INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning 300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA 800-521-0600



.

Surface Morphology of Polyethylene Blown Films

By Zuojian Tang

Department of Chemical Engineering McGill University, Montreal November 2000

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements of the Degree of Masters of Engineering

©Zuojian Tang 2000. All rights reserved



National Library of Canada

Acquisitions and Bibliographic Services

395 Wellington Street Ottawa ON K1A 0N4 Canada Bibliothèque nationale du Canada

Acquisitions et services bibliographiques

395, rue Wellington Ottawa ON K1A 0N4 Canada

Your the Vote nitionnos

Our Be Nore référence

The author has granted a nonexclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission. L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-70254-5

Canadä

Abstract

The properties of blown polyethylene (PE) films depend on various factors, including crystallinity, morphology, and orientation, in addition to chemical composition. It has been shown that the optical properties are strongly influenced by surface morphology. In this project, we use non-contact atomic force microscopy (AFM) and polarized light microscopy (PLM) to visualize surface and bulk morphology. Various techniques, such as surface and line roughness, surface and line fractal dimension, pair-correlation function and nearest neighbor distance distribution function, are employed to quantify the description of morphology and to compare the morphological characteristics of a number of polyolefin films of commercial interest. A comprehensive quantitative analysis of surface topography has been performed. The co-monomer of the PE resins was found to play a significant role in the formation and the orientation of spherulite-like domains. The film cross-section microstructure has been evaluated qualitatively by using both AFM and PLM. However, quantitative analysis of bulk morphology cannot be obtained due to knife effects.

Resume

Les proprietés des films de polyethylene soufflés (PE) dependent en de nombreux facteurs, incluant la crystallinité, la morphologie, et l'orientation, en addition de la compostion chimique. Il a été demontré que les proprietés optiques sont fortement influence par la morphology de la surface. Dans ce projet, nous utilisons, la microsopie a force atomique sans contact (AFM) et la microscopie en lumiere polarisée (PLM) pour vizualiser la morphologie de la surface et du volume interieur. Differentes techniques, tel que la mesure de la rugosité de la surface et de la ligne, de la dimension fractal de la surface et de la ligne, de la function de paire-correlation, et la function de distribution de la distance du plus proche voisin, sont employées pour quantifier la description morphologique et comparer les caracteristiques morphologiques d'un grand nombre de film polyolefin d'intérets commerciaux. Une analyse quantitative compréhensive de la topographie de la surface a été realisé. Le co-mono-mere de la resinse de PE s'est averer jouer un role signifiant dans la formation et l'orientation des domaines de type spherulitiques. Les sections diagonal de la microstructure ont été evalué qualitativement par AFM et PLM. Cependant, l'analyse quantitative de la morphologie du volume interieur ne peut etre obtenu a cause des effets de coupure.

Acknowledgments

First of all, I would like to express my deep gratitude to my supervisor, Professor Musa R. Kamal. His profound insights in the polymer science and engineering field have enlightened and guided me immensely.

I would like to thank Dr. Tao Huang for his advice and guidance in my entire research work, especially, on aspects of advanced image analysis.

I would also like to thank Dr. Lei Wang for his assistance in operating the AFM/NSOM system.

I owe special thanks to Mr. E. Siliauskas for helping me with the operation of the profiler instrument.

Finally, I deeply appreciate my parents and my sister for their encouragement throughout my studies. Special thanks to my husband for his support, understanding and patience.

Table of Contents

1. Introduction	1
1.1. Overview	1
1.2. Objectives	2
2. Technical Background	
2.1. Relationship of Resin Chemical Structure, Process	
and Properties of Polyolefin Blown Films	3
2.2. Basic Process Characteristics of Polymer Film Blowing	5
2.3. Morphology of Polyolefin (Ethylene-Copolymers)	8
2.4. Microscopy and Polymer Morphology	10
2.4.1. Polarized Light Microscopy (PLM)	12
2.4.2. Atomic Force Microscopy (AFM)	
2.5. Microstructure Development of PE Blown Films	14
2.6. Gloss and Haze of Polyolefin Blown Films	16
3. Experimental Methods	20
3.1. Materials	
3.2. TopoMetrix Aurora 2100 Near-field Scanning	
Optical Microscope/Atomic Force Microscope	21
3.2.1. Apparatus	25
3.2.2. Sample Preparation and Apparatus Adjustment	29
3.2.2.1. Sample preparation	29
3.2.2.2. Apparatus adjustment	
3.2.2.2. Apparatus adjustment	
3.2.2.2. Apparatus adjustment	
 3.2.2.2. Apparatus adjustment	
 3.2.2.2. Apparatus adjustment	
3.2.2.2. Apparatus adjustment 3.3. Cross-section Morphology 3.3.1. Cryo-Ultramicrotome 3.3.2. Sectioning Condition 3.3.3. Sample Preparation 3.3.4. Sectioning	
 3.2.2.2. Apparatus adjustment 3.3.1. Cryo-Ultramicrotome 3.3.2. Sectioning Condition 3.3.3. Sample Preparation 3.3.4. Sectioning 3.4. PLM: Polarized Light Microscopy 	

3.5.1. Profiler	
3.5.2. Sample Preparation	
3.5.3. Experimental Techniques	
4. Results and Discussion	40
4.1. Analysis of Surface Texture	
4.1.1. AFM Image observation	40
4.1.2. Roughness	46
4.1.2.1. Surface Roughness	
4.1.2.2. Line Roughness	49
4.1.3. Fractal Dimension	53
4.1.3.1. 2D Fractal Dimension	
4.1.3.2. Line Fractal Dimension	56
4.2. Spatial Distribution of Surface Domains	60
4.2.1. Pair Correlation Function	60
4.2.2. Nearest Neighbour Distance Distribution Function	69
4.3. Observation of Cross-section Morphology	
4.3.1. PLM Cross-section Images	
4.3.2. AFM Cross-section Images	
4.4. Characterization of the Effect of Blow-up Ration (BUR)	
4.4.1. Profile Images	83
4.4.2. Roughness and Waviness	
5. Conclusions and Recommendations	
5.1. Conclusions	
5.1.1. Surface Morphology Characteristics	89
5.1.2. Surface Topography: Roughness and Fractal Dimension	
5.1.3. Spatial Distribution of Surface Domains	
5.1.4. Cross-section Morphology	
5.1.5. Surface Profiles and Waviness	
5.2. Recommendations	
Reference	
Appendix A	
Appendix B	
Appendix C	

1. Introduction

Blown polyethylene films account for 70% of the market of linear low density polyethylene (LLDPE). For the majority of the end uses of LLDPE blown film, the optical properties, which usually refer to gloss and haze, are very important since they could contribute to the appeal of the packaged products. Optical clarity is mainly dependent on the intrinsic characteristics of the material and morphological properties of the film. Good optical properties are associated with high gloss and low haze. Gloss is related to the specular reflection of incident light upon the rough surface of polymer films, which is determined by the film reflective index and the film surface topography. Haze refers to the wide-angle light scattering by the film, which is the combined result of the scattering by the bulk domains in the film and by the rough surface. Therefore, the refractive index and the film bulk and surface morphologies are important factors for film optical properties. The direct measurement of light scattering for a given wavelength of incident light and a given film thickness shows that the surface topography is the dominant factor in film light scattering. The bulk crystallinity and morphology are also contributing factors.

1.1 Overview

Many studies have attributed the scattering of light by polymer films to the structure in the bulk of the film and to both air-film interfaces [1-7]. It has been indicated that light scattering is caused mainly by the rough film surface. In LDPE films, it has been suggested that the main contribution to scattering was from the surface of films, and that such scattering was qualitatively correlated with surface roughness. There are at least two mechanisms causing surface roughening and surface haze, namely extrusion haze and crystallization haze. Reducing both extrusion haze and crystallization haze. Reducing both extrusion haze and crystallization haze can yield a high optical clarity film. In order to identify the contribution of the surface roughness and crystallinity to the light scattering of polyethylene blown films, experiments have been carried out by using UV/visible spectrophotometry, x-ray diffraction and reflectometry [8]. The results show that surface roughness is mainly caused by the film

surface crystallization during the film blowing process, and light scattering of polyethylene films is caused very largely by rough film surfaces. Therefore, the understanding and control of the morphologies of the film are crucial for film optical properties. Though many techniques have been used for this purpose, the surface topography and the bulk morphologies of blown films remain in need of higher and more detailed resolution.

Smith et al [9] employed the Atomic Force Microscope (AFM) to examine the surfaces of commercial blown polyethylene films. It revealed that the optical haze and gloss of films are related to surface roughness. Recently, Wang, Huang and Kamal [10] presented a comprehensive characterization of the surface roughness of polyethylene blown films based on a variety of resins by AFM. The quantitative description of surface roughness was achieved using a number of statistical parameters. Surface gloss of the sample films was calculated using the general Kirchhoff solution [11] for rough surfaces. The calculated gloss values showed good agreement with experimental measurements. Wang also discussed the potential advantages of using near-field scanning optical microscopy (NSOM) [12].

1.2 **Objectives**

In order to obtain a dependable analysis of film optical properties, it is necessary to characterize the surface topography and bulk morphology of the films. The objective of this thesis is to study the morphology of blown films by using AFM, PLM, and a surface profiler, in order to:

- develop techniques of the sample preparation and the observation of bulk morphology.
- obtain quantitative analysis and characterization of surface topography.
- improve our basic understanding of blown film morphology.

This project is part of a larger research program with the broad objective of studying and optimizing the film blowing process and the properties of linear low density polyethylene blown films.

2. Technical Background

Generally speaking, the optical properties of polyolefin blown films are determined mainly by the intrinsic material characteristics and the morphological features. The morphological features are the result of the coupling of the complex thermo-mechanical history and crystallization behavior of the material. The thermal history, temperature gradients, rheological characteristics, stress, deformation, and pressure history strongly affect nucleation and growth of crystallites during polymer processing. Because the domain size and shape, which determine the surface topography and global bulk morphologies of blown films, are in the nanometer scale, the AFM has been selected for film surface microstructure characterization. The systematic studies on film morphology by AFM are essential. As indicated in chapter 1, this project aims to enhance our understanding of the morphology of crystalline polymer films, especially morphological aspects that relate to the optical properties, particularly haze, transparency, and gloss, of polyolefin blown films. In this chapter, we present a brief review of various issues regarding the morphological aspects in polyolefin blown films.

2.1 Relationship of Resin Chemical Structure, Process and Properties of Polyolefin Blown Films

The study of composition-process-microstructure-property interactions is the backbone of materials science. Figure 2-1 shows a schematic of interactions between primary molecular structure and processing-induced film structure with the mechanical, thermal, and optical properties of polyolefin blown films. The properties of a film are a consequence of its structure, which may be considered at different levels of size, ranging from the molecular to the macroscopic. Various properties depend differently on the structural manifestations. The thermodynamic properties and electrical properties depend upon the molecular organization, whereas transparency, smoothness and some mechanical properties depend on larger structures. The flexibility of crystalline polymers, for example, depends to a great extent upon the size, perfection and organization of the

crystals. Again, the optical properties of polyolefin blown films are determined mainly by both the intrinsic material characteristics and the morphological features. Gloss is primarily a function of surface roughness and refractive index. The principal contributors to forward light transmission and light scattering by films are surface roughness, refractive index, domain size, and volume fraction of the spherulites on the surface.

The discussion in the following sections outlines the main features of the approach that we propose to use for establishing the relationships between resin-processmorphology-optical properties. However, emphasis is placed on the morphological aspects relating to optical properties. The roles of the resin chemical structure and the process should become obvious from the discussion, because these factors determine crystallization behavior in blown films and, eventually, form the morphology of such blown films.



Figure 2-1: Schematic of interactions between primary molecular structure and processing induced film structure on the mechanical, thermal, and optical properties of polyolefin blown films.

- 4 -

2.2 **Basic Process Characteristics of Polymer Film Blowing**

Polymer processing is defined as the "engineering specialty concerned with operations carried out on polymeric materials or systems to increase their utility" [13]. The film blowing process is of great industrial importance, since the majority of polymer films are manufactured by this process. In the film blowing process, molten polymer is extruded through an annular die, and the molten tube leaving the die is drawn upwards by the nip rolls. At the same time, air is introduced through an opening in the center of the die inflating the tube. Biaxial stretching takes place in the melt before the point at which the polymer is solidified at the frost line. The biaxial stretching from the molten state of the polymer is achieved by stretching the tubular bubble simultaneously in the machine direction (MD) with the take-up rolls, and in the transverse direction (TD) by bubble inflation. The film properties are precisely controlled by adjusting the axial drawing velocity and the pressure of air inside the bubble.

Figure 2-2 shows a schematic of the basic process characteristics of polymer film blowing. First of all, rheologically there are three different flow regions. The shear flow region is the region inside the die where the polymer melt undergoes uni-dimensional steady shear flow, assuming negligible entrance and exit effects. The transition region is near the die exit. It consists of the confined flow in the die and the extensional flow in the extrudate swell region. In the die, the flow is essentially shearing, with the extensional component just starting to develop. In the extrudate swell region, the flow becomes mainly extensional, with the shearing flow rapidly decreasing. Consequently, the flow field is very complicated in the transition region, at die exit. The pure extensional flow region, between the transition region and the frost line, involves free surface non-uniform biaxial extensional flow. The deformation regime lies somewhere between biaxial extension and planar extension.



Figure 2-2: Schematic of blowing film processing and its rheology and temperature characteristics.

In the extensional flow region, the strain rate, upon neglecting the shear components of the deformation rate, may be written as [14-15]:

$$\dot{\gamma}_{11} = 2\frac{dv_z}{dz} + 2v_z \left(\frac{dr}{dz}\right)\frac{d\theta}{dz}$$
$$\dot{\gamma}_{33} = 2\frac{v_z}{r}\frac{dr}{dz}$$

where, $\dot{\gamma}_{11}$ and $\dot{\gamma}_{33}$ are MD shear rate and TD shear rate respectively. (r, θ , z) is cylinder coordinates and v_z is draw-up velocity.

An expression for the stress as a function of z is obtained:

$$\sigma_{11}(z) = \frac{F_e - \pi \Delta P(r_f^2 - r(z)^2)}{2\pi r(z)h(z)\cos[\theta(z)]}$$
$$\sigma_{33}(z) = \frac{R_t(z)}{h(z)} \left[\Delta P - \frac{h(z)}{R_m(z)} \sigma_{11}(z) \right]$$

where R_t and R_m are the radii of curvature in the machine direction (MD) and the transverse direction (TD), respectively. F_c is the take-up force, ΔP is the internal bubble

pressure. Finally, if R_f is the final radius, and H_f is the final thickness, the equations for stress at the points beyond the freeze line are obtained:

$$\sigma_{11} = \frac{F_e}{2\pi R_f H_f}, \qquad \sigma_{33} = \frac{R_f}{H_f} \Delta P$$

Let us consider the process parameters: the blow-up ratio, $B_R = R_f/R_0$, and the draw ratio, $D_R = V/v_0$, and then the final film thickness, $H_f = H_0/(B_R D_R)$, where H_0 is the initial film thickness or the die gap (see Figure 2-2 for identification of critical parameters). If the B_R is increased and the film thickness is kept constant, the MD stress, $\sigma_{1/}$, decreases and the TD stress, σ_{33} , increases. The decrease of MD stress is understandable with increasing B_R and constant thickness the D_R decreases. Experimentally, the stress in MD is always higher than the stress in TD. Although, with increasing B_R , the stress ratio (MD/TD) may become smaller, it will always be considerably larger than unity. Increasing the B_R and keeping the film thickness and the freeze line height constant, the stress ratio (MD/TD) may approach unity, but this is more a result of the decrease of $\sigma_{1/}$ than the increase of σ_{33} .

The blow-up ratio, coupled with the rate of draw, permits both the control of film thickness and the degree of uni- and biaxial orientation introduced into the film by this process. Hence the blow-up ratio (i.e., the ratio of the diameter of the bubble to that of the die) is of great importance. It determines the orientation in the transverse direction (TD), see Figure 2-2. The draw speed determines the draw-down ratio in the machine direction (MD) and, consequently, the orientation in that direction.

The film is cooled by an air ring over the die. The tubular film extrudate thins out axially because of the internal pressure applied by the central air stream and by an axial tension that is deliberately imposed by the rotation of the nip rolls. This is why the orientation is biaxial to degrees that can be varied by manipulating the internal pressure and the axial tension. The bubble diameter increases and reaches a constant value R_f in the neighborhood of the freezing line. At the freezing line, the film temperature is approximately equal to the solidification temperature. The axial distance between the die

exit and the freezing line is controlled by the rate of cooling supplied by cold air jets from an air ring. The nip rolls act as a seal for the film bubble. After the nip rolls, the flattened bubble is cut at the creases and wound onto two separate rolls.

2.3 Morphology of Polyolefin (Ethylene-Copolymers)

The common morphology of semicrystalline polymers is spherulitic. The microstructure of spherulites consists of amorphous and crystalline phases. In crystalline regions, major structural units are the platelet-like crystallite (folded chain) aggregates or lamellae, which are separated by amorphous regions inside the spherulite. The spherulites exhibit radially symmetric growth of the lamellae from a central nucleus, while the molecular chains run perpendicular to the spherulite radius. The platelets also grow in the branch direction. Spherulites generally impinge upon one another, resulting in polyhedral shapes. When viewed with a crossed polarizer, the spherulites appear bright, because they are anisotropic and crystalline in nature.

The size of spherulites affects not only the optical properties of polymers, but also their mechanical response. Monitoring this property can be important in structureproperty determinations. It is evident that spherulitic morphology strongly depends on crystallization temperature [16]. At the low temperature, polymer crystalline morphology is "grainy", consisting of many small spherulites, because of the high nucleation rate. Such structures are mechanically ductile due to a quantity of molecular ties and amorphous phase between the small spherulites. Also, such polymers have a lower modulus and are optically uniform. On the other hand, spherulites can grow to be larger at high crystallization temperatures, because the nucleation rates are lower and growth rates are high. Such spherulitic morphology, which comprises more perfect crystals, results in high moduli, brittle, and optically non-uniform substances. In brief, the crystallinity, the number and size of spherulites, and the rate of crystallization depend strongly on not only the crystallization (annealing) temperature but also on the degree of macromolecular orientation during crystallization. The properties of crystalline polymers ultimately depend on the structural and morphological features of the system. These features are controlled by the kinetics and mechanisms of crystallization. A variety of studies with different homo-polymers have clearly established the important role of molecular weight in controlling the crystallization process and thus the resulting properties [17]. Similar factors should also be important in the crystallization of polyolefin, or ethylene-copolymers. In this case, beside molecular weight, the influence of co-unit content needs to be assessed. Although there are many reports of the crystallization kinetics of copolymers, there is a lack of studies with various molecular weights and composition fractions of random copolymers [18].

The two basic processes in crystallization are initiation or nucleation, by which a new phase is initiated within a parent phase, and subsequent growth of the new phase at the expense of the parent. Both processes have been analyzed in monomeric systems and in long-chain molecules. The former may occur homogeneously, by statistical fluctuations in the parent phase, or by formation of nuclei catalyzed by heterogeneities or impurities present in the melt. Two main theories describing crystallization of polymers have been developed. One uses a thermodynamic approach [17] and provides a description of crystallization and morphology, and the other offers a kinetic description of the formation and growth of the nuclei [17]. The crystallization rate depends mainly on the temperature. Because crystallization is described by a nucleation and growth mechanism [10], the temperature coefficient observed in the transformation must be explained in terms of the temperature coefficients of these two processes.

Nuclei can be formed either homogeneously by means of statistical fluctuations in the parent phase or heterogeneously, catalyzed by the presence of heterogeneities. In the latter process, nucleation starts on or in surfaces, cavities, and cracks of insoluble impurities. An example of heterogeneous nucleation is self-nucleation, caused by crystals chemically identical with the polymer. When impurities or residual crystals are present, the nucleation rate depends on the thermal history of the polymer and, more specifically, on the previous melting temperature; eventually, a temperature is reached at which all the possible seeds are destroyed. Therefore, polymer crystallization, whether manifested by observation of the growth of specific crystal faces, the spherulite growth rate, or the overall crystallization rate, is a result of the rate of formation and growth of stable nuclei as well as the rate at which untransformed chain units are brought to the growing faces.

Alamo and Mandelkern have reviewed the overall crystallization kinetics of a set of random ethylene copolymers [18]. The copolymers, with ethyl and butyl branches, covered a wide range in molecular weights and co-unit contents. The influence on the crystallization process of molecular weight at a fixed co-unit content, as well as that of co-unit content at a fixed molecular weight, could be assessed by the appropriate choice of fractions. Studying the overall rate of crystallization removes the restriction of having to focus on the growth of well-defined morphological forms, such as spherulites. This latter method severely limits the range of molecular weights and copolymer compositions that can be studied. On the other hand, it has been well established that the salient features of the crystallization process, such as the temperature coefficient and delineation of regimes, can be obtained with equal reliability by either of the two experimental methods. The most general features of the crystallization process are very similar to those of homopolymers. However, some important exceptions are found. Foremost among these is the fact that the isotherms do not superpose one with the other; deviations from the Avrami [19] relation occur at low levels of crystallinity; and only relatively low levels of crystallinity can be attained after crystallization for a long time. These phenomena can be explained by the changing composition of the melt during isothermal crystallization, the restraints that are placed on the concentration of sequences that can participate in steady-state nucleation, and the theoretical limitations on the true equilibrium crystallinity levels.

2.4 Microscopy and Polymer Morphology

The morphology of polymers is evaluated by a wide range of optical, electron and scanning probe microscopy techniques. Table 2-1 is a listing of the more commonly

employed microscopy techniques [20]. The size and distribution of spherulites can be observed by optical techniques, but more detailed study requires electron and scanning probe microscopy. The conventional optical microscope gives lower magnification than electron and scanning microscopy. One advantage of the light microscope is that larger fields can be imaged. Therefore, a larger area of the specimen can be observed. Transmission Electron Microscopy (TEM) is widely used to evaluate the local organization and orientation of lamellae orientation. Small-Angle X-ray Scattering (SAXS), Wide-Angle X-ray Scattering (WAXS), and Small Angle Light Scattering (SALS), as well as the infrared dichroism technique are used to examine the molecular orientation. Because the domain size and shape associated with surface topography and global bulk morphologies of blown films are in the nanometer scale, Atomic Force Microscopy (AFM) is most suited for characterization of microstructure.

Туре	Features	size range	magnification
Optical			
Bright field	Macro-, microstructures, Color, homogeneity	acro-, microstructures, $1 \text{ cm} - 0.3 \mu \text{m}$ 1 - 1000× olor, homogeneity	
Polarized light	Spherulitic textures	1cm - 0.5μm	1 - 1000×
Phase contrast	Phase variations, refractive index differences	100μm - 0.2μm	50 - 1200×
Electron	· · · · · · · · · · · · · · · · · · ·		
Scanning (SEI)*	Surface topography	1mm - 5nm	10 - 50000×
Scanning (BEI)*	Atomic number contrast	1mm - 20nm	10 - 10000×
Transmission	Internal morphology, lamellar and crystalline structures	10μm - 0.2nm	2000-5×10 ⁶ ×
STEM	Internal morphology, lamellar and crystalline structures	100µm - 1nm	300-0.3×10°×
Scanning probe			
STM	Surface topography	10µm - 0.2nm	2000-5×10 ⁶ ×
AFM	Surface topography of insulators	10μm - 0.4nm	2000-1×10 ⁶ ×
FFM Friction and surface Chemistry		10μm - 1nm	2000-1×10 ⁶ ×

Table 2-1:	Microscopy	techniques
------------	------------	------------

*Note: SEI - secondary electron image

BEI - backscattered electron image

2.4.1 Polarized Light Microscopy (PLM)

As an object is illuminated, it scatters, reflects or transmits the light. A system of lenses is used to collect this light to form an image. All of these functions can be executed by the optical microscope. The polarized light microscope is an optical microscope. It is used to study the microstructure of objects by the interaction with polarized light. The method is widely applied to polymers and to liquid crystals [21]. Polarized light microscopy involves the interaction of materials that have anisotropic optical properties with polarized light. If there is no birefringence in specimen, the field of view in the crossed polars should be completely dark. The image of polymeric specimen produced by PLM is due to the birefringence of polymer chains.

An application of PLM in industrial films is to observe spherulitic texture. In a spherulite, the crystals grow radially outwards from the center, so orientations are present at all angles. Under polarized light, the spherulite is bright and visible except at the four perpendicular radial directions where the crystals are in the extinction position. This produces the well-known Maltese cross extinction pattern. The Maltese cross image of spherulitic morphology is related to the crystallization conditions of the polymer. An observation of spherulitic size/shape and distribution is very useful for understanding the effects of process variables. Figure 2-3 is an example of the spherulitic texture observed by PLM of a thin cross section of a high-density polyethylene [22].



Figure 2-3: A fine spherulitic texture of a high-density polyethylene cross-section taken in polarized light [22].

2.4.2 Atomic Force Microscopy (AFM)

The scanning tunneling microscope (STM) was invented in 1982 by Binning and Rochrer at IBM [23]. It was the first of a new class of microscopes, which are generally referred to as near-field or scanning probe microscopes (SPM). In 1986, Binning et al invented the atomic force microscope, which is one of the most versatile types of SPM [24]. These novel imaging techniques have a common character, in that the image is produced by scanning a sharp tip on the surface of a specimen and detecting the interaction between the tip and sample surface. Compared to the electron microscope, AFM, especially in the non-contact mode, does not damage the specimen surface. Moreover, it can image the structures at various length scales, from sub-nanometer to hundreds of microns with ease and minimal sample preparation. The images are obtained at very high resolution.

Smith *et al.* [9] used the AFM to examine surface morphology of blown polyethylene films by scanning the inner and outer film surfaces, and the surface roughness was determined. They concluded that in blown films, the surface roughness might be attributed to the exposed crystalline features, which cause much of the haze. Recently, Wang, Huang and Kamal [10] presented a comprehensive AFM characterization of the surface roughness of polyethylene blown films based on a variety of resins.

Topography visualization of film surfaces and cross-sections with AFM can be clear and sharp. An accurate exaggerated relief map of the surface height can be exactly produced. The magnification perpendicular to the plane of the film can be ten or a hundred times, thus revealing surface structure clearly. In the present study, we employ AFM to perform direct measurement of the surface roughness, fractal dimension, distribution of spherulites and relative size of spherulites quantitatively.

2.5 Microstructure Development of PE Blown Films

It is well known that spherulitic morphology is commonly observed in semicrystalline polyolefins formed during solidification from the melt in the absence of stress. However, the row nucleated structure is often observed due to stress effects. In order to understand this phenomenon, we need to recall the morphological development of spherulites under stress or strained conditions. Figure 2-4 shows the deformation of the spherulite under different strained conditions [25]. Without strain, the shape is basically spherical. With increasing strain, the magnitude of molecular chain orientation increases. Experimental results have shown that when stress is smaller than 102 kPa, the spherulites shape is basically spherical. When stress is greater than 104 kPa, shish-kebobs start to appear.





The irregularities on the surface of blown polyolefin films have been attributed to extrusion defects originating from the complex melt flow behavior of the polymer during die flow and by the growth of crystalline aggregates on or near the surface. Kwack and Han [26-27] studied the crystalline structure of LDPE blown films by WAXS, SAXS and SEM. They claimed that the biaxial stress ratio appears to be a determining factor in the distribution of fibrous nuclei and crystalline texture, as well as film anisotropy. Similar results by White and coworkers [28-31] proposed that the changes in crystalline morphology and surface roughness were produced by flow defects generated during extrusion. They concluded that below a stress value of about 10^5 Pa. the crystallite is spherulitic. The row nucleated structure could be observed when the magnitude of the applied stress exceeds about 10^7 Pa. Prud'homme [32] guantified and characterized the molecular orientations induced in low-density polyethylene films prepared by the tubular film blowing process using pole figures obtained by wide-angle X-ray diffraction. The type and orientation of the morphology within the films were determined using smallangle X-ray scattering. It was also shown that molecular orientation measurements could be used to verify the consistency of the processing conditions in blown film production.

Simpson and Harrison [33] have investigated the effects of processing conditions on crystalline and amorphous morphologies. They found that increasing the take-up ratio (TUR) causes lamellae to become more perfectly stacked and amorphous orientation to increase in the MD. Increasing the blow-up ratio (BUR) increases lamellar disorder and amorphous orientation in the TD. Increasing the frost line height (FLH) causes no significant changes in crystalline and amorphous morphologies. Van Gurp *et al.* [34] found that, with increasing extrusion temperature, the twisting of the lamellae increasing. Haber and Kamal [35] reported that resin rheolgical properties have a profound influence on the orientation. Due to its strain-softening behavior, LLDPE exhibits the lowest stress orientation, while LDPE exhibits an intermediate stress orientation due to its strainhardening behavior. Babel, Nagarajan and Campbell [36] tested the relationship between process kinematics, film structure, and the physical properties of the final polyethylene blown film. Orientation was determined experimentally using polarized infrared radiation. They concluded that the amount of strain put in the film once it starts to freeze, defined here as plastic strain here, has the dominant effect on the film properties. On the basis of their studies, they proposed a two-phase model of the blown film process for partially crystalline polymers. They computed a 2-D heat transfer analysis, with consideration of the heat generation due to crystallization. The results indicate a correlation between the plastic strain (or its derivatives), dichroic ratio, and the ultimate physical properties of the blown film.

The morphological features are the result of the coupling of the complex thermomechanical history and crystallization behavior of the material. The thermal history, temperature gradients, the rheological characteristics, stress, deformation, and pressure history strongly affect nucleation and growth of crystallites during polymer film blowing [37].

2.6 Gloss and Haze of Polyolefin Blown Films

Many works reported that the scattering of light from films might be attributed to the structure in the bulk of the film and to both air-film interfaces. Other studies have indicated that light scattering is caused mainly by the rough film surface [1-3]. The irregularities on the surface have been attributed to extrusion defects originating from the complex melt flow behavior of the polymer during die flow and by the growth of crystalline aggregates on or near the surface. This has been supported by the works of Stein *et al.* [4], Hashimoto *et al.* [5], Stehling, Speed and Westerman [6], and Ashizawa, Spruiell and White [7]. By using SEM to evaluate surface roughness, small angle x-ray scattering (SAXS), wide angle x-ray scattering (WAXS) and small angle light scattering (SALS) to evaluate crystalline and lamellar morphology, Stehling *et al.* [6] further confirmed that the main contribution to scattering was from the surface of films, and that such scattering was qualitatively correlated with surface roughness for LDPE films.

Gloss is defined as the optical property that measures the ratio between specularly reflected intensity and the incident light intensity. Because the reflection of incident light

intensity depends largely on the surface upon which the reflection occurs, gloss is closely associated with the surface roughness of the material. In the case of polymer films, gloss is not only a function of the surface profile but also the intrinsic property as well, i.e. the refractive index of the polymer film. For the same polymer resin, the refractive index of the crystalline state is usually different from that of the amorphous state. However, such difference is small and is usually neglected in the study of surface reflections. Therefore, the refractive index of a polymer film here depends only on the chemical composition of the resin from which the film is made [12].

The surface roughness is described using parameters such as the standard deviation of surface heights, lateral correlation length and fractal dimension. Resin composition and structure appear to play a critical role in the formation of surface roughness. Wang et al. [10, 12, 38] developed a model to compute the reflection of light by the rough surface of polymer films based on the theory of the general Kirchhoff solution [11] of the reflection of electro-magnetic waves. The gloss of films was computed by combining this model with the results of the statistical characterization of surface morphology of the films. A comparison between computed gloss values and the corresponding experimental measurements, for the various polyethylene films included in this study, is presented in Figure 2-5 [10, 12, 38]. There is good agreement between the theoretically computed gloss values and the experimental measurements. The actual gloss measurement may include both the reflection from the top film surface and the reflection by the surface of the background on which the film is placed for measurement [39]. Such an effect would be strong for highly transparent films, yielding higher measured gloss values. This effect is not taken into consideration in the theoretical assessment of gloss from the surface profile. It explains the discrepancy between theoretical prediction and experimental measurements for high clarity film samples in Fig. 2-5 [10, 12, 38]. The effect of background reflection is less significant for less transparent samples, in which case, better agreement between the theoretical values and the experimental measurements would be expected.



Figure 2-5. Comparison between the experimental gloss and haze measurements and values calculated from morphological information [10, 12, 38].

Unlike gloss, which is only a function of surface morphology, light transmission is dependent upon the surface as well as the bulk morphology. It is known that the reduction from perfect transparency for polyethylene blown films is mainly due to the scattering of light. Haze is defined as the percentage of transmitted light which, in passing through a specimen, deviates from the incident beam by more than 2.5° from the normal incident beam [40]. In the study of light transmission and forward scattering by polymer films, the parameters of interest are direct transmittance, total transmittance and haze. Haze is defined as the cloudy or turbid aspect or appearance of an otherwise transparent specimen caused by light scattered from within the specimen or from its surfaces.

Wang *et al.* [10, 12, 38] proposed a model for the calculation of haze of polyolefin films based on the surface morphology of these films. Figure 2-5 [10, 12, 38] also shows the computed values of haze for 13 different blown polyethylene film samples. These are compared to experimental measurement. There is good agreement between experimental measurements and the theoretical values computed from the morphology information. The theoretical predictions are in general lower than the experimental values. This discrepancy is attributed to neglecting scattering in the bulk. As pointed out by Smith [9], the main contribution to transmission haze comes from the surface. The measurements of haze for polyethylene blown films before and after oil immersion showed up to 70% reduction in transmission haze. However, a fair amount of light is scattered by the bulk of the film. Because of the assumption that the bulk of film does not contribute to light scattering, the calculated haze includes only the contribution of the surface. To include the effect of bulk on the light scattering as well as transmission haze, a detailed knowledge of the internal structure of the spherulites is essential.

3. Experimental Methods

3.1 Materials

The materials included in this study were based on low density polyethylene, LDPE, and linear low density polyethylene, LLDPE, supplied by NOVA Chemicals, Calgary, Canada. Structural data for these resins were also supplied by NOVA Chemicals. The LDPE and LLDPE blown films made from these resins were supplied by NOVA Chemicals. These blown films were obtained under the similar processing conditions, which are approximately: barrel temperature = 420° F, die temperature = 440° F, melt temperature = 430° F, line speed = 67.4 ft/min, output = 40 lb/hr and BUR = 2.5. Table 3-1 shows the structural information and Table 3-2 shows the film serial number provided by NOVA Chemicals. Also, film C was obtained with six different blow-up ratios, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4 (BUR), as shown in Table 3-3.

Resin	Сото	Med/Cat	Co-me	Branc	Mn	Mw	Mw/Mn	Density
			%	B/KC	(g/mol)	(g/mol)		(g/cm3)
В	BUT	Gas/ZN	4.03	20.20	24200	98700	4.1	0.9194
Н	BUT	Sol/ZN	3.80	18.90	24900	120000	4.8	0.9190
A	HEX	Gas/ZN	3.94	19.72	30000	111000	3.7	0.9208
С	HEX	Gas/ZN	3.77	18.87	36000	111300	3.1	0.9234
D	HEX	Gas/Met	3.08	15.41	44000	98000	2.2	0.9192
Е	HEX	Gas/Met	2.56	12.80	43000	94000	2.2	0.9194
M	HEX		4.50		20600	74200	3.64	0.9192
G	OCT	Sol/ZN	3.20	15.80	17000	106000	6.2	0.9200
I	OCT	Sol/Met	5.00	24.80	22000	53000	2.4	0.9070
J	OCT	Sol/Met	3.20	15.80	38000	70000	1.8	0.9180
L	ОСТ	Sol/ZN	2.80		25900	114000	4.4	0.9212
F	LDPE	Gas			12000	88000	7.3	0.9190
K	LDPE	Gas			16000	66200	4.1	0.9203

Table 3-1: Resin information

Como: Comonomer; Co-me: Copolymer-content

Med: Reaction Medium - Gas Phase or Solution; Cat: Catalyst - Ziegler-Natta or Metallocene Branc: Branching Frequency in Branches per 1,000 Carbon Atoms Mn: Number Average Melecular Weight Mn: Weight Average Melecular Weight

Mn: Number Average Molecular Weight; Mw: Weight Average Molecular Weight

Film	Serial Number	Film	Serial Number
В	P972403:978586	G	P972403:978583
н	P971664:975866	I	N/A
A	P972403:978585	J	N/A
С	P972403:978587	L	P970268:970703
D	P972403:978582	F	P971351:974751
E	N/A	к	P971351:974752
M	P9807250:9807251		

 Table 3-2: Blown film serial number

Table 3-3: Films based on Resin C with different BUR

BUR	Serial Number	BUR	Serial Number
2.4	9801749	3.0	9801752
2.6	9801750	3.2	9801753
2.8	9801751	3.4	9801754

3.2 TopoMetrix Aurora 2100 Near-field Scanning Optical Microscope/Atomic Force Microscope

The TopoMetrix Aurora 2100 Near-field Scanning Optical Microscope/Atomic Force Microscope (NSOM/AFM), shown in Figure 3-1, was used in this study. The NSOM/AFM was used to obtain images of both the inside and outside surface textures. AFM measures the interaction force between the tip and surface. The tip may be dragged across the surface, or may vibrate as it moves. Image data indicate the surface height. NSOM systems are used to scan an optical fiber probe over the sample. A laser light is emitted through the aperture. Image data can be gathered by the detection of this light energy. The atomic force microscope combines the principles of the scanning tunneling microscope and the stylus profilometer. It has been used in a wide variety of disciplines, including fundamental surface science, routine surface roughness analysis, three-dimensional imaging down to nanometer scale. Also it is used to investigate both conductors and insulators from the atomic to the micron level. As shown in Figure 3-2, the basic principle of AFM is that the probe tip, which interacts with the sample, is mounted on a cantilever (also called spring lever). The role of a cantilever is to translate the forces acting upon the tip into a measurable quantity. Either the sample or the cantilever assembly is mounted on an XYZ piezoelectric scanner, which is controlled from a computer that enables raster scanning in the X and Y directions, where Y is taken as the direction of the slow scan. Typically, in order to simplify the detection scheme, it always moves the sample driven by scanner under the tip, although it is also possible to scan the tip over the sample.

During the scanning, the cantilever is deflected due to its probe tip interaction with the sample surface. Either the amount of motion of the cantilever or the change of resonant frequency of the cantilever can be measured by a position-sensitive detector. This means that the light from a diode laser is reflected from the cantilever and the cantilever deflection is translated into a change in the reflectance angle, which can then be monitored by the use of a four-section photodetector. Then these data regarding the deflection of the cantilever are converted into the Z direction data and are collected by the computer, while a raster scan along the surface is performed. Meanwhile, the XY coordinates of points on the surface are also collected in the same manner. These coordinates can then be stored and processed to produce a space-filling three-dimensional image.

As the probe is brought close to the sample, it is first attracted to the sample surface, and then when the probe gets very close to the surface, the electron orbital of the atoms on the surface of the probe and the sample start to repel each other. As the gap decreases, the repulsive forces neutralize the attractive forces, and then become dominant. Depending on the force between the probe tip and sample, the AFM imaging modes can be classified as follows: contact mode, non-contact mode and intermittentcontact mode. The contact mode is operated in the repulsive region, on the other hand, the non-contact mode is operated in the attractive region. The intermittent-contact mode is intermediate between the above two modes.

The contact mode is the most commonly employed mode for visualization. In this case, the cantilever is held less than a few angstroms from the sample surface. This mode produces higher resolution, but it can easily lead to deformation and drag. A positionsensitive photodetector is used to detect displacements of light projected on the top of the tip. It generates the topographic data set by operating in either a constant-height mode or a constant-force mode. On the other hand, in the non-contact mode, a stiff cantilever vibrates at its resonant frequency, and a feedback system is used to detect changes in the resonant frequency or vibration amplitude during the scanning. According to the relationship between the resonant frequency and the force gradient, the system can control the scanner up or down by keeping the resonant frequency or amplitude constant. Meanwhile, the system also keeps the average tip-to-sample distance constant. The motion of the scanner is used to generate the data set. Operation in the non-contact mode does not cause damage of the sample surface, since it keeps the tip away from the surface at a distance in the order of tens to hundreds of angstroms. Therefore, the force between the tip and the sample in the non-contact mode is lower, and the image resolution is also lower compared to the contact mode. The non-contact mode is most suitable for the soft or elastic samples.

Near-field scanning optical microscopy (NSOM) is a new microscopic method, which simultaneously provides high-resolution optical and topographic information. Since its development, NSOM has proven powerful for nanometer to micrometer scale imaging of a variety of materials, and polarization-modulation NSOM has been shown to be particularly useful for the detailed characterization of optically anisotropic samples, and for studying local molecular organization. Such observations in conventional farfield polarization microscopy are, however, limited in spatial resolution by diffraction. This far-field diffraction limit to resolution can be overcome by resorting to NSOM. The operational principle behind near-field optical imaging involves illuminating a specimen through a sub-wavelength sized aperture whilst keeping the specimen within the nearfield regime of the source. Broadly speaking, if the aperture-specimen separation is kept roughly less than the half of the diameter of the aperture, the source does not have the opportunity to diffract before it interacts with the sample. Therefore, the resolution of the system is determined by the aperture diameter as opposed to the wavelength of the light used. An image is built up by raster-scanning the aperture across the sample and recording the optical response of the specimen through a conventional far-field microscope objective.



Figure 3-1: TopoMetrix Aurora 2100 Near-field Scanning Optical Microscope/Atomic Force Microscope (NSOM/AFM) [41].



Figure 3-2: The principles of surface scanning of Atomic Force Microscopy [42].

3.2.1 Apparatus

The TopoMetrix Aurora 2100 Near-field Scanning Optical Microscope/Atomic Force Microscope (NSOM/AFM), shown in Figure 3-1, including the laser source, microscope and viewing monitor was used in the present study. This is a new class of microscope combining the interaction mechanisms of optical microscopy with the high resolution of the scanning probe methods [43]. This means that it has both the NSOM and AFM functions. The Aurora NSOM/AFM instrument consists of two major components: the head and the stage, shown in Figure 3-3 and 3-4. In the present research on polyethylene blown films, only the AFM mode is used. However, the operating system is not exactly the same as for the normal AFM microscope. The scanning tip is also a NSOM tip. There is an aperture at the end of a sharp tip, and the tip is fabricated from conventional quartz, single-mode optic fiber. The tip is pulled to a sharp point and coated with an aluminum opaque material, in order to obtain a very small aperture at the end of the tip. During NSOM scanning, the tip is maintained very close to the sample surface. Thus, only a very small area is illuminated, and resulting in optical resolution that is limited by the size of the aperture and the tip-to-sample separation, not by the wavelength of illuminating light. Normally, the aperture is approximately 50nm and much smaller than the wavelength of light. Therefore, the NSOM produces images with very high spatial resolution.

When the AFM option is employed, the microscope operates in the non-contact mode. The basic principle is analogous to that of the common AFM microscope, except that the tip is mounted on a vertical piezo and does a raster-scan vertically. During the AFM scanning, the tip oscillates at its fundamental resonance frequency, as the tip approaches the sample surface, shear forces between the tip and the sample can produce a resonance shift and change the amplitude and phase of the tip oscillation. This change is monitored by a feedback system by shining a laser (I = 670nm) on the top of tip. The light will reflect off the tip and up towards the photo detector. The four-section photo detector detects the reflected intensity and generates the change in direction. The resulting signal is then normalized and demodulated to yield an amplitude or phase sensitive signal. By comparing with a reference signal in a standard feedback circuit linked to the vertical motion of the scan piezo, the control system will then adjust the absolute probe position to maintain a constant force between tip and sample, and also a constant average distance between the tip and the sample. The apparatus scan range is from $1\mu m \times 1\mu m$ to $35\mu m \times 35\mu m$. The scan resolution can be up to 1000 lines per μm . The NSOM/AFM Instrument Technical Information is listed as the following:

- Photonmultipler Tube
- Cathode: Bi-Alkali detector
- Voltage: 0 to 1200 V
- NSOM Probe
- Type: Single-mode fiber optic
- Diameter: 125 µm
- Aperture: 50 nm (nominal)
- Output: 10nW (nominal)

- Force Feedback
- Detection: Phase
- Frequency: 45 to 120 kHz
- Resolution: 1 nm vertical
- Tip-to-sample Separation: 2 to 15 nm
- X-Y Sample Positioner
- Type: Piezoelectric
- Travel: 7 mm, X and Y
- Resolution: 0.1 µm
- Laser Excitation Source
- Type: Argon ion
- Wavelength: 488 nm
- Output power: 15 mW
- Power source: 100 to 120 V, 10 A, 50 to 60 Hz
- Cooling: Air


Figure 3-3: TopoMetrix Aurora 2100 Near-field Scanning Optical Microscope/Atomic Force Microscope.



Figure 3-4: The head and the stage of Aurora NSOM/AFM instrument.

3.2.2 Sample Preparation and Apparatus Adjustment

3.2.2.1 Sample Preparation

AFM instruments acquire images by scanning a probe very close to the sample surface, and determining variations in the sample surface topography or other characteristics. This requires that the surface remains unchanged during the analysis. If loose material is on the sample surface, it may interfere with the image. Loose dirt particles can be removed by using pure compressed air. In case of solid film surface, e.g. with grease or fingerprint, acetone or alcohol can be used to remove the contaminants. This is achieved by placing some acetone or alcohol on the film surface and wiping it across the sample surface slowly. Sometimes, the film can be dipped into the liquid for cleaning.

After cleaning, the sample is simply cut to obtain a small piece of film, which is around $10mm \times 10mm$. The sample is now ready to be placed on a glass slide.

The polymer film is a soft material. It is important in imaging soft samples that they are securely held without deforming the surface. It is also important to avoid surface deformation due to tip-sample forces or mechanical interaction. In order to hold the sample securely onto a glass slide and eliminate static charge on the sample surface, the selection of adhesives becomes very important. After many trials of different kinds of liquids, an embedding medium, which is a leak detection compound made by CANTESCO, was used for this purpose. Pure compressed air was used to force out the air bubble between the sample and glass slide. The sample sticks securely to the glass slide due to capillary action.

Finally, the sample is placed on the scanning stage of the NSOM/AFM instrument. Scotch tape is used to fix the glass slide onto the scanner stage. The film is ready for scanning.

3.2.2.2 Apparatus Adjustment

The following procedure was used for apparatus adjustment.

First of all, mount a sharp tip on the NSOM/AFM head, and turn the Photo Diode Laser on. Aim the laser onto the end of the tip. Turn the laser off, and adjust the focus on the reflection objective to fix the distance between the shadow of the tip and the tip at about 1-2cm. This means that the tip is close enough to the sample surface without touching the sample. Turn the laser back on, and adjust the photo detector to maximize the sensor feedback from the reflection of the tip. At the beginning, under the non-contact mode, set MODE to phase, DRIVE AMPLITUDE to 1-2, SCAN RANGE to required range, SET POINT to 0na and SCAN RATE to half of the scan range.

The next step is to determine the resonance frequency of the tip. Scan the frequency range from 45 kHz to 250 kHz or from 5 kHz to 120 kHz, and check all phase angles from 0 to 270 to choose the most negative internal sensor signal, which gives the maximum sensor feedback. The resonance frequency is different for different probes and different probe-sample interactions. This means that the resonance frequency needs to be determined each time when either the probe or the sample is changed.

Once the resonance frequency is determined, change SET POINT to half of this negative value, and set the probe to false feedback state. After incrementing the DRIVE AMPLITUDE voltage, start line scan for adjusting PID, i.e. proportional, integral and derivative, feedback control parameters and scan speed. During line scanning, the probe will scan one certain line repeatedly, in order to check the reproducibility and the accuracy. When the line scanning is stable and repeatable for a randomly selected line, the apparatus adjustment is finished, and the microscope is ready to use for scanning.

The images are monitored in real time and recorded using the computer system. Since this is a very sensitive instrument, the scanning procedure could involve various complications. If the adjustment is not correct, it will cause AFM image artifacts from various sources. The artifact problems are discussed in Appendix B.

3.3 Cross-section Morphology

An Ultracut ultramicrotome, with the cryo-attachment, was used to prepare blown films for measurement by NSOM. The ultramicrotome cuts 500-1000 angstrom thick slices, or sections, of the sample using a diamond knife. The blown film bulk morphology was observed on sections cut in MD and TD cross-section directions, using both NSOM/AFM and PLM instruments.

3.3.1 Cryo-Ultramicrotome

Microtomy or sectioning involves the preparation of thin slices of material for microscopy observation [20]. It is one of the most widely used methods in the preparation of polymers for electron microscopy and scanning probe microscopy. Microtomy permits the observation of the actual structure in the bulk of the material, which is not possible by methods such as thin film casting or surface replication. The microtome is the instrument used for this purpose. Generally, microtomy refers to sectioning for observation with an optical microscope by transmitted light. The microtomed sections are about 1-40 μ m thick and are cut with steel or glass knives. Ultramicrotomy is a sectioning technique that advances a specimen past a cutting knife to prepare ultrathin sections of material for observation in the electron microscope or the scanning probe microscope [44]. Ultrathin sections are cut with either a glass or a diamond knife in the ultramicrotome (also called ultratome) to about 30-1000 nm thickness. Ultramicrotomy is very commonly used in the preparation of polymer materials for electron microscopy and scanning probe microscopy. The materials must be carefully fixed, stained and embedded prior to sectioning. Ultramicrotomy has been used to prepare cross-sections from a variety of materials, such as metals, composites, ceramics, and plastics. This technique presents many advantages, the first being the possibility of obtaining relatively thin sections of uniform thickness. The sectioning process does not affect the chemistry of the sample; there is no redeposition or preferential etching, as is possible when preparing samples by

conventional ion beam milling. Therefore, ultramicrotomy is suitable for the preparation of specimens from materials with phases of very different chemistry [45].

Polymers are generally easier to prepare, prior to sectioning, but are much more difficult to section than biological materials. Some polymers that have a glass transition temperature below room temperature are too soft to be sectioned at room temperature and must be hardened either chemically or by cooling below room temperature during microtomy. This latter method is called cryosectioning (also call cryomicrotomy). Cryomicrotomy and cryoultramicrotomy are sectioning methods performed at low temperatures to produce thin or ultrathin sections, respectively. Sectioning in the -20 to 40° C range is fairly straightforward as liquids may still be used to separate sections off the knife. At lower temperatures, such as -120° C, sectioning is more difficult as a dry knife must be used. Cryosectioning has several advantages: specimen embedding and hardening is not performed by a chemical reaction, which limits the potential of chemical reaction. Soft polymers can be sectioned, which may not be possible at room temperature. Disadvantages include: it is time consuming; special equipment is required to control knife and specimen temperature; static charge affects picking up of sections; and frost buildup limits the method.

A cryoultramicrotome REICHERT ULTRACUT S system from Leica Microsystem with a REICHERT FCS chamber system attachment has been used in the present work. Photographs of these systems are shown in Figure 3-5 and Figure 3-6.

The computers of the ULTRACUT S system are:

- The Ultracut S microtome
- The stereomicroscope
- The drive system

The computers of the FCS system are:

- Cryochamber
- Control unit

- Dewar vessel for liquid nitrogen on mobile trolley
- Liquid nitrogen pump

The FCS is specifically designed for routine ultrathin frozen sectioning. With the addition of the FCS to the ULTRACUT S, the ultramicrotome is quickly converted to a cryoultramicrotome. The ULTRACUT S/ FCS cryoultrathin system is designed to give the best results for any cryoultrasectioning purpose. The cooling chamber is mounted on the shell of the ULTRACUT S and is thereby isolated from the base of the ultramicrotome. The system cutting ranges from 95nm to 5μ m by using glass knife or diamond knife. The maximum cooling temperature is -160° C.



Figure 3-5: REICHERT ULTRACUT S system with cryochamber FCS control system.



Figure 3-6: Leica ULTRACUT S microtome cryochamber.

3.3.2 Sectioning Condition

Microtomy method:	Dry cryo-ultrathin microtomy to obtain less distortion, less
	knife scratches. Also it is easier to hold this sample.
Sectioning temperature:	-160°C. For the PE blown film, glass transition temperature
	is lower than -120°C.
Sectioning speed:	5mm/s
Sectioning knife:	45° glass knife or 45° histo-cryo or ultrathin-cryo diamond
	knife.
Knife clearance angle:	6°
Cryogen:	a frozen tissue embedding media from Stephens Scientific,
	water-soluble
Sectioning thickness:	5µm

3.3.3 Sample Preparation

Cut the film into $4\text{mm} \times 3\text{mm}$ specimens. During the cutting, the film direction, MD or TD, as shown in Figure 2-2, should be carefully indicated. Here, the MD is the film process machine direction, and TD is the film process transverse direction, as discussed earlier. There are also three other instrument specified section-directions: parallel to film surface (PL) direction, vertical to film surface (VL) direction and 45° direction, shown in Figure 3-7. All these three directions are named artificially. The next step is the immersion cryofixation. On the top of the special small sample holder, place one drop of the cryogen, which is the frozen tissue embedding media to block the film square. The cryogen is a water-soluble and colorless compound of polyvinyl alcohol and polyethylene glycol liquids made by Stephens Scientific. Insert the shaped film block into the cryogen liquid vertically by using the tweezers and dip the holder and sample together into the liquid nitrogen and allow both film block and embedding medium to be vitrified, which requires a few seconds. Then, take the sample holder out of the vessel

and quickly place it in the microtome chamber in the desired direction. The chamber has been already cooled down to -160° C. Take a new glass knife or diamond knife and install it into the knife holder. Set the knife clearance angle at 6°. Hold this system conditions for 10 - 15 minutes, in order to reach an equilibrium temperature for the chamber, the knife and the sample. Every time when the sample or knife is changed, a certain period is needed to reach equilibrium. The sample is ready to be trimmed and sectioned.



Figure 3-7: Three specified section-directions: PL direction, VL direction and 45° direction.

3.3.4 Sectioning

Before cutting, it is necessary to clean the glass microscope slide. Firstly, trim the sample in the PL direction by using the side edge of the knife. After trimming, turn the sample in the VL direction for cutting, and move the sample to the center of the knife-edge. In the PL direction, there is less mechanical stress and cutting is easy. However, because of static charge and stress, the sample will curl heavily, and it is unable to spread out due to its small size. On the other hand, in the VL direction, because the film thickness is very small, about 25 μ m, the sectioned slice is just a very narrow ribbon, and

it hardly roll up except for twisting sometimes. It is easier to obtain a straight ribbon slice compared to cutting in the PL direction. After positioning the sample, cut it in different thicknesses, $1 - 5 \mu m$, and speeds, 1 mm/s, 5mm/s, and 8mm/s. During the sectioning, follow the cutting operation with the stereomicroscope. Upon finding a good ribbon, stop the sectioning and use the tweezers carefully to remove the sample from the knife. Place the sectioned part on the glass slide and cover it inside the chamber. The sample is ready for microscopic observation. Sectioning parameter optimization adjustment is very an important skill for the microtomy. A detailed discussion of this aspect is presented in Appendix C.

3.4 PLM: Polarized Light Microscopy

A polarized microscope is a transmitted light microscope that has a rotatable stage; a polarizer that produces polarized light from an input of unpolarized or natural light, and an analyzer between the objective and eyepiece. Both the polarizer and analyzer are rotatable and polars, which means that they selectively transmit light polarized in one specific plane. They are made from polaroid filters. By far, the most polarizing microscope is crossed polar. The transmitted polarization planes of the two polars are set to be perpendicular or crossed, so that the analyzer does not transmit light transmitted by the polarizer. When an anisotropic, birefringent material, such as a crystalline polymer, is placed between the crossed polars. The incident plane polarized light is split into two components, plane polarized along the principal directions. One component will be retarded relative to the other. In general, the altered polarization state leaving the specimen will have a certain portion of the components passing through the analyzer. Therefore, all anisotropic specimens are bright between crossed polars regardless of their orientation, whereas isotropic materials appear dark in the crossed polars due to exhibiting the same properties in all directions.

The apparatus used in this study is the OLYMPUS polarizing microscope, BX50. The lens is 100× with transmitted light.

3.5 Surface Profile

In the previous sections, we described the surface microstructure measurement by using NSOM/AFM instrument. However, this instrument is only available for flat surface measurement up to 0.5 microns, due to the NSOM tip. For a very rough and steep surface texture, the NSOM tip cannot trace the change very well, and the tip could be damaged very seriously. In order to explore the surface texture of such films, a profiler has been used. This study was used to characterize the surface of LLDPE blown films C with different blow-up rations (BUR).

3.5.1 Profiler

A profiler is a surface texture measuring system that accurately measures surface texture below submicro-inch. The measurements are made electromechanically by moving the sample beneath a diamond-tipped stylus. The high precision stage moves a sample beneath the stylus according to a user-programmed scan length, speed and stylus force. The stylus is mechanically coupled to the core of a linear variable differential transformer (LVDT). As the stage moves the sample, the stylus rides over the sample surface. Surface variations cause the stylus to be translated vertically. Electrical signals corresponding to the stylus movement are produced as the core position of the LVDT changes respectively. An analog signal proportional to the position change is produced by the LVDT, which in turn is conditioned and converted to a digital format through a high precision, integrating analog-to-digital converter. The digitized signals from a single scan are stored in computer memory for display, manipulation, measurement, and print.

A Dektak³ST profiler from Veeco/Sloan Instruments Inc. has been used in this research. The apparatus is a very high precision measuring instrument capable of measuring minute physical surface variations and is very sensitive to the environment in which it is operated. A stylus based surface profiler measures the actual physical surface of the sample. The radius of the standard diamond stylus is 2.5 microns.

3.5.2 Sample Preparation

As mentioned before, the principle of AFM is similar to that of the profiler, whereby a stylus is dragged over the sample surface to image the surface texture, except that the AFM is much more sensitive and can scan the surface texture down to nanometer scale. Therefore, the sample preparation in this study is the same as for NSOM/AFM scanning. Sample preparation involves binding a clean 10mm × 10mm square film to the top of a glass microscope slide firmly by using an embedding medium.

After starting the profiler instrument, the computer control system automatically operates the scanning setting program. According to the scanned material properties, set suitable scanning parameters. Place the sample on the sample stage and position it for scanning using the stage translation, rotation, and leveling controls. The next step is scanning. When a scan is run, the stylus is lowered onto the sample surface, and the stage moves the sample to do the line scan as the stylus rides over the surface features. The video monitor allows the operator to view both the physical scanning of the sample and the plotting of the data simultaneously. At the end of the scan, the stylus automatically retracts and the system is immediately ready for the next scan. The surface features encountered by the stylus are represented as a two dimensional profile which is plotted, scaled, and displayed on the video monitor. After completing the profile, use system software to conduct the analyses of roughness and waviness, and save the plot and the data.

3.5.3 Experimental Techniques



	Scan Resolution	0.125µm/sample
	Measurement range	655 kA
	Profile	hills and valleys
	Stylus force	10mg
Displa	y parameters	
	R. cursor	100.00µm
	M. cursor	900.00µm
	Display range	auto
	Display data type	raw
Rough	ness and waviness filters	
	Short pass filter cutoff	10µm
	Long pass filter cutoff	100µm

4. **Results and Discussion**

In this section, the results of detailed qualitative observation and quantitative examination of images will be reported. Quantitative analysis is performed using a variety of methods, including line and area analysis (roughness, fractal) and spatial correlation (pair correlation, nearest neighbor distance distribution).

4.1 Analysis of Surface Texture

The surface of an object is the boundary that separates that object from another object, substance, or space. Any manufactured surface will normally have a large number of irregularities, due partly to the nature of the material, but, to a large extent, due to the finishing operation used. According to American National Standard B46.1-1985 [46], surface texture is the repetitive or random deviation from the nominal surface that forms the three-dimensional topography of the surface.

4.1.1 AFM Image Observation

By using the AFM/NSOM microscope, both the inside and outside surface texture of LLDPE and LDPE blown films are imaged. The scanning size is $35\mu m \times 35\mu m$, and the scanning rate is half of the scanning range per second or slower. The scanning resolution is 300×300 pixels. Although this apparatus has the ability to scan images up to $1\mu m \times 1\mu m$, the large size scanning image is still chosen because it contains much more data points and thus lowers statistical bias. Therefore, it should produce a more accurate statistical representation of surface morphology. Also, the smaller scan range can be strongly affected by the location on the film surface. Therefore, a smaller scan range results in less reliability. Due to the above reasons, $35\mu m \times 35\mu m$ scanning size was selected and has been shown to yield the best reproduability. Figure 4-1 demonstrates the reproducibility of AFM surface images of different scans of film D at different locations. The surface roughness standard deviation is 3.66 and the surface 2D fractal dimension standard deviation is only 0.02. In all of the AFM images during this project, the machine direction is the vertical direction with respect to the page.



R	loot-Mean-Square roughness(Rms, nm)	2D fractal dimension
D ₁	40.5701	2.46
D_2	41.5923	2.51
D_3	37.7318	2.47
\mathbf{D}_4	34.4682	2.44
D ₅	43.8037	2.46
D_6	43.8354	2.47
Average R _{ms}	40.3336	2.47
Standard Deviati	ion 3.6638	0.0232

Figure 4-1: Film D AFM surface image reproducibility

Figure 4-2 shows the AFM images of the inside surface topography of various PE resins. All the images are filled with dense stacked spherical domain structures. These spherical domains, we believe, are spherulites. They are the result of crystallization, on and beneath the surface, during the film blowing process. The main difference among the different films is the domain size. For example, film D average surface domain size is larger than for the other films.

The shapes of the domains and their spatial distributions are generally dependent on crystallization behavior, which strongly depends on the thermal history, the resin composition and the polymer structure, i.e. molecular weight distribution, long or short chain branching, and co-monomer type and content. If ellipse shaped spherulites or rowcrystallized morphology are observed, then uniaxial and biaxial extensional flow or strong shear deformation during the film blowing process have an influence on the crystallization during film blowing. Since all sample films are produced under similar processing conditions, it is considered that the effect of the mechanical history during the process on the differences in surface morphology between sample films are less significant than the effects of crystallization behavior, which strongly depends on the thermal history, the resin composition and the polymer structure.



Figure 4-2: Surface AFM images of sample A, D, H and G (inside) scanning size : $35\mu m \times 35\mu m$ scanning rate: the half of the range per second

Figure 4-3 shows the surface profile of sample film D. Spherical domain structure is clearly observed, and there are no indications of ellipse shaped spherulites or rownucleated morphology. This implies that uniaxial and biaxial extensional flow and shear deformation do not have a significant influence on the observed surface morphology of this film.

Chapter 4: Results and discussion



ստ Սատ

Figure 4-3: Surface AFM images 3D profile of film D, inside.

Figure 4-4 shows the inside and outside AFM surface images of films A and D. It shows that both sides appear to have the similar surface texture, which is fully covered with spherical domains. It can be also seen that the average size of domains on the inside surface is slightly larger than those on the outside surface. This may be explained by the fact that, during the blowing process, especially as the film leaves the die, the outside of film bubble is cooled by an air-ring and the inside of the bubble is cooled by stagnant air. This means that the outside cooling rate is higher than the inside cooling rate. Therefore, the outside growth stops earlier than inside growth. The result is that the outside domain size is smaller and more uniform than the inside domain size.

The surface topography of all the given sample films is shown in Appendix A. None exhibit strong orientation, neither in the shape of the domains nor in the aggregation of clusters. On average, the domains in Sample D appear to be larger than the domains observed for other film surfaces. The outside and inside surface topography of all samples suggests three-dimensional spherulitic structures.



Figure 4-4: Surface AFM images of sample A and D, (inside and outside), scanning size : $35\mu m \times 35\mu m$, scanning rate : the half of the range per second

4.1.2 Roughness

Roughness consists of the fine irregularities of the surface texture, usually including those irregularities that result from the inherent action of the production process. These are considered to include traverse feed marks and other irregularities within the limits of the roughness sampling length. It is a measure of the topographic relief of a surface. Surface relief includes sample intrinsic marks during the process, machining marks on machined surfaces, or marks left by rollers on sheet stock. Roughness can be obtained directly from AFM images or from surface-profile measurements (also called line roughness).

More than 200 different surface-texture parameters have been developed. However, the most two common definitions are root-mean-square roughness (RMS) R_{ms} and average roughness R_a . The RMS roughness is defined as the square root of the mean value of the square of the distances Z_i of the points i from the mean surface level:

$$R_{ms} = \sqrt{\frac{1}{N} \bullet \sum_{i=1}^{N} Z_i^2}$$
 (4-1)

The mean surface level is defined as the line about which roughness is measured and a line parallel to the general direction of the profile within the limits of the sampling length, such that the sums of the areas contained between this line and those parts of the profile that lie on either side are equal. Suppose surface height variation is measured as Z_i in the $\pm Z$ direction. Then, mathematically, the mean surface level is defined to satisfy the following equation:

$$\sum_{i=1}^{N} Z_i = 0 \tag{4-2}$$

If the measurement is the surface profile, the R_{ms} will in general depend on the profile length, which, in our research, is 35µm. On the other hand, if the data points represent averages of height variations over small areas on the surface, the R_{ms} value will depend on the size of the areas, which is 35µm×35µm in this work.

The average roughness R_a is the average of the absolute values of the surface height variations Z_i measured from the mean surface level, as given by the following equation:

$$R_{a} = \frac{1}{N} \sum_{i=1}^{N} |Z_{i}|$$
(4-3)

Generally, if a surface is flat and contains no large deviations from the mean surface level, R_{ms} and R_a will be similar. However, if the surface is very rough and there are appreciable numbers of large bumps and holes, the value of Z_i will dominate the surface statistics and R_{ms} will be larger than R_a . The R_{ms} roughness is generally used to describe the finish of optical surfaces [47], which is important in our study. On the other hand, R_a is normally used for roughness of machined surfaces [46]. In our study, we used both types of roughness to characterize AFM surface images.

4.1.2.1 Surface Roughness

An AFM surface image can yield quantitative surface height data and allow measuring the surface roughness. In this study, by using the NSOM/AFM instrument software, both surface R_{ms} and R_a have been calculated for the inside and outside surfaces of all the PE blown films, from A to M. The results are shown in Table 4-1 and Figures 4-5 and 4-6.

The results show that the surface roughness of films F and K, which are based on LDPE resins, have the highest outside surface roughness.

	R _{ms} (inside)	R _{ms} (outside)	R _a (inside)	R _a (outside)
В	22.1197	23.0386	17.4501	18.6101
Η	30.0089	25.0441	24.0271	19.798
Ā	39.5158	38.4883	31.9853	30.7535
С	46.6635	45.1499	37.8099	36.536
D	37.7318	31.814	29.0574	25.2706
Ε	67.8047	49.6476	55.0448	38.7875
Μ	27.699	50.5604	22.2764	38.5051
G	44.1985	40.6692	35.7561	32.5181
I	25.2717	32.7409	20.1201	26.4963
J	24.5472	28.5616	19.8146	23.0914
L	28.4443	24.5882	22.3937	19.7193
F	85.0106	109.1162	67.9543	88.6318
K	43.4964	62.0929	34.8421	50.411

Table 4-1: Film A - M Surface Roughness (both R_{ms} and R_a units are nm)

Area Roughness (RMS)



Figure 4-5: Film surface roughness – Root-Mean-Square-roughness (RMS)



Figure 4-6: Area Roughness - Average-Roughness (Ra)

4.1.2.2 Line Roughness

Surface roughness gives a good indication of surface statistics and provides a quantitative comparison among the different films. However, it does not describe the distribution and orientation preference over the entire area. By measuring different surface profiles along randomly chosen lines in both the horizontal and vertical directions, height variations on a surface and line roughness can be obtained directly, as shown in Tables 4-2, 4-3, 4-4, 4-5 and Figures 4-7, 4-8. Three different horizontal lines and three different vertical lines have been chosen. For each image, the number of both horizontal lines and vertical lines is the same. The results show that, for each side of one film, line roughness parameters, along the six lines are similar but with slight irregularity. This means that there is no specific orientation of the surface domains. The slight irregularity of line roughness reflects the variation of surface height.

Horizontal line	line 78	line 153	line 224
В	14.35	19.01	19.24
H	26.79	16.68	25.17
A	32.69	29.65	29.09
С	39.66	34.34	34.48
D	27.26	21.03	34.08
E	42.76	47.64	56.65
Μ	23.64	18.48	22.62
G	38.32	32.98	34.13
Ι	18.23	17.9	26.56
J	17.84	20.28	18.51
L	25.26	18.27	15.01
F	76.57	73.16	65.91
K	30.91	41.25	29.57

 Table 4-2: Film A - M Inside Line Average Roughness (units are nm)

Table 4-3: Film A - M Inside Line Average Roughness (units are nm)

Vertical line	line 78	line 153	line 224	
В	14.26	15.53	15.83	
Н	25.84	22.83	18.79	
A	29.93	35.5	24.99	
С	39.42	42.9	30.94	
D	32.66	18.29	21.27	
E	64.08	49.98	39.51	
М	17.57	21.49	17.94	
G	36.16	30.97	33.58	
Ι	23.88	18.82	13.3	
J	19.92	19.09	20.72	
L	24.71	20.58	18.9	
F	84.98	73.12	43.92	
K	38.16	29.75	37.37	

Horizontal line	line 78	line 153	line 224	
В	16.12	13.72	16.64	
Н	19.08	19.24	14.9	
Ā	29.28	28.41	26.45	
С	39.71	39.23	36.95	
D	22.38	26.16	26.78	
E	34.21	33.07	32.71	
Μ	23.75	32.07	31.4	
G	23.64	38.56	36.95	
I	26.35	19.49	29.45	
J	18.51	21.88	19.26	
L	22.28	17.72	13.72	
F	82.07	105.3	61.22	
K	30.65	61.39	44.64	

 Table 4-4: Film A - M Outside Line Average Roughness (units are nm)

 Table 4-5: Film A - M Outside Line Average Roughness (units are nm)

Vertical line	line 78	line 153 line		
В	20.99	21.6	10.2	
Н	22.91	19.23	18.33	
A	25.3	27.76	28.76	
С	36.86	36.54	26.91	
D	23.69	20.93	22.81	
Е	53.66	46.23	34.03	
М	32.61	25.92	37.56	
G	30.2	39.16	23.24	
I	35.78	25.23	22.82	
J	24.65	19.03	20.96	
L	21.58	15.63	17.26	
F	87.62	102.7	68.09	
K	52.48	65.18	38.79	



Inside Line Roughness (Ra) Comparision

Figure 4-7: All films horizontal line roughness





4.1.3 Fractal Dimension

The previous two roughness measurements are the most common parameters that are used to quantify surface characteristics. However, these parameters simply compress all the complex surface information into only one number and mainly emphasize surface height difference. In the past few years, fractal analysis [48] has become a popular and powerful tool to describe the roughness spectrum of line profiles, and the geometric, structural properties of surfaces. The fractal dimension method can give a detailed description of the domain distribution and orientation. It shows how broken a surface is, but it does not provide detailed height information. In this section, the "lake pattern" method is used to estimate the surface fractal dimension, according to the methodology proposed by Gomez-Rodriguez and Baro [49]. Also the box-count method is used to calculate line fractal dimension, according to Chesters et al [50].

4.1.3.1 2D Fractal Dimension

The Lake Pattern method has been used for the processing of three-dimensional AFM images. It is based on the fact that the intersection of a given Z plane with a surface image generates self-similar lakes or islands. For each lake or island, we identify the lake perimeter L and the lake area A. At the area below the given Z plane, by simulating the filling with "water" up to such Z directional level of image, it creates an imaginary lake. Therefore, a series of corresponding L and A pairs will be calculated by computer and further to obtain the fractal dimension of film surfaces. The calculation results are at the nanometer scale.

The fractal dimension is defined according to the following equation:

$$L(\delta) = \alpha D A^{\frac{D}{2}}$$
 (4-4)

where α is a constant, D' is the fractal dimension of the lakes' coastlines, and δ is the yardstick length. The fractal dimension of the three-dimensional surface (D) can be calculated from the following equation:

D' = D - 1

(4-5)

Thus, the fractal dimension of the surface image can be calculated in a straightforward way from a log L versus log A plot.

Table 4-6 and Figure 4-9 show the 2D fractal dimensions of the different PE films for the inside and outside surfaces. Films F and K, which are LDPE films, have the lowest 2D fractal dimension. On the other hand, they have the highest surface roughness. This means that the surfaces of films F and K have a lower frequency of the lakes and higher amplitude of the roughness. Figure 4-10 shows the images of film D and film F 2D fractal dimensions. Comparing both images and 2D fractal dimension values, it appears that film D has a lower surface roughness and a higher 2D fractal dimension. This means that film D has a more broken surface but flatter than film F. These effects can be also observed from the original images, shown in Appendix A.

We have used both roughness and fractal dimension parameters to describe film surface texture. Surface roughness parameter corresponds to surface flatness information. On the other hand, the fractal dimension parameter refers to surface smoothness, which may be related to cleanability.

Film	Surface Fractal Dimension (inside)	Surface Fractal Dimension (outside)
В	2.6	2.52
H	2.56	2.53
A	2.62	2.65
С	2.63	2.59
D	2.47	2.49
Ε	2.53	2.5
Μ	2.52	2.63
G	2.56	2.55
I	2.53	2.56
J	2.62	2.61
L	2.5	2.48
F	2.27	2.3
K	2.35	2.36

Table 4-6: Film A - M Surface Fractal Dimension



Figure 4-9: All films surface 2D fractal dimension (both inside and outside)







Film F (inside), D = 2.27 Ra = 67.9543 nm, Rms = 85.0106 nm



4.1.3.2 Line Fractal Dimension

According to the dimensions of Euclidian geometry, the integers 0, 1, 2, and 3 correspond to dots, lines, planes, and bodies, respectively. However, this simple classification is only suitable for regularly shaped objects. As we know, there are many examples of very irregular shape substances and artificial geometrical objects. In order to organize and compare such objects, one can intuitively assign intermediate dimensional values to them. For example, a broken line could have a dimension between 0 and 1 and a jagged curve, which partly fills a certain plane, could have a dimension between 1 and 2. This non-integer "fractal dimension" was invented by Mandelbrot [48]. It is used to describe the surface irregular texture and roughness.

Roughness profiles are analyzed in terms of a "roughness spectrum" which gives the fractal dimension as a function of feature size. A box dimension method [51] is used to determine the fractal dimensions. In brief, this method overlays the profile with a uniform grid or a set of "boxes" of side length, b, and a count is made of the non-empty boxes (N) for which any portion of the profile falls within the box. Then the box size is divided in half and the count is repeated. The box dividing process continues until the box size is very close to the pixel size. Finally, the counts are plotted against each box size on a log-log scale to obtain a boxcount plot. The box sizes can be interpreted as the physical heights, which can correspond to the height of the profile; therefore, the boxcount plot represents counts versus "feature size" instead of box size. The absolute value of the slope of the plot gives the fractal dimension value, which is also referred to as fractal-based roughness, R_F [52]. The R_F value of a rough profile will be larger than that of a smooth profile. This is because, if a profile is perfectly smooth and level, such as a straight line, then the fractal dimension R_F equals one, because the number of boxes, which are needed to cover such a perfect profile will change in exactly linear proportion to the box size, $N \propto b^{-1}$. On the other hand, if the profile is a very ragged curve, the number of boxes, which are required to cover it, will increase faster than the decrease of box size, $N \propto b^{-R_F}$, where R_F is between 1 and 2. In the extreme case, R_F approaches 2.

The fractal roughness technique shows good correlation between the measured fractal roughness values R_F and the visual roughness impression of a surface. The treatment of surfaces as fractal objects provides another means of characterizing and understanding the effects of surface texture from the molecular to the macroscopic scale [50].

Tables 4-7 and 4-8 and Figures 4-11 and 4-12 show the line fractal dimensions for the surfaces of the various films. As in the case of line roughness measurements, three different lines are chosen randomly in both the horizontal and vertical directions. The same lines are used for all films. These results are similar to those obtained for line roughness. The line fractal dimensions for each side of one film have similar values. Also the results indicate that the entire rough surface is isotropic, and spherical domains are distributed randomly. There is no orientational preference of surface spherulites due to the extensional flow during the film blowing process.

Film	line78	line153	line224	line78	line153	line224
В	1.52	1.54	1.55	1.49	1.52	1.5
H	1.6	1.6	1.62	1.63	1.63	1.63
Ā	1.62	1.62	1.62	1.64	1.64	1.61
С	1.63	1.63	1.63	1.62	1.64	1.6
D	1.51	1.51	1.55	1.57	1.57	1.56
Ε	1.59	1.61	1.57	1.53	1.54	1.56
Μ	1.61	1.6	1.59	1.54	1.57	1.56
G	1.61	1.61	1.58	1.62	1.62	1.62
Ι	1.56	1.58	1.56	1.56	1.57	1.59
J	1.66	1.64	1.64	1.61	1.62	1.61
L	1.58	1.58	1.58	1.58	1.58	1.58
F	1.43	1.44	1.43	1.44	1.47	1.41
K	1.49	1.49	1.42	1.45	1.47	1.51

Table 4-7: Film A - M Inside Line Fractal Dimension

Table 4-8: Film A - M Outside Line Fractal Dimension

Film	line78	line153	line224	line78	line153	line224
В	1.57	1.57	1.53	1.61	1.60	1.60
Η	1.63	1.63	1.58	1.62	1.62	1.61
A	1.56	1.57	1.59	1.55	1.59	1.57
С	1.62	1.64	1.62	1.61	1.63	1.61
D	1.58	1.58	1.58	1.60	1.60	1.58
Ε	1.50	1.50	1.50	1.43	1.43	1.43
Μ	1.49	1.44	1.45	1.48	1.55	1.53
G	1.62	1.62	1.63	1.60	1.61	1.58
I	1.59	1.59	1.60	1.61	1.60	1.61
J	1.65	1.63	1.60	1.63	1.64	1.62
L	1.60	1.60	1.60	1.64	1.64	1.64
F	1.39	1.39	1.39	1.46	1.43	1.42
K	1.48	1.52	1.48	1.46	1.47	1.48



Figure 4-11: All films horizontal line fractal dimension



Outside Line Fractal Dimension Comparision



4.2 Spatial Distribution of Surface Domains

In order to quantitatively characterize the spatial distribution of the surface domains and surface domain size distributions, we calculated the pair correlation function and nearest neighbor distance distribution function.

4.2.1 Pair Correlation Function

A direct imaging program was used to determine the pair correlation function [53]. The pair correlation function is the probability of finding another particle j, as a function of distance from the center of a particular particle i, statistically averaged over the system. Defining \vec{r} as the position vector of a given particle, the pair correlation function, $g(\vec{r})$ is defined as:

$$g(\vec{r}) = \frac{1}{\rho} \left\langle \frac{1}{N} \sum_{i,j=1; i \neq j}^{N} \delta(\vec{r} - (\vec{r}_i - \vec{r}_j)) \right\rangle$$
(4-6)

where N is the total number of particles, which are confined in a macroscopic test volume, and $\delta(\vec{r})$ is the Dirac Delta function. The density ρ is the statistical average of the particle positions:

$$\rho(\vec{r}) = \left\langle \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_{i}) \right\rangle$$
(4-7)

The measurement of the pair correlation function for two-dimensional images was performed in this way: let $\langle n(r) \rangle$ be the average number of nuclei situated at a distance between r and r+ δr from a given nucleus, see Figure 4-13, then the pair correlation function in 2D is calculated according to the following formula [22]:

Chapter 4: Results and discussion

$$g(\mathbf{r}) = \frac{1}{\rho} \left(\frac{\langle \mathbf{n}(\mathbf{r}) \rangle}{2\pi r \delta r} \right) = \frac{A}{N} \left\{ \frac{1}{N-1} \frac{\sum_{i=1}^{N} n_i(\mathbf{r})}{2\pi r \delta r} \right\}$$
$$= \frac{A}{N(n-1)2\pi r \delta r} \sum_{i=1}^{N} n_i(\mathbf{r})$$
(4-8)

where N is the total number of nuclei, which are confined in a test area A of a frame of the image.



Figure 4-13: The measurement of the pair correlation function for two-dimensional images

We also employ another way to determine the pair correlation function, which is based on stochastic geometry [53]. It turns out that the two methods give the same results. There were typically 400 domains in the frame of an AFM image of the experimental sample. This set of domains in the observation window is typical and representative. To achieve unbiased statistical measurement, we used the standard techniques of Minus sampling and Multi-sampling to correct for edge effects [42]. Generally, the graph of the pair correlation function gives information above the spatial distribution of the particles. There is one characteristic value, which is the first maximum $g_{first-max}(r)$ of the first sharp peak, located at a characteristic distance. This characteristic distance corresponds to the average distance to the next particle. The characteristics of the pair correlation function yields the following information:

- If $g_{first-max}(r) > 1$, and, with increasing r, $g(r) \rightarrow 1$ and oscillates around 1, then there is short-range order in the system.
- If g(r) oscillates around 1, then the spatial distribution of the particles is random.

Experimental results from the characterization of the pair correlation function show that there is clear correlation between the spatial distribution of the surface domains of blown films and the chemical structure of the resins for similar processing condition. There is no long-range order for the domains on the surface. Two types of the graphs of the pair correlation function were obtained, indicating the behavior of the various resins: one is short-range order, the other is the random distribution.

Typical results are presented in Figures 4-14, 4-15 and 4-16. With respect to chemical structure, the following conclusions may be made:

- 1. For films based on ethylene-octene copolymers, e.g. samples of **G**, **J**, **I** and **L**, short-range order was observed, see Figure 4-16.
- For films based on ethylene-hexene copolymers, e.g. samples of A, C, D, E and M, random distribution prevailed, see Figure 4-15.
- 3. For films based on ethylene-butene copolymers, e.g. samples of **B** and **H**, random distribution was noted for **B** and short-range order was found for **H**, see Figure 4-14.

The details of the physics and dynamics of crystallization and their influence on the above observations are beyond the scope of this thesis. Pair correlation function (B film)



(a)

Pair correlation function (H film)



(b) Figure 4-14: Pair correlation function of film B and H
Pair correlation function (A film)



(a)

Pair correlation function (C film)



(b) Figure 4-15: Pair correlation function of film A, C, D, E and M



Pair correlation function (D film)

(c)

Pair correlation function (E film)



(d) Figure 4-15: Pair correlation function of film A, C, D, E and M

Pair correlation function (M film)



(e) Figure 4-15: Pair correlation function of film A, C, D, E and M



Pair correlation function (G film)

(a)

Pair correlation function (I film)



(b) Figure 4-16: Pair correlation function of films G, I, J and L



Pair correlation function (J film)

(c)

Pair correlation function (L film)



(d) Figure 4-16: Pair correlation function of films G, I, J, and L

4.2.2 Nearest Neighbor Distance Distribution Function

The nearest neighbor distance distribution function is defined as the distribution of pairs with a separating distance d_{NN} , which is determined by the edge length of the Delaunay triangulation, as shown in Figure 4-17 [54]. The physical significance of the data regarding the density function of nearest neighbor distance distributions is summarized below:

- There is one critical mean nearest neighbor distance, d_{NN} , which may be considered as the most probable size for the surface domains for the specimen.
- The broadness of the nearest neighbor distance distribution function can be used to evaluate the diversity of surface domain sizes in relation to the most probable size. The broader the distribution curve, the wider is the diversity of surface domain sizes.

Experimental results from the characterization of the nearest neighbor distance distribution function show that there is clear correlation between the nearest neighbor distance distribution function of the surface domains of blown films and the resin used to process the film under similar conditions. Two significant results of the graphs of the nearest neighbor distance distribution function function are summarized below:

- The most probable distance between nearest pairs of film surface domains on the inside surface is greater than that on the outside;
- The diversity of surface domain sizes in relation to the most probable size on the inside surface is greater than that on the outside.

Typical results are presented in Figures 4-18, 4-19 and 4-20. With respect to the resin chemical structure, the following conclusions may be made:

- For films based on ethylene-octene copolymers, e.g. samples of G, J, I and L, the most probable distance between nearest pairs for film surface domains on the inside surface is slightly larger than that on the outside. The broadness of the nearest neighbor distance distribution functions for inside and outside surfaces are almost the same, except for sample I, see Figure 4-20.
- 2. For films based on ethylene-hexene copolymers, e.g. samples of A, C, D, E and M, the most probable distance between nearest pairs for film surface domains on the inside surface is much larger than that on the outside. The broadness of the nearest neighbor distance distribution functions on the inside surface is much greater than that on the outside surface, except for sample C, see Figure 4-19.
- 3. For the films based on ethylene-butene copolymers, e.g. samples of B and H, the most probable distance between nearest pairs for film surface domains on the inside surface is same as that on the outside surface for B, but much greater for H. The broadness of the nearest neighbor distance distribution functions for inside and outside surfaces are almost the same for both B and H, see Figure 4-18.

These results showed only one critical mean nearest neighbor distance for each film. The experimental data are not consistent with random distribution. The distances are not completely ordered, which would lead to a delta distribution, but instead they fit a Gaussian curve. The details of the physics and dynamics of crystallization and their influence on the above observations are beyond the scope of this thesis.



Figure 4-17: The dual of the Voronoi diagam (the thick-line network) is the Delaunay triangulation (the thin-line network). The network with the thick solid lines is the real-space graph (the

Voronoi diagram) and the network with thin solid lines (the Delaunay triangulation) is the dual network. The duality relationship maps all vertices to the faces of the dual, and the edges to edges. If vertices in the real-space graph are triply connected, the faces of the dual network are triangles, and the dual is a triangulation [54].



Density of the Nearest Neighbor Distance Distribution d(r) (B film)

(a)

Density of the Nearest Neighbor Distance Distribution d(r) (H film)



(b) Figure 4-18: The Nearest Neighbor Distance Distribution of films B and H



Density of the Nearest Neighbor Distance Distribution d(r) (A film)

(a)

Density of the Nearest Neighbor Distance Distribution d(r) (C film)



(b) Figure 4-19: The Nearest Neighbor Distance Distribution of films A, C, D, E and M



Density of the Nearest Neighbor Distance Distribution d(r) (D film)

(c)

Density of the Nearest Neighbor Distance Distribution d(r) (E film)



(d) Figure 4-19: The Nearest Neighbor Distance Distribution of films A, C, D, E and M



Density of the Nearest Neighbor Distance Distribution d(r) (M film)

(e)

Figure 4-19: The Nearest Neighbor Distance Distribution of film A, C, D, E and M



Density of the Nearest Neighbor Distance Distribution d(r) (G film)

(a)

Density of the Nearest Neighbor Distance Distribution d(r) (I film)



(b) Figure 4-20: The Nearest Neighbor Distance Distribution of films G, I, J, and L



Density of the Nearest Neighbor Distance Distribution d(r) (J film)

(c)

Density of the Nearest Neighbor Distance Distribution d(r) (L film)



(d) Figure 4-20: The Nearest Neighbor Distance Distribution of films G, I, J, and L

4.3 Observation of Cross-section Morphology

4.3.1 PLM Cross-section Images

Cross-section samples were cut with different thicknesses in both machine (MD) and transverse directions (TD) using the ultracut cryogenic microtome at -160^oC. Blown film cross-section images were captured under the PLM by transmitted light, as shown in Figure 4-21 and Figure 4-22.

Figure 4-21 shows images in both the MD direction and the TD direction. The images suggest that the two directions are similar, exhibiting stacked crystalline spherulites. Figure 4-22 shows PLM images for samples with different thickness. It is seen that resolution improves as the thickness becomes smaller, since the images were taken by transmitted light. However, the optimum thickness was found to be $5\mu m$, considering the balance between ease of sectioning and resolution. Very thin samples, for example 0.1 μm thick, are easily distorted by the stress of the knife during cutting. Also, static electricity makes it difficult to handle the thinner ribbons. Scratches are the most common sectioning problem in microtomy. Very thin and very soft slices are more easily and severely scratched.

Figure 4-23 shows typical film cross-section morphologies, as observed with PLM. It is evident that the cross-section of the film is filled with spherulite-like domain structures. The spherulites are densely stacked. This is quite similar to film surface topology. The spherical domains are distributed randomly. This suggests that, even in the inside of the film, the mechanical history, in particular biaxial extension, does not have a strong influence on the bulk morphology. However, a quantitative analysis is not possible since the resolution is not of a quality amenable to quantitative analysis.



MD direction

TD direction

Figure 4-21: Bulk Morphology from PLM. Sectioning thickness is 5µm.







D film TD direction with diamond knife $5\mu m$ thickness



G film TD direction 5µm thickness



D film MD direction with diamond knife 5µm thickness



G film MD direction 5µm thickness

Figure 4-23: Surface AFM images of sample A and D: Inside and Outside Scanning size: 35µm x 35µm Scanning speed: 50% of range.

4.3.2 AFM Cross-section Images

The cross-section ribbons of PE blown films cut with the cryo-ulatramicrotome were imaged by using the NSOM/AFM instrument. Scanning size was $20\mu m \times 20\mu m$ due to the film thickness being only about $25\mu m$. Scanning rate was 50% - 60% of the range per second. The resolution is 300×300 pixels.

Figure 4-24 shows the AFM cross-section image for film D. The film is shown in the MD. The cutting direction is VL, and the thickness is 5μ m. The image appears to be quite similar to the surface AFM images, which are formed by fully impinged spherical domains. The size of these domains appears to be uniform. Also, the images indicate that there is a tendency for the spherulites to line up in columns. Each column consists of densely stacked spherulites. The knife cutting direction, which is also the direction of knife scratches, is the same as the column direction. In order to distinguish the column formation from knife marks, a different cutting direction was evaluated. Figure 4-25 shows an AFM cross-section image of film G in the TD. The cutting direction was 45° (see Figure 3-7) and the thickness was 5μ m. The image indicates clearly that knife scratches are an important factor in column formation. In fact, the spherulite domains are randomly distributed. Knife scratches seriously affect the image analysis. Thus, so far we can only observe microstructure qualitatively, and it is not possible to obtain a reliable quantitative description.



Figure 24: AFM cross-section morphology of film D, MD direction, 5 microns thickness





4.4 Characterization of the Effect of Blow-up Ratio (BUR)

4.4.1 Profile Images

Tests were carried out on a set of samples blown from resin C. The films were produced at different blow-up ratios, namely 2.4, 2.6, 2.8, 3.0, 3.2, 3.4. The film surface textures were very ragged with steep changes. Thus, they were not suitable for the NSOM/AFM instrument. A Veeco/Sloan profiler was used to measure the surface roughness. Both the inside and outside surfaces were scanned for each film. Ten scans were performed randomly on each side of the film to obtain a statistically useful evaluation.

Figures 4-26 and 4-27 show the surface profiles for the original film C and for the specimens with different BUR. The latter specimens exhibit very rough surface texture compared to the original film C. This may be due to the presence of fillers or additives that appear on the surface of the film.

Surface Profile of Film C (inside)



Figure 4-26: One of the original film C surface profiles, inside



Surface Profile 1 of Film C with BUR=2.5 (inside)

Surface Profile 1 of Film C with BUR=2.8 (inside)









Surface Profile 1 of Film C with 8UR=3.4 (inside)



Figure 4-27: Surface profiles of film C with different BUR, inside.

4.4.2 Roughness and Waviness

The six different films of C with BUR 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, were scanned for surface texture. Surface profile roughness parameters, R_a and R_{ms} , and waviness parameters, W_a and W_{ms} , were calculated.

Average roughness and root-mean square roughness have the same definitions as those used for AFM surface roughness. R_a is the arithmetic average deviation from the mean line, and R_{ms} determines the root-mean-square value of roughness corresponding to R_a . Strictly, surface texture includes closely spaced random roughness irregularities and more widely spaced repetitive waviness irregularities. Roughness represents the finer random irregularities of surface texture, which usually result from the inherent action of the production process, and waviness represents the wider-space repetitive deviation, which is usually attributed to the characteristics of an individual machine or to external environmental factors. For an optical surface, surface roughness always causes light scattering and is typically separated by submicrometers to fractions of a millimeter; however, surface waviness contributes to small-angle scattering and is separated by larger distances, from hundreds of micrometers to several millimeters.

According to ANSI/ASME B46.1-1985 [46], waviness is the more widely spaced component of surface texture and includes all irregularities whose spacing is greater than the roughness sampling length and less than the waviness sampling length. The waviness height W is calculated as the difference between the maximum peak-to-valley measurement of the total profile within a waviness sampling length and the average peak-to-valley roughness value within that length. Average waviness, W_a , is the average deviation of waviness from the mean line and it corresponds to R_a . Root-mean-square waviness, W_{ms} , is the root-mean-square value of waviness and corresponds to R_{ms} .

Figures 4-28 and 4-29 show R_a , R_{ms} and waviness W_a , W_{ms} for the C films under consideration. They clearly show that, as the blow-up ratio (BUR) increases from 2.4 to

3.4, both roughness and waviness trendlines show a negative slope, which means that the film surface texture becomes smoother and less rough. Also, the results indicate that, on the average, the roughness and the waviness of the inside film surface are higher than those for the outside surface.



Film C with different BUR inside surface roughness (Ra)

Film C with different BUR inside surface roughness (Rms)







Film C with different BUR inside surface roughness (Wa)







5. Conclusions and Recommendations

5.1 Conclusions

It has been shown that the optical properties, such as, gloss, haze and total transmission of polymer blown films are strongly influenced by surface morphology, in addition to the film bulk morphology. Various advanced characterization techniques have been employed to visualize and characterize the surface and bulk morphology, including the non-contact atomic force microscopy (AFM), the polarized light microscopy (PLM) and a Veeco/Sloan surface profiler. The following aspects have been studied:

- 1. Surface topography has been analyzed systematically based on the measurement of line and surface roughness and surface fractal dimensions for the complete set of blown films.
- Spatial distribution of spherulitic surface domains has been quantitatively characterized by the pair-correlation function and the nearest neighbor distance distribution function, based on AFM images for the first time, with the aid of an image analysis program.
- 3. Cross-section morphology has been successfully visualized for the first time, although some problems need to be overcome in cryosectioning, before an accurate quantitative description may be obtained.
- 4. Rapid surface profiling has been used for quantifying the surface profiles and the average waviness of a number of polyolefin films.

5.1.1 Surface Morphology Characteristics

Morphological observation by AFM has shown that the outside and inside surface topography of all samples exhibits three-dimensional spherulitic structures. There is no regular clustering, nor preferred orientation in either distribution or the shape of individual spherulites on all the samples. The shapes of the domains and their spatial distributions are generally dependent on crystallization behavior, which strongly depends on the thermal history, the resin composition and the polymer structure, i.e. molecular weight distribution, long or short chain branching, and comonomer type and content.

Neither ellipsoidal-shaped spherulites nor row-crystallized morphology are observed, indicating that uniaxial and biaxial extensional flow or strong shear deformation during the film blowing process have no strong effects on the crystallization during the film blowing.

5.1.2 Surface Topography: Roughness and Fractal Dimension

An AFM surface image can yield quantitative surface height data and allows measurement of the surface roughness. In this study, both line and surface roughness and line and 2D fractal dimension have been calculated to quantify the surface information. The former one is the most commonly used parameter to quantify surface characteristics. It mainly emphasizes surface height differences. However, it does not provide complete information regarding surface characteristics. The fractal dimension method can give detailed information regarding the domain distribution and orientation. It shows how broken a surface is, but it does not provide detailed height information. The surface roughness parameter provides surface flatness information. On the other hand, the fractal dimension parameter refers to surface smoothness, which may be related to cleanability.

The surface information results show that the surface roughness of films F and K, which are LDPE, have the highest outside surface roughness and the lowest fractal dimension. Line information results show that both line roughness and line fractal dimensions for each side of the same film have similar values. Also the results indicate that the entire rough surface is isotropic, and spherical domains are distributed randomly. There is no orientational preference of surface spherulites due to the extensional flow during the film blowing process.

5.1.3 Spatial Distribution of Surface Domains

Experimental results from the characterization of the pair correlation function show that there is clear correlation between the spatial distribution of the surface domains of blown films and the chemical structure of the resins under similar processing condition. There is no long-range order for the domains on the surface. Two types of the graphs of the pair correlation function were obtained indicating the behavior of the various resins: one is short-range order, the other is the random distribution, which is mainly related to the chemical structures for similar process condition.

- 1. For films based on ethylene-octene copolymers, e.g. samples of G, J, I and L, short-range order was observed.
- For films based on ethylene-hexene copolymers, e.g. samples of A, C, D, E and M, random distribution prevailed.
- 3. For films based on ethylene-butene copolymers, e.g. samples of **B** and **H**, random distribution was noted for **B** and the short-range order was found for **H**.

Experimental results from the characterization of the nearest neighbor distance distribution function show that there is clear correlation between the nearest neighbor distance distribution function of the surface domains of blown film and the resin used to process the film under similar process condition. Two significant results of the graphs of the nearest neighbor distance distribution function are summarized below:

- The most probable distance between nearest pairs of film surface domains on the inside surface is greater than that on the outside surface;
- The diversity of surface domain sizes in relation to the most probable size on the inside surface is greater than that on the outside.

This is also mainly related to the chemical structures for similar process condition. The following conclusions may be made:

- 1. For films based on ethylene-octene copolymers, e.g. samples of G, J, I and L, the most probable distance between nearest pairs of film surface domains on the inside surface is slightly larger than that on the outside. The breadth of the nearest neighbor distance distribution functions for inside and outside surfaces are almost the same, except for sample I.
- 2. For films based on ethylene-hexene copolymers, e.g. samples of A, C, D, E and M, the most probable distance between nearest pairs of film surface domains on the inside surface is much larger than that on the outside. The breadth of the nearest neighbor distance distribution functions on the inside surface is much greater than that on the outside surface, except for sample C.
- 3. For the films based on ethylene-butene copolymers, e.g. samples of B and H, the most probable distance between nearest pairs of film surface domains on the inside surface is same as that on the outside surface for B, but much greater for H. The breadth of the nearest neighbor distance distribution functions for inside and outside surfaces are almost same for both B and H.

5.1.4 Cross-section Morphology

Experimental observation by both AFM and PLM shows that the cross-section of the film is filled with spherulite-like domain structures. The spherulites are densely stacked. This is quite similar to film surface topology. The spherical domains are distributed randomly and appear to be formed by fully impinged spherical domains. The size of these domains appears to be uniform.

5.1.5 Surface Profiles and Waviness

For the films which exhibit high roughness and change, or with higher electrostatic surface change, the NSOM/AFM was not suitable. Therefore, a Veeco/Sloan profiler was used to measure the surface roughness. Both the inside and outside surfaces were scanned for each film.

The six different films of C with BUR 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, were scanned for surface texture. Surface profile roughness parameters, R_a and R_{ms} , and waviness parameters, W_a and W_{ms} , were calculated.

The results clearly show that, as the blow-up ratio (BUR) increases from 2.4 to 3.4, both roughness and waviness trendlines show a negative slope, which means that the film surface texture becomes smoother and less rough. Also, the results indicate that, on the average, the roughness and the waviness of the inside film surface are higher than those for the outside surface.

5.2 Recommendations

The film bulk morphology shows that even in the inside of the film, the mechanical history, such as biaxial extensional flow does not have a strong influence on the bulk morphology. The cross-section of film is filled with spherulite-like domain structures. The spherulites are densely stacked together. This is quite similar to film surface topography. We also observe that the spherical domains are distributed randomly. However, the quality of AFM image is not satisfaction for quantitative description. The glass knife scratches seriously affect the images. A proper diamond knife may improve the AFM image quality and provide a suitable basis for quantitative analysis.

Experimental results from the characterization of the pair correlation function and the nearest neighbor distance distribution function show that there is clear correlation between the spatial distribution of the surface domains and the nearest neighbor distance distribution of the surface domains, on one hand, and chemical structure on the other hand. It would be useful to study these correlations in detail to obtain appropriate quantitative relationships.

Reference:

- 1. G. H. Meeten, **Optics of polymers**, Elsevier Applied Science, New York (1986), and reference therein.
- P. J. Perron and P. D. Lederman, "Effect of molecular weight distribution on polyethylene film properties," *Polym. Eng. Sci.*, p.340, 12(5) (1972).
- 3. T. Fujiki, "Concept of secondary heterogeneous structure of long-chain branched polyethylene," J. Appl. Polym. Sci., p.47, 15 (1971).
- 4. R. S. Stein and R. S. Finkelstein, "Optical properties of polymers," Annu. Rev. Phys. Chem. P.207, 24 (1973).
- T. Hashimoto, A. Todo, Y. Murakami and H. Kawai, "Light scattering from crystalline superstructure in tubular-extruded polybutene-1 films," J. Polym. Sci. Polym. Phys., p.501, 15 (1977).
- 6. F. C. Stehling, C. S. Speed and L. Westerman, "Causes of haze of low-density polyethylene blown films," *Macromolecules*, p.698, 14 (1981).
- H. Ashizawa, J. E. Spruiell, J. L. White, "An investigation of optical clarity and crystalline orientation in polyethylene tubular film," *Poly. Eng. and Sci.*, p.1035, 24(13) (1984).
- A. Larena and G. Pinto, "The effect of surface roughness and crystallinity on the light scattering of polyethylene tubular blown films," *Polym. Eng. and Sci.*, p.742, 33(12) (1993).
- P. F. Smith, I. Chun, G. Liu, D. Dimtrievich, J. Rasburn and G. J. Vancso, "Studies of optical haze and surface morphology of blown polyethylene films using atomic force microscopy," *Polym. Eng. and Sci.*, p.2129, 36(16) (1996).
- 10. L. Wang, T. Huang, M. R. Kamal, A. D. Rey and J. The, "Surface topography and gloss of polyolefin blown films," *Polym. Eng. and Sci.*, p.747, 40(3) (2000).
- 11. R. Alexander-Katz and R. G. Barrera, "Surface correlation effects on gloss," J. Polym. Sci. Part B: Polym. Phys., p.1321, 36(8) (1998).
- 12. L. Wang, "Morphology and optical properties of polyolefin blown films," *Ph.D. thesis*, McGill University, (1999).

- 13. H. R. Jacobi, "The historical development of plastics processing techniques," Kunststoffe, 55 (1955).
- 14. J. R. A. Pearson and C. J. S. Petrie, "The flow of a tubular film. Part 1. Formal mathematical representation," J. Fluid Mech., p.1, 40 (1968). "The flow of a tubular film. Part 2. Interpretation of the model and discussion of solutions," J. Fluid Mech., p.609, 42 (1970).
- 15. C. J. S. Petrie, "Memory effects in a non-uniform flow. Behavior of a tubular film of viscoelastic fluid," *Rheol. Acta*, p.92, 12(2) (1973).
- 16. Z. Tadmor and C.G. Gogos, **Principles of polymer processing**, Wiley-Interscience, (1979).
- 17. L. Mandelkern, Crystallization of polymers, Springer, (1964).
- 18. R. G. Alamo and L. Mandelkern, "The crystallization behavior of random copolymers of ethylene," *Thermochimica Acta*, p.155, 238(1-2) (1994).
- M. Avrami, "Kinetics of phase change. I*," J. Chem. Phys., p.1130, 7 (1939);
 "Kinetics of phase change. II*, transformation-time relations for random distribution of Nuclei," J. Chem. Phys., p.212, (8) (1940); "Granulation, phase change, and microstructure, kinetics of phase change. III*," J. Chem. Phys., p.177, (9) (1941).
- 20. L. C. Sawyer and D. T. Grubb, Polymer microscopy, Chapman and Hall, (1996).
- 21. N. H. Hartshorne, The Microscopy of liquid crystals, Microscope, (1974).
- 22. T. Huang, "Nucleation and growth of spherulitic domain structure in semicrystalline polymer thin films," *Ph.D. thesis*, McGill University, (1997).
- 23. G. Binning, H. Rochrer, C. Gerber and E. Weibel, "Surface studies by scanning tunneling microscopy," Zurich Res. Lab., IBM, Ruschlikon, Switz., Phys. Rev. Lett. P.57, 49(1) (1982).
- 24. G. Binning, C. F. Quate and C. Gerber, "Atomic force microscope," Phys. Rev. Lett., p.930, 56(9) (1986).
- 25. A. Keller and W. H. Kolnaar Hans, "Flow-induced orientation and structure formation," *Mater. Sci. and Technol.*, p.189, 18 (1997).



- 26. C. D. Han and T. H. Kwack, "Rehology-Processing-Property relationships in tubular blown film extrusion. I. High-pressure low-density polyethylene," J. Appl. Polym. Sci., p.3399, 28 (1983).
- 27. T. H. Kwack, C. D. Han and M. E. Vickers, "Development of crystalline structure during tubular film blowing of low-density polyethylene," J. Appl. Polym. Sci. p.363, 35(2) (1988).
- 28. K. J. Choi, J. E. Spruiell and J. L. White, "Orientation and morphology of highdensity polyethylene film produced by the tubular blowing method and its relationship to process conditions," J. Polym. Sci. Phys. Ed., p.27, 20 (1982).
- 29. H. Ashizawa, J. E. Spruiell and J. L. White, "An investigation of optical clarity and crystalline orientation in polyethylene tubular film," *Polym. Eng. Sci.*, p.1035, 24 (1984).
- 30. Y. Matsukura and J. L. White, "Experimental study of the mechanisms of light scattering and surface roughness of tubular film," ANTEC 86, Conference Proceedings Society of Plastics Engineers 44th Annual Technical Conference & Exhibit, p.888 (1986).
- 31. E. Maemura, M. Cakmak and J. L. White, "Characterization of crystallinity, orientation, and mechanical properties in biaxially stretched poly(p-phenylene sulfide) films," *Polym. Eng. Sci.*, p.140, 29(2) (1989).
- 32. R. Pazur and R. E. Prud'homme, "X-ray Pole Figure and Small Angle Scattering Measurements on Tubular Blown Low-Density Poly(ethylene) Films," *Macromolecules*, p.119, 29(1) (1996).
- 33. D. M. Simpson, and I. R. Harrrison, "A study of the effects of processing parameters on the morphologies and tensile modulus of HDPE blown films: application of composite theories on a molecular level to characterize tensile modulus," J. Plast. Film & Sheeting, p.302, 10(4) (1994).
- 34. M. van Gurp, B. J. Kip, J. P. C. van Heel and S. de Boer, "Study of development of orientation in LDPE blown films," J. Plast. Film & Sheeting, p.156, 10(2) (1994).
- 35. A. Haber and M. R. Kamal, "Structure of blown PE film goes with the resin's flow," *Plast. Eng.* p.43, 43(10) (1987).



- 36. A. K. Babel, G. Nagarajan, G. A. Campbell and B. S. Cao, "Kinematics, structure, and properties relationship of polyethylene blown films," *Annu. Tech. Conf. - Soc. Plast. Eng.*, p.2112, 2 (1996).
- 37. T. Huang and M. R. Kamal, "Morphological modeling of polyolefin blown films: effects of temperature distribution and stress," to be published.
- 38. L. Wang and M. R. Kamal to be Published.
- 39. E. M. Mount III, "Optics-Principle sources of haze and gloss," ANTEC Proceedings, p.194, 45 (1987).
- 40. ASTM D1003: Standard test method for haze and luminous transmittance of transparent plastics, (1992).
- 41. http://monet.physik.unibas.ch/snom/instrumentation.htm
- 42. http://www.mobot.org/jwcross/spm
- 43. E. Betzig and J. K. Trautman, "Near-field optics: microscopy, spectroscopy, and surface modification beyond the diffraction limit," *Science*, p.189, 257(5067) (1992).
- 44. R. Phillips, Diamond "knife ultra-microtomy of metals and the structure of microtomed sections," Brit. J. App. Phys., p.554, 12 (1961).
- 45. T. F. Malis and D. Steele, "Ultramicrotmy for materials science. In: Workshop on Specimen Preparation for TEM of Materials. R. Anderson. ed.," Mater. Res. Symp., Proc. Mater. Res. Soc., p.3, 199 (1990).
- 46. Surface texture (surface roughness, waviness, and lay), ANSI/ASME B46.1 1-1985, *The American Society of Mechanical Engineers*, 345 East 47th Street, New York, N. Y. 10017.
- 47. J. M. Bennett and L. Mattsson, Introduction to surface roughness and scattering, Optical Society of America, (1989).
- 48. B. B. Mandelbrot, The fractal geometry of nature, Freeman, (1983).
- 49. J. M. Gomez-Rodriguez and A. M. Baro, "Fractal characterization of gold deposits by scanning tunneling microscopy," J. Vac. Sci. Technol. B., p.495, 9(2, Pt.2) (1991).
- 50. S. Chesters, H. C. Wang and G. Kasper, "Atomic force microscopy of gas-surface corrosion in stainless steel," *Solid State Technol.*, S9-S12, 34(6) (1991).

- 51. B. B. Mandelbrot, "Fractals in physics," Proc. Sixth Trieste Int'l Symp., L. Pietronero, E. Tosatti, eds., Elsevier Sci. Publ. Co., New York, p.10, (1986).
- 52. S. Chesters, H. Y. Wen, M. Lundin and G. Kasper, "Fractal-based characterization of surface texture," *Appl. Surf. Sci.*, p.185, 40(3) (1989).
- 53. D. Stoyan and W. S. Kendall, Stochastic geometry and its applications, (1995).
- 54. M. R. Kamal, T. Huang and A. D. Rey, "Topological properties of polymer spherulitic grain patterns from simultaneous nucleation," J. Mater. Sci., p.4085, 32(15) (1997).

Appendix A

Appendix A

AFM surface morphology of all films

(Both inside and outside surfaces)






Inside





















Inside















Outside

Inside













Figure A-13: Film K inside and outside surface AFM images, P971351:974752

Appendix B

Artifacts in AFM Images

This Appendix is mainly based on "A Practical Guide to Scanning Probe Microscopy," by *ThermoMicroscopes*, Plumsteadville, PA, 18949, USA. Some of the text has been taken from the above reference and modified to fit the experiments carried out in this work.

Any measurement that results in an image differing from the actual sample surface is an artifact. AFM artifacts can come from many sources, such as probe geometry, non-ideal performance of piezoelectric scanner, static electric charge, and feedback control.

1. Probe Geometry

A NSOM/AFM magnifies the image in three dimensions, the x, y and z axes, and the maximum resolution in each of these axes is determined by different factors. Resolution in the z-axis is limited by the level of vibrations between the probe and surface. It is possible to build mechanical structures to stabilize the vibration to within a fraction of an angstrom. However, the maximum achievable resolution in the plane formed by the x and y axes is established by the geometry of the probe itself. Since image quality is determined by probe geometry, the tip diameter and aspect ratio, shown in Figure B-1, and the shape of the probe tip are critical to the AFM imaging.



Figure B-1: Probe geometry.

Appendix B

Most imaging artifacts in an AFM image arise from a phenomenon known as tip convolution or tip imaging. Every data point in an image represents a spatial convolution of the shape of the tip and the shape of the feature imaged. As long as the tip is much sharper than the feature, the true edge profile of the feature is represented. However, when the feature is sharper than the tip, the image will be dominated by the shape of the tip. In the AFM imaging process, the basic principle relies on the assumption that the contact point between the sample and the tip is at the top of tip. This may be achieved in the case of a flat surface, but when the tip encounters an object of comparable size, the first point of contact is no longer at the apex. The result is that the object will appear wider, however, one consolation is that the height of the feature is reproduced accurately. Thus, height measurements and roughness statistics remain undeformed by the tip [B-1]. Tip imaging is a common problem in images because many samples have features with steep sides. Sidewall angles on images should be measured routinely to determine whether the slope is limited by that of the tip or truly represents the topography of the sample. This is an important aspect of calibration process. To recognize tip imaging, look for a particular shape that is repeated throughout an image. The tip can appear in different sizes, as the tip is convolved with features of different sizes, but it will always maintain the same orientation. Thus, if the tip is dominating the image, the orientation of the tip shape will be the same before and after rotation during scanning. If the image is a true representation of the surface, the shapes in the image will rotate along with the sample; otherwise, they remain the same. If the image is dominated by tip-convolution effects, then the tip is very dull, has large radius, or lower aspect ratio and should be changed.

2. Non-ideal performance of piezoelectric scanner

For all NSOM/AFM, a piezoelectric scanner is used as an extremely fine positioning stage to move the probe over the sample (or the sample under the probe). The NSOM/AFM electronics drive the scanner in a type of raster pattern, as shown in Figure B-2. The scanner moves across the first line of the scan, and back. It then steps in the perpendicular direction to the second scan line, moves across it and back, then to the third line, and so forth. NSOM/AFM data are collected in only one direction - commonly

called the fast-scan direction. The perpendicular direction, in which the scanner steps from line to line, is called the slow-scan direction. The spacing between the data points is called the step size. The step size is determined by the full scan size and the number of data points per line.

Piezoelectric scanners for NSOM/AFM are usually fabricated from piezoelectric materials, which are ceramics that change dimensions in response to an applied voltage. Conversely, they develop an electrical potential in response to mechanical pressure. Piezoelectric scanners can be designed to move in x, y, and z by expanding in some directions and contracting in others. As an ideal situation, the strain in a piezoelectric scanner varies linearly with applied voltage. However, in practice, the behavior of piezoelectric scanners is not so simple. The relationship between strain and electric field diverges from ideal linear behavior. These divergences can come from scanner nonlinearities, such as intrinsic nonlinearity, hysteresis, creep, and cross coupling. All of the imperfect performances can result in three-dimensional image distortions. There are several manifestations of these non-linearitries in both the x-y plane and z direction. First of all, intrinsic nonlinearity, which means that the scanner does not move linearly with applied voltage, the measurement points are not equally spaced. In the plane of the sample surface, the effect of intrinsic nonlinearity is distortion of the measurement grid of raster pattern. As a result, an image of a surface with periodic structures will show nonuniform spacing and curvature of linear structures. Perpendicular to the plane of the sample surface (in the z direction), intrinsic nonlinearity causes errors in height measurements. Secondly, hysteresis and creep result from time-dependent behavior of the piezoelectric ceramic. In the x-y plane, the effect of hysteresis and creep is scanning position shift between the fast-scan direction and slow-scan direction. Also, it causes a slowdown of the work, when trying to zoom in on a feature of interest. In the z direction, they can cause step-height profiles. Thus, it causes formation of ridges and trenches as the scanner creeps in response to the sudden changes in voltage necessary to allow the tip to negotiate the step. The term cross coupling refers to the tendency of x-axis or y-axis scanner movement to have a spurious z-axis component, which means that the electric field is not uniform across the scanner and the strain fields are not simple constants, but

Appendix B

actually complex tensors. Some "cross talk" occurs between x, y, and z electrodes. Cross coupling can cause an AFM to generate a bowl-shaped image of a flat sample. Traditionally, the nonlinear behavior of piezoelectric scanners has been addressed imperfectly using software corrections, which always do re-calibration when scan conditions change. Some systems on the market use hardware solutions that eliminate most of the nonlinearities instead of correcting them, which sense the actual position of the scanner with external sensors. Hardware solutions are divided into optical, capacitive, and strain-gauge techniques. The best systems combine hardware and software corrections. Also, during practical operation, in order to minimize line-to-line registration errors that result from scanner hysteresis, the data are always collected in only one direction. Moreover, in order to minimize creep problems, the scanning speed is slowed down, and repeat scans are made over the same area a few times until the image is recorded without shift and distortion.





Another artifact originating from the scanner is a dynamic range artifact. Piezoelectric ceramics have a limited physical range. If the change in sample height exceeds this range, such as irregular surface feature size, large roughness on the surface or dirty objects on the sample surface, no meaningful data will be collected for the sample beyond the dynamic range and will appear as a flat spot on the sample. The common treatment for this problem is to increase the tip driving amplitude and to clean the sample surface carefully.

3. Static between the Probe Tip and the Sample Surface

Another common problem that we always meet during the scanning is static charge. It can build up on the surface of some samples or between the tip and the surface. These static charges could be caused by a variety of factors, such as the sample intrinsic characteristics, ambient air, friction between the film and other objects prior to sample preparation. It can seriously interfere with AFM imaging because the static electricity generates a force between the tip and the surface. Typical artifacts that result from static charges are lots of random spikes and glitches on the image surface, the low frequency noise on the internal sensor feedback, and many scratch lines on the AFM image due to the unstable scanning. These deformations of the surface profile cannot be reduced by adjusting the feedback system. In some serious situation, the obvious tip vibration can be observed and the reproductivity of line scan is very poor. Several methods can be used to reduce or eliminate these problems, such as grounding the sample and the scanning stage, wipe the sample surface, and change the embedding. However, since PE blown films are dielectric, grounding is not a feasible way after trying. Wipe film surface doesn't look like very effective since the film is clean itself. Various embedding media have been used to minimize the electric charge on the sample surface. It is found that 2.3M sucrose has a significant effect in reducing the electric charge of samples.

4. Feedback Artifacts

Once feedback is established and a scan is in progress, it is important to adjust the feedback loop to be optimized, further to optimize the system performance. To achieve this, it is necessary to adjust the set point, scan rate, and PID gain. This is a complicated and important step for AFM imaging. If the feedback loop of an AFM is not optimized, the image can be affected. When feedback gains are too high the system can oscillate, generating high frequency periodic noise in the image. This may occur throughout the image or may be localized in features with steep slopes. On the other hand, when feedback gains are too low, the tip cannot track the surface well. In the extreme case, the image loses detail, appearing smooth or "fuzzy". On sharp slopes, an overshoot can appear in the image as the tip travels up the slope, and a undershoot can appear as the tip travels down the slope. This feedback artifact commonly appears on steep features, represented as bright ridges on the uphill side and/or dark shadows on the downhill side of the feature.

Ambient condition can also affect the image quality, such as undesired vibration. In order to avoid this, the microscope is placed on an air-pressure table for vibration isolation. The air pressure of the table is maintained at 100 psi.

In summary, whenever an image is suspected to contain artifacts, follow these steps:

- 1. Repeat the scan to ensure that it looks the same.
- 2. Change the scan direction and take a new image.
- 3. Change the scan size and take an image to ensure that the features scale properly.
- 4. Rotate the sample and take an image to identify tip imaging.
- 5. Change the scan speed and take another image to identify periodic or quasiperiodic features.
- 6. Change the tip to identify tip convolution.

B-1: U.D. Schwarz, H. Haefke, P. Reimann and H. Guentherodt, "Tip artifacts in scanning force microscopy," J. Microsc., p.183, 173(3) (1994).

Appendix C

Optimization of Sectioning Parameters

This Appendix is mainly based on "Development and Application of a Dry Ultramicrotomy Technique for the Preparation of Galvanneal Sheet Coatings," by M. P. Barreto, R. Veillette and G. L'Esperance, *Microscopy Research and Technique*, p.293, 31 (1995).

During the sectioning, the effects of different parameters, such as knife angle and clearance angle, cutting medium, sectioning thickness and cutting speed, are very important. An optimization of the cryo-ultramicrotomy technique for the preparation of the film sample has been carried out.

1. Knife angle

For microtomy, glass or diamond knives is available with different angles, see Figure C-1. In general, a larger angle knife will give better edge durability but more curling of the section. On the other hand, a low angle knife appears to reduce the compression when cutting ductile materials. However, the fact is that for different materials, the sectioning process is different. For the harder and more brittle materials, it is possible that the section follows more of a cleavage/fracture mechanism, which means that cracks may form ahead of the knife edge, shown in Figure C-2. A greater knife angle can promote the formation of cracks further into the materials are sectioned more by a shear mechanism, therefore, increasing the knife angle will then impose a greater amount of compression on the section and it is easier to deform the section. In our study, cryoultrasectioning was carried out at very low temperature, -160°C. The film and embedding media are vitrified and can be considered as a hard and brittle materials. 45° glass knives and diamond knife were used in the study.



Figure C-1: Schematic diagram of the sectioning process. The section is cut when the moving sample comes in contact with the edge of the knife.





Water is generally used to help cutting and section retrieval and to reduce damage to the knife because it acts as a lubricant. However, some materials are susceptible to attack when in contact with water. Thus, one of the advantages of dry ultramicrotomy is that the chemistry of the sample is not altered. During the cryosectioning, especially at a very low temperatures, such as -160°C, only dry sections are available. However, the dry sections tend to accumulate at the edge of the knife, making it much harder to retrieve them. Also because of the static charge, the ribbon is more difficult to pick up. As a result, it is generally necessary to cut more sections when cutting dry than when using water, in order to obtain a good section that is well-positioned. We also note that dry ultramicrotomy is much more affected by knife edge defects, where the knife marks (also called knife scratches), more often found in the absence of a lubricant, sometimes cause tearing. Therefore, more frequent changing the glass knife is required. In using a diamond knife, there is also a large buildup of debris along the knife edge. The solution is to clean the knife more frequently.

2. Sectioning thickness

The aim is to obtain sections thin enough to carry out high spatial resolution micro-analyses while imaging under the NSOM/AFM and PLM instruments. In general, we collected specimens with thickness of $0.1\mu m$, $0.5\mu m$, $1\mu m$ and $5\mu m$. Generally, sections tend to be folded for larger thickness settings on the ultramicrotome, especially when cut dry. On the other hand, the thinner the sections, the more brittle they are and the harder they are to retrieve, even more so during dry cutting. It is very difficult to obtain good sections with very small thickness setting on the microtome.

3. Cutting speed

The cutting speed may affect the sectioning mechanism and can result in vibrations that diminish the quality of the sections. We used the following cutting speeds: 1mm/s, 5mm/s, and 8mm/s. Dry cryoulatrasectioning can be affected by the cutting speed

and further the cutting speed can affect the quality of the sections. At larger speeds, vibrations can be created and static electricity is increased. As the cutting speed increases, there is more compression due to an increase in friction between the sample and the knife edge and it is harder to collect the section due to lack of adhesion to the knife edge. In this work, the cutting speed was finally set at 5mm/s.