of samples being crystallized under combined orientation and pressure effect available in a capillary rheometer, by assuming a very high orientation of the "c" axis and a high degree of crystallinity that could minimize the intensity of light scattering.

On the other hand, Wang and Chen (81) supported the view that smaller sizes of crystallites accounted for the transparency of quenched- rolled polyethylene film.

Hawkins and Richards (30) studied light transmission and the formation and decay of spherulites in polyethylene. They reported that (1) more crystalline samples formed from less branched molecules are more opaque, (2) rapid cooling yields more amorphous samples, which are more transparent, (3) for samples of the same degree of crystallinity, transparency tends to increase with molecular weight. Light transmission was studied as a function of temperature (see Figure 2.6). They related their findings to spherulite formation and accompanying changes in refractive index.

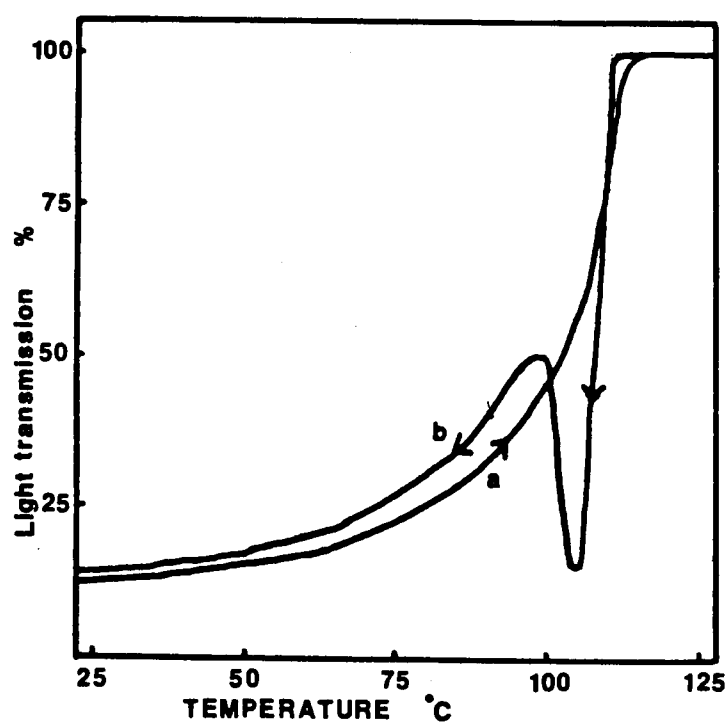


Figure 2.6. Light transmission of polyethylene sheet as a function of temperature.

2.4 Light Scattering from Rough Surfaces

The light incident on a rough film surface is partially reflected and partially refracted. Refracted light may emerge after internal reflections. The light so emerging and the light directly reflected from the outer surface both contribute to the total scattering by the film.

In spite of the fact that the haze of thin blown LDPE film is caused mainly by scattering from rough film surface (26, 27, 33, 56, 64), there have been only a few studies done about film surface roughness and scattering behavior (32, 33, 64).

In optics, however, surface roughness is a most important problem, since the light scattered from rough surfaces of the optical components lowers the performance of the optical system itself. The problem of scattering from rough surfaces has been placed on a firm theoretical and experimental basis. This is reviewed by Elson, Bennett and Bennett (25).

There are several kinds of irregularities which may cause surface scattering: (1) irregularities which are large relative to the wave length of the incident light, (2) isolated irregularities which are comparable to or smaller than the wavelength of the incident light, and (3) irregularities which are small relative to the wavelength but which are so closely spaced that they can not be treated as independent scattering centers. In case of blown film, especially polyethylene blown film, irregularities commonly termed "extrudate distortion", "melt fracture", etc., involve gross distortion of extrudates, or surface

roughness known as "shark-skin" as well as scratches belong to category (1). Those irregularities such as "grain" in extruded blown film belong to the category (2), and those irregularities such as so-called "extrusion haze" in blown film belong to the category (3). (Refer to section 2.6 for definitions of film surface irregularities.)

The appropriate theoretical treatment of scattering depends on which of the above categories the scattering centers fall into. If the dimensions of the irregularities are large compared with the wave length of the incident light, the reflectance of a surface is determined entirely by geometrical optics and is a function only of the inclinations of the facets. When the irregularities become comparable to or smaller than the wave length of the incident light, the scattering problem becomes a diffraction problem, and geometrical optics is no longer adequate. A great simplification occurs, however, if the scattering centers can be considered to act independently. Mie scattering theory (49), of which Rayleigh scattering (59) is a special case, can then be used. The scattering caused by so-called "micro-irregularity," which is mentioned above (category 3), has been studied by several authors based on the Kirchoff-method in diffraction theory. The most comprehensive development has been given by Beckmann and Spizzichino (7). However, most of the work in this area has been done in the past 20 years and it is still continuing.

2.5 Measurements and Characterization of Surface Roughness

A. Measurement of Surface Roughness

Qualitative evaluations of film surface roughness have been done mainly using the scanning electron microscope (32, 33, 64).

Howell and Benbow (32) reported that the size of small defects on blown LDPE film surface, which is thought to be the main cause of haze, is about 1 μm . Stehling et al., based on SEM photographs, reported that these small scale defects form mounds which are a few micrometers (μm) in diameter and protrude from the surface by about 1 μm or less.

Several methods of measuring the statistical character of surfaces have been developed (25). Statistical surfaces having fine scale roughness may be measured using stereo electron microscopy (17), multiple-beam interferometry (9) or surface profiling instruments (24).

Stereo electron microscopy involves making a replica of the surface for observation in a transmission electron microscope, taking stereo pairs of electron micrographs, and then measuring heights of surface features using a stereo viewer and parallax bar. Multiple-beam interferometry is a method for obtaining statistics of surface features which have lateral separation of the order of several micrometers.

Surface profiling instruments (58) use a diamond stylus to trace over the surface. The radius of the standard (conical) stylus is about 8 μm , and several styluses having radii in the 0.5 ~ 2.5 μm range are available. The stylus loading is continuously adjustable from about 1 to 40 mg. A loading of 2 mg is generally used with standard stylus for

optical surface measurement to insure good contact without permanently marking the surfaces (24).

B. Characterization of Random Rough Surfaces

The fine scale surface roughness of the LDPE blown film appears to be a random process. Random surfaces such as terrain, sea, atmospheric layers, etc., are best described by the values of appropriate statistical parameters (7, 8).

Consider a one dimensional random surface profile (see Figure 2.7), where X is the horizontal coordinate and $h(x)$ is the height coordinate of the random rough surface. We define δ as the separation parameter

$$\delta = X_2 - X_1 \quad (X_1, X_2 \text{ are arbitrary}) \quad (2.13)$$

L is the measured length along the X axis.

Assuming the random process of the surface roughness is stationery and ergodic, we can characterize the roughness of the surface using two statistical functions.

That is, the statistical distribution of height deviation from a certain mean level gives us information about heights of hills, and the correlation function or autocorrelation coefficient gives us information about how the hills and the valleys of the surface are crowded close together or far apart. These functions are defined as follows.

The standard deviation σ of height $h(x)$ is

$$\sigma^2 = \lim_{L \rightarrow \infty} \frac{1}{L} \int_0^L [h(x) - \langle h(x) \rangle]^2 dx \quad (2.14a)$$

$$= \langle h(x)^2 \rangle - \langle h(x) \rangle^2 \quad (2.14b)$$

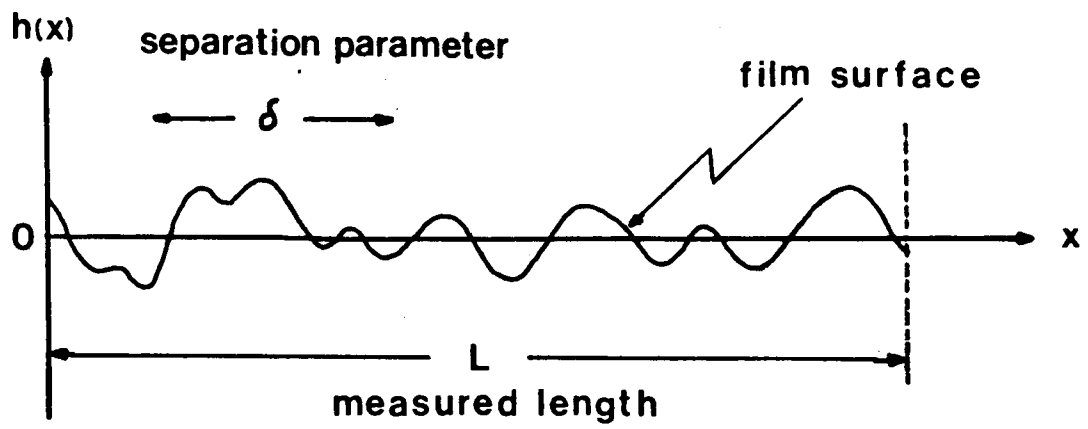


Figure 2.7. Coordinates of random surface profile.

where $\langle h(x) \rangle$ is the mean value of the height given by

$$\langle h(x) \rangle = \lim_{L \rightarrow \infty} \frac{1}{L} \int h(x) dx \quad (2.15)$$

The correlation function is

$$B(\delta) = \lim_{L \rightarrow \infty} \frac{1}{L} \int h(x)h(x + \delta) dx \quad (2.16)$$

And its normalized correlation function (autocorrelation function) is

$$C(\delta) = \frac{B(\delta) - \langle h(x) \rangle^2}{\langle h(x)^2 \rangle - \langle h(x) \rangle^2} \quad (2.17)$$

For a purely random surface, $C(\delta)$ will decrease monotonously from its maximum value

$$C(0) = 1 \quad \text{to} \quad C(\infty) = 0 \quad . \quad (2.18)$$

And the correlation distance D_c which can be thought of as a measure of the density of the roughness on a horizontal scale is defined to be the distance at which $C(\delta)$ drops to the value of $1/e$ (see Figure 2.8).

These statistical parameters, σ , $C(\delta)$ and D_c , can be evaluated from surface profile data obtained using a stylus.

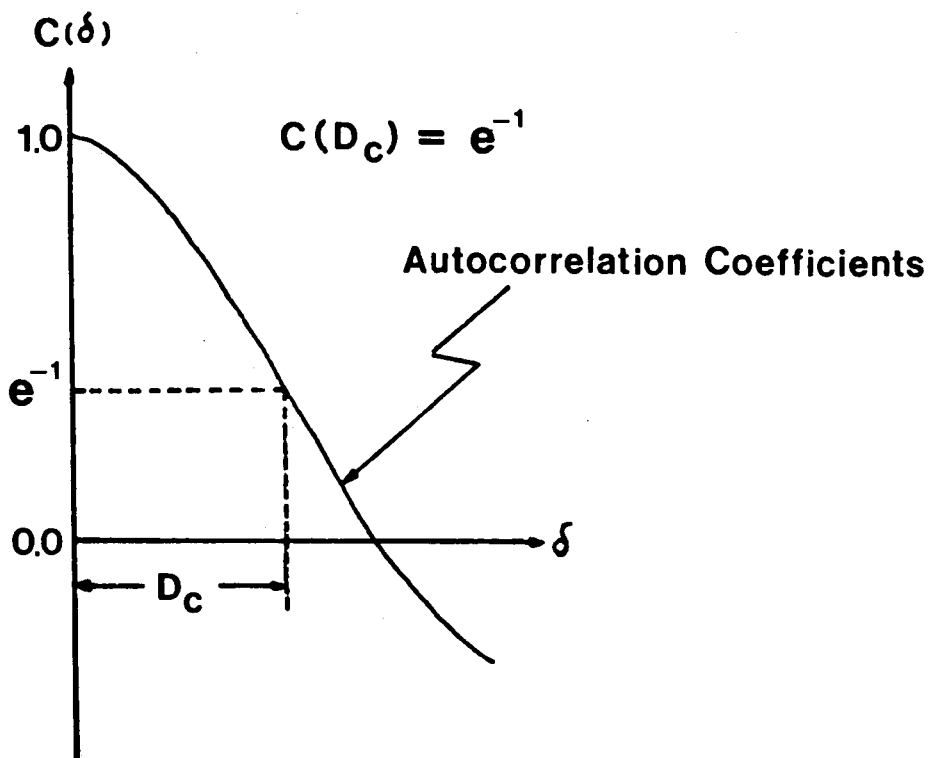


Figure 2.8. Definition of correlation distance.

2.6 Surface Roughness on Polymer Film

A. Cause of Surface Roughness

There appear to be two major types of optical irregularities on the surface of blown crystalline polymer film, although light will also be scattered at inhomogeneities such as grain, microgels, and particulate additives. These arise from surface irregularities caused by melt flow phenomena, and surface irregularities caused by crystallization-behavior (32).

Several kinds of surface irregularities, known as flow defects, are observed and categorized.

1. Extrudate distortion, described as "waviness", "knobbliness" by Clegg (14) and as "melt fracture" by Tordella (79, 80), is recognized as a departure from smooth flow which arises because polymer melts are elastic as well as viscous. This phenomenon has been extensively studied by several researchers (i.e., 80, 84).

2. Surface irregularities, known as "shark skin" or "matness", have depth of more than 50 μm . This phenomenon is considered as a surface defect arising at the die exit where a velocity discontinuity occurs owing to polymer-metal adhesion. The correlation between "shark skin" and the cohesive failure of polymer melts was studied by Cogswell (16).

3. Surface irregularities, known as "extrusion haze" (33), is a structure about 1 μm in size. Although this kind of irregularity seems to be mainly related to haze of thin LDPE blown film as well as

irregularities caused by crystallization-behavior, it is still incompletely explained because of its fine structure (32, 33, 64).

Fine surface irregularities caused by crystallization-behavior have been studied only briefly (32, 33, 64). Huck and Clegg concluded that these surface irregularities arise from the growth and aggregation of crystallites at or near the surface which buckle the surface of the film. Stehling et al. suggested that so-called crystallization haze is caused by stress-induced crystallization close to the film surface during blown film operations.

B. Effect of Processing Conditions

Huck and Clegg (33), who first showed the existence of extrusion haze, suggested how the degree of surface roughness depends upon the principal extrusion conditions in the blown film polyethylene process. According to their interpretation, during the film forming operation there will be a change in the texture of the surface of the melt because of a decrease in the height of the extrusion defects and an increase in their length and breadth as the melt is drawn lengthways and blown sideways and the overall magnitude of the extrusion defects will decrease under the influence of surface tension. On the other hand surface irregularities arising from the growth and aggregation of crystallites, which is mainly influenced by the temperature gradient at the frost line, the frost-line height, and the cooling time, will increase as the frost-line height (the cooling time) increases. These two opposing effects should contribute to the total haze of LDPE (see Figure 2.9).

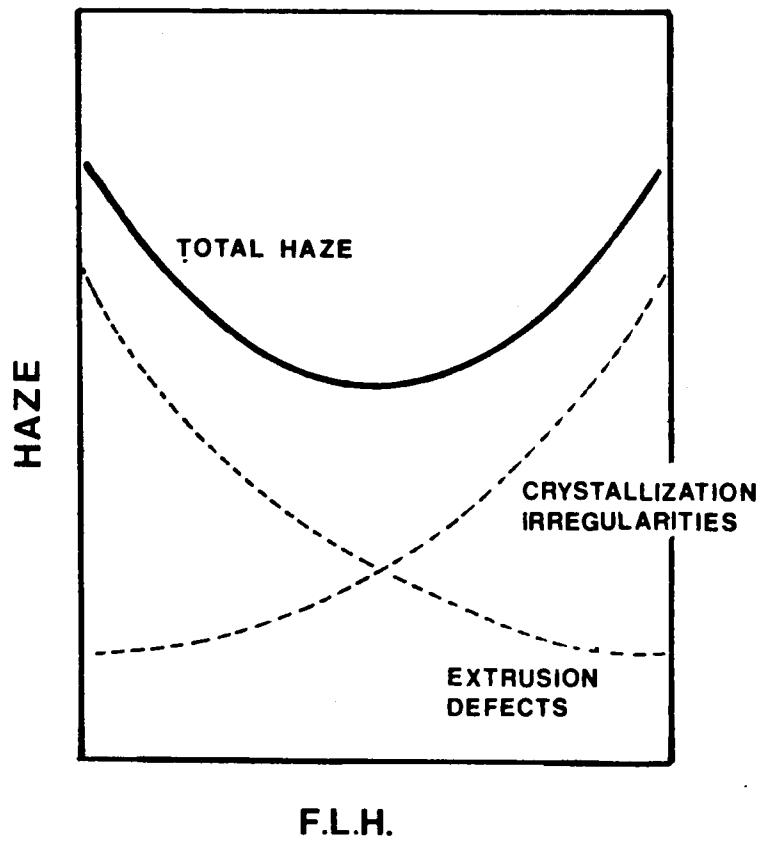


Figure 2.9. Haze value as a function of frost line height (33).

Using these hypotheses, they rationalized many of the effects of film fabrication conditions on film haze.

Howells and Benbow (32) experimentally showed that the surface haze which must be associated with mainly the extrusion haze component decreases with decreasing draw-down ratio. They noted that this decrease in extrusion haze is partly accountable by the greater relaxation occurring between the die and the frost line at low draw-down ratio (see Figure 2.9). And they suggested that in order to generate extrusion haze it is necessary to apply both melt shear (as in the film die) and a simple melt deformation (as in the draw down or blow up) and one of these processes alone is not sufficient, and that extrusion haze may originate in the immediate vicinity of the die exit but relaxes rapidly unless a restraint is imposed.

Recently Stehling and his coworkers (64) carried out on-line haze measurement to confirm Huck and Clegg's hypotheses using flat films extruded from a slit die. It was assumed that for these films the mechanisms of haze formation are similar to that of blown films. Haze was measured as a function of distance from the die. Their measurements on LDPE (see Figure 2.10) showed monotonically increasing haze from the die exit to far down stream instead of the postulated initial decrease. They also carried out on-line small angle light scattering measurements. And for the reason that haze increases rather than decreases after exit from the die, they suggested that the spatial rearrangement of the surface features generated at the die exit possible causes an increase rather than a decrease in haze.

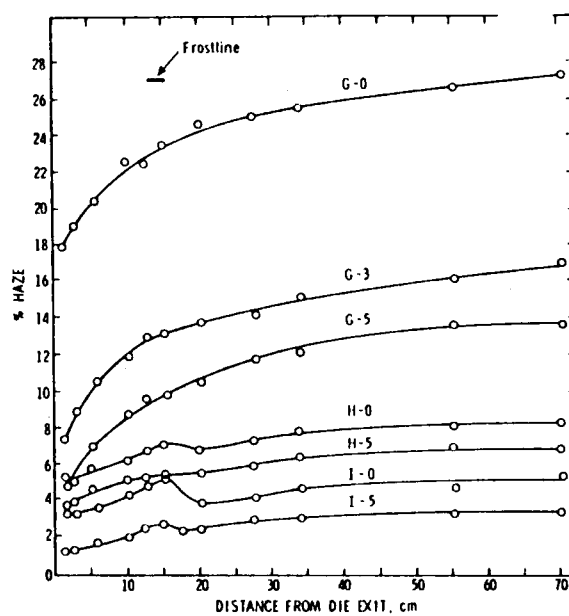


Figure 2.10. Haze value as a function of distance from die exit in LDPE blown film (64).

It is well known that the haze of LDPE film can be reduced by subjecting the polymer melt to a mechanical deformation in an intensive mixer before extrusion (2). Although this process is commonly used in the film industry, the mechanism is poorly understood. A number of workers have proposed that polymer melt elasticity is closely related to blown film haze. According to Huck and Clegg (33), the haze of LDPE film increases as extrudate die swell increases. Shroff et al. (63) used entrance pressure drop for flow into a capillary, P_0 as a measure of melt elasticity and concluded that the haze of blown poly (ethylene-co-vinyl acetate) film increased as P_0 increased. Howell and Benbow (32) reported, without supporting data, that mechanical treatment reduced LDPE melt elasticity without molecular weight changes. A similar but better documented conclusion was obtained by Fujiki (27) and Rokudai (60), who further noted that reduction in elasticity (die swell and entrance pressure drop) was accompanied by a decrease in film haze. Howells and Benbow (32) stated that the reduction in elasticity could be almost completely reversed by holding the melt at high temperatures for long times and by dissolving and reprecipitating the polymer, but no data to support these assertions were given. They interpreted the reduction and recovery of elasticity in terms of a reversible disentanglement-reentanglement mechanism.

On the other hand Albright (2) attributed the reduction of film haze resulting from mechanical deformation of the melt to polymer chain scission, but he presented no data to support this view. Stehling et al. (64) carried out haze measurement on LDPE blown films which were

reextruded several times. From data obtained from GPC measurements and measurements of die swell recovery with different residence times in a capillary rheometer, they concluded that mechanical deformation reduces melt elasticity and haze by a reversible physical mechanism that generates a long-lived nonequilibrium melt structure.

C. Effect of Molecular Structure

The effect of polymer chain structure on LDPE film haze has been only briefly investigated. Perron and Lederman (56) concluded from GPC examination of a few LDPE resins that broadening of molecular weight distribution caused an increase in haze. However, no allowance was made for long-chain branching of LDPE in the analysis of the GPC chromatographs. Foster (26) concluded that the total haze of LDPE blown films increased as the number of long branches in the resin increased. Stehling et al. (64) reported that the haze of blown LDPE film increased with increase of molecular weight distribution, the concentration of large size molecules and the number of long branches in a weight-average molecule from their GPC measurement. They also suggested that by introducing more irregularity into the polymer chain by copolymerization or by increasing short-chain branching, haze arising from crystallization may possibly be reduced.

2.7 Structure and Crystalline Orientation Development for Blown PE Film

Film structural studies of polyethylene related to blown film processing conditions (i.e., various blow-up ratios) was carried out by

Homes and Palmer (31) with flat-plate x-ray diffraction and birefringence. They concluded that the a axis of the unit cell lies along the extrusion (machine) direction and the c axis, the polymer chain direction, tends to orient perpendicular to the extrusion direction.

However, Keller (34, 35) proposed an alternative interpretation, termed row orientation, in which the b axis take up a preferred orientation perpendicular to the machine direction, and the a and c axes are randomly distributed with cylindrical symmetry about the b axis.

Lindenmeyer and Lustig (38) investigated crystalline orientation in HDPE and LDPE films, using WAXS and constructed pole figures. At low blow-up ratios, the crystalline orientations of the HDPE and LDPE are approximately the same, but at high blow-up ratio the LDPE film showed b axis perpendicular to the film and the a and c axes uniformly distributed in the plane of the film. Desper (20) carried out pole figure measurements for LDPE blown film with various quenching conditions (various frost line heights), and calculated the crystal orientation functions derived by Desper and Stein (22). They reported that equal degrees of a and c axes orientation parallel to the machine direction at low quench rates, and increasing a axis orientation as the quenching rate increases, coupled with a shift in the c axis from parallel to perpendicular orientation.

More recently Maddams and Preedy (41-43) have presented a series of papers about the orientation of HDPE blown films. Two types of crystalline orientations are described. One is the a and c axes

inclined at an angle to the plane of the film, which was developed by Keller and Machin (36). The other type is the c axis distributed substantially along the machine direction and the a_x and b_x axes rotated around the c_x axis, which is found in cold drawn polyethylene (46, 46). These types of orientation depend upon the blow-up ratio, draw-down ratio, cooling condition and sample. They found out that for some HDPE samples under very low stress conditions, there was almost pure "a" axis orientation, and under very high draw-down conditions, there was substantial "c" axis orientation, both with reference to the machine direction and commercial blowing conditions gave rather high stresses and the a axis was inclined at 60° to the machine direction in the sheet-normal direction plane. They also found out that high draw-down ratio and low extrusion temperature were the most effective in promoting high stress crystallization.

Choi, White and Spruiell investigated the orientation in blown film of polystyrene (12) and high density polyethylene (11) as a function of processing conditions. They found that the orientation was determined by the stresses at the point of solidification. The results were interpreted in terms of White-Spruiell biaxial orientation factors (13) which are given by the expressions

$$f_{1j}^B = 2 \overline{\cos^2 \phi_{1,j}} + \overline{\cos^2 \phi_{2,j}} - 1 \quad (2.28a)$$

$$f_{2j}^B = 2 \overline{\cos^2 \phi_{2,j}} + \overline{\cos^2 \phi_{1,j}} - 1 \quad (2.28b)$$

for the case of crystalline polymers, where j represents the a , b and c crystallographic axes, 1 and 2 represent the reference directions (e.g., machine and transverse directions, respectively), ϕ is the angle between the crystallographic axis and the reference direction.

They found that the polyethylene films showed much higher levels of crystalline orientation from WAXS than would be expected from the Rheo-Optical Law (39, 40). This is due to oriented nucleation and growth of crystals. However, for the polystyrene films, they showed that orientation in the films was exactly that predicted from the Rheo-Optical Law. The stresses were found from balance of forces in blown film process developed by Pearson and Petrie (53). A similar situation exists for melt spun polystyrene (51) and polyethylene filaments (19).

They also found that in the uniaxial polyethylene films, a row structure, first described by Keller, was favored and a biaxially oriented sample exhibited a morphology appearing to be approximately equivalent to a superimposed row structure as illustrated schematically in Figures 2.11 and 2.12.

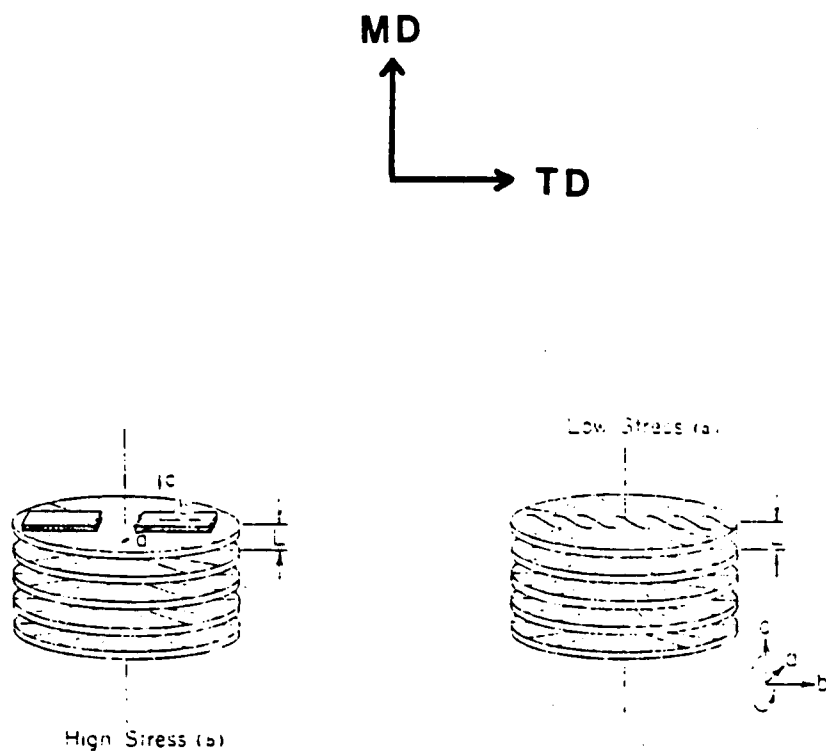


Figure 2.11. Keller-Martin row structure for strictly uniaxial polyethylene fiber.

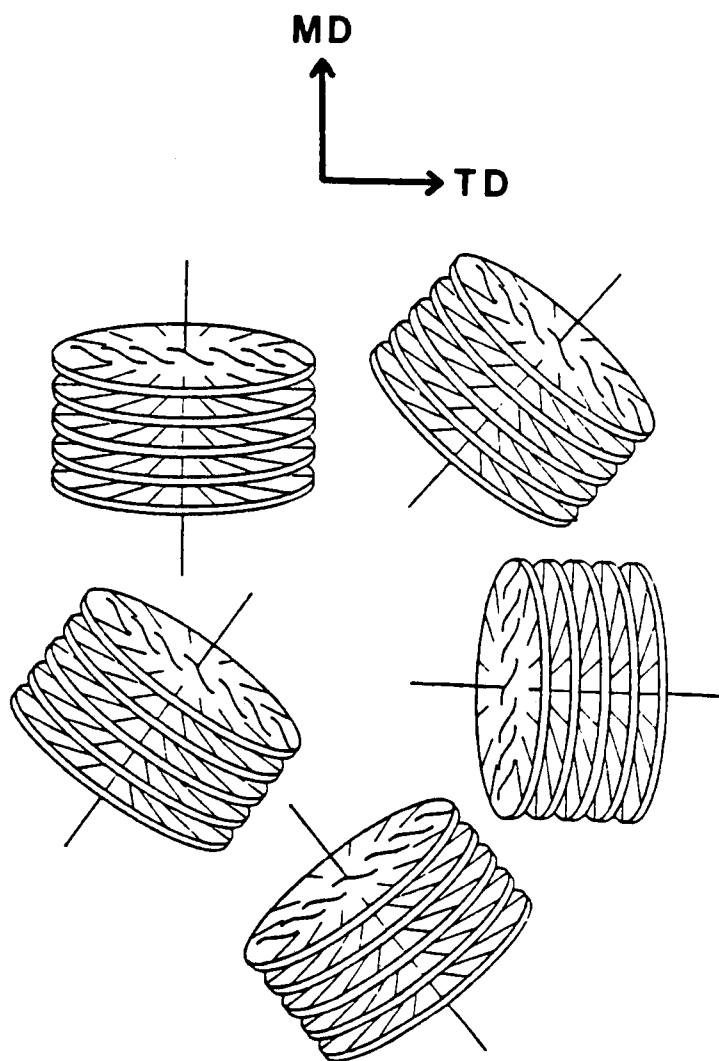


Figure 2.12. Morphological model for polyethylene blown film with equal biaxial orientation.

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURES

3.1 Materials

The polymers used in these experiments were a commercial linear low density polyethylene, UCC GRSN 7040 (MI = 2.0, density = 0.921), and low density polyethylene, UCC DFD 0332 (MI = 1.0, density = 0.918).

Several other kinds of blown films produced by our laboratories (C-2, 62) were also used for characterization of their optical properties and surface roughness. These polymers were a commercial high density polyethylene Chemplex 6009 (MI = 0.98, density = 0.960), Chemplex 6109 (MI = 0.8, density = 0.960) and polypropylene Hercules Pro-fax PD195 (MI = 1.5) and HDPE (Chemplex 6109)-PP (Pro-fax PD195) blends with various weight compositions (PE/PP = 75/25, 50/50, 25/75).

3.2 Film Extrusion Apparatus and Operating Conditions

Linear low density polyethylene and low density polyethylene blown films were produced using a 3/4 inch Rainville screw extruder with an annular blown film die (inside diameter = 1.496 cm and outside diameter = 1.605 cm). A schematic diagram of the die is given in Figure 3.1.

The operation temperature was set at 180°C throughout the system (barrel, adaptor, die) and the out-put was kept constant for all

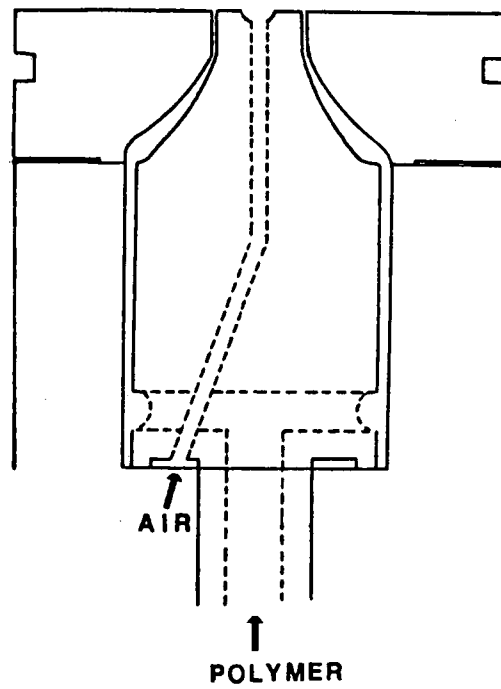


Figure 3.1. Schematic diagram of the blown film die.

experiments ($Q = 12.5$ g/min). A photograph of the apparatus is shown in Figure 3.2.

Several samples of linear low density polyethylene and low density polyethylene blown films were produced with various draw-down ratios ($1.0 \sim 8.0$), blow-up ratios ($1.0 \sim 4.5$) and frost-line heights ($2.5 \sim 12$ cm).

The time it takes for the molten polymer to travel from the die exit to the frost line was measured using a movie camera. The solidification temperature at the frost line was measured using a pyrometer. These data were used to calculate the apparent cooling rate on the film surface. These studies were carried out in conjunction with T. Konai.

Linear low density polyethylene blown films and low density polyethylene blown films were labeled LL and L, respectively.

A detailed summary of preparation conditions is presented in Table 3.1.

Other films whose optical properties and surface roughness were characterized in this research are listed with their preparation conditions in Table 3.2.

3.3 Direct Transmission Factor Measurements

The direct transmission factor of the blown film was measured using wide angle light scattering apparatus, Model 6000 Light Scattering Monophotometer (C-7). A source of monochromatic light whose wavelength is 5460A provided incident light. A schematic diagram of the equipment is shown in Figure 3.3.

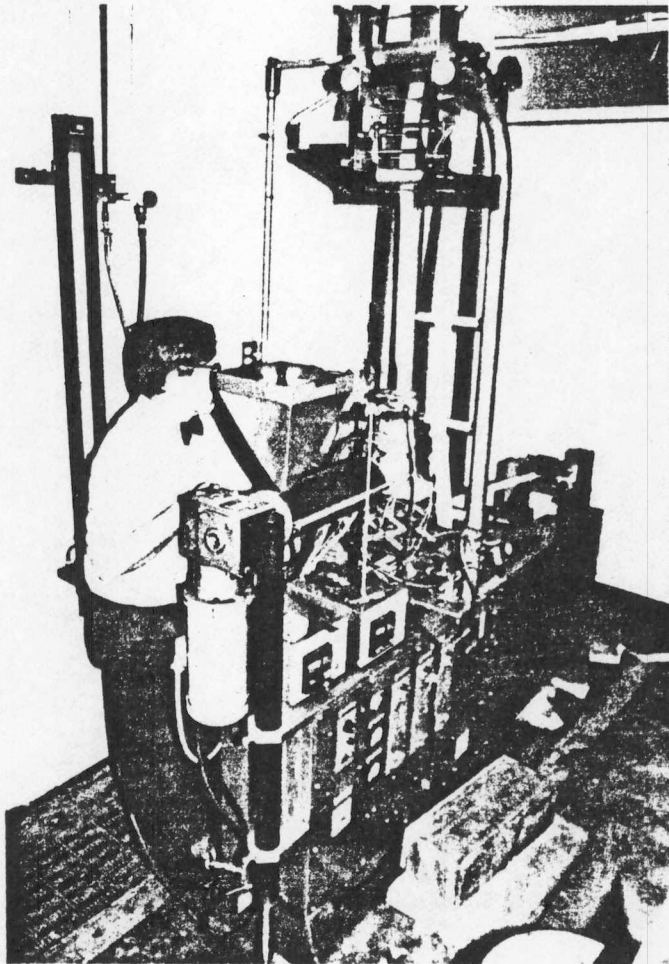


Figure 3.2. Blown film apparatus.

Table 3.1. Operation Conditions for L-LDPE and LDPE Blown Films

Materials	Sample #	D.D.R. (-)	B.U.R. (-)	F.L.H. (cm)
L-LDPE GRSN 7040 and LDPE DFD 0332	L-1,LL-1	4.0	3.5	12
	L-2,LL-2	4.0	3.5	9
	L-3,LL-3	4.0	3.5	6
	L-4,LL-4	4.0	3.5	2.5
	L-5,LL-5	1.0	2.5	9
	L-6,LL-6	2.0	2.5	9
	L-7,LL-7	4.0	2.5	9
	L-8,LL-8	6.0	2.5	9
	L-9,LL-9	8.0	2.5	9
	L-10,LL-10	4.0	1.0	9
	L-11,LL-11	4.0	4.5	9

Output = 12.5g/min; Temp. = 180°C.

Table 3.2. Operation Conditions for HDPE, PP and Blend Polymer Blown Films

Materials	Sample #	D.D.R. (-)	B.U.R. (-)	F.L.H. (cm)
<u>HDPE Chemplex 6009</u>				
	4	3.4	2.2	~15
	6	10.6	2.3	~15
<u>HDPE Chemplex 6109</u>				
	E31	3.0	1.0	~22
	E33	3.0	3.0	~22
<u>HDPE/PP Blend</u>				
75/25	EP91	3.0	1.0	~22
	EP93	3.0	3.0	~22
50/50	EP72	3.0	1.0	~22
	EP74	3.0	3.0	~22
25/75	EP61	3.0	1.0	~22
	EP63	3.0	3.0	~22
<u>PP Pro-Fax PD195</u>				
	P102	3.0	1.0	~22
	P104	3.0	3.0	~22

Temp. = 200°C for #4, #6; Temp. = 210°C for others.

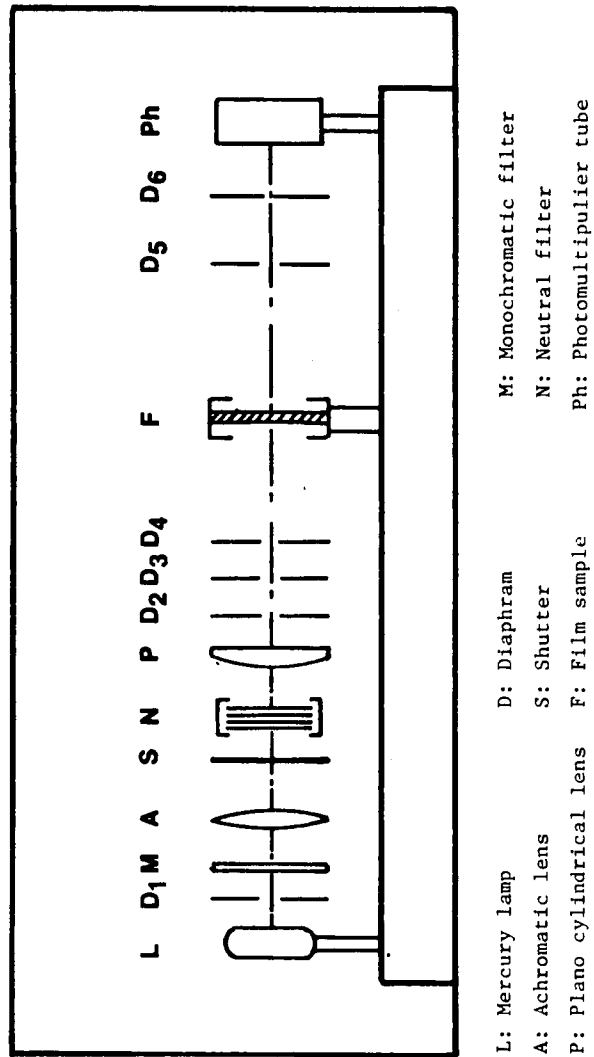


Figure 3.3. Schematic diagram of Light Scattering Monophotometer Model 6000.

The direct transmission factors of surface phase, T_S , and bulk phase, T_B , were obtained using the immersion method. First the direct transmission factor of a single blown film, T , was measured by immersing the blown film in Glycerol ($C_3H_8O_3$, $n = 1.47$) whose refractive index is similar to that of polyethylene ($n = 1.50 \sim 1.54$). A pair of glass microscope slides were used to hold the film and the liquid. Since the direct transmission factor of the single blown film is a product of transmission values of each phase (L-5)

$$T = T_S \cdot T_B \quad (3.1)$$

The direct transmission factor of the surface phase, T_S , can be calculated using the above equation.

The turbidity, τ , of the bulk phase was also calculated using the equation

$$T_B = \exp(-\tau \Delta l) \quad (3.2)$$

For some blown films, direct transmission factors of inner surface phase, T_{si} , and that of outer surface phase, T_{so} , were obtained with a method similar to that of Clampit (13).

Using the same idea mentioned previously, the direct transmission factor of the single blown film, T , can be expressed by

$$T = T_{so} \cdot T_{si} \cdot T_B \quad (3.3)$$

where T_{so} and T_{si} are direct transmission factors of outer surface phase and inner surface phase, respectively.

By placing the outer surface of two identical films together with a liquid in between, the two contributing surfaces will be the inner surface, and vice versa (see Figure 3.4).

For two films placed with the outer surfaces together Eq. (3.3) becomes

$$[T]_{\text{so-so}} = (T_{\text{si}})^2 \cdot (T_{\text{B}})^2 \quad (3.4)$$

and for two films placed inner surface to inner surface together

$$[T]_{\text{si-si}} = (T_{\text{so}})^2 \cdot (T_{\text{B}})^2 \quad (3.5)$$

The equations (3.3), (3.4) and (3.5) may be solved simultaneously to yield values for T_{B} , T_{so} , T_{si} .

For the bulk phase direct transmission factor

$$T = \left(\frac{[T]_{\text{so-so}} \cdot [T]_{\text{si-si}}}{T} \right)^{\frac{1}{2}} \quad (3.6)$$

for the outer surface phase direct transmission factor

$$T_{\text{so}} = \frac{T^2}{[T]_{\text{so-so}}} \quad (3.7)$$

and for the inner surface phase direct transmission factor

$$T_{\text{si}} = \frac{T^2}{[T]_{\text{si-si}}} \quad (3.8)$$

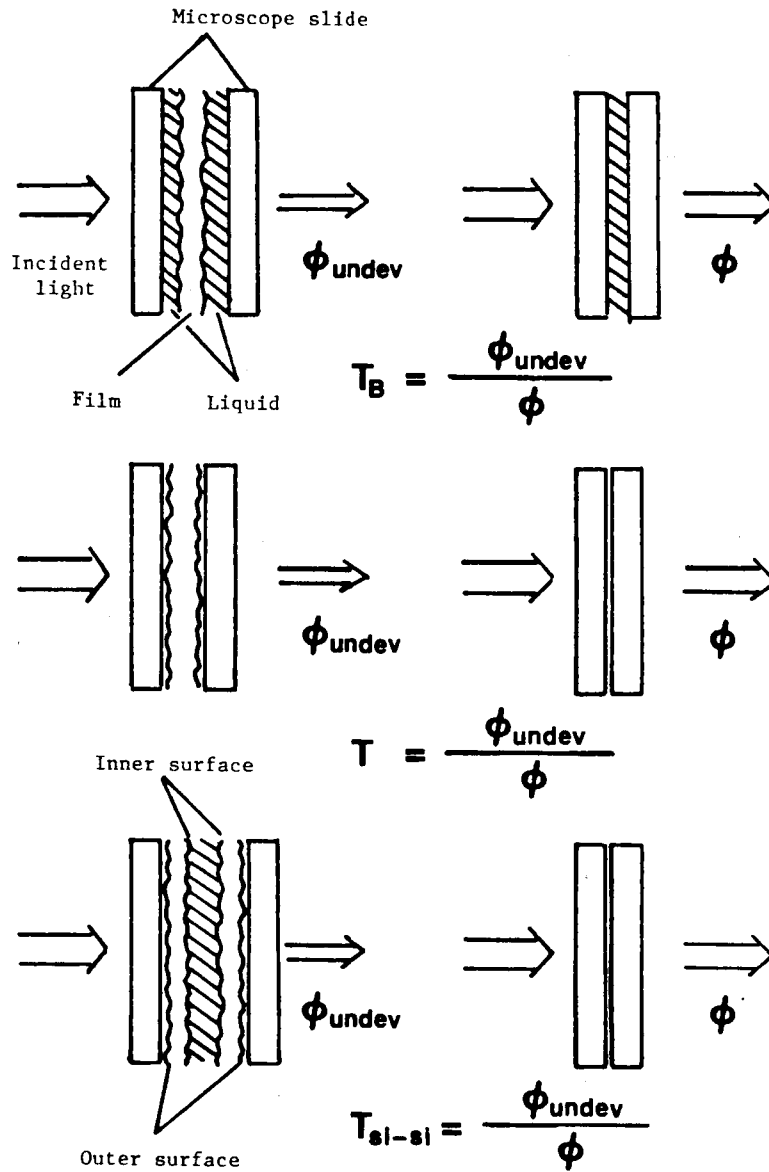


Figure 3.4. Measurement of direct transmission factor.

Experimentally, three direct transmission factors, T , $[T]_{so-so}$ and $[T]_{si-si}$ were measured and direct transmission factors of each phase were calculated using the above equations.

Here again a pair of glass microscope slides was used to hold the films and the liquid during measurement.

For the calculations of T , $[T]_{so-so}$ and $[T]_{si-si}$ an undeviated beam of incident light passing through a pair of glass microscope slides was measured as an incident light flux, and for the calculation of the values of T_B an undeviated beam flux through a pair of glass microscope slides with the liquid in between was measured as an incident light flux.

3.4 Microscopic Examination

A microscopic examination of the film surface was done using a scanning electron microscope, AMR Model 900 high resolution electron microscope.

The film samples were coated with gold-palladium in a vacuum chamber to eliminate charging of the films by electrons. The scanning electron microscope was operated at 6 kv and 40 mA. This low voltage operation was chosen particularly to eliminate the destructive effects of the electron beam on the film surface. Generally two different magnifications ($\times 2000$ and $\times 5000$) were used for the observation of the film surfaces.

3.5 Measurement of Surface Profile and Its Characterization

A. Measurement of Surface Profile

A profile of the surface roughness of each blown film was obtained using a Tencor Alpha-Step surface profiler (78). The radius of the diamond stylus used in this experiment was about 2 μm and the stylus loading was adjusted to about 3 mg to produce good contact with the polyethylene film surfaces. The total possible stylus travel across the sample is 3 mm, but 0.4 mm-long scans were generally used for the surface statistics.

Several different vertical magnifications (1000 kA° full scale – 1000 A° full scale) are available, 25 kA° , 10 kA° and 5000 A° full scale magnifications were used generally according to the degree of surface roughness. Two stylus traverse speeds are available, the slowest one, 10 $\mu\text{m}/\text{sec}$, was used for the surface statistics. The schematic diagram of the surface profiler is shown in Figure 3.5.

Six sets of data (three sets along machine direction and three sets along transverse direction) were sampled from different places for each film. The surface profiles obtained by the surface profiler were digitized for statistical calculations using the TEKTRONIX 4953 Graphics Tablet system. The computer program for the system used is given in Appendix A. The horizontal spacing between adjacent points on the surface is 2.0 μm and the vertical spacing are 0.0127 μm for 25 kA° full scale, 0.0051 for 10 kA° full scale and 0.0025 μm for 5000 A° full scale.

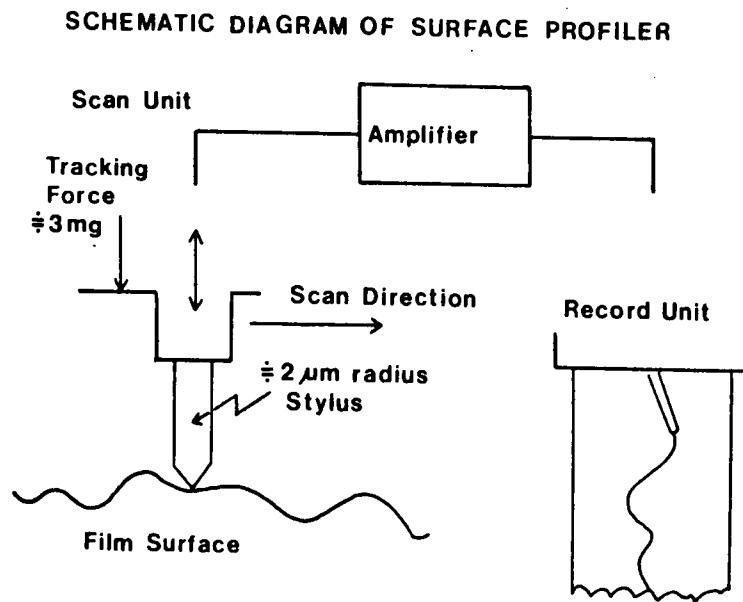


Figure 3.5. Schematic diagram of the surface profiler.

B. Characterization of Surface Roughness

Surface roughness of blown film was assumed to be randomly distributed. First a least squares straight line was calculated for each 0.1 mm-long scan to eliminate the effect of large bumps as well as instrument drift and sample tilt. These four sets of a least squares straight lines were considered as the mean surface level and differences were calculated for all points from the straight lines. These differences were considered to be the basic surface profile data $h(n)$ (see Figure 3.6).

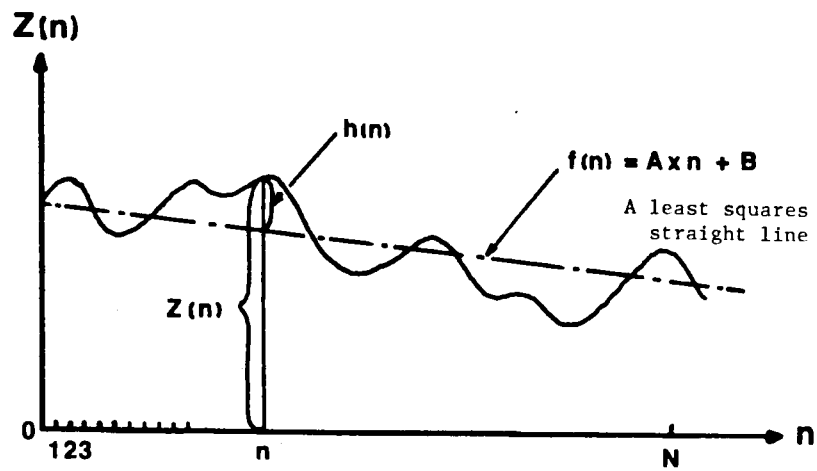
Standard variation of height, σ , and autocorrelation coefficient, $c(\sigma)$, were calculated using the following equations.

$$\sigma = \left[\frac{1}{N} \sum_{n=1}^N \{h(n)\}^2 \right]^{\frac{1}{2}} \quad (3.1)$$

$$\begin{aligned} C(\delta) &= \frac{B(\delta)}{\sigma^2} \\ &= \frac{\frac{1}{N} \sum_{n=1}^{N-\delta} h(n)h(n + \delta)}{\sum_{n=1}^N \{h(n)\}^2} \end{aligned} \quad (3.2)$$

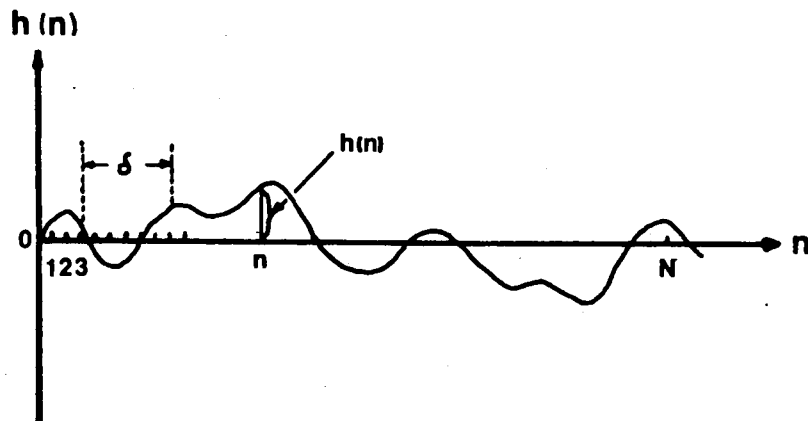
where $n(=1, 2, 3 \dots)$ is each data point, $N(=200)$ is the total number of data points and $\delta(=1, 2, 3 \dots)$ is the separation factor. It should be noted that for the above calculations the mean value of $h(n)$, $\langle h(n) \rangle$, is zero. Correlation distance, D_c , was determined from the relation

$$c(D_c) = e^{-1} \quad (3.3)$$



Actual digitized surface profile data $Z(n)$

$$h(n) = Z(n) - f(n)$$



Basic digitized surface profile data $h(n)$

Figure 3.6. Treatment of surface profile data.

All calculations were done using the DEC-10 computer system. The computer program used for these calculations is given in Appendix B.

3.6 Density Measurement and Determination of Crystallinity

The density of polyethylene was determined at 23°C using a distilled water-isopropyl alcohol density gradient column with a range of 0.9200 ~ 0.9700 g/cm³.

The crystalline fraction was obtained through

$$X = \frac{\rho_c}{\rho} \cdot \frac{(\rho - \rho_a)}{(\rho_c - \rho_a)} \quad (3.4)$$

where X is the crystalline fraction, ρ_c is the crystalline density of polyethylene ($\rho_c = 1.002$), ρ_a is the amorphous density ($\rho_a = 0.855$) and ρ is sample density measured.

3.7 Birefringence Measurements

Both "in-plane" and "out-of-plane" birefringences were measured. The "in-plane" birefringence represents the difference of index of refraction between the machine and transverse directions, Δn_{12} , and the "out-of-plane" birefringence represents the difference in index of refraction between the machine and thickness direction, Δn_{13} . This was accomplished using an instrument equivalent to that of Stein (65) which allows a sample to be rotated and tilted in the incident polarized light beam. The governing equation given by Stein for obtaining the "out-of-plane" birefringence is

$$\Delta n_{13} = \frac{\lambda_0}{d_0} \left[\frac{R_0 (1 - \sin^2 \phi / n^2)^{1/2} - R_0}{\sin^2 \phi / n^2} \right] \quad (3.5)$$

where n is the average index of refraction of the film, λ_0 is the wavelength of the light used in vacuum, d_0 is the thickness of the film, 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 .

3.8 X-Ray Pole Figure Determinations and Evaluation of Orientation Functions

A. X-Ray Pole Figure Determinations

A General Electric X-ray diffractometer equipped with a single crystal orienter was used. The radiation used was crystal-monochromated Cu-K_α of wave length 1.542 Å. The X-ray unit was operated at 40 KV and 15 mA. Films were stacked and glued with epoxy glue at their edges and mounted on the single crystal orienter. The amorphous (110) and (200) intensity data were corrected for overlap by the method of Nichols (50), and Aggarwal and Tilley (1). Detailed data recording and pole figure plotting procedures are given by Choi (11).

B. Evaluation of Orientation Functions

To obtain White-Spruiell biaxial orientation functions, four of six cosine square averages $\overline{\cos^2 \phi_{1a}}$ $\overline{\cos^2 \phi_{2a}}$ $\overline{\cos^2 \phi_{1b}}$ $\overline{\cos^2 \phi_{2b}}$ for polyethylene, must be measured. Both $\overline{\cos^2 \phi_{1a}}$ and $\overline{\cos^2 \phi_{2a}}$ were obtained from the 200 pole figure. Since the intensity of the (020) is much weaker than that of (200) or (110), it is often preferable to obtain

data from the 110 reflection rather than the 020 reflection. For this reason, $\overline{\cos^2 \phi_{1b}}$ and $\overline{\cos^2 \phi_{2b}}$ were evaluated from the 200 and 110 pole distribution using Stein's treatment (66) expressed by

$$\overline{\cos^2 \phi_{1b}} = \frac{\overline{\cos^2 \phi_{1,110}} - 0.308 \overline{\cos^2 \phi_{1a}}}{0.692} \quad (3.6a)$$

$$\overline{\cos^2 \phi_{2b}} = \frac{\overline{\cos^2 \phi_{2,110}} - 0.308 \overline{\cos^2 \phi_{2a}}}{0.692} \quad (3.6b)$$

CHAPTER 4

INTERNAL STRUCTURE OF POLYETHYLENE FILMS

4.1 Results

A. Crystallinity

The densities measured on the L-LDPE and LDPE films and calculated crystallinities are listed in Tables 4.1 and 4.2.

L-LDPE films have slightly higher densities and crystallinities than LDPE. In spite of preparation condition differences, the crystallinity of these films does not change significantly.

B. Birefringence

The birefringences measured on the L-LDPE and LDPE blown film samples are listed in Tables 4.1 and 4.2, respectively. The Δn_{12} , Δn_{13} and Δn_{23} are plotted as a function of draw-down ratio and blow-up ratio in Figures 4.1 and 4.2. Although the magnitudes of the birefringences measured are very small, slight changes with change in preparation conditions are observed.

For L-LDPE films, all birefringences increase monotonically with draw-down ratio with

$$\Delta n_{13} > \Delta n_{12} \sim \Delta n_{23} \quad (4.1)$$

As blow-up ratio increases, both Δn_{12} and Δn_{13} decrease while Δn_{23} increases. In case of the approximately biaxial film (LL-11)

Table 4.1. Birefringences, Densities, Calculated Crystalline Fraction of L-LDPE Blown Films

Sample #	$\Delta n_{12} \times 10^4$	$\Delta n_{13} \times 10^4$	$\Delta n_{23} \times 10^4$	ρ (g/cc)	X (%)
LL-2	1.90	6.49	4.58	.919	47.5
LL-6	2.58	3.78	1.20	.919	47.5
LL-7	4.30	7.50	3.20	.919	47.5
LL-8	3.68	8.38	4.70	.918	46.8
LL-9	4.09	9.13	5.04	.917	46.1
LL-10	10.5	11.6	1.13	.919	47.5
LL-11	1.36	6.68	5.32	.919	47.5

Table 4.2. Birefringence, Densities, Calculated Crystalline Fraction of LDPE Blown Films

Sample #	$\Delta n_{12} \times 10^4$	$\Delta n_{13} \times 10^4$	$\Delta n_{23} \times 10^4$	ρ (g/cc)	X (%)
L-2	-14.7	-6.95	-7.73	.921	48.7
L-6	1.49	5.65	4.16	.921	48.7
L-7	0.13	6.95	6.81	.921	48.7
L-8	1.75	9.65	7.90	.920	48.2
L-9	1.03	9.60	8.57	.920	48.2
L-10	9.13	10.8	1.63	.921	48.7
L-11	-18.3	-10.9	-7.48	.920	48.2

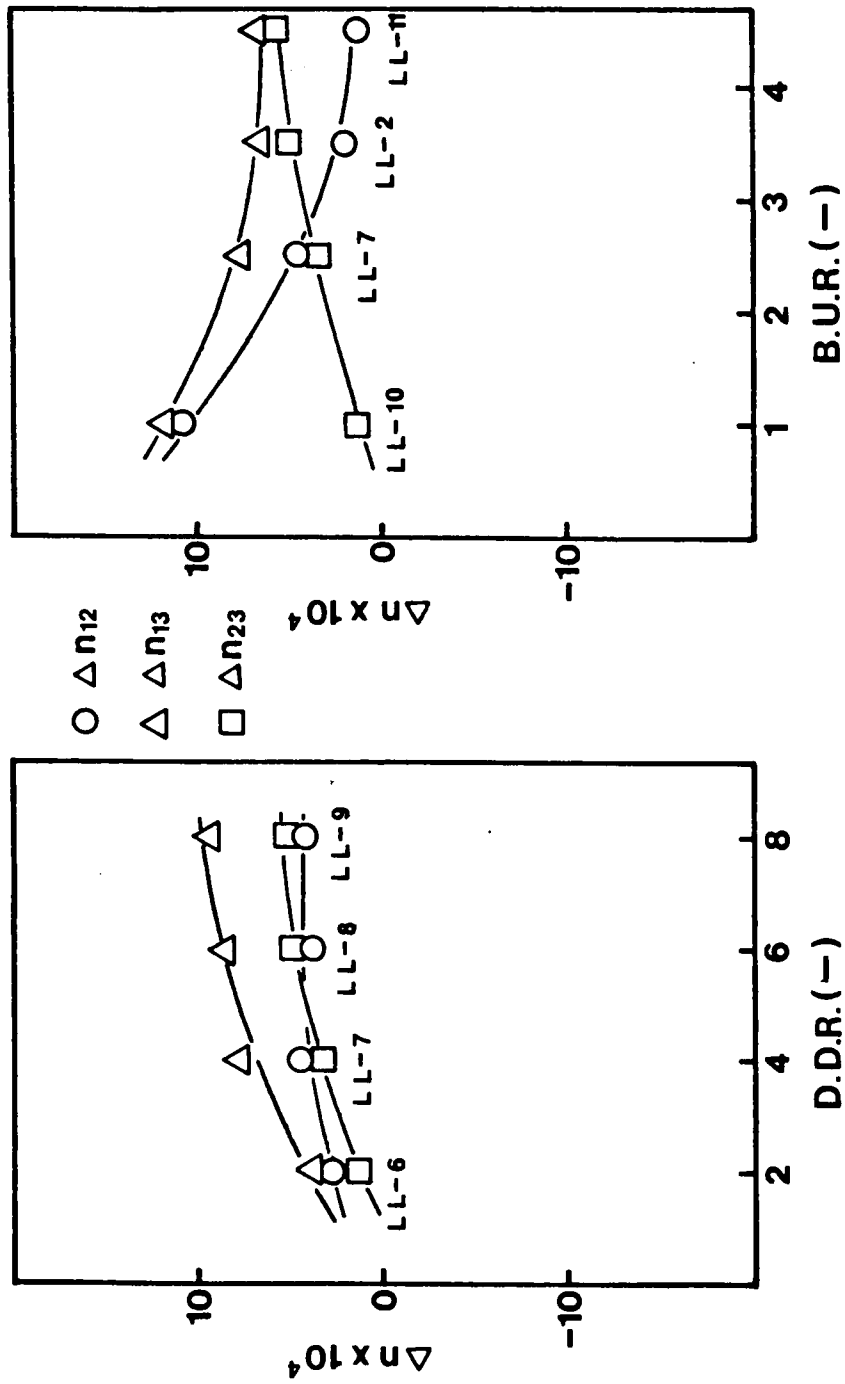


Figure 4.1. Birefringences of L-LDPE blown film as a function of draw-down ratio and blow-up ratio.

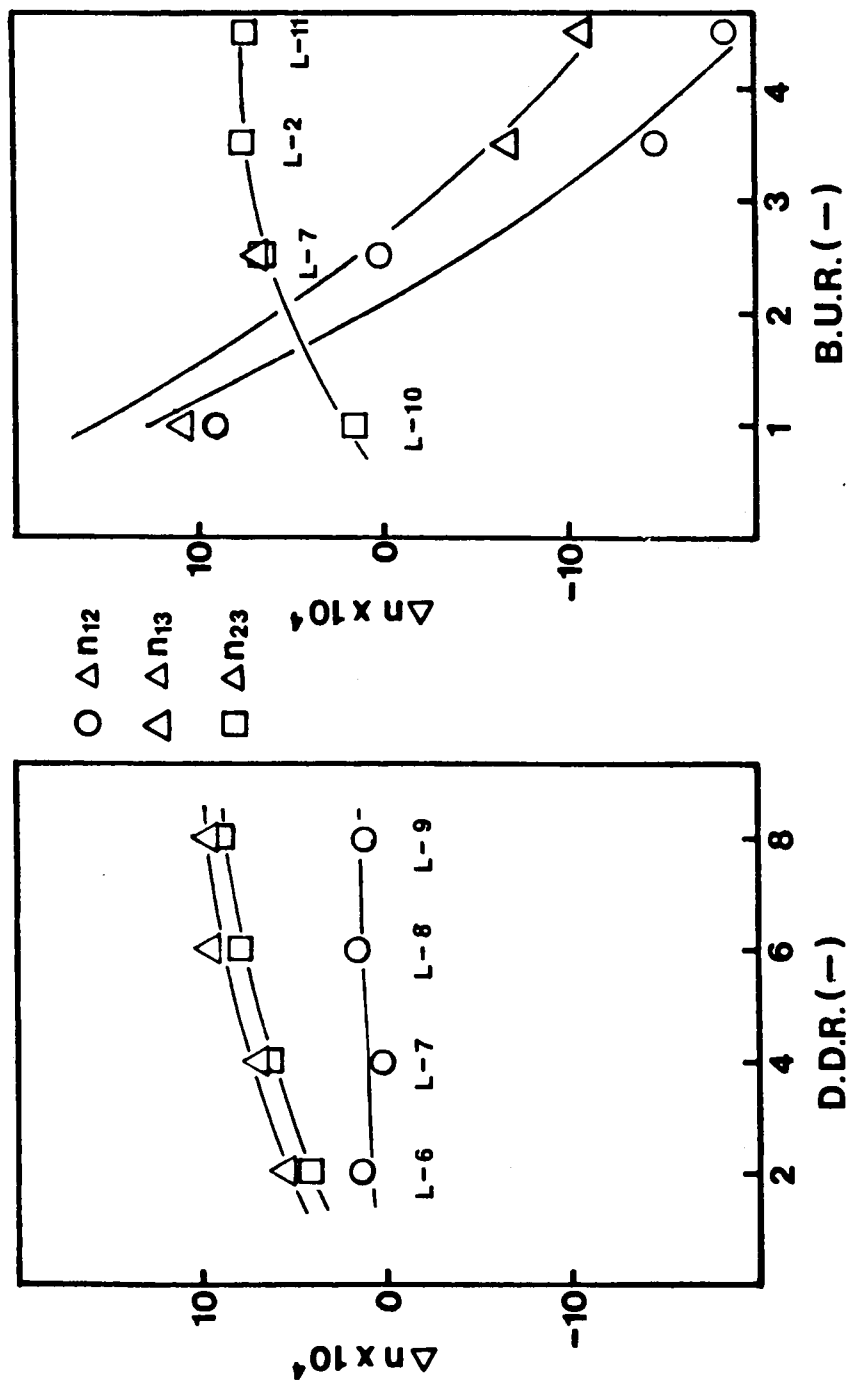


Figure 4.2. Birefringences of LDPE blown film as a function of draw-down ratio and blow-up ratio.

$$\Delta n_{12} = 1.36 \times 10^{-4} \quad (4.2)$$

and

$$\Delta n_{13} = 6.68 \times 10^{-4} \sim \Delta n_{23} = 5.32 \times 10^{-4} \quad (4.3)$$

For the pure biaxial case, Δn_{12} equals zero.

Similar behavior is observed for LDPE films, but the magnitude of each birefringence is slightly different. As draw-down ratio increases, all birefringences increase with

$$\Delta n_{13} > \Delta n_{23} \gg \Delta n_{12} \quad (4.5)$$

With blow-up ratio increasing, Δn_{12} , Δn_{13} decrease and Δn_{23} increases. At higher blow-up ratios Δn_{12} and Δn_{13} become negative. Sample L-7 (VL/VO = 4, B.U.R. = 2.5) shows approximately biaxial orientation with

$$\Delta n_{12} = 0.13 \times 10^{-4} \quad (4.6)$$

and

$$\Delta n_{13} = 6.95 \times 10^{-4} \sim \Delta n_{23} = 6.81 \times 10^{-4} \quad (4.7)$$

C. Crystalline Orientation

Crystalline orientation of L-LDPE and LDPE films were studied by preparing pole figures using WAXD techniques. Samples examined are L-LDPE (LL-7, LL-9, LL-11) and LDPE (L-7, L-9, L-11). Examples of the 200 and 020 pole distributions (pole figures) are presented for four cases in Figures 4.3 through 4.10. The figures present the results for samples LL-9, LL-11, L-9 and L-11, respectively. Samples LL-9 and L-9

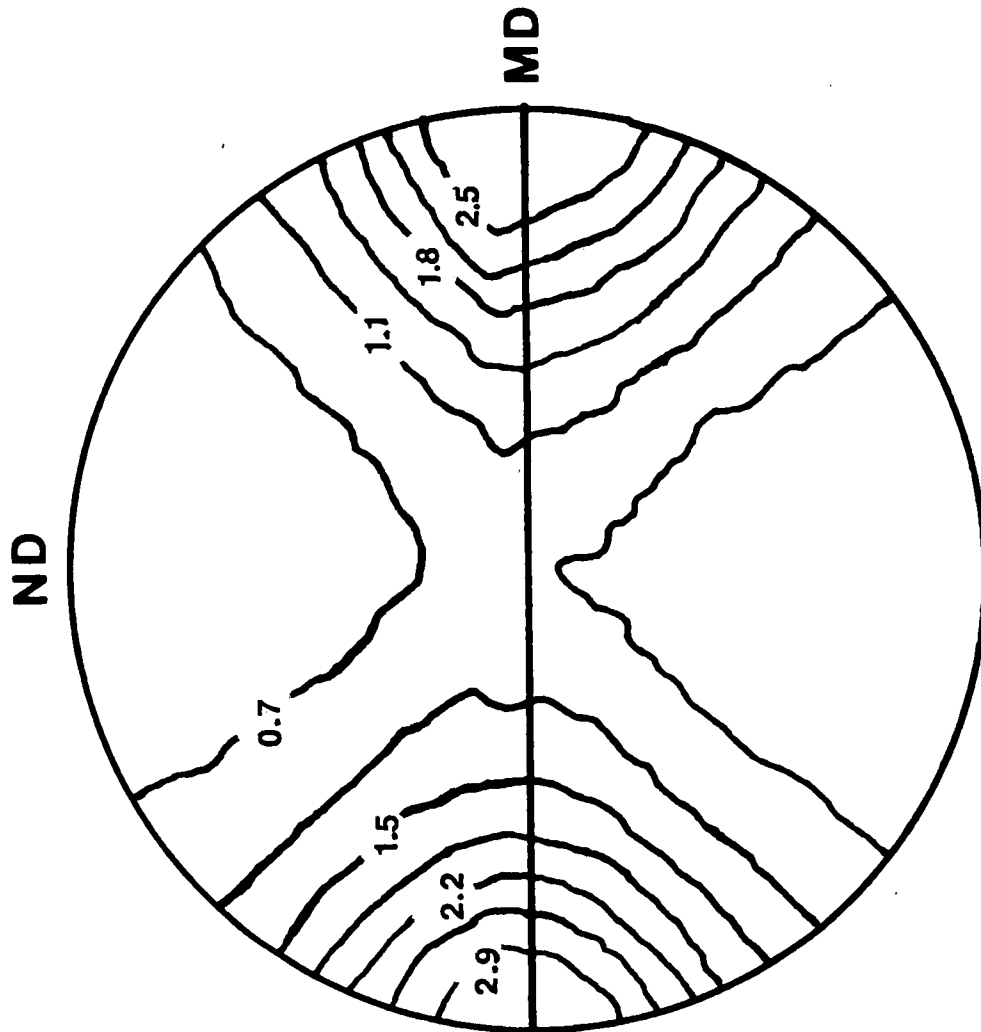


Figure 4.3. Pole figure (200) of sample LL-9.

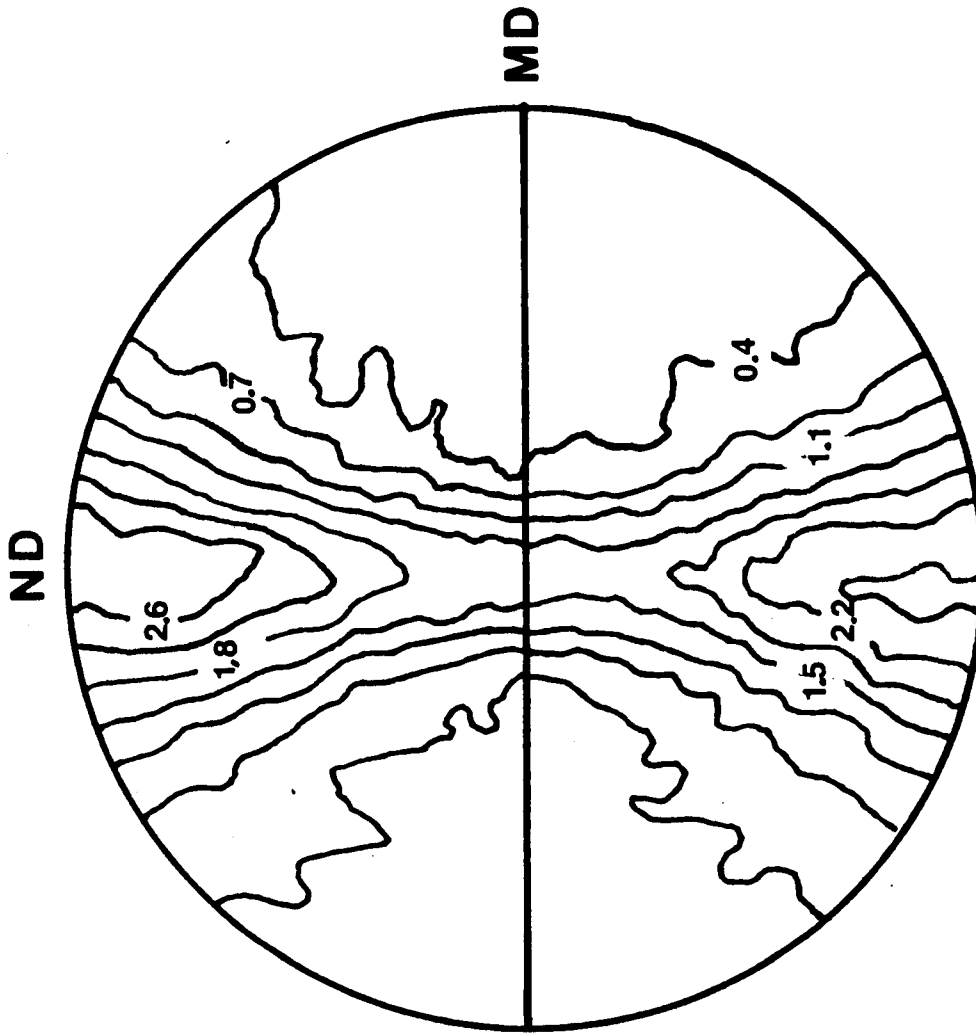


Figure 4.4. Pole figure (020) of sample LL-9.

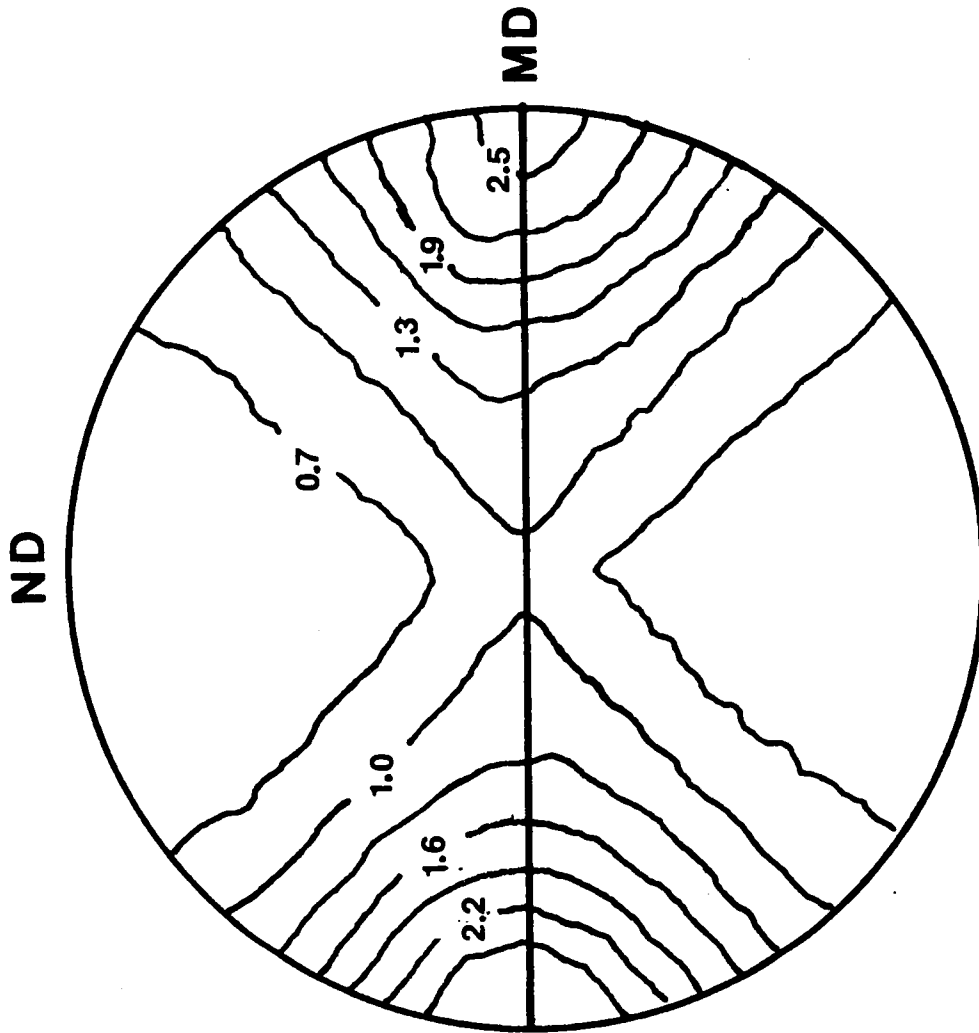


Figure 4.5. Pole figure (200) of sample LL-11.

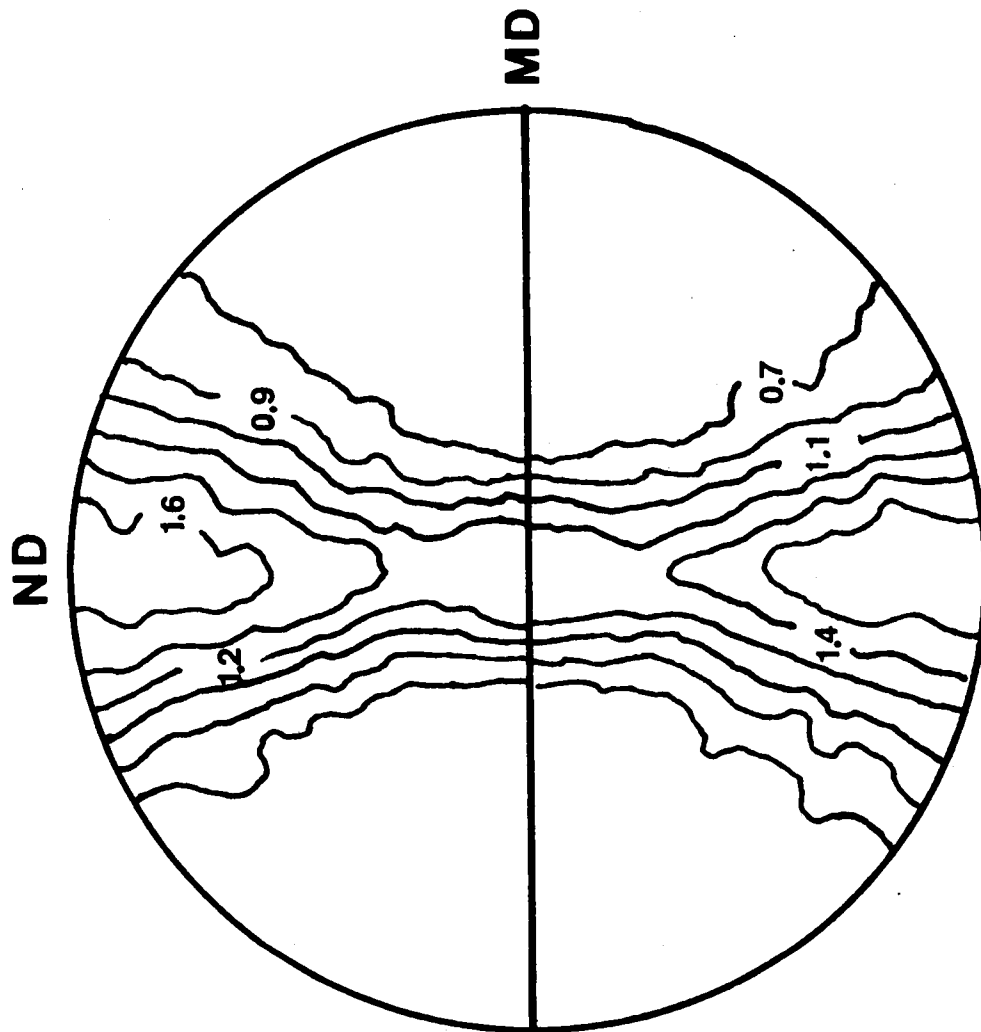


Figure 4.6. Pole figure (020) of sample LL-11.

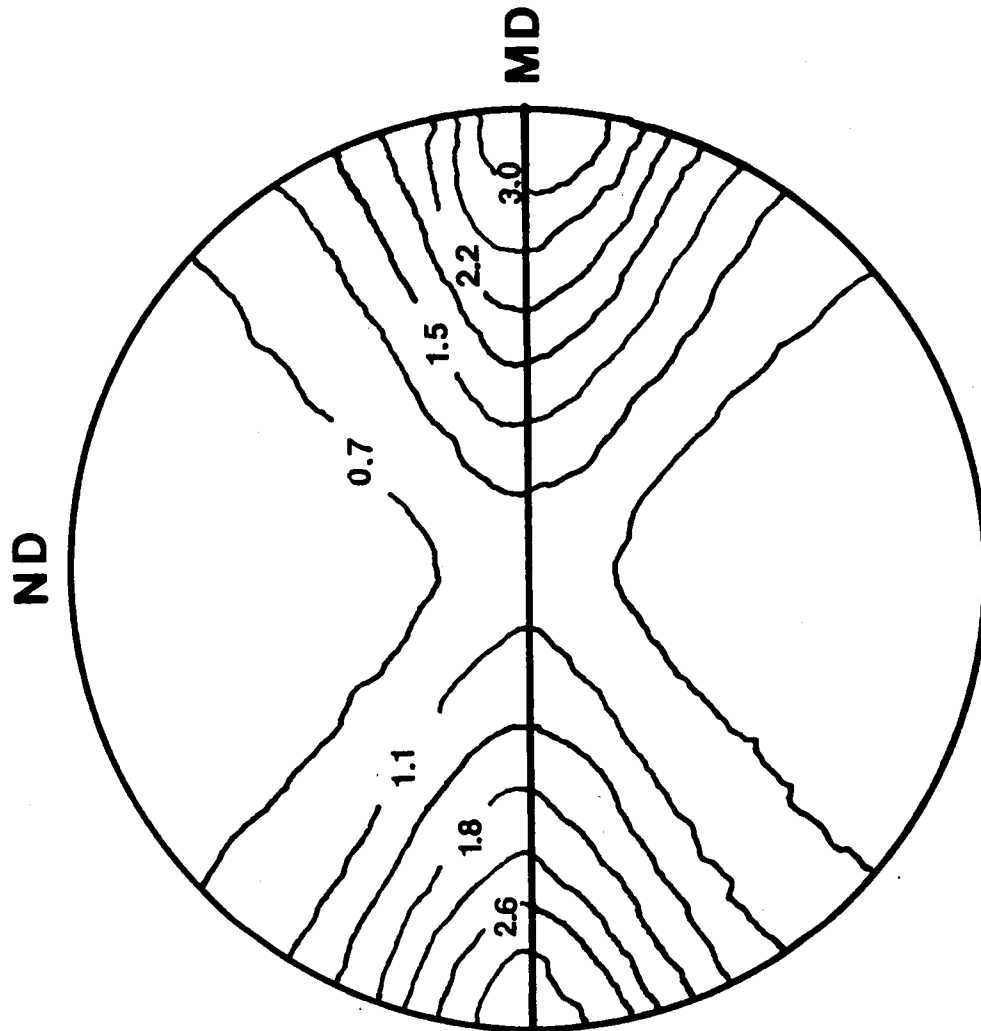


Figure 4.7. Pole figure (200) of sample L-9.

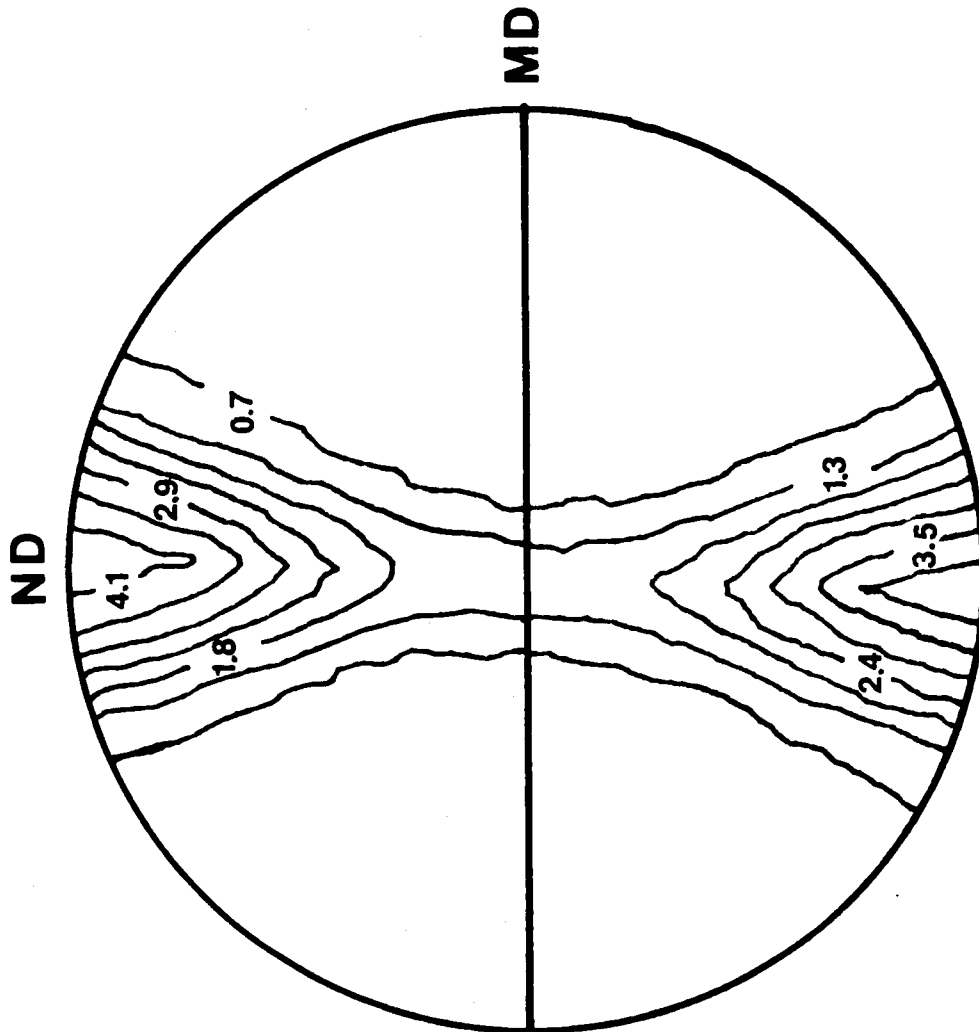


Figure 4.8. Pole figure (020) of sample L-9.

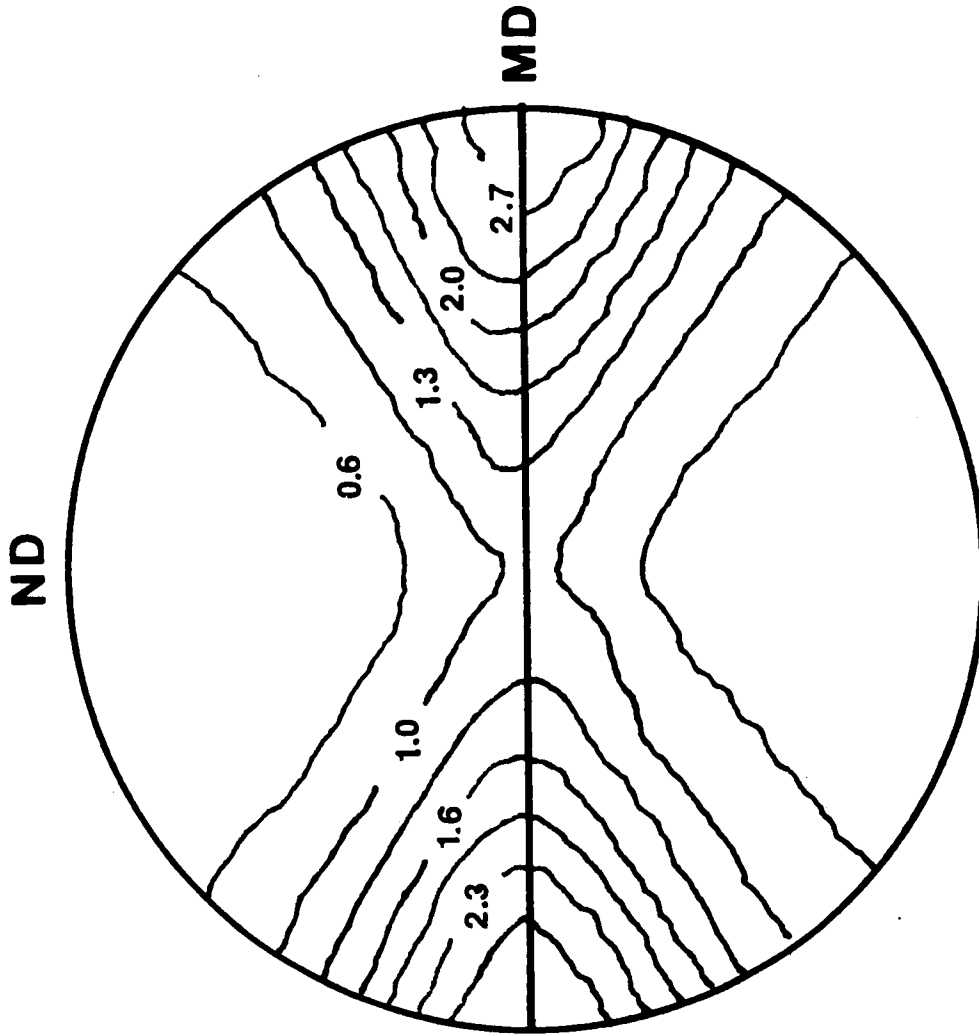


Figure 4.9. Pole figure (200) of sample L-11.

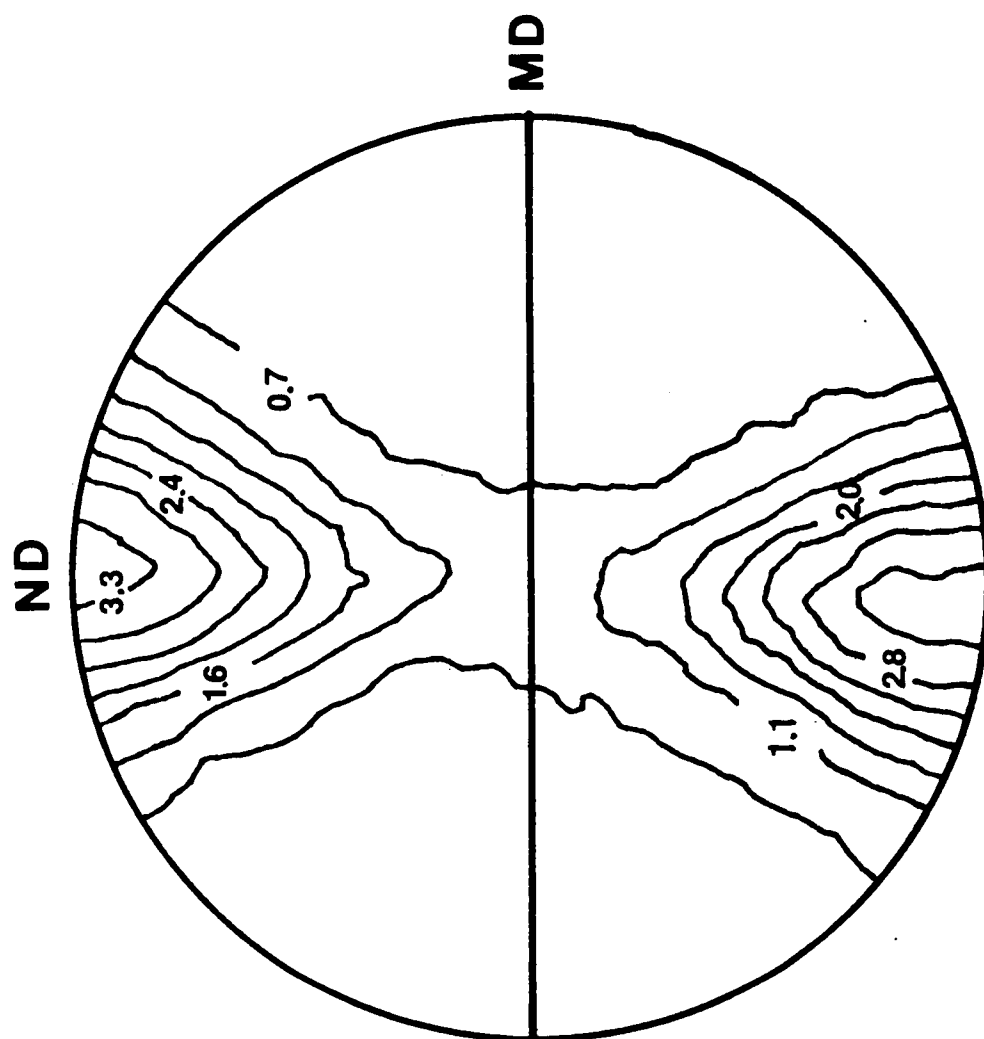


Figure 4.10. Pole figure (020) of sample L-11.

have the highest draw-down ratio (8.0) and relatively lower blow-up ratio (2.5). Samples LL-11 and L-11 are approximately the kinematically biaxial case corresponding to the highest blow-up ratio (4.5) and draw-down ratio (4.0). The pole figures for the remaining samples (LL-7 and L-7) and 110 pole figures of LL-9, LL-11, L-9 and L-11 are presented in Appendix C.

A similar tendency can be observed for both L-LDPE and LDPE except that LDPE has slightly higher concentrations of the 200 poles near the ND than does L-LDPE. For each case, a tendency for a-axis orientation along the machine direction is observed. The b-axes are almost perpendicular to MD and tend to concentrate toward the normal direction. As draw-down ratio increases and blow-up ratio decreases, the concentration of a-axes toward MD and that of b-axes toward ND increases. However, the change is very small.

4.2 Discussion

The crystalline orientation and birefringence results presented above may be interpreted quantitatively in terms of White and Spruiell's orientation factors.

The six cosine squared values, $\overline{\cos^2 \phi_{1a}}$, $\overline{\cos^2 \phi_{2a}}$, $\overline{\cos^2 \phi_{1b}}$, $\overline{\cos^2 \phi_{2b}}$, $\overline{\cos^2 \phi_{1c}}$, $\overline{\cos^2 \phi_{2c}}$, calculated from the pole figure data of each sample are listed in Table 4.3. These cosine squared values can be expressed in terms of White-Spruiell's biaxial orientation factors through equations (2.28a) and (2.28b). Here, subscripts 1, 2 and 3 correspond to machine direction, transverse direction and normal direction (toward film), respectively. These are given in Table 4.4.

Table 4.3. Cosine Squared Values of Blown L-LDPE and LDPE Films

Sample #	$\cos^2 \phi_{1a}$	$\cos^2 \phi_{2a}$	$\cos^2 \phi_{1b}$	$\cos^2 \phi_{2b}$	$\cos^2 \phi_{1c}$	$\cos^2 \phi_{2c}$
LL-9	0.445	0.279	0.127	0.350	0.428	0.371
LL-7	0.424	0.286	0.183	0.342	0.393	0.371
LL-11	0.435	0.292	0.158	0.338	0.407	0.370
L-9	0.478	0.297	0.089	0.317	0.433	0.386
L-7	0.455	0.312	0.122	0.304	0.423	0.384
L-11	0.466	0.308	0.116	0.301	0.419	0.391

Table 4.4. Orientation Factors of Blown L-LDPE and LDPE Films

Sample #	Crystalline orientation factors					Amorphous orientation factors		
	f_{1a}^B	f_{2a}^B	f_{1b}^B	f_{2b}^B	f_{1c}^B	f_{2c}^B	f_1^B	f_2^B
LL-9	0.170	0.004	-0.397	-0.174	0.227	0.170	-0.29	-0.24
LL-7	0.135	-0.003	-0.291	-0.132	0.157	0.135	-0.20	-0.20
LL-11	0.162	0.018	-0.345	-0.165	0.184	0.147	-0.25	-0.21
L-9	0.253	0.072	-0.505	-0.276	0.252	0.205	-0.35	-0.29
L-7	0.223	0.080	-0.452	-0.270	0.229	0.190	-0.33	-0.28
L-11	0.239	0.081	-0.468	-0.282	0.229	0.201	-0.44	-0.29

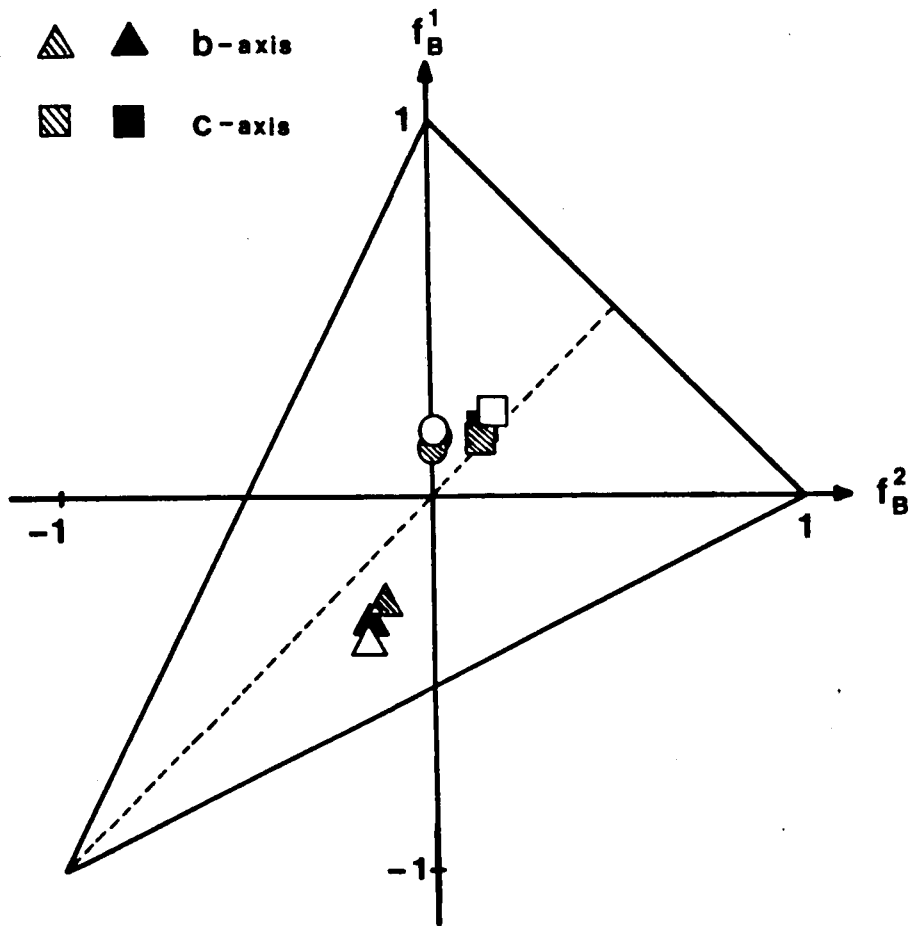
These orientation factors are plotted in Figure 4.11(a) and (b) as f_1^B versus f_2^B on the isosceles triangle diagram (85). As we can expect from the pole figures and birefringence measurements, only a small change of each factor is observed. LDPE seems to have slightly higher orientation than L-LDPE. For all samples the c-axis orientation factor lies near the line at 45° to either coordinate axis indicating a biaxial orientation of the chains. The a-axes always lie on or near the f_1^B axis indicating that they are distributed in a nearly uniaxial manner about MD. The b-axes have f_1^B values which are near $-1/2$ indicating that they tend to be perpendicular to MD. The fact that the f_2^B values for the b axes are also negative indicates that there is a slight tendency for the b-axes to become perpendicular to TD. This tendency is greater for the LDPE than for the L-LDPE. These results indicate a very complex texture for these samples.

These results may be compared with data previously published by Desper (20) and Maddams and Preedy (43). Desper's pole figures for LDPE blown films at cooling rate 32A and 32B show very similar tendency to those of the LDPE and L-LDPE investigated here. The tendency for b-axis orientation towards the film normal is probably a result of preferential nucleation at the surface of the film as discussed by Desper (20). This a-axis orientation along MD is also found in Maddams and Preedy's HDPE blown films under low stress conditions.

L-LDPE and LDPE are semicrystalline polymers but its crystallinity is less than 50% (see Table 4.3). Therefore orientation in the amorphous regions may be considered. This amorphous orientation factor

LL-9, LL-7, LL-10

○	◐	●	a-axis
△	◑	▲	b-axis
□	◒	■	c-axis



(A)

Figure 4.11. Representations of crystalline biaxial orientation factor of L-LDPE blown film on a triangular diagram.

L-9,L-7,L-10

○	◐	●	a-axis
△	◑	▲	b-axis
□	◒	■	c-axis

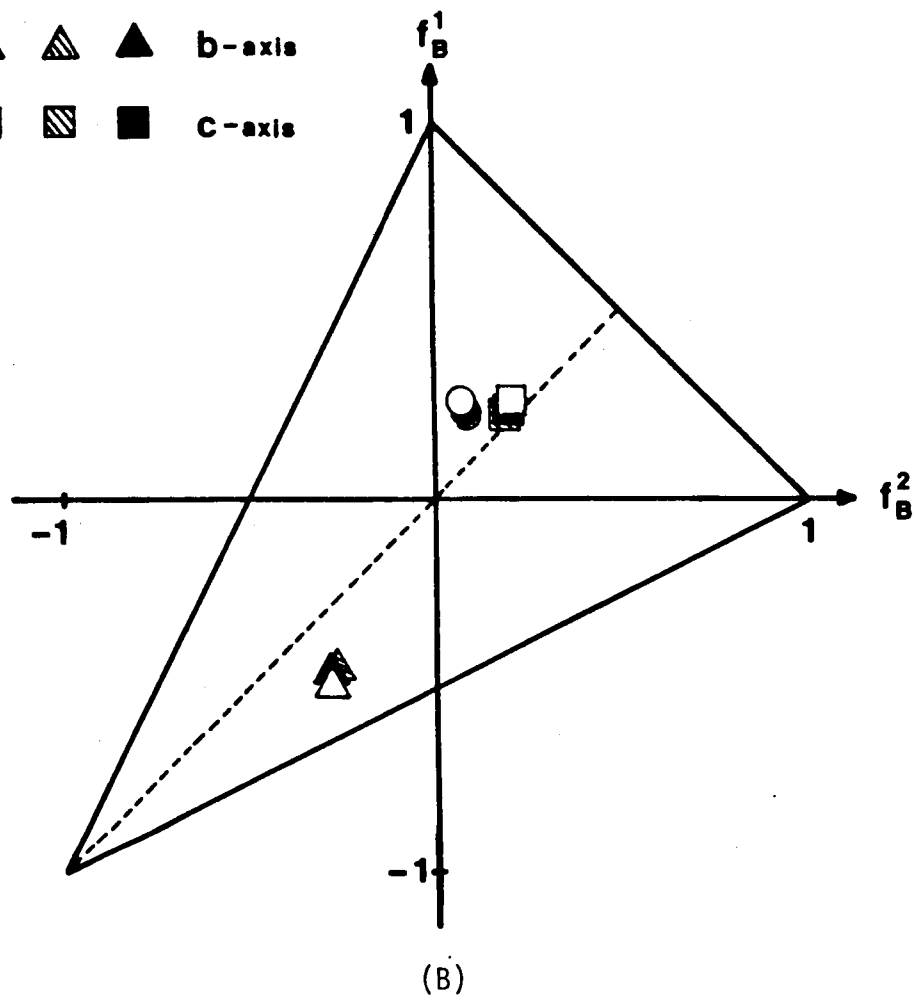


Figure 4.11 (continued)

can be calculated from several measured or calculated results using the following equations derived by White and Spruiell (84)

$$\begin{aligned} \Delta n_{13} = & X(\Delta_{ca}^{oc} f_{1c}^B + \Delta_{ba}^{oc} f_{1b}^B) \\ & + (1 - X)\Delta^{oa} f_{1cm}^B + (\Delta n_{13})_{form} \end{aligned} \quad (4.8a)$$

$$\begin{aligned} \Delta n_{23} = & X(\Delta_{ca}^{oc} f_{2c}^B + \Delta_{ba}^{oc} f_{2b}^B) \\ & + (1 - X)\Delta^{oa} f_{2cm}^B + (\Delta n_{23})_{form} \end{aligned} \quad (4.8b)$$

$$\Delta_{ca}^{oc} = n_c - n_a \quad (4.9a)$$

$$\Delta_{ba}^{oc} = n_b - n_a \quad (4.9b)$$

where n_c is the refractive index along the c crystallographic axis of a polyethylene single crystal, n_b the refractive index along the b crystallographic axis, and n_a along the a crystallographic axis. Δ^{oa} is the maximum (intrinsic) birefringence of the amorphous component and $\Delta(n_{13})_{form}$ and $(\Delta n_{23})_{form}$ are form birefringence due to the phase distribution. f_1^B and f_2^B are orientation factors for the amorphous regions. A problem is that the final calculated value of amorphous orientation factor involves accumulated errors from each of the measured or calculated results. The results of such calculation must thus be viewed and interpreted with caution. These calculated orientation factors are given in Table 4.4, and plotted on the isosceles triangle diagram as f_1^B versus f_2^B in Figure 4.12. For all samples, both f_1^B and f_2^B

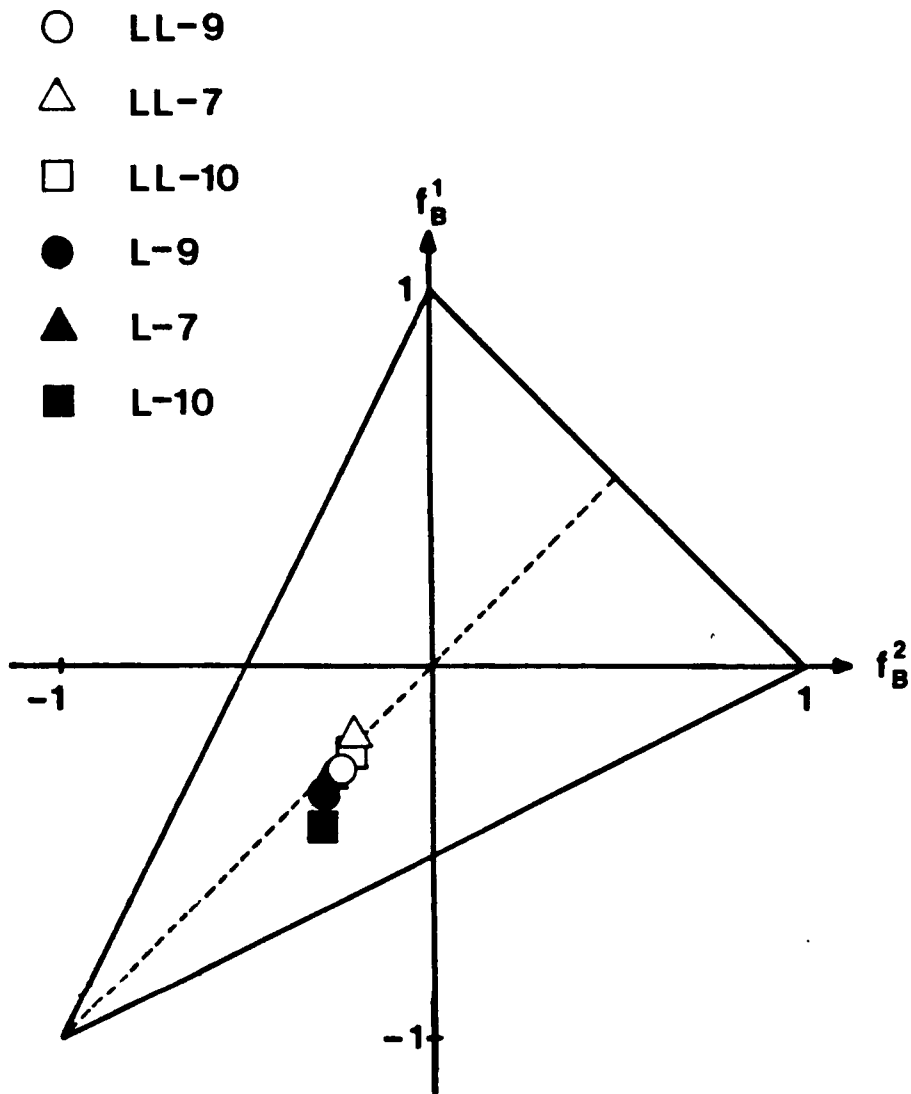


Figure 4.12. Representation of amorphous biaxial orientation factors of L-LDPE and LDPE blown films on a triangular diagram.

show negative values and chains in the amorphous region tend to be perpendicular to the film surface. One possible interpretation of these results is that the chains that are more highly oriented along MD (or TD) in the melt crystalline more readily during freezing. This produces crystals with their chain axes approximately parallel to either MD or TD and depletes the remaining amorphous material of chains having these orientations. This remaining amorphous material is left with chain orientations which tend to be perpendicular to both MD and TD.

CHAPTER 5

CLARITY OF POLYETHYLENE FILMS

5.1 Direct Transmission Factors of PE Films

Direct transmission factors and turbidities measured on the L-LDPE, LDPE and HDPE are listed in Tables 5.1 and 5.2. For L-LDPE films direct transmission factors of each surface phase (outer and inner) and apparent cooling rates are also given.

A. Results

HDPE blown films have much lower values of T , T_S and T_B than L-LDPE and LDPE. LDPE shows highest values among them. Direct transmission factors of each phase, T , T_S , T_B and turbidity, τ , are plotted as a function of frost-line height, draw-down ratio and blow-up ratio for L-LDPE and LDPE in Figures 5.1, 5.2 and 5.3, respectively. In Figures 5.2 and 5.3, values for T and T_B are converted to those of films having thickness of 54 μm using τ values in order to eliminate effects of thickness.

Similar tendencies of T , T_S , T_B and τ on film preparation conditions are observed for L-LDPE and LDPE. Surface phase direct transmission factors of L-LDPE are much lower (5-20%) than those of LDPE. Bulk phase direct transmission factors of L-LDPE are also lower than those of LDPE, but the difference is very small (0-5%). For L-LDPE films direct transmission factors of the inner surface phase are a little higher (0-3%) than those of the outer surface phase.

Table 5.1. Direct Transmission Factor of Blown L-LDPE Film
($\lambda = 5460 \text{ \AA}$)

Sample #	Thickness (μm)	T (%)	T _s (%)	T _{os} (%)	T _{is} (%)	T _B (%)	τ (cm^{-1})	$\Delta\theta$ (oc/sec)
LL-1	31.8	67.4	71.2	86.2	86.9	94.8	16.9	7.5
LL-2	33.0	69.0	72.4	85.6	87.4	95.3	14.5	9.6
LL-3	36.8	72.7	76.1	88.7	88.5	95.5	12.4	12.5
LL-4	34.3	79.2	81.5	89.5	95.0	97.1	8.4	--
LL-5	241.3	48.0	81.0	94.1	90.4	59.3	21.7	5.2
LL-6	95.3	66.4	80.8	87.3	91.4	82.2	20.5	7.7
LL-7	47.0	70.7	75.1	87.1	87.8	94.1	12.9	11.7
LL-8	36.8	73.5	76.7	86.6	87.8	95.9	11.4	15.7
LL-9	30.5	73.1	75.1	86.3	87.7	97.3	9.0	17.2
LL-10	112.0	68.3	80.5	89.8	91.8	84.8	14.8	--
LL-11	22.9	72.2	74.6	86.0	88.4	96.8	14.2	8.2

Table 5.2. Direct Transmission Factor of Blown LDPE, HDPE Films
($\lambda = 5460 \text{ \AA}$)

Sample #	Thickness (μm)	T (%)	T _s (%)	T _B (%)	τ (cm^{-1})
L-1	38.1	77.6	83.0	93.4	17.8
L-2	48.3	81.1	85.8	94.5	11.7
L-3	44.5	82.3	84.7	97.1	6.5
L-4	44.5	83.6	86.6	96.5	8.0
L-5	208.3	64.8	87.0	72.8	15.3
L-6	114.3	75.9	89.1	85.2	14.1
L-7	53.3	82.3	85.8	95.8	8.0
L-8	33.0	84.2	86.9	96.9	9.5
L-9	26.7	86.2	88.3	97.5	9.3
L-10	147.3	80.0	91.1	87.8	8.8
L-11	22.9	83.7	85.4	98.0	8.6
4	45.7	39.2	45.6	85.9	33.3
6	14.0	39.6	41.3	95.9	29.8

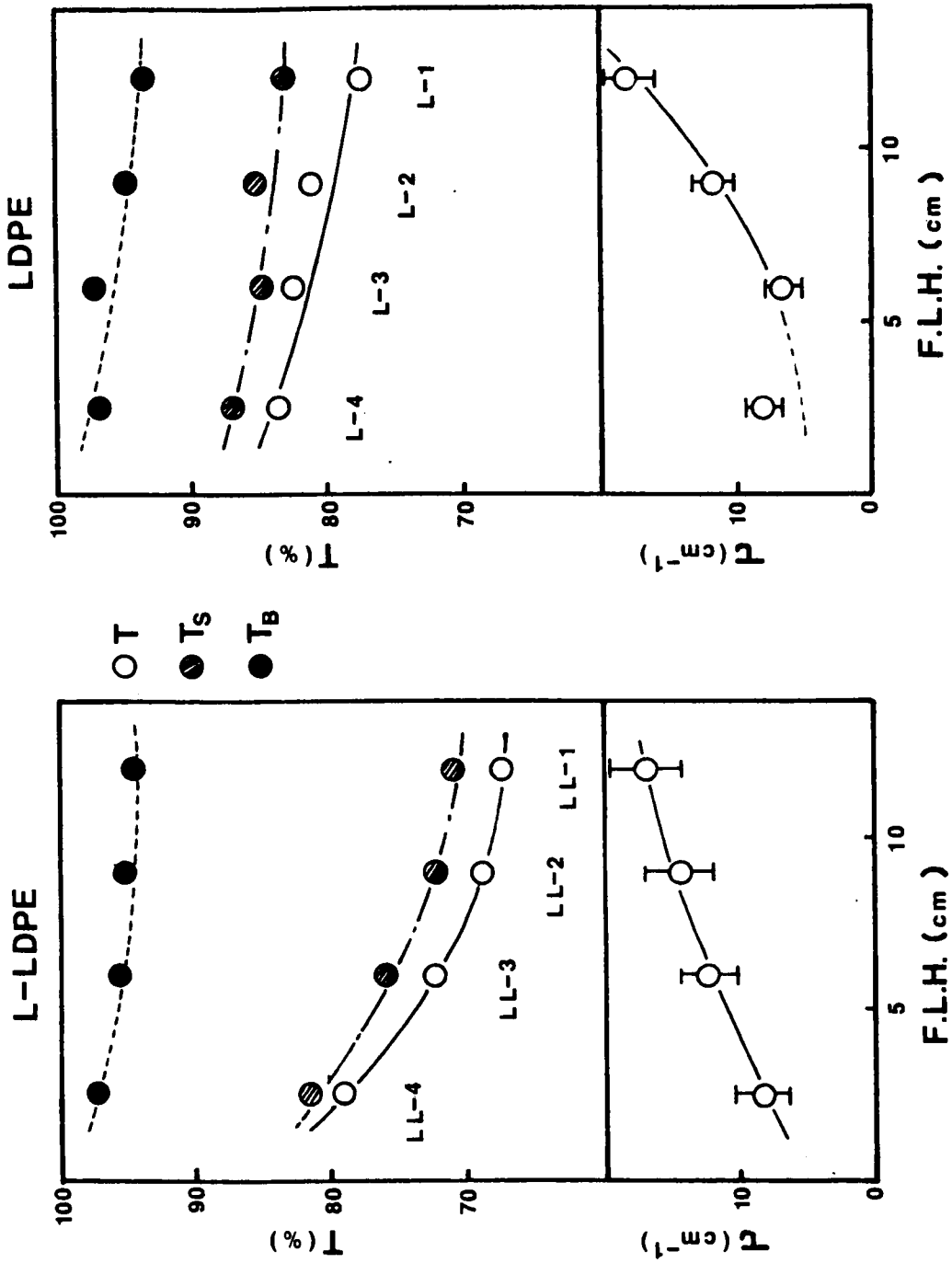


Figure 5.1. Direct transmission factors and turbidities of blown PE film as a function of frost line height.

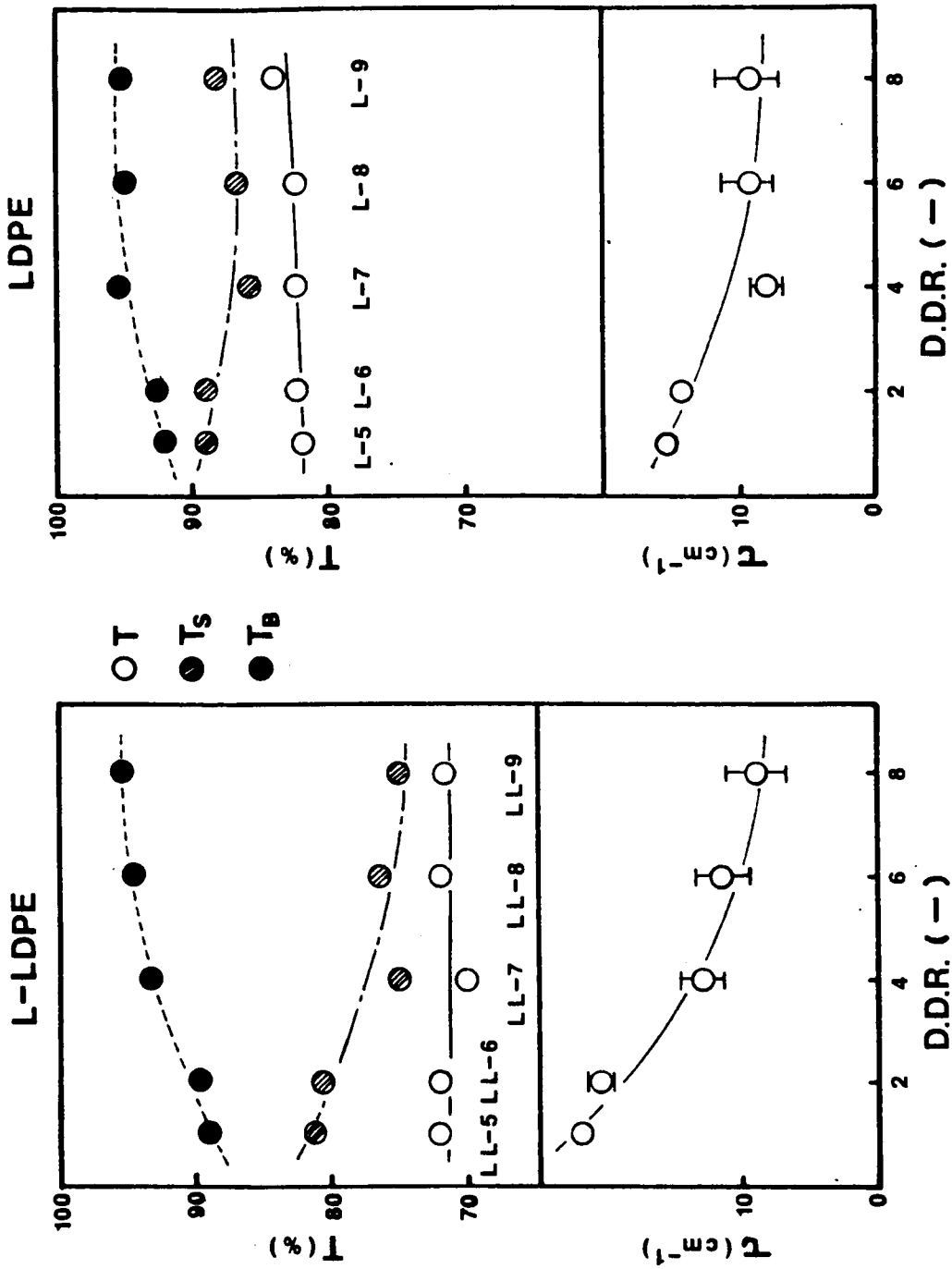


Figure 5.2. Direct transmission factors and turbidities of blown PE film as a function of draw-down ratio.

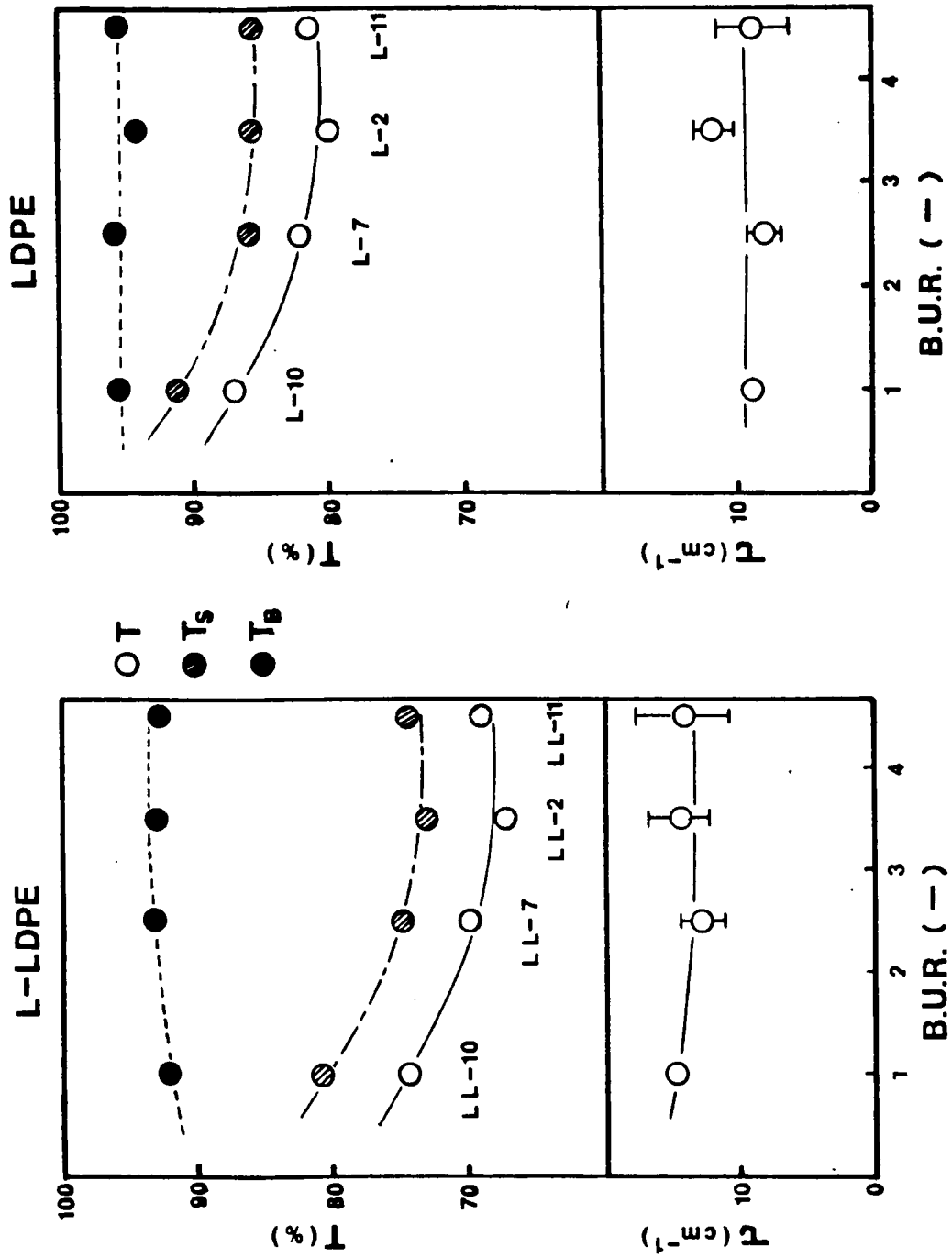


Figure 5.3. Direct transmission factors and turbidities of blown PE film as a function of blow-up ratio.

In Figure 5.1, as frost-line height increases, both T_S and T_B decreases. As a result T , which is a product of T_S and T_B , also decreases. In all cases T_S is smaller than T_B and is more important in determining the value of T .

In Figure 5.2, T_B increases with draw-down ratio. On the other hand T_S decreases. As a result T remains almost constant. In Figure 5.3, T_B increases very slightly with increase in blow-up ratio while T_S decreases substantially. This results in a decrease of T .

In Figure 5.4, τ values of L-LDPE films are plotted as a function of apparent cooling rate, $\Delta\theta$. The τ values are strongly dependent on their apparent cooling rates. As $\Delta\theta$ increases τ decreases.

B. Discussion

For all samples examined the surface phase direct transmission factor, T_S , is lower than the bulk phase direct transmission factor, T_B . This indicates that the overall direct transmission factor is controlled primarily by effects at or near the surface. Presumably the low values of T_S are due to scattering from rough surfaces.

There are changes in both T_S and T_B with film processing variables. A decrease of overall direct transmission factor, T , with frost-line height is due to a decrease of both the surface phase direct transmission factor, T_S , and the bulk phase direct transmission factor, T_B . As frost-line height increases, larger crystalline aggregates are formed because of slower cooling rate. It is suggested that these larger crystalline aggregates produce more light scattering from the bulk phase thus lowering T_B . The larger crystalline aggregates at or near the film

surface may also cause more surface irregularities. There are, however, only small changes of refractive index at those internal optical irregularities compared to that of air-film-surface boundaries. As a result, roughness of the film surface becomes the dominant cause of light scattering from blown films.

In spite of an increase of the bulk phase transmission factor, T_B , with both draw-down ratio and blow-up ratio, the surface direct transmission factor, T_S , decreases. This decrease of T_S must be associated with the same kind of flow defects (the extrusion haze) and not with the crystallization. This conclusion is based on the presumption that higher draw-down ratio and blow-up ratio increase the cooling rate and hence produces less surface roughness due to crystallization (smaller crystalline aggregates). This interpretation is in agreement with the observed decrease of turbidity with increased cooling rate (see Figure 5.4).

Huck and Clegg (33) suggested that with increasing draw-down ratio or blow-up ratio the total haze of the film decreases since surface tension would smooth the extrusion defects. However our result does not agree with their explanation. Howells and Benbow (32) suggested that a decrease of extrusion haze is partly accountable by the greater relaxation of surface defects occurring between the die and frost-line at low draw-down ratio. Our result seems to support Howells and Benbow's explanation.

Although turbidity, τ , shows strong dependency on the apparent cooling rate, $\Delta\theta$, the temperature gradient at the frost-line and the

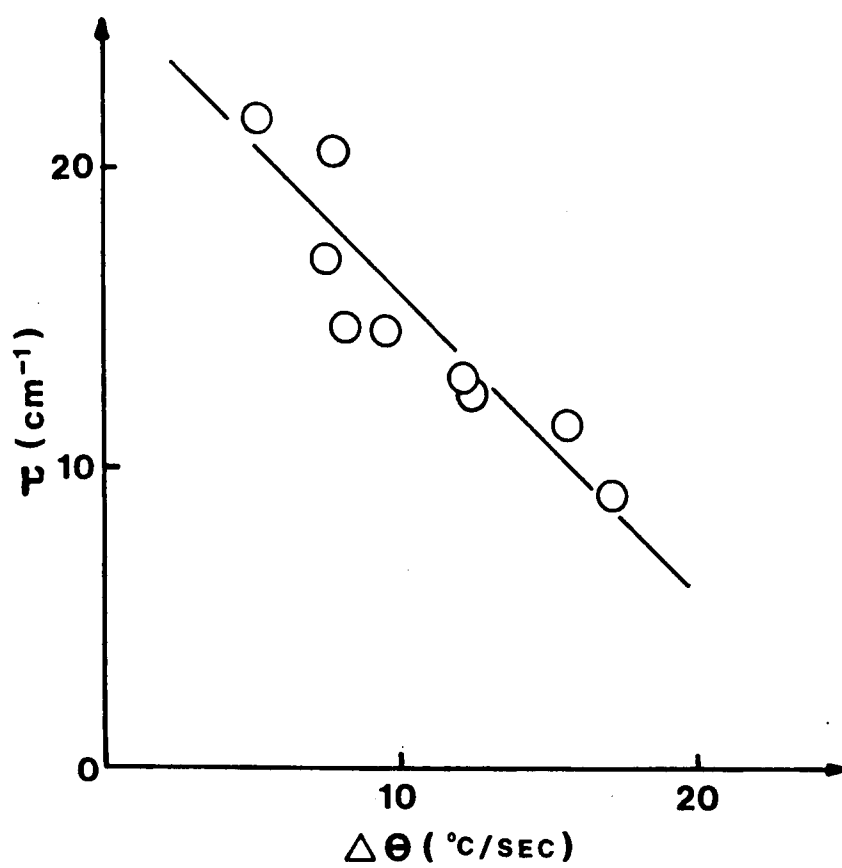


Figure 5.4. Turbidity as a function of apparent cooling rate.

deformation rate of polymer melt might be expected to have effects on τ . These effects have not been separated from the effect of cooling rate alone in this investigation. They may be responsible for some of the scatter observed in Figure 5.4.

5.2 Direct Transmission Factors of Blend Films

A. Results

Direct transmission factors and turbidities measured on HDPE/PP blend films are listed in Table 5.3, and these values are plotted as a function of weight composition in Figure 5.5.

PP blown films have higher values of T , T_S and T_B than HDPE. Maxima of T_S are observed at HDPE/PP = 50/50 weight composition and minima of T_B are observed at HDPE/PP = 25/75-50/50 weight composition.

B. Discussion

Here again HDPE blown films have lower values of T , T_S and T_B than L-LDPE and LDPE as found in section 5.1. PP blown films have higher values of T , T_S and T_B than HDPE but lower than L-LDPE and LDPE.

The maxima of T_S and τ observed in blend films seem to correspond with the minima of viscosity at HDPE/PP - 25/75-50/50 weight composition reported by Shimomura et al. (62). A fine morphological structure of blend polymer could possibly reduce its melt viscosity and relate to the maxima of T_S . And the maxima of τ may be related to the differences of index of refraction in going from HDPE to PP in the incompatible blends, that is scattering from the HDPE-PP interfaces. The morphology of these

Table 5.3. Direct Transmission Factor of Blown HDPE, PP, PE/PP Blend Films ($\lambda = 5460 \text{ \AA}$)

Sample #	Thickness (μm)	T (%)	T _s (%)	T _B (%)	τ (cm^{-1})
E31	116.8	19.5	34.1	57.0	48.1
E33	50.8	33.4	40.0	83.4	35.7
EP91	106.7	22.3	42.4	52.7	60.0
EP93	50.8	38.7	46.6	83.2	36.3
EP72	132.1	28.1	51.0	85.1	45.1
EP74	35.6	57.0	61.5	92.6	21.6
EP61	160.0	25.5	42.7	59.8	32.1
EP63	40.6	53.1	56.4	94.0	15.2
P102	94.0	49.5	56.1	88.3	13.2
P104	40.6	54.1	57.0	95.1	12.5

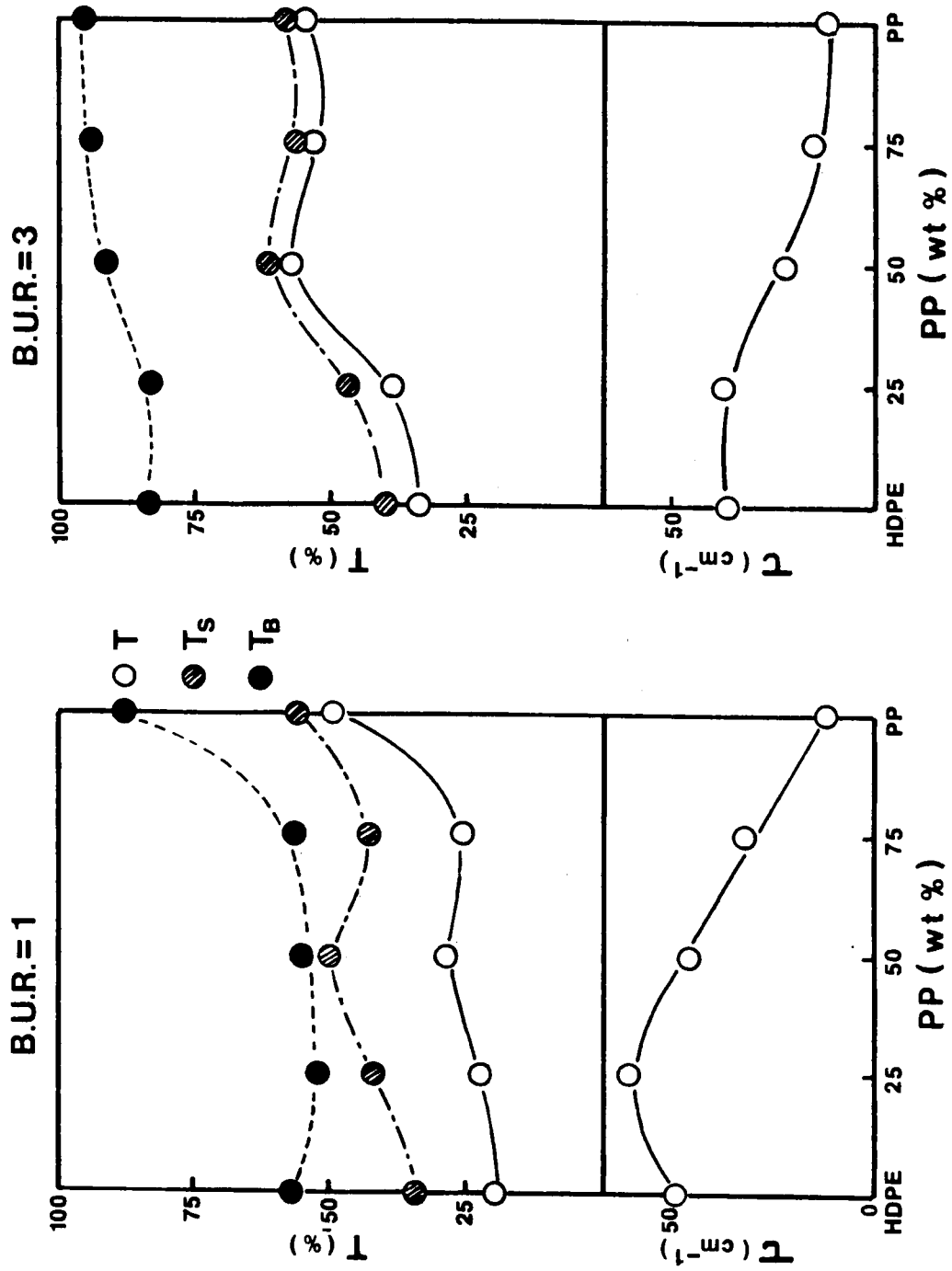


Figure 5.5. Direct transmission factors and turbidities of HDPE/PP blend film as a function of weight composition.

may change with weight composition. However, to explain this unusual phenomena a further investigation is needed.

5.3 Microscopic Examinations

A. Results

Micrographs of blown HDPE, L-LDPE and LDPE are shown in Figures 5.6 through 5.10, respectively. It is clear that HDPE has the roughest surface among them and its surface structure is different from that of L-LDPE and LDPE. The surface of L-LDPE is rougher than that of LDPE with the same film processing conditions.

B. Discussion

In Figure 5.6 we see row-nucleated, rod-like structures for which the rod axes are oriented parallel to the machine direction. There are also fibrous-appearing or perhaps, lamellar striations oriented perpendicular to the machine direction. The spacing between rods is less than a few micrometers.

As shown in Figures 5.7 and 5.8 the appearance of the surface of blown L-LDPE film differs from that of HDPE. The surface of L-LDPE appears much smoother than HDPE. Here again we see a lamellar structure but the orientation of the lamellae is not only machine direction but also transverse direction.

These microscopic observations reveal that the direct transmission factors of the blown film surfaces are directly related to the degree of surface roughness.

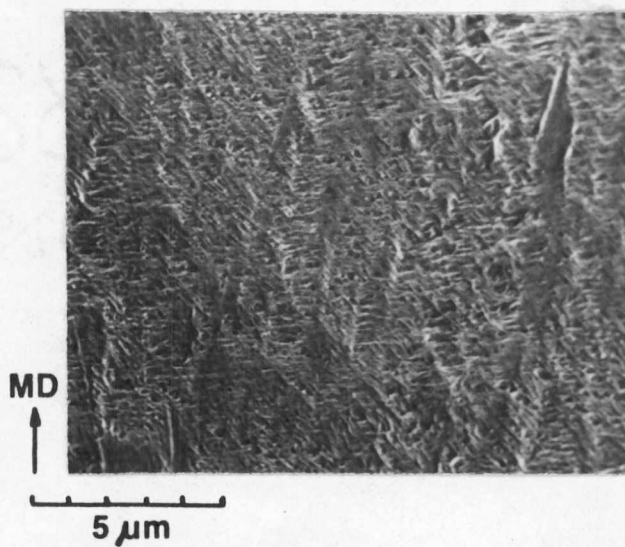
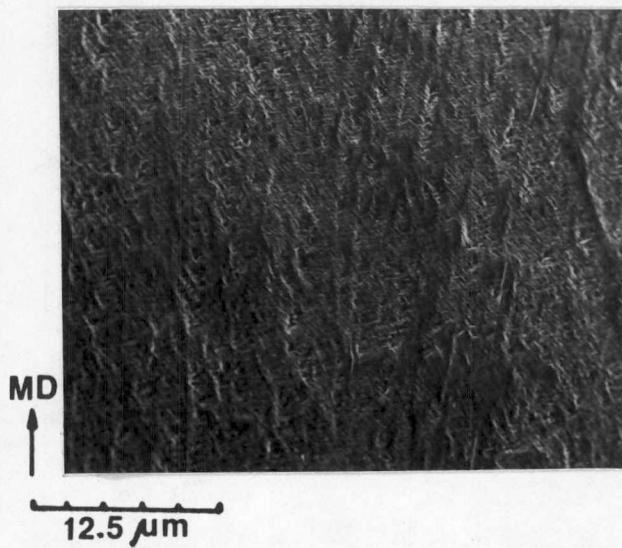


Figure 5.6. SEM micrographs of blown HDPE film (4).

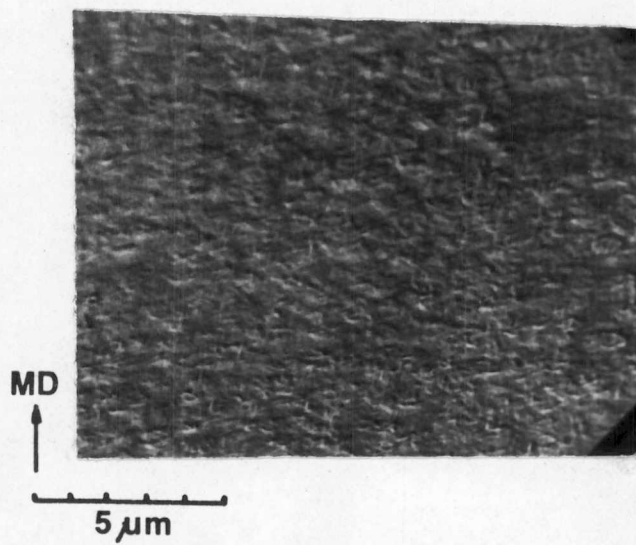
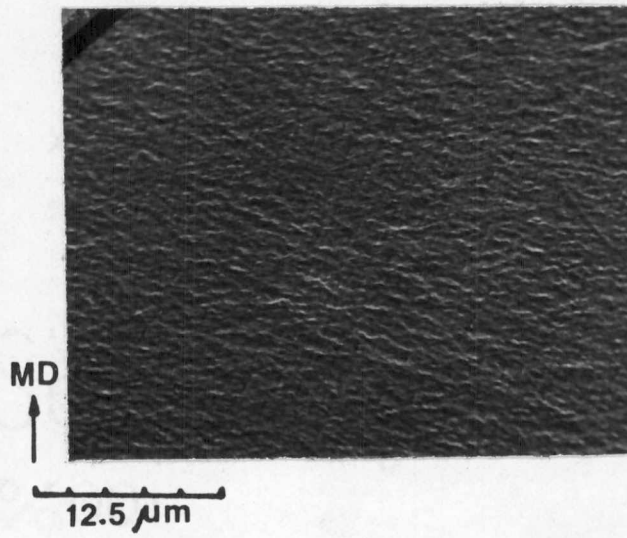


Figure 5.7. SEM micrographs of blown L-LDPE film (LL-2).

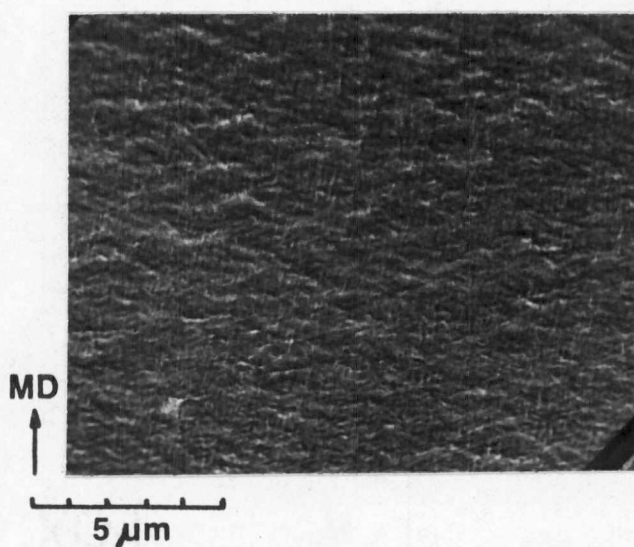
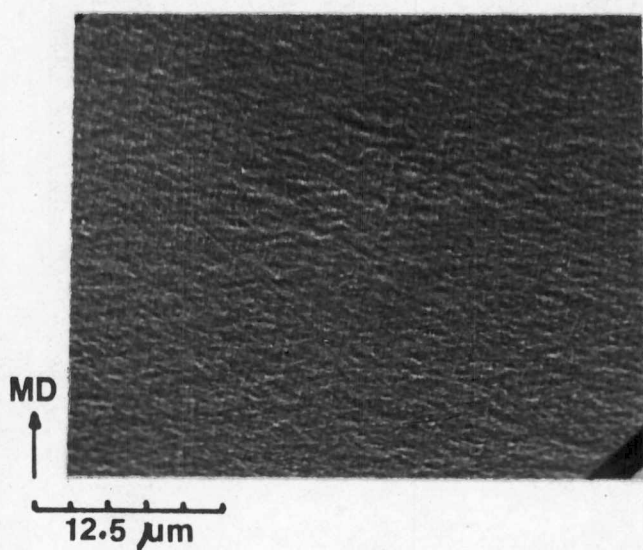


Figure 5.8. SEM micrographs of blown L-LDPE film (LL-4).

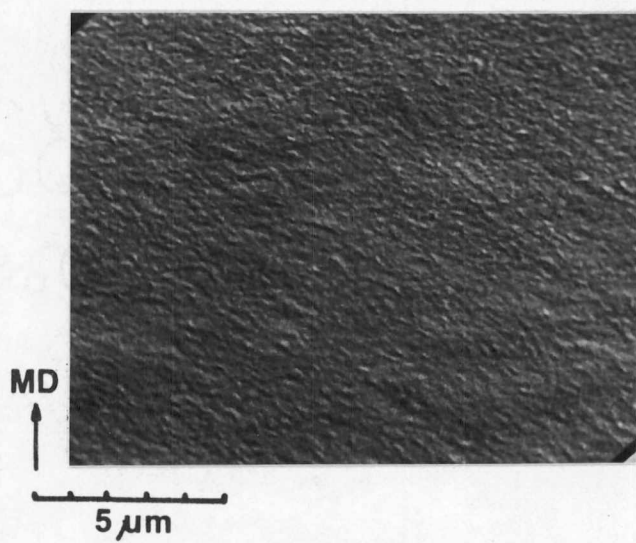
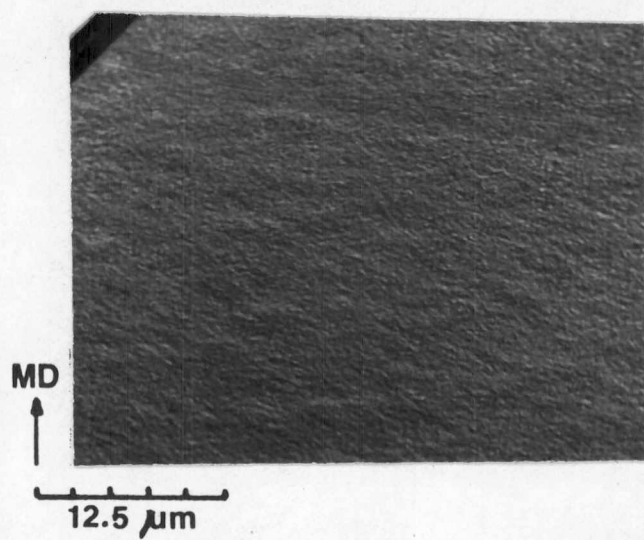


Figure 5.9. SEM micrographs of blown LDPE film (L-2).

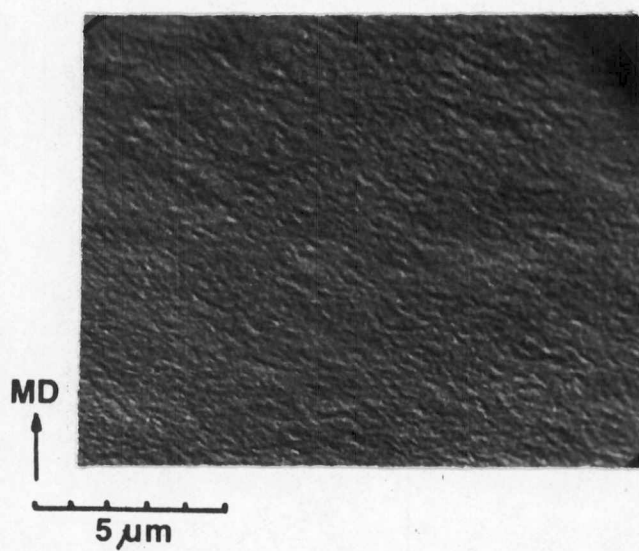
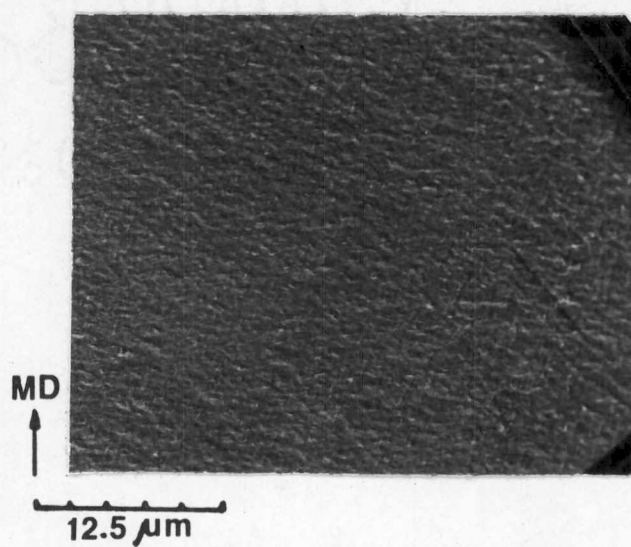


Figure 5.10. SEM micrographs of blown LDPE film (L-4).

5.4 Surface Profiles of Blown PE Films

A. Results

Surface profiles of blown PE films were measured on HDPE (4, 6), L-LDPE (LL-2, LL-3, LL-4) and LDPE (L-2, L-3, L-4). Typical surface profiles of each PE film are shown in Figure 5.11. Characteristic values of surface roughness, as measured by σ and D_c , are listed in Table 5.4.

HDPE films have much rougher surface than L-LDPE and LDPE. Mounds on the surface protrude from the bottom about a few thousands of Angstroms and have 5-10 μm periods. Besides these micro irregularities, large waveness having longer periods ($\sim 50 \mu\text{m}$) are observed.

L-LDPE films have rather smooth surface and mounds protrude only about 2000 $\text{\AA}$ at most.

LDPE films show the smoothest surface; here the mounds protrude about 1000 $\text{\AA}$ at most and are packed very closely together.

B. Discussion

The qualitative features of the surface profiles described above are directly related to the standard variation of height (σ) and the correlation distance (D_c). HDPE films have ~ 5 times larger values of σ than L-LDPE and ~ 10 times larger than LDPE. The longer period of mounds of HDPE can be seen in larger values of D_c which are $\sim 50\%$ larger than those of L-LDPE and LDPE.

Two examples of histograms of height distribution generated from surface profile data are shown in Figure 5.12. In this figure the curves represent a Gaussian function

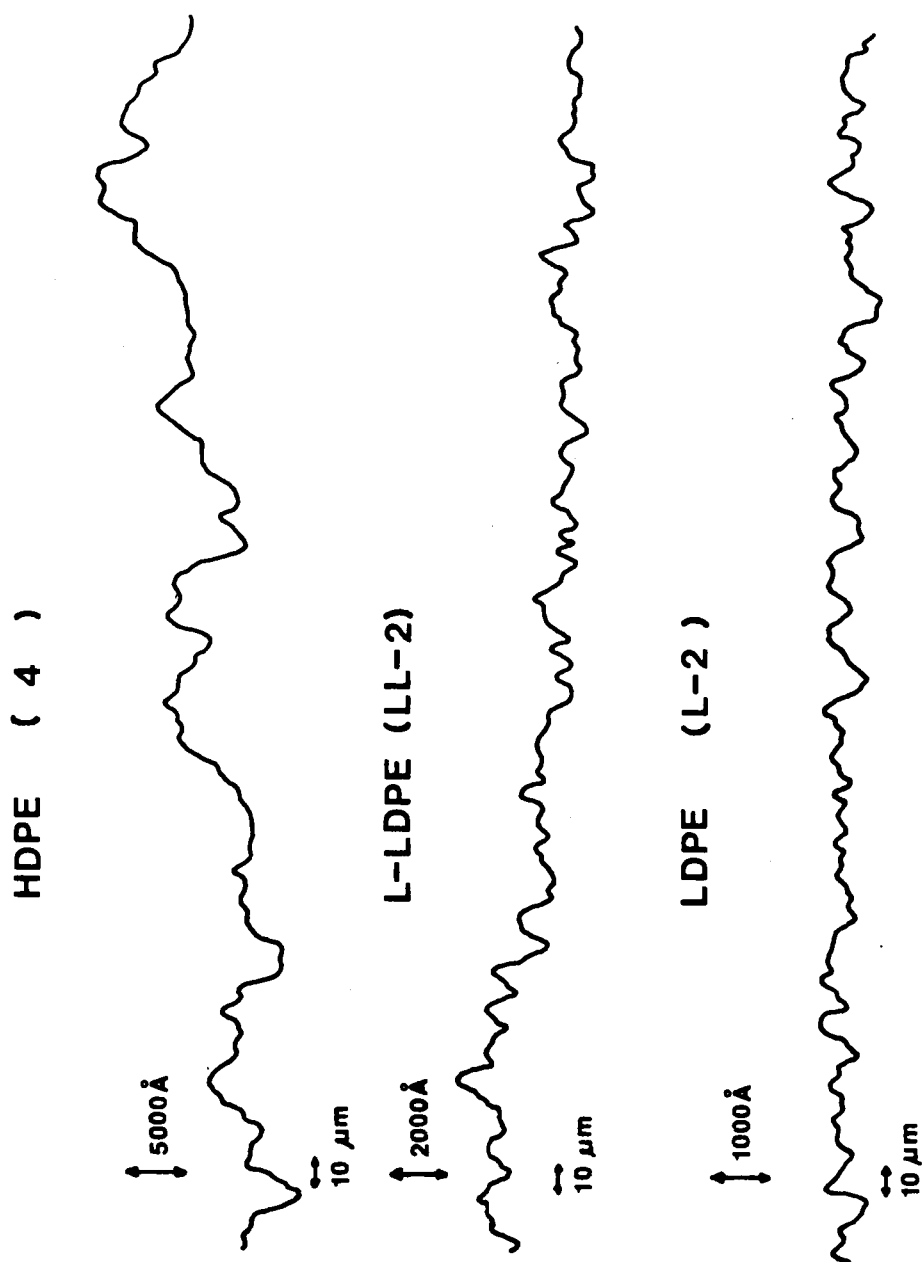


Figure 5.11. Typical surface profiles of various PE blown films.

Table 5.4. Characteristic Values of Surface Roughness

Sample #	Traverse Direction	σ (μm)	D_c (μm)	Average of MD&TD	
				σ	D_c
4	MD	.206	10.1	.206	9.2
	TD	.205	8.2		
6	MD	.127	6.2	.162	6.8
	TD	.197	7.3		
LL-2	MD	.043	4.7	.047	5.4
	TD	.050	6.0		
LL-3	MD	.039	5.4	.043	5.4
	TD	.046	5.4		
LL-4	MD	.028	5.7	.030	6.9
	TD	.032	8.0		
L-2	MD	.020	4.5	.020	4.8
	TD	.020	5.0		
L-3	MD	.022	4.3	.022	4.7
	TD	.021	5.1		
L-4	MD	.016	4.7	.016	5.3
	TD	.016	5.8		

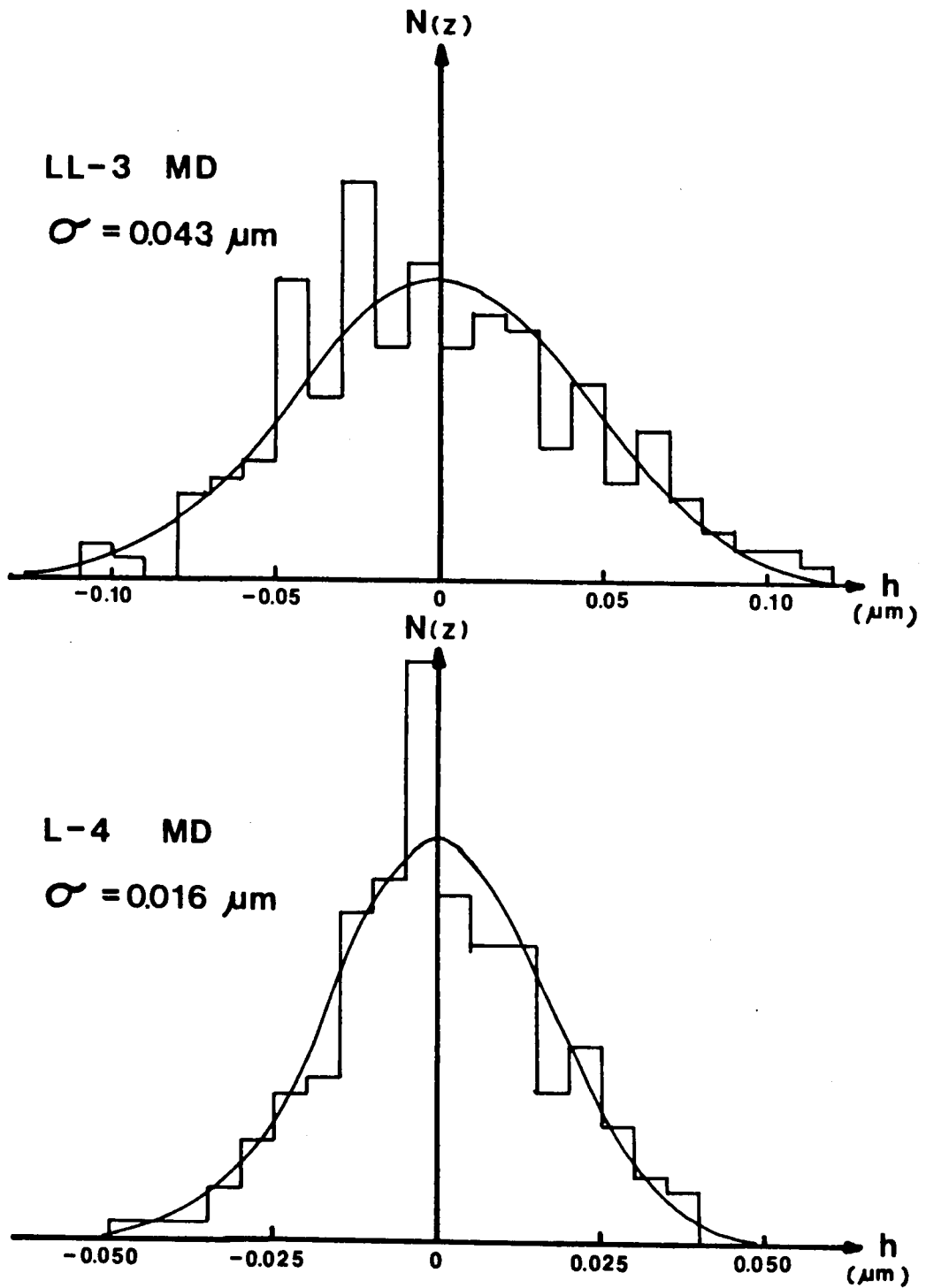


Figure 5.12. Histogram of the height deviations from mean surface level.

$$N(Z) = \frac{1}{\sigma(2\pi)^{1/2}} \exp \left(-\frac{z^2}{2\sigma^2} \right) \quad (5.1)$$

with σ obtained from surface profile measurement. The curves of Gaussian function are a good match to the histograms. This suggests that the roughness of the PE film surfaces is Gaussian in distribution.

σ values are plotted as a function of direct transmission factor of film surface, T_S , in Figure 5.13. A good correlation between σ and T_S is obtained. As σ decreases T_S increases.

Since a surface having random roughness can be considered to be composed of a two-dimensional superposition of sinusoidal gratings having different amplitudes, periods and phases, an insight into angular scattering can be obtained by considering the angular scattering from a single sinusoidal grating having an amplitude A , measured from the mean surface level and grating spacing d . For normally incident light the angle of scattering is given by the grating equation

$$\sin \theta = m(\lambda/d) \quad (5.2)$$

where m is the order of interference and λ the wavelength. The intensity I of light scattered into m th order is proportional to

$$I \sim (A/\lambda)^2 |m| \quad (5.3)$$

Therefore for microrough surfaces whose period is longer than the wavelength, the grating spacing d affects the scattered intensity I (25). Here the amplitude A is analogous to σ and grating spacing d is analogous to D_c . However the correlation distance (D_c) seems not to affect the surface phase direct transmission factor much in our result.

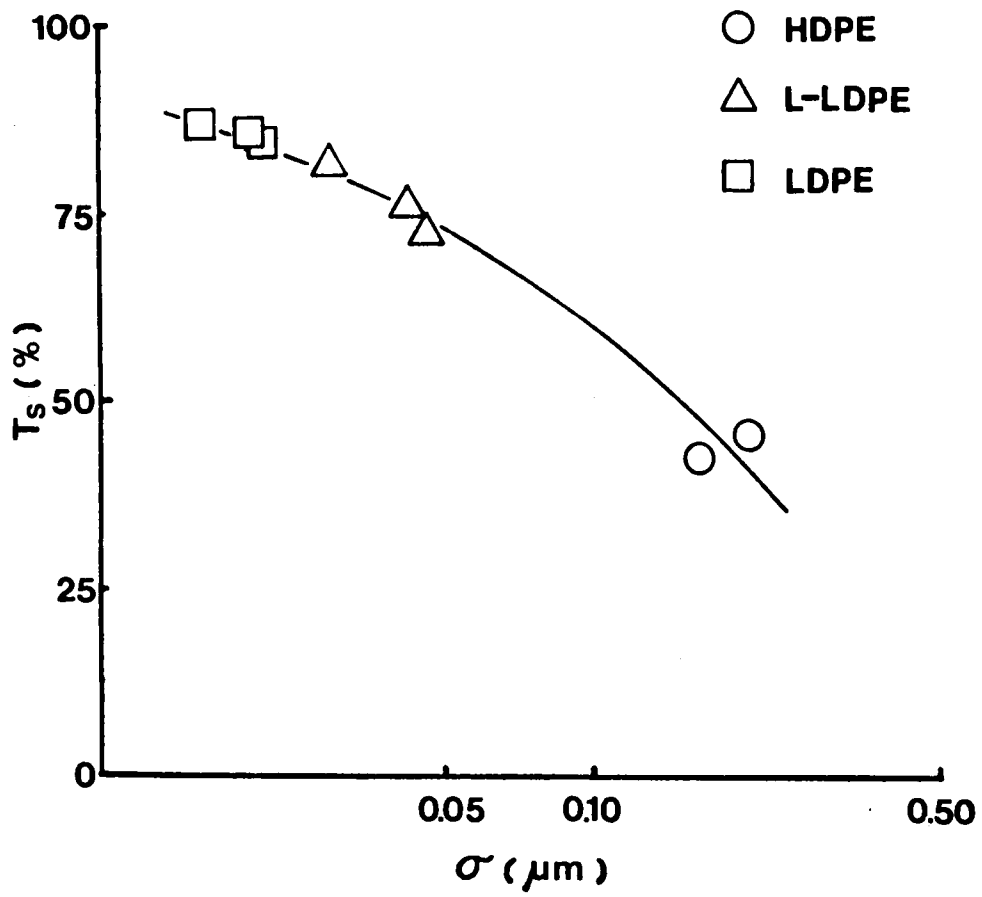


Figure 5.13. Direct transmission factor of blown PE film surface as a function of standard deviation of surface roughness.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

The clarity of blown polyethylene film highly depends on their molecular structure characteristics. Of the three different kinds of polyethylene studied (HDPE, L-LDPE, LDPE), the HDPE showed the lowest direct transmission factor and LDPE showed the highest direct transmission factor. The cause of opaqueness of thin blown PE films is mainly due to light scattering from their rough surfaces and the contribution of their internal optical irregularities is small especially for L-LDPE and LDPE. As expected, films having lower surface-phase direct transmission factors showed larger irregularities on their surfaces. A good correlation was obtained between the standard variation of height deviation of the film surface irregularities and the film's surface phase direct transmission factor. Surface irregularities of blown PE film are affected by crystallization mechanisms near or at the film surface and flow defects caused by deformations within the die and beyond the die exit. Higher deformation causes greater surface irregularities. Increasing the cooling rate reduces both surface irregularities and internal optical irregularities significantly. This is presumably due to the formation of smaller crystalline aggregates at the higher cooling rates.

Both L-LDPE and LDPE blown films showed a typical a-axis orientation along the machine direction with the b-axes concentrated towards the normal direction. Within the range of processing conditions used here, the orientation does not change much. There must, however, be a sufficient change in the nature of crystalline aggregates with processing variables to account for the observed effect of cooling rate on turbidity and crystallization related surface roughness changes.

6.2 Recommendations

The following recommendations for further study of the problem of the blown film surface irregularities, optical properties and internal structure are made:

1. For films having rather smooth surfaces, a scattered portion of light should be measured in addition to the direct transmitted portion.
2. Crystallization induced surface roughness should be eliminated. For further investigation of the extrusion haze, surface irregularities of amorphous polymer blown film should be studied to eliminate crystallization induced surface roughness.
3. For studies of internal structure, a wider range of operation conditions should be used.

LIST OF REFERENCES

LIST OF REFERENCES

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APPENDIXES

APPENDIX A

APPENDIX A

```

.SOS HIROG.FOR
EDITING DSKB:HIROG.FOR
*P:
00100      C          GRAPHICS TABLET
00200      DIMENSION IX(3000),IXR(3000),IYR(3000),
00300      1      IXD(1000),IYD(1000)
00400      CALL INITT
00500      CALL TABINT (0,1,1)
00600      CALL ONEPNT (IXR(1),IYR(1))
00700      IXD(1)=IXR(1)
00800      IYD(1)=IYR(1)
00900      WRITE (21,60) IXD(1),IYD(1)
01000      CALL BELL
01100      IC=IXD(1)+4
01200      J=2
01300      DO 10 I=2,3000
01400      CALL ONEPNT (IXR(I),IYR(I))
01500      IF (IXR(I).GT.900) GO TO 30
01600      IF (IXR(I).EQ.IC) GO TO 20
01700      GO TO 10
01800      20      IXD(J)=IXR(I)
01900      IYD(J)=IYR(I)
02000      WRITE (21,60) IXD(J),IYD(J)
02100      60      FORMAT (2G15.6)
02200      J=J+1
02300      IC=IC+4
02400      CALL BELL
02500      10      CONTINUE
02600      30      CONTINUE
02700      CALL ANMODE
02800      CALL MOVABS (IXD(1),IYD(1))
02900      NUM=J-1
03000      DO 40 J=2,NUM
03100      CALL DRVABS (IXD(J),IYD(J))
03200      40      CONTINUE
03300      50      CONTINUE
03400      CALL FINITT (0,0)
03500      END
*

```

APPENDIX B

APPENDIX B

```

..SOS ASHIR.FOR
EDITING DSKB:ASHIR.FOR
*P:*
00100      C          RANDOM PROCESS
00200      DOUBLE PRECISION FILE
00300      DIMENSION W(1000),IXD(1000),IYD(1000),V(1000)
00400      1      ,Z(1000)
00500      DIMENSION XY(1000,2),ALBAP(3),DES(5),ANOVA(14),
00600      1      STAT(9),PRED(1,7)
00700      IX=1000
00800      WRITE(5,50)
00900      50      FORMAT( ' INPUT FILE NAME ',1H$)
01000      READ(5,100) FILE
01100      100     FORMAT(A6)
01200      OPEN(UNIT=21,FILE=FILE)
01300      DO 200 I=1,4
01400      IA=I*50
01500      IB=IA-49
01600      IC=0
01700      DO 160 J=IB,IA
01800      READ (21,150) IXD(J),IYD(J)
01900      WRITE (1,150) IXD(J),IYD(J)
02000      150     FORMAT (2G15.6)
02100      IC=IC+1
02200      XY(IC,1)=IXD(J)
02300      XY(IC,2)=IYD(J)
02400      160     CONTINUE
02500      N=IC
02600      IMOD=0
02700      IPRED=0
02800      ALBAP(1)=0.05
02900      ALBAP(2)=0.05
03000      IP=1
03100      NN=7
03200      CALL RLONE(XY,IX,N,IMOD,IPRED,ALBAP,DES,ANOVA,
03300      1      STAT,PRED,IP,NN,IER)
03400      IF(IER.EQ.0) GOTO 16
03500      WRITE(5,116) IER
03600      116     FORMAT(' ERROR NUMBER ',14)
03700      16      CONTINUE
03800      WRITE(5,250)DES(2),DES(4),DES(5),STAT(1),STAT(5)
03900      250     FORMAT(' MEAN= ',G15.6,/, ' SIGM= ',G15.6,/, ' RE.COEFF= '
04000      1      ,G15.6,/, ' SLOPE= ',G15.6,/, ' INTERSEPT= ',G15.6)
04100      A=STAT(1)
04200      B=STAT(5)
04300      DO 200 K=IB,IA
04400      Z(K)=IYD(K)-IXD(K)*A-B
04500      200     CONTINUE
04600      IC=IA
04700      FIC=FLOAT(IC)
04800      DO 500 I=1,IC
04900      AL=AL+Z(I)
05000      AMEAN=AL/FIC
05100      DO 600 I=1,IC
05200      D=D+(Z(I)-AMEAN)**2
05300      600     CONTINUE
05400      VARI=D/FIC
05500      SIGM=VARI**0.5
05600      M=50
05700      DO 700 I=1,M
05800      G=0
05900      NM=IC-I-1
06000      DO 700 J=1,NM
06100      K=J+1-1
06200      G=G+(Z(J)-AMEAN)*(Z(K)-AMEAN)
06300      V(I)=G/NM
06400      700     CONTINUE
06500      W(I)=V(I)/VARI
06600      WRITE(22,800) AMEAN,SIGM
06700      800     FORMAT(' MEAN= ',G15.6,/, ' SIGM= ',G15.6)
06800      WRITE(22,900) (W(I),V(I),I=1,M)
06900      900     FORMAT(G15.6,G15.6)
07000      WRITE(22,1000)IC
07100      1000    FORMAT(' DATA PTS= ',G15.6)
07200      CLOSE (UNIT=21,FILE=FILE)
07300      STOP
07400      END

```

APPENDIX C

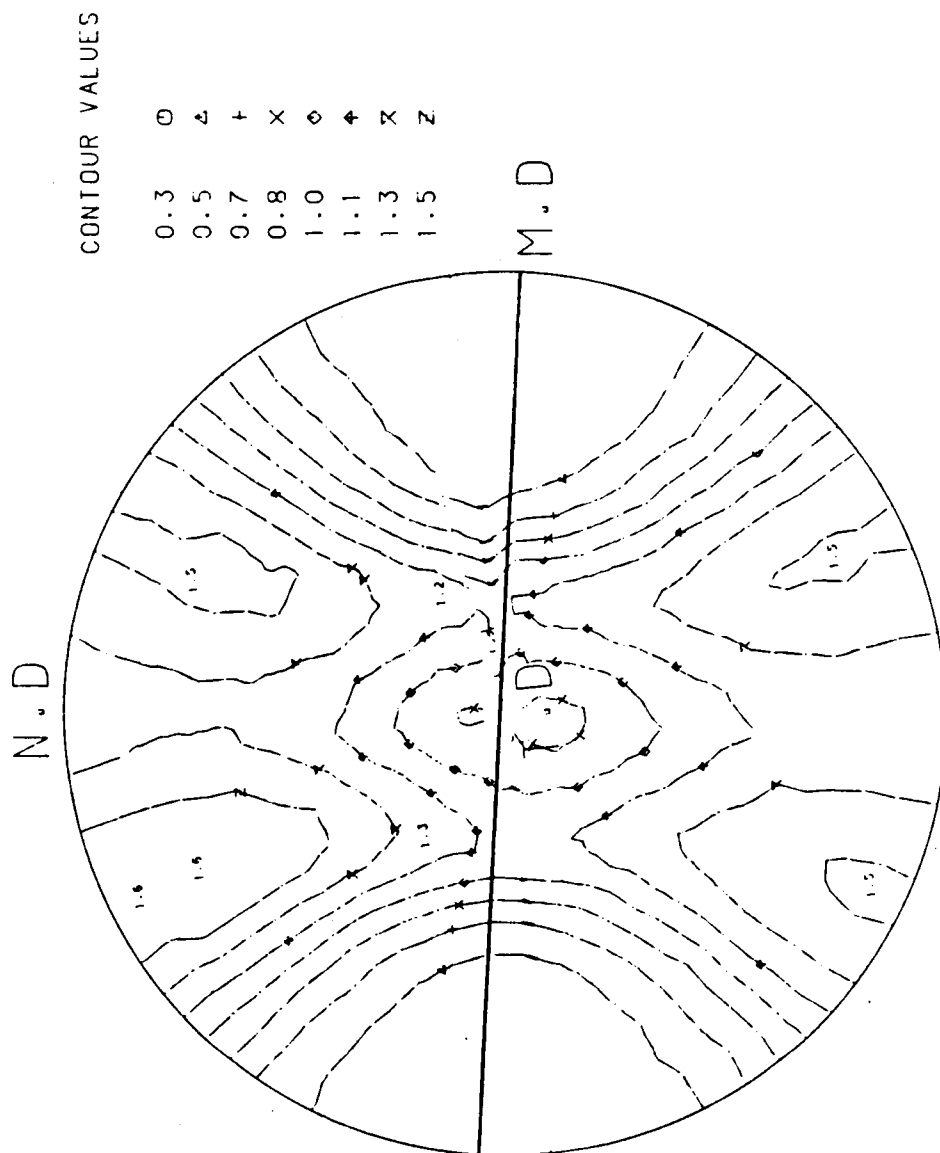


Figure C.1. Pole figure (110) of sample LL-9.

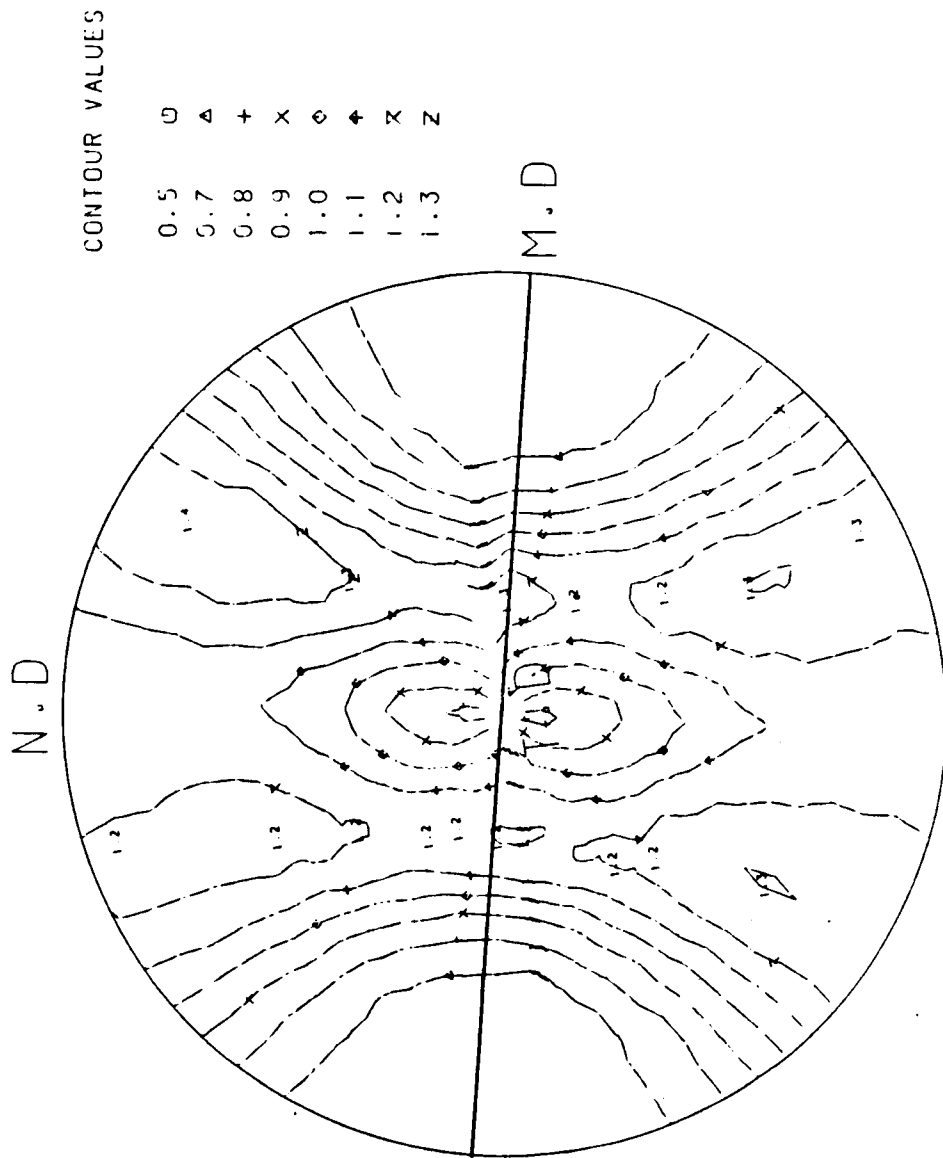


Figure C.2. Pole figure (110) of sample LL-11.

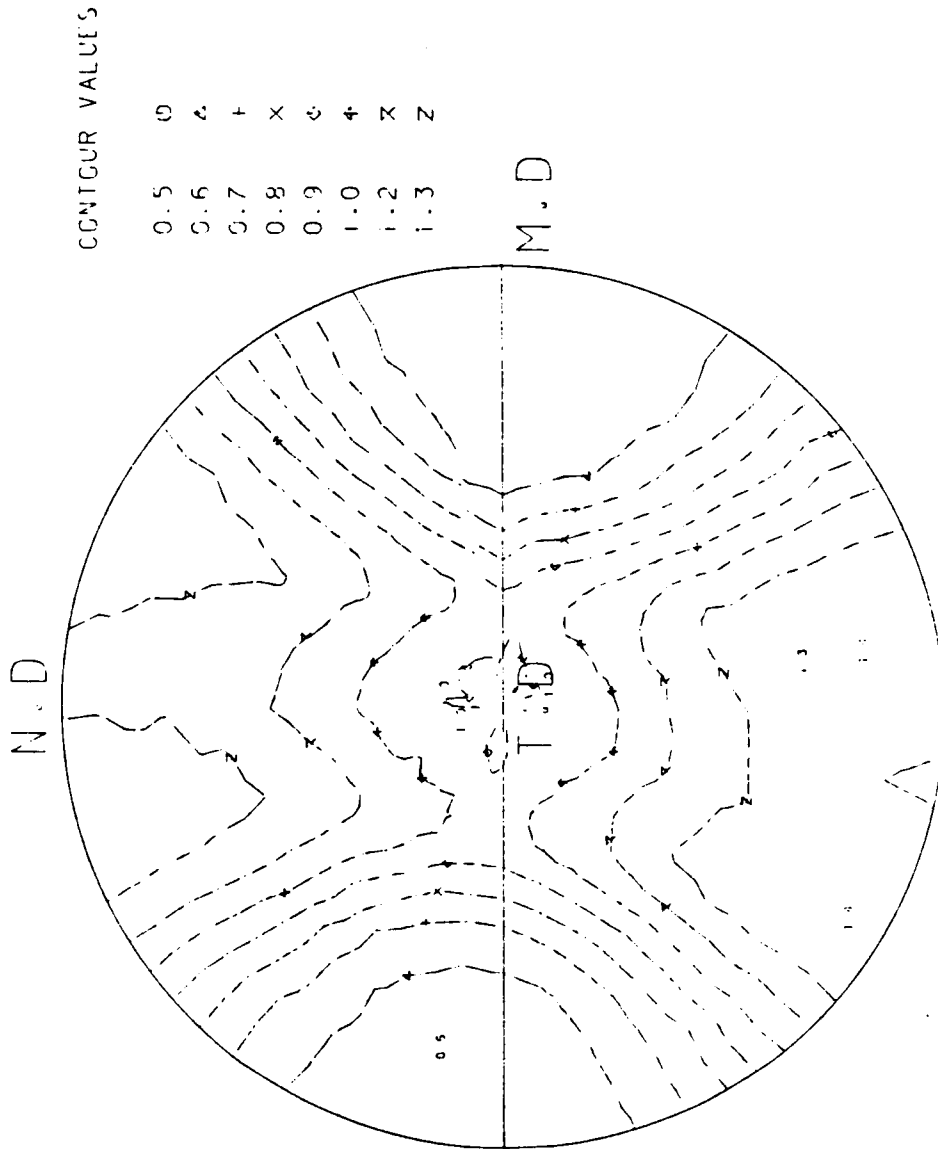


Figure C.3. Pole figure (110) of sample LL-7.

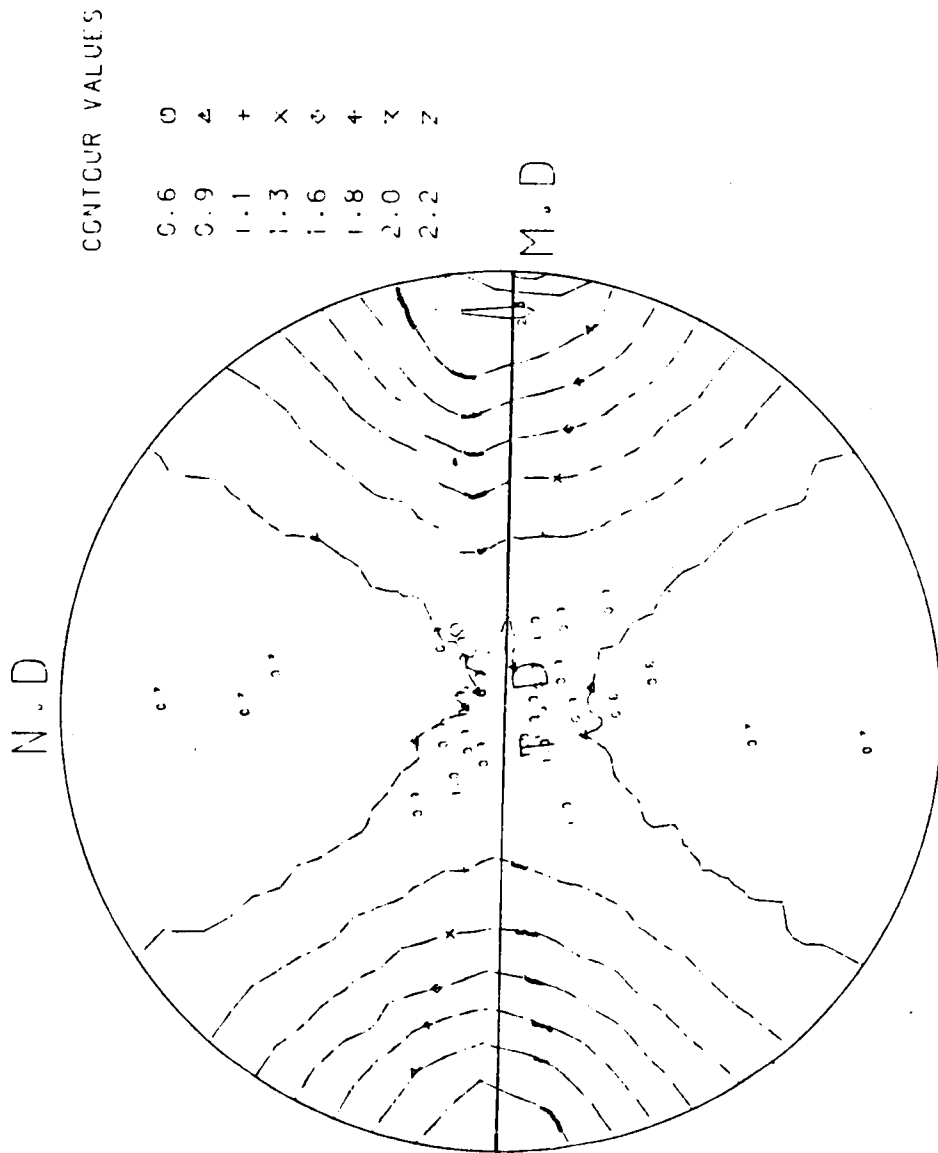


Figure C.4. Pole figure (200) of sample LL-7.

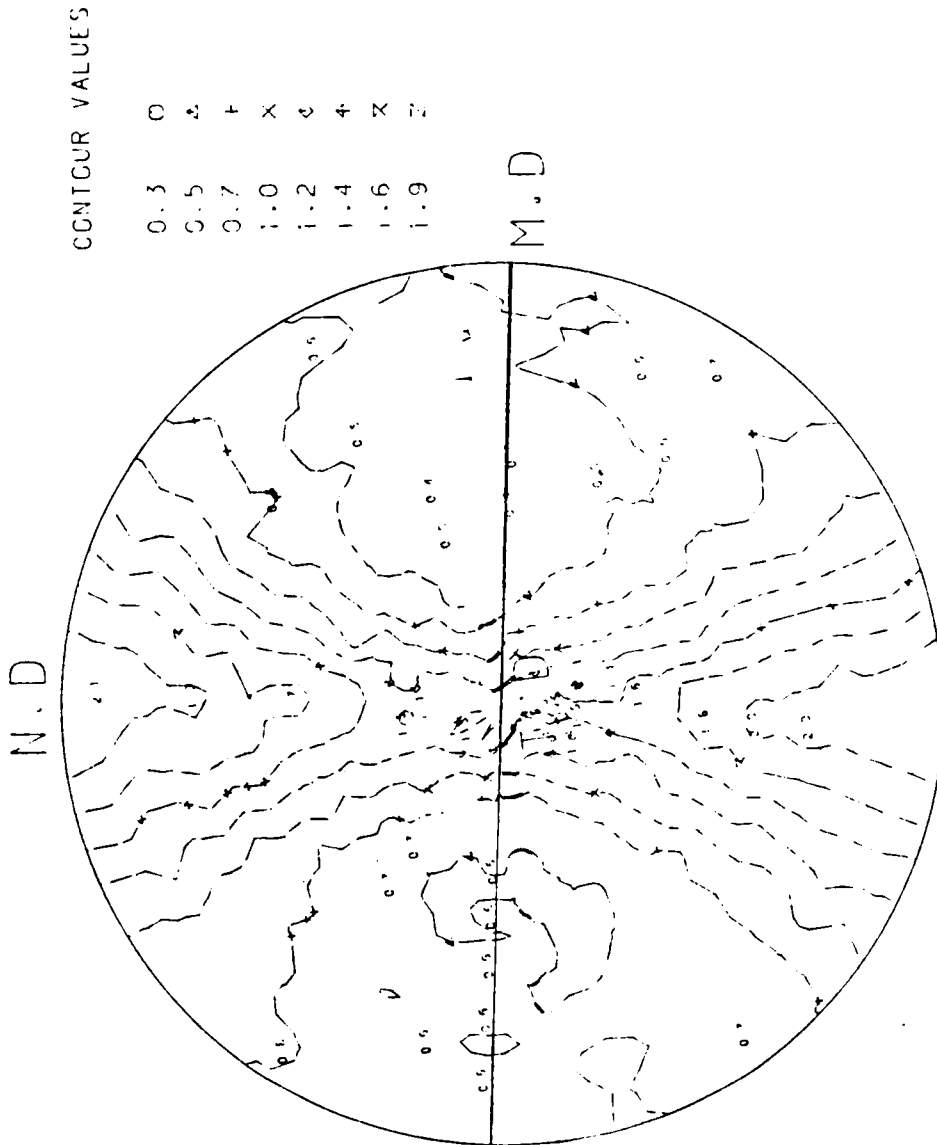


Figure C.5. Pole figure (010) of sample LL-7.

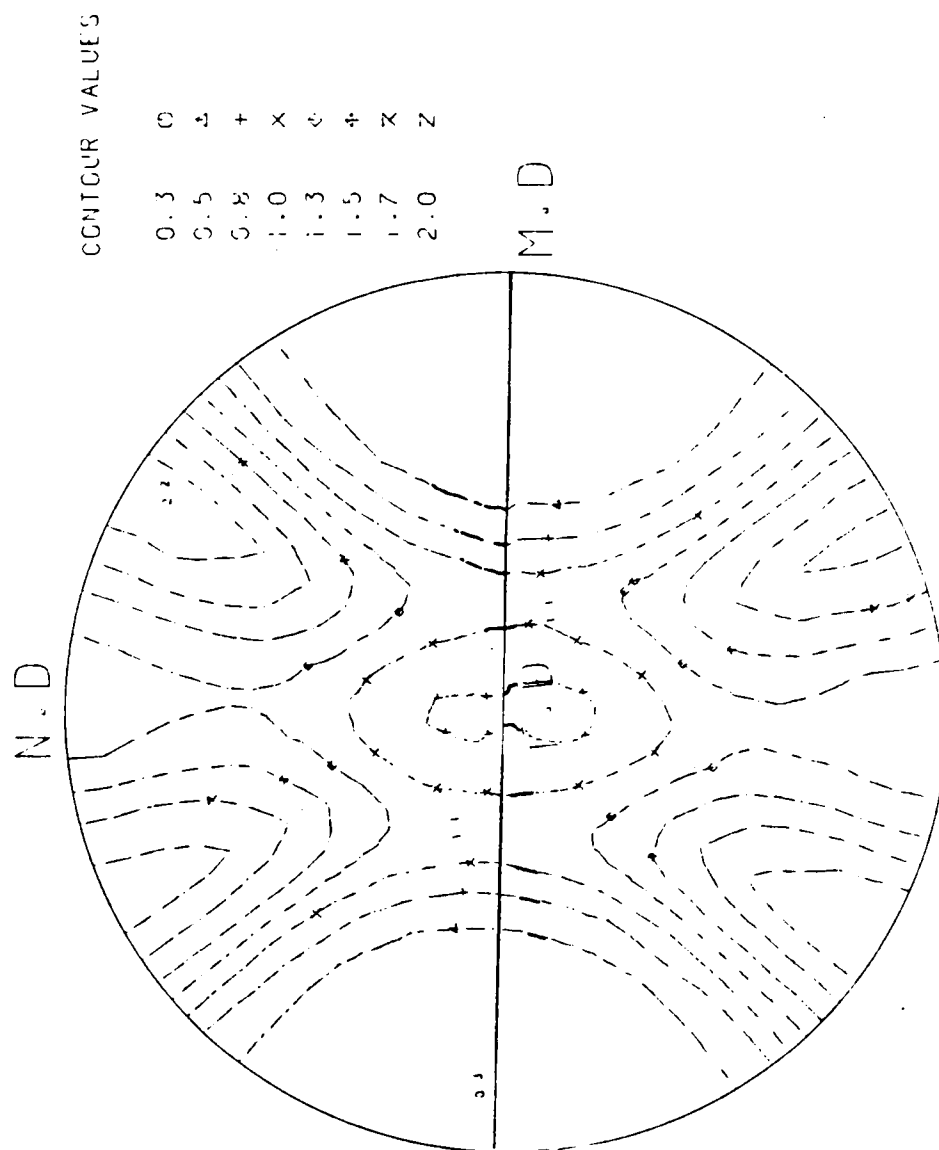


Figure C.6. Pole figure (110) of sample L-9.

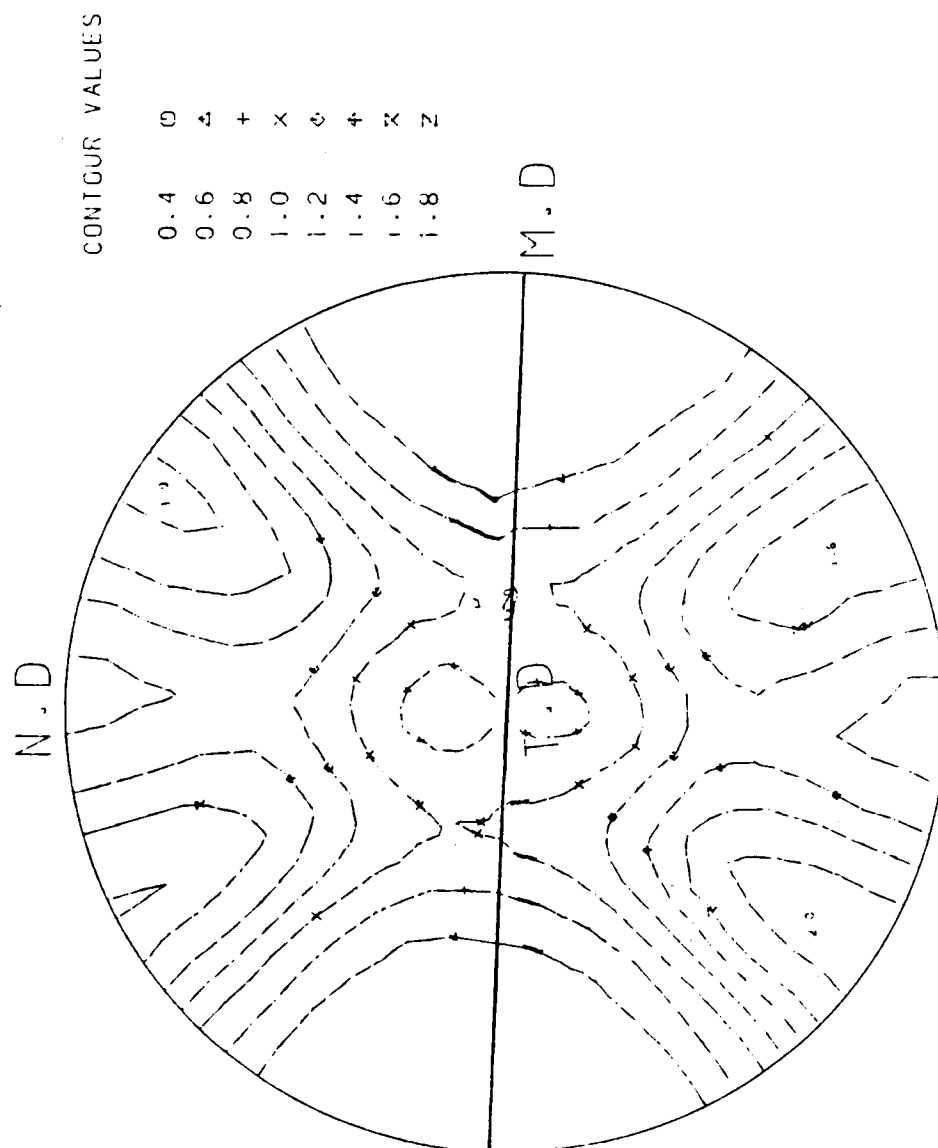


Figure C.7. Pole figure (110) of sample L-11.

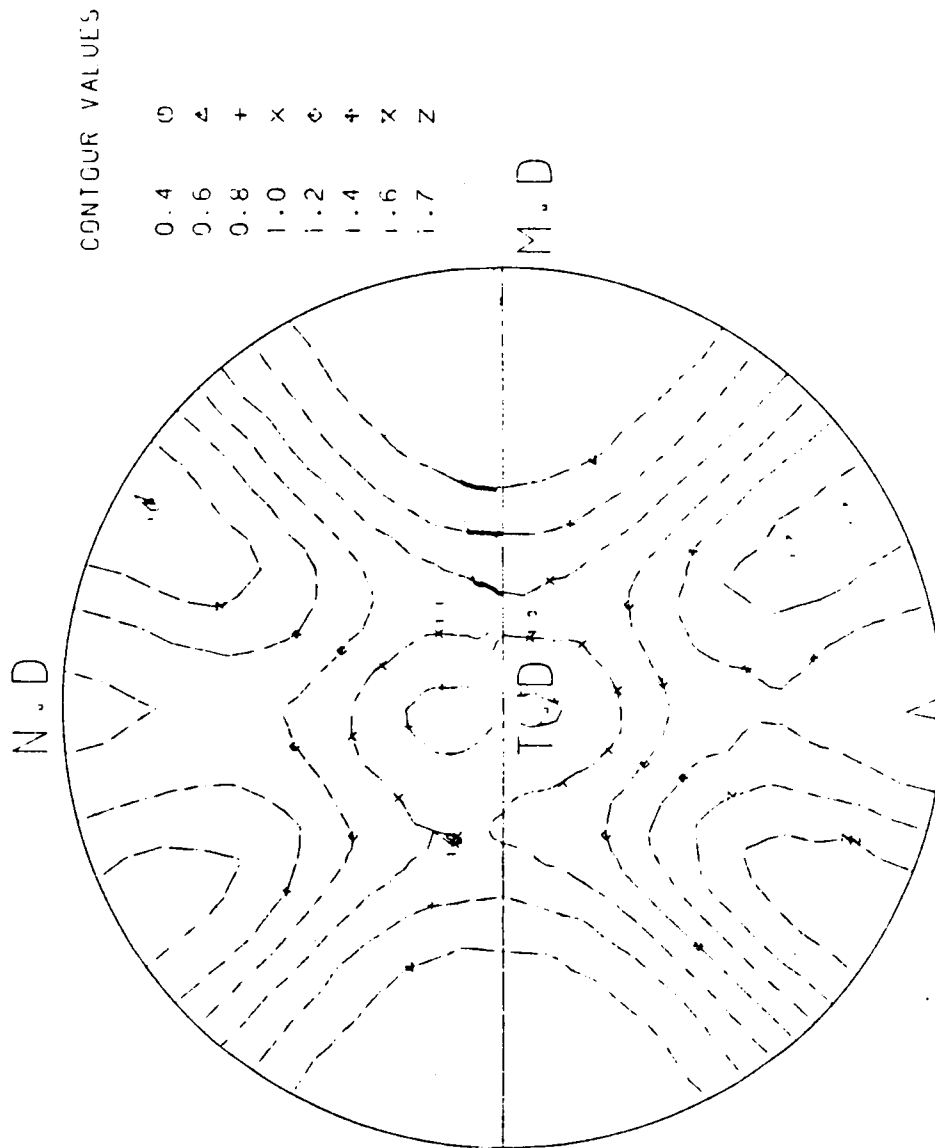


Figure C.8. Pole figure (110) of sample L-7.

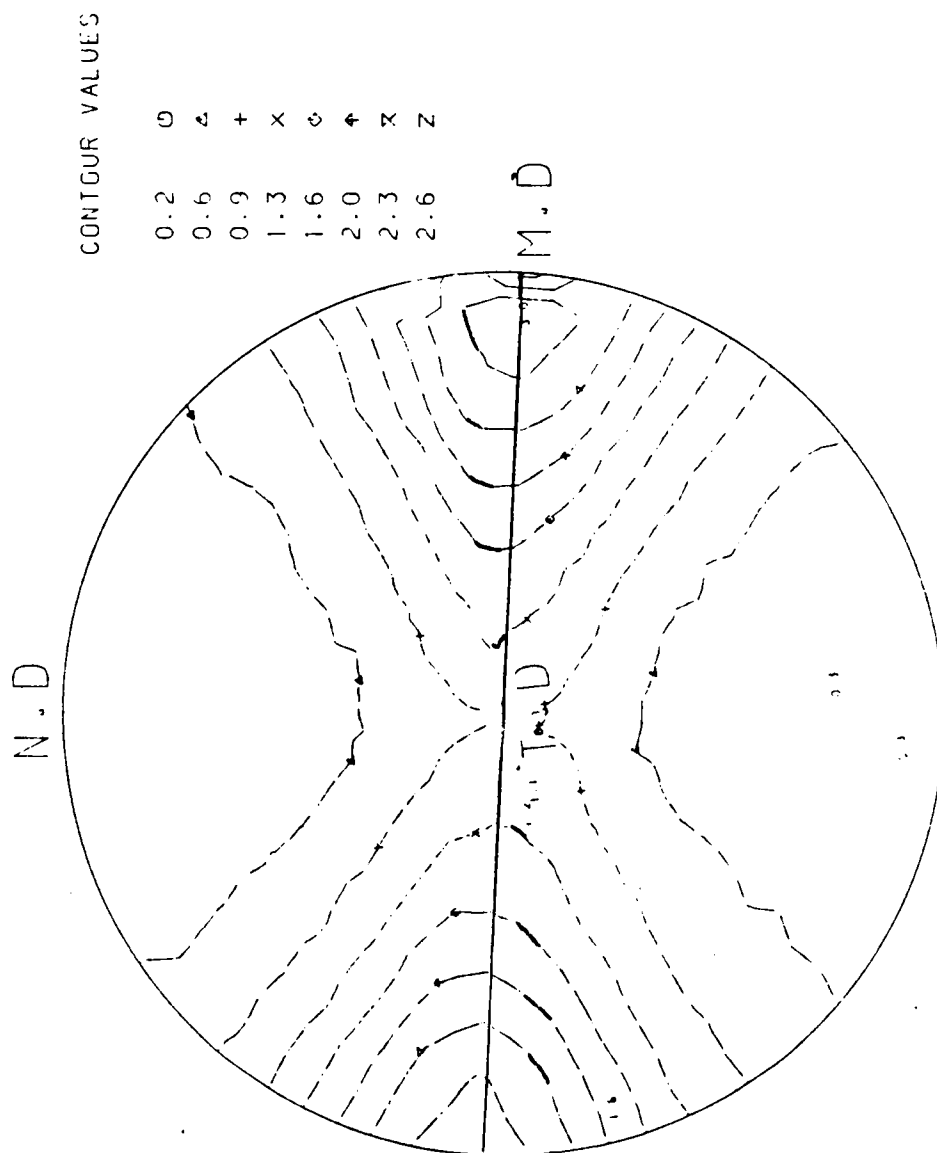


Figure C.9. Pole figure (200) of sample L-7.

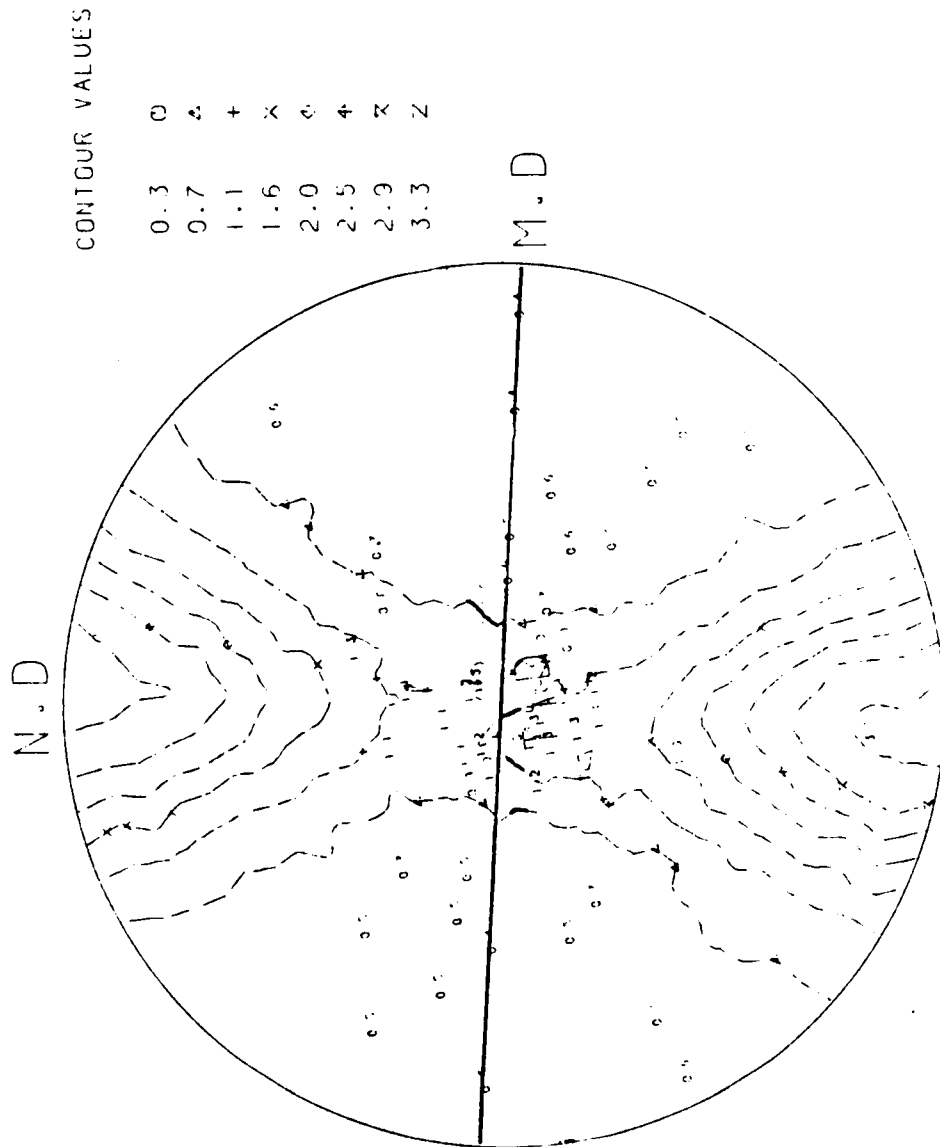


Figure C.10. Pole figure (020) of sample L-7.

VITA

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