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OPTICAL PROPERTIES AND ORIENTATION IN POLYETHYLENE BLOWN
FILMS

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Dedicated to

**My Mom, Kanchan A. Bafna whose love and care has been a constant source of
encouragement and has helped me achieve my goals.**

ABSTRACT

In this thesis we report structural factors affecting the optical properties of blown polyethylene films. Two types of blown polyethylene films of similar degree of crystallinity were made from 1) single-site catalyst HDPE (STAR α) and 2) Ziegler-Natta catalyst HDPE (ZN) resins. The STAR α film exhibited high clarity and gloss, while the ZN film was turbid. Small-angle x-ray scattering (SAXS), small-angle light scattering (SALS) and optical microscopy gave quantitative and qualitative information regarding structure and orientation in the films. A new approach is described for determining the 3-dimensional lamellar normal orientation from SAXS.

Both the clear STAR α and turbid ZN films had similar lamellar crystalline structures, long periods and degree of crystallinity but displayed different degrees of nano-scale orientation. It is demonstrated that optical haze is related to surface features that seem to be linked to the bulk morphology. The relationship between haze and structural orientation is described. The lamellar orientation was linked to rod like structures seen in optical microscopy and SALS through stacked lamellae or cylindrite morphology on the nano-scale. The micron-scale rod-like structures seem directly related to surface roughness by comparison of index matched immersion and surface micrographs. The higher haze and lower gloss of the ZN film was shown to be caused by extensive surface roughness, not observed in the STAR α film.

Keywords: HDPE, blown films, haze, 3-d orientation, SAXS, SALS, optical microscopy.

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1. INTRODUCTION

1.1 General

Close to five million metric tons of polyethylene are converted into film products in USA every year [1]. Polyethylenes are available as, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and high density polyethylene (HDPE). Major applications for LDPE film include heavy-duty sacks, refuse sacks, carrier bags and for general packaging. LDPE films are also used extensively in the building industry. The LDPE film market has now been partly eroded by LLDPE. Along with its ease in manufacturing, LLDPE films also have some technical advantages over the LDPE films. The LLDPE films have comparatively higher impact strength, tensile strength and extensibility. Such properties allow the possibility of making film of lower gauge but with the same mechanical properties. Low cost HDPE film is being increasingly used for carrier bags. It is also finding rapid acceptance as a wrapping material instead of paper for food products, which is largely a consequence of its crisp feel and greaseproof nature. HDPE film is also used in monoaxially stretched form when it is slit into tape and also to some extent in the manufacture of fibrillated tape.

Packaging applications dominate the utilization of polyethylene film not only in the American, but also in the European and Asian markets. Some examples of packaging applications include food packaging, trash and can-liners, shrink film, stretch film, and merchandise packaging. The market for polyethylene film is enormous and is continually growing. Polyethylene in the form of blown film is one of the most important polymer products. Since most of the films are blown using a film blowing process, understanding

the process both theoretically and experimentally is very important especially in controlling processing/ structure/ property relationships. For these materials a principle property is film clarity, which is the subject of this thesis.

1.2 Polyethylene

Polyethylene (PE) is one of the most widely used commercial thermoplastics in the world today. PE counts for nearly 40% of the total thermoplastic production in the United States [1]. Since 1930, when it was discovered extensive research has been carried out in understanding its morphology and structure-property relationship [2-6]. The low cost (~49 cents/lb.) of PE, plus versatility of attainable properties with modifications in its molecular weight and chain architecture has generated a plethora of commercial applications for PE.

The properties of PE are primarily dependent on the type, crystallinity, branch content and molecular weight. Modulus increases as density increases, so does melting point, strength, and hardness. Advances in catalyst technologies such as the new single site catalysts have permitted the production of low crystallinity PE grades, which display ‘elastomeric’ properties. On the other end of the crystallinity spectrum, are ultra high molecular weight / ultra oriented polyethylenes (UHMWPE), which offer a modulus comparable to highly crystalline graphite (~ 200 GPa) and unusually high strength (~ two times that of highly crystalline graphite).

PE can be classified into three main categories according to the architecture of its main chain. The three principal types of PE, which are used extensively in commercial film processing, are, high density polyethylene (HDPE), low density polyethylene (LDPE), and linear low density polyethylene (LLDPE).

Some typical applications for PE are, UHMWPE- Low coefficient of friction applications such as bearings, sprockets, gaskets; LDPE- bags, textile products, moisture barriers, greenhouses, cable insulation; HDPE- bottles, pails, tubes, caps, uses where injection molding of complex shapes is required but low load is required, film, sheet, wire and cable insulation, pipes and drums.

High density PE consists predominantly of linear chains with few side branches. Its density ($> 0.95 \text{ g/cc}$) as well as crystallinity (60%-85%) is higher than the low density and linear low density resins, HDPE is commercially synthesized by either a gas phase or a slurry process. HDPE can be synthesized in molecular weights as high as 6 million. The molecular architecture of HDPE imparts it with good mechanical properties.

The second type of PE is low density PE (LDPE). This grade has a density range of ($0.90 \text{ g/cc} - 0.94 \text{ g/cc}$) and shows a low degree of crystallinity ($\sim 30\%$). LDPE has a distribution of short and long chain branches. Its melting point is around 115°C . It is commercially produced by high-pressure free radical polymerization. The low crystallinity imparts good optical properties such as gloss to the finished film. There is however a penalty in terms of reduced mechanical properties. The short chain branches in

the backbone of the LDPE chains lower the crystallinity. Branches also enhance shear thinning thus decreasing the energy expended during its processing.

The third type of polyethylene, LLDPE, is made using a Zeigler-Natta catalyst, which is a low-pressure process and has controlled short chain branches along its main chain. The short chain branches (3-8 CH₂ units) can be introduced by copolymerizing the ethylene with α -olefins like 1-butene, 1-hexene or 1-octene. The catalysts used in the synthesis usually have more than one active site, which reduces the precise control over the branching distribution, leading to multi-modal branching distributions. The short chain branches allow LLDPE to be tailored to give properties lying between the HDPE and LDPE resins. LLDPE can be synthesized in a range of crystallinity and densities. Unfortunately, LLDPE does not perform as well as LDPE in extrusion. LLDPE has lower elongational viscosities at lower shear rates thereby reducing bubble stability. LLDPE, especially the octene branched grades, have a balance of excellent mechanical properties and good optical properties.

Dow, Exxon and Phillips are some of the companies, which produce LLDPE's using metallocene catalysts. These catalysts systems have a single reactive site, which allows precise control over the chain architecture. Tailored branch content and narrow molecular weight distribution endows these resins with better properties as compared to the conventional LLDPE's. Although, the high cost of these specialty resins have forced the processor to blend them with conventional Zeigler-Natta catalyzed LLDPE's in order

to attain the desired properties. Some typical features of the three grades of PE are tabulated below in Table 1.

Resin	Molecular Weight Distribution	Short Chain Branching	Long Chain Branching	Mechanical Properties	Optical Properties
HDPE	Broad	Low	Low	Excellent impact and stiffness, poor MD tear	Poor
LLDPE	Narrow (Bimodal)	High 4, 6 and 8 carbon atoms	None	Excellent impact, tear and puncture	Good
LDPE	Broad	Some	High	Good	Excellent

Table 1. Characteristics of film grade polyethylenes [3].

1.3 Film blowing process

The wide variety of applications for PE films has lead to developments of new technologies for their manufacture. In most of the applications the polymer end product is rarely in the isotropic state. The processing methods impart orientation to the polymer thereby varying it's morphology as well as it's properties. One such processing technique is blown film extrusion, which is widely used in the polyolefin industry to make films.

Figure 1. Schematic of a film blowing process.

In a typical blown film process, polymer extrudate is turned through a right angle (so that it is moving vertically upwards), separated in an annulus, and then forced upwards through a thin circular slit, finally emerging into the atmosphere as a thin-walled ($\sim 1/16$ inch) continuous tube. The tube is then, and very rapidly ($\sim 3^{-10}$ sec)

- Drawn upwards (Machine direction, MD) by the pull rollers,
- Expanded laterally (Transverse direction, TD) by internal pressure, inflated into a sausage-shaped bubble, and at the same time
- Acted upon by cooling air jets from the air-blower, which cause it to solidify at the frost line height, some tens of centimeters above the shaper lips.

The tubular film extrudate thins out axially because of the internal pressure applied by the central air system and by a axial tension imposed by the nip-rolls. This is why the

orientation is biaxial to degrees that can be varied by varying the internal pressure and the axial tension [7]. After these operations the bubble is collapsed and the film is rolled on to a wind-up roll. The stability of the bubble is a matter of great importance to the film fabricator.

Film blowing is described by several control parameters: Draw down ratio, DDR, is the ratio of the line speed to the melt extrusion speed at the die. Blow up ratio of the film is the ratio between the diameter of the final film tube and the diameter of the orifice. As the film leaves the die, the tube is transparent. Where the polyethylene crystallizes (solidifies), it becomes translucent or “hazy.” This level is called the frost line height. Blown film is cooled by air blown against the surface. The level of frost line height depends on several variables: rate of extrusion, thickness and temperature of extrudate, and volume, heat capacity of the polymer, thermal conductivity of the polymer and temperature of cooling air. Cooling faster lowers the frost line height. The frost line height is generally associated with bulk crystallization although, as shown in this thesis, the development of haze in these films is mainly a result of surface scattering.

Therefore widely used parameters for the characterization of the blowing process are the melt temperature T , the thermal dependence of viscosity (WLF), the draw down ratio, DDR (degree of axial stretching of the extruded melt), the blow up ratio, BUR, the thickness of the blown film, the frost line height, FLH and the axial take off velocity at the nip rollers, which transport and seal the film tube.

Once the tubular shape is being satisfactorily extruded and has been threaded through the collapsing tower and take-up roll, sufficient air is introduced through a port in the mandrel into the area between the die and the pinch rolls to form a bubble of the volume necessary to produce film of desired width and thickness. The air remains within the bubble surrounded by passing film and requires little augmentation. Expanding the bubble also imparts some transverse orientation to the film for added strength. Blown films display biaxial orientation due to the combination of machine and transverse direction drawing.

Film blowing is widely used in the manufacture of polyethylene and other plastic films. The advantage of blown films over cast films formed by a coat-hanger die or calendar films include: the systems adaptability to producing tubing, both flat and gusseted, in a single operation; the relative ease of changing the film width and caliber by controlling the volume of air in the bubble and the relative high rate of production; the elimination of the edge-effects that result from flat die film extrusion; and the capability of biaxial orientation as the film is stretched during the bubble blowing process.

During the film blowing process axial stress acts in the machine direction and lateral stress acts in the transverse direction. There is no stress in normal direction as the surfaces are free. These stress fields are functions of melt viscosity, extrusion rate, takeoff rate, blowup ratio, temperature profile and die size. Acting against the development of orientation during film blowing, however, are a number of molecular

and physical relaxation processes. These depend primarily on the solidification time of the melt in the freezing zone, the melt temperature T and the strain rate dependent melt viscosity. The solidification involves partial crystallization to between 30 to 90% by volume. Crystallinity is the main morphological mechanism for retention of orientation in blown films.

The material properties of blown films change with varying processing conditions due to the dependence of viscosity and crystallization rate on shear rate and temperature. In many applications isotropic elastic modulus and tensile strength are desired in the film. Other applications of blown films require high strength and modulus in a particular direction, as for instance in the case of PE filmstrips made by cutting and uniaxial drawing of blown films.

The optical properties of films (such as haze, transparency or clarity, and transmittance) are key issues in packaging applications because they allow the consumer to see what is contained within the package. Hence, optical property is also an important feature in the marketability of a particular product. A fundamental understanding of the morphological basis for haze, for instance, is largely absent from the literature because the morphologies are complex, anisotropic and generally not amenable to simple models. In the case of blown polyethylene films, light scattering and reflection/refraction occur because of both bulk and surface structures. Scattering may take place due to the presence of morphologies that may be related to structures either in bulk or on the surface of the films. The degree of scattering depends on the size of the structures present. If such

crystalline structures exist on the scale of the wavelength of light, considerable diffuse reflection, refraction and scattering occurs resulting in turbidity. Thus, the size and organization of micron-scale crystalline structures play an important role in deciding the optical properties of the films. In blown films the morphologies tend to be oriented and a relation between orientation, structure and surface roughness may lead to an understanding of haze in blown films.

The nature of crystalline orientation to some extent depends on the fraction of crystallinity, branch content, and branch length. The later two have a dramatic effect on melt elasticity. The degree and 3-d nature of crystalline orientation as well as degree of crystallinity determine most film properties.

1.4 Background of Semi-crystalline Morphology

This thesis will discuss morphological consequences of the film blowing operation. A brief summary of semi-crystalline morphology in polymers is presented for background.

Semi-crystalline polymers account for a large portion of the total plastic consumption each year. This has forced a better understanding of their morphology and structure-property relationship with an aim at modifying their morphology to achieve the required property.

Much of the present knowledge about semi-crystalline morphology is based on extensive studies carried out on polyethylene. Some factors like simple molecular

architecture and its technological importance of polyethylenes has made its study very important. At first glance the morphology of the polyethylenes seems very simple, but there are a number of variations in it and various morphological concepts have still remained unexplained.

The two most important modes of crystallization for semi-crystalline polymers are 1) from solution and 2) from melt. The crystals obtained by crystallizing from a dilute solution of the semi-crystalline polymer are more ordered or perfect because there are fewer chains in the solution, which leads to better ordering of these chains in the solution crystal (lamellae). In melt crystallization the high concentration of the chains causes the melt crystallized macro aggregates (spherulites) to be comparatively less ordered. The size of these two types of morphologies differs by an order of magnitude. So as the concentration of the melt is increased from dilute solution to concentrated, the crystal morphology changes from a simple lathe like crystal to a spherical macro-aggregate crystal (spherulites) [8]. The main difference being isolation of a single chain (dilute solution), weakly interpenetrating chain (semi-dilute) and strongly entangled (melt). In most commercial processing, the polymer exists in its melt state and the processing conditions and the nature of the entangled state usually influences the morphologies of commercial polymers. Although in the film blowing operation the polymer exists in its melt state, the spherulitic morphology is rarely seen since the spherulites are destroyed/or cannot form during biaxial stretching of the films. A brief description of both model modes of crystallization is given below.

1.5 Solution crystallization

The single crystals developed in semi-crystalline polymers crystallizing from dilute solutions are usually lath or lozenge like having high aspect ratios, i.e. the growth in one direction is much larger than in the remaining two directions. The PE crystals display a large aspect ratio, the lateral dimension being an order of magnitude higher than their thickness. High density polyethylene (HDPE) forms crystals, which have a lateral dimension of 1-2 μm and a thickness of 100Å-200Å. In order to accommodate itself the long chain ($\sim 1 \mu\text{m}$) undergoes chain folding. This chain folding was first proposed by Keller [9].

Figure 2. Chain folding morphology as proposed by Keller [9].

1.6 Melt crystallization

The primary mode of crystallization in commercially processed polymers is from the melt state. Some characteristics of solution grown crystals, such as high aspect ratio lath like crystals exhibiting chain folding, are also present in crystals grown from the melt. There are several structures, which are unique to this route. Polymers crystallize from the melt into more complex forms, which are dependent on various external factors such as processing conditions, temperature and pressure. The nucleation density is substantially higher in the melt as compared to the dilute solution [11, 12]. Generally from the melt, semi-crystalline polymers crystallize into macro-aggregates, which are called spherulites. These are spherical shaped structures, which have a central nucleus from which the sub-crystals ‘lamellae’, radiate outwards. The spherulitic size is dependent on the undercooling, at high undercooling the nucleation rate is higher leading to numerous small spherulites and at low undercoolings there are few nucleation sites present, which leads to few large spherulites. The lamellae are universal to solution as well as melt crystals.

Keith and Padden [13] have explained spherulitic formation on the basis of two prominent characteristics; non-crystallographic branching and a fibrous growth pattern. In case of polymers crystallizing in the melt such a fibrous growth may be caused by the impurities in the melt. To describe this, they introduced parameter d that is related to the lateral dimension of the radially out growing fibrils or the “coarseness” of the spherulitic structure. d has units of length and is given as,

$$\delta = D/G \quad (1)$$

Where, D is the diffusion coefficient of the impurities present in the melt and G is the growth rate of the spherulities. Thus, the lamellae width is dependent upon impurities in the form of uncrystallizable segments of the chain, branches, dirt etc. and also on entanglements and lamellar branching.

External factors such as the processing conditions lead to variations in the melt crystallized morphology although these variations are ill described in the literature. Spherulitic morphology is rarely seen in oriented films or fibers. Here it is replaced by either pillared lamella morphology in blown PE films or by shish-kebob morphology seen in UHMWPE fibers. There are numerous other forms of melt crystals, which occur under special conditions such as high pressure. In this study the focus is on oriented lamellar morphologies with oriented rod-like micron-scale morphologies as described below.

Morphologies in semi-crystalline polymers have been documented extensively in the literature. Still there are several unresolved issues in understanding, which make this puzzle incomplete. In the past, researchers have focussed on individual components of the whole semi-crystalline morphology. Tagawa et al. [14] focused on the formation of pillared lamellae structures while Stehling et al. [15] focused on the scattering of light from micron-scale structures on the surface of blown polyethylene films. No one has approached the overall crystalline morphology from the point of view of quantifying the manner in which the individual building blocks (lamellae) come together and arrange themselves to form the micro-scale rod-like crystalline structures, i.e. no one has detailed

how the lamellae organize into the rod-like structures. Knowledge of the characteristic arrangement of the individual lamellae inside the rod-like structures would promote a better understanding of the effects of the crystalline structures on the final properties of the blown film. For instance the optical properties of commercial polyethylene blown films are controlled by their crystallinity and the orientation of their lamellae, which are dependent upon the processing conditions. Hence, measuring the lamellar orientation and calculating lamellar dimensions would allow the processor to tailor the end-use properties by modifying the lamellar morphology. Knowledge of the lamellar dimensions such as thickness, lateral width, packing efficiency in the lamellar stack and periodicity of the stacks (correlation distance) would be beneficial in understanding the behavior in these blown films.

In this thesis we have put forward the hierarchical structure i.e. the arrangement of the nano-scale crystalline lamellae (oriented along the film TD) in the micron-scale rod-like structures (oriented along the film MD) present on the surface of the film. The lamellae bundles come together to form the crystalline rod-like structures. This arrangement is explained in detail later.

1.7 Literature re view

1.7.1 Morphology

Several reports exist in the literature concerning blown film morphology. Among these,

Tagawa et al. [14] made a basic study about the morphology of HDPE films. They studied the surface of blown polyethylene film and the surface of a necked region formed by drawing the film in the machine direction, using a high-resolution scanning electron microscope equipped with a field emission source. They showed that the internal texture of the film consisted of piled-lamellae units. The piled-lamellae units were stacked perpendicular to the MD (lamellar normal in MD). They consisted of three to ten lamellae crystal sheets and acted as a single unit even during deformation. They showed that the piled-lamellae units protrude from the film surface in the fashion of an open pine cone, when the film is deformed in the MD. They also showed the formation of many tie fibrils between adjacent piled-lamellae units after the deformation. When the film was extensively deformed along the MD they observed a very large reorientation of the lamellae or lamellae piles. The lamellae-piles rotated about the axis along the film normal direction.

1.7.2 Relation between film morphology and resin characteristics

Studies made by several authors related the resin characteristics to the morphology of the film.

Prasad et al. [16] studied the effect of melt relaxation time and melt elasticity on the properties of blown medium molecular weight (MMW) HDPE films. They used SAXS data to obtain lamellar orientation function using the Herman's orientation function approach. The Herman's orientation function is widely used to describe uniaxial

orientation in x-ray diffraction. Herman and coworkers had initially formulated this function to measure axial orientation in fibers. The function is given as follows,

$$f_{\phi} = \frac{1}{2} (3\langle \cos^2 \phi \rangle - 1)$$

Where, $\langle \cos^2 \phi \rangle$ is the average cosine of the angle between the normal to the lamellae surface and the machine direction (reference axis). The function takes a value of + 1 (at $\langle \phi \rangle = 0$) for perfectly alignment or orientation, a value of $-1/2$ (at $\langle \phi \rangle = 90$) for perfectly perpendicular orientation and finally a value of 0 for completely random orientation. The films studied had different degree of long chain branching (LCB). Their study showed the affect of degree of LCB on the melt relaxation time and the degree of lamellae orientation.

Krishnaswamy et al. [17] studied the relationship between the resin characteristics and the film properties. In their study they used films with different MWD. They studied the effect of relaxation behavior on the melt elasticity and lamellae orientation in blown LLDPE films and finally linked the lamellae orientation to the Elmendorf tear resistance of the films.

1.7.3 Relation between film processing conditions and film morphology

Various studies related the processing conditions of the film to the final morphology obtained in the film.

Jianjun et al. [18] studied the effect of the processing conditions on the morphology of two blown LDPE films. The films were made of the same resin but under

different conditions. They showed how the processing conditions affected the crystalline texture in the films. According to their study films blown using conventional bubble geometry had lamellar structures growing with their b-axis along the transverse direction (TD) without any kind of twisting and their c-axis along the machine direction (MD).

Smith et al. [19] studied optical haze in PE films and related this to the surface morphology using wide-angle x-ray diffraction (WAXD) and atomic force microscopy (AFM). In this study they concluded that the surface roughness was due to exposed crystalline features, which contributed majorly towards haze. They studied the variation in degree of roughness by varying the frost line, height and the extrusion temperature. According to their study the higher the frost line, the higher is the degree of crystallinity and roughness. No clear explanation was made regarding how these crystalline features formed on the surface in their study.

Pinto et al. [20] studied the effect of crystallization and surface roughness on light scattering in blown polyethylene films. They varied the extrusion temperature and studied its effect on the surface roughness and crystallization. According to their study increasing the extrusion temperature increased the degree of crystallization but decreased the surface roughness. From their study they concluded that light scattering from surface features was a major cause of haze but they did not put forward any theory regarding the kind of surface features present and how they formed.

Wilkes et al. [21] studied the effect of variation in relaxation behavior on the orientation and the morphology of polyethylene uniaxially oriented tubular films. They showed that the melt relaxation behavior could be controlled by varying the processing conditions to produce films with or without the direct observation of fiber nuclei. This fibril nuclei structure proposed was similar to the ‘row orientation’ concept proposed by Kellar [22]. According to this concept the lamellar overgrowth occurs epitaxially from the c-axis oriented fibril. The fibril behaves as nuclei for the lamellar overgrowth. As the lamellae grow outwards they gradually twist about the b-axis, which stays perpendicular to the c-axis of the central fibril. They also showed how the presence of fiber nuclei affected the mechanical properties of the films. No observation was made in the context of the affect of the relaxation time on the surface features of the film.

1.7.4 Relation between resin characteristics / morphology /processing conditions to the film optical properties

Several authors related the resin properties or, the morphology of the film or, its processing conditions to the optical properties of the film.

Shroff et al. [23] studied the effect of melt elasticity and crystallization kinetics on the optical properties of LDPE blown films. They presented data for LDPE resins, which were subjected to melt histories involving shear and heat before film blowing which caused deterioration in the optical properties of the blown films. The resins were subjected to repeated passes through a commercial (Banbury) batch finisher. Shroff et al. observed permanent changes in the molecular structure (content of high molecular weight

species increased) as a result of multiple passes through the finishing line. This in turn increased the melt elasticity. They then showed that the increase in melt elasticity deteriorated the optical properties of the blown films. Overall, from their study, they concluded that the crystallization kinetics had a small effect on the optical properties while the melt elasticity played a major role in determining the optical properties, which is consistent with our study.

Wilkes et al. [24] later studied the affect of relaxation behavior on the optical properties of blown and cast LLDPE films using wide angle x-ray scattering (WAXS), small angle x-ray scattering (SAXS) and atomic force microscopy (AFM). The two films studied were blown under identical conditions. The only parameter varying between the films was that one of the films had a narrow molecular weight distribution (MWD) while the other had a broad MWD. They showed that the films with narrow MWD had lower relaxation time and developed micron size spherical superstructures on its surface. They claimed that these superstructures scattered light and hence the film with narrow MWD and lower relaxation time had deteriorated optical properties.

Bheda et al. [25] studied the light transmission properties of polypropylene tubular blown films. They studied the effect of both, processing conditions and the resin variables on optical properties of PP blown films. They showed that, decreasing the melt flow rate, narrowing the MWD, addition of nucleating agent, increasing the blow up ratio (BUR), increasing the draw down ratio (DDR) and decreasing the frost line height (FLH) generally improved the optical properties of the films. They made their conclusions based

on studying both the surface texture and the bulk morphology. They concluded that, surface roughness was the major cause of light scattering while, the scattering taking place from the bulk played a secondary role.

Stehling et al. [15] studied the causes of haze in LDPE blown films using scattering electron microscopy (SEM), small angle light scattering (SALS), gel permeation chromatography (GPC) and a hazemeter. They studied two mechanisms, a) extrusion haze and b) crystallization haze, which were responsible for light scattering from the films. They also tried to put forward techniques by which light scattering could be reduced. According to their study surface roughness was the major cause of haze in the films. This surface roughness was due to presence of irregularities produced either, during extrusion of films (extrusion haze) or, due to crystallization near the surface (crystallization haze). They concluded that reducing the melt elasticity could reduce the extrusion haze. To reduce the melt elasticity they suggested to either, select a resin with lower concentration of large molecules or, by mechanically treating the resin before blowing. Increasing the structural irregularities in the polymer chain, which would reduce crystallization, could reduce the crystallization haze.

Kojima et al. [26] studied the structure and morphology of biaxially oriented polyethylene films. Three different resins, HDPE, LLDPE and LDPE copolymer were studied using SAXS, SEM, TEM, and AFM. They studied the formation of crystalline lamellae on both, inner and outer surfaces of the films. Surfaces investigated by AFM, TEM and SAXS measurements showed morphologies of comparable dimensions while

the dimensions obtained from SEM overestimated the basic crystalline sizes. The SEM micrographs exhibited dimensions that were an order of magnitude larger than the lamellar sizes determined by other techniques. They proposed that the lamellar crystals collapse together to form crystalline aggregates. They also proposed that these aggregates scatter light from the surface of the films.

1.7.5 Relation between resin characteristics and film morphology / mechanical properties

Several authors reported on the relationship between the resin properties and its effect on the film morphology and its mechanical properties.

Kim et al. [27] studied the effect of the length and distribution of short chain branching on the Elmendorf tear resistance and dart drop impact strength of blown films of LLDPE's having similar melt index and density. They showed that the Elmendorf tear resistance for all the films was higher along the transverse direction (TD) than that along the machine direction (MD). This was due to crystal cleavage along the MD. As the length of the short chains increased the Elmendorf tear resistance increased. This was due to increase in length of the short chains, which produced fewer amounts of crystal imperfections. Hence larger and perfect crystals were formed which increased the Elmendorf tear resistance.

Kim et al. [28] used two different HDPE resins one with unimodal molecular weight distribution and the other with bimodal molecular weight distribution to blow

films and study the effect of molecular weight distribution on the film morphology and its properties. They also studied the effect of molecular weight distribution on the preferential orientation of the crystallographic axes a, b and c along the machine direction (MD), transverse direction (TD) and the normal direction (ND). They studied the effect of increase in large molecular weight chain content on the orientation of the crystalline lamellae. The orientation of the c-axis along the MD increased with the large molecular weight chain content. They also studied the effect of the processing conditions on the film morphology. They observed morphology similar to the shish-kebob morphology on increasing the draw ratio (DR) and decreasing the blow up ratio (BUR).

Kim et al. [29] studied the tearing and tensile deformation behavior and the dart drop impact strength of unimodal and bimodal HDPE blown films. In their earlier publication they had concluded that the bimodal HDPE's have a well-developed network structure of lamellar stacks. In the present study they observed that this level of interconnectivity of lamellar stacks play a critical role in dart drop impact resistance of the blown HDPE films. They also observed that the orientation distribution of the lamellae stacks played a significant role in deciding the tear and the tensile deformation of the films.

1.7.6 Relation between resin characteristics and superstructure formation

Several authors have reported the relationship between the resin properties and formation of micron-scale superstructure on the surface of the films, which finally lead to turbidity in the blown films.

Hashimoto et al. [30] reported the formation of sheaf-like superstructures on the surface of tubular extruded polybutene-1 films. They studied light scattering from the surface of the films. Light scattering patterns and electron micrographs were used to investigate the crystalline superstructures and the deformation mechanism. They showed that the sheaves were aligned side by side with axis oriented perpendicular to the machine direction i.e. direction of stress. They suggested that these sheaf like superstructures were a result of anisotropic crystal growth due to molecular orientation in the melt. From their study they concluded that these sheaf-like structures caused light scattering in the blown films.

Stehling et al. [15] reported the formation of rod-like superstructures on the surface of blown LDPE films. They related the surface roughness to the melt elasticity and showed that the roughness increases with increasing melt elasticity.

Samuels et al. [31] reported that rod-like, fibrillar structures (1-3 μm) form on the surface of water-soluble hydroxy-propylcellulose. These structures are reminiscent of those reported by Stehling et al. [15].

1.7.7 Summary

Various studies proposing the effect of, resin properties like molecular weight and molecular weight distribution, film processing conditions and film morphology on the final film properties has been made.

The lamellar structure and their orientation are important factors in determining the structure-property relations in blown films. Although there are prior studies in the literature where lamellar orientation, as determined by small angle x-ray scattering, has been correlated to micro properties such as permeability and tear strength, no such study was found which correlated this lamellar orientation to the macro-scale orientation in the films which in turn affected the optical properties of the film. The main thrust of past and recent studies in the literature has been devoted to understanding the effect of processing parameters such as, FLH, BUR and take-up speed of the bubble to the structure and properties of blown films. From this literature review and the above discussion it is clear that the lamellar orientation in blown polyethylene films plays an important role in determining the final film properties and is so explained in brief below.

1.8 Orientation in PE blown films

1.8.1 Orientation measurement

The inherent orientation induced in the film and the constraints (rapid crystallization times) imposed upon it by the processing technique lead to non-spherulitic morphologies in blown films. The chains undergo row nucleation and then crystallize epitaxially in the form of lamellar stacks. As noted above Tagawa et al. [14] have done extensive investigation towards elucidating the morphology of PE blown films using high resolution scanning electron microscopy. They have reported that HDPE blown films show lamellae arranged in piles or stacks of three to ten individual lamellar sheets. The lamellar piles are arranged perpendicular to the machine direction. Considerable amount

of literature exists about correlation of morphology in these films to the final properties [32-36].

The lamellar structure and their orientation are important factors in determining the structure-property relations in the blown films. Although there is evidence of prior studies in the literature where the lamellar orientation as determined by small angle x-ray scattering has been correlated to micro properties as permeability and tear strength, no such study was found which related this lamellar orientation to the macro-scale orientation in the films which mainly affected the optical properties. The main thrust of past and recent studies in the literature has been devoted to understanding the effect of processing parameters such as, FLH, BUR and take-up speed of the bubble to the structure and properties of blown films.

Processed plastics are usually anisotropic in nature due to the orientations imparted while processing. In the blown film process the orientation is imposed upon the film in both the machine direction (MD) as well as in the transverse direction (TD), although the machine direction orientation is usually several orders of magnitude higher than that in the TD. This plays an important role in deciding the final mechanical properties, which are superior in the MD. The measurement of orientation thus provides vital information for comprehending the structure-property relations.

Three common techniques used in the past to quantify orientation in processed polymers are wide angle x-ray scattering (WAXS), FTIR dichroism and birefringence [3,

4, 37]. WAXS is a powerful technique to probe the crystalline orientation of the unit cells in a semi-crystalline polymer. Wilchinsky [38-39] has measured the orientation of the c-axis in polypropylene films using x-ray diffraction. Roe et al. [40-42] have studied crystalline orientation in polycrystalline materials using x-ray diffraction. Maddams and Preedy have applied the pole figure analysis to blown PE films [43]. Birefringence is used to measure the molecular orientation of the amorphous and crystalline phase in the polymer. Through this technique one can obtain the total molecular orientation of the sample, although knowledge of the intrinsic birefringence of the crystalline and amorphous regimes is necessary in order to arrive at accurate conclusions. Neither birefringence nor WAXS directly probe structures in the size scale of those structures (lamellae), which play a vital role in determining macro properties such as permeability, tear strength in PE blown films. In the past several researchers have discovered unique methods for quantifying this orientation.

In blown films the macro properties such as the moisture permeability and tear strength are controlled by morphological features (lamellae) that are several orders of magnitude higher than what can be effectively probed by WAXS. The oriented lamellae would cause the mechanical properties to be higher in the direction of orientation of the lamellae normal, which in case of most blown films is the machine direction. Thus quantitative knowledge of the orientation of the lamellae normal would be helpful in establishing structure-property relationships. One way of quantifying lamellae orientation is by using the Herman's orientation function, through which the orientation of the lamellar normals is calculated with respect to the reference axis, which in the case of

blown films is the machine direction axis. Herman's orientation function (explained earlier) is widely used to describe uniaxial orientation in x-ray diffraction and IR spectroscopy [37]. Small angle x-ray scattering (SAXS) is a useful technique for tackling the issue of lamellar orientation. The lamellae in blown films, which are 100 to 300 Å thick, fall in the size range observable by SAXS measurements, viz. 0.002 to 0.4 Å⁻¹. For this reason SAXS has been extensively used and described in detail in our study.

2. EXPERIMENTAL AND RESULTS

2.1 Introduction

Two films studied had identical degree of crystallinity by DSC. Sample ZN was manufactured from HDPE synthesized with a Ziegler-Natta third generation titanium complex catalyst on an inorganic support, while sample STAR α was manufactured from HDPE synthesized with a single-site catalyst. The film designated as ZN had broad molecular weight distribution (MWD) while the other film designated as STAR α had narrow MWD. The film with STAR α was glossy and transparent while the film ZN was hazy. The aim behind this study was to find the reason for haziness in the film ZN. A film looks hazy only when major part of the incident light is scattered. This scattering from the film can take place due to several reasons, some of which are as follows:

- Presence of large crystals (with size comparable to the wavelength of light) in the bulk and on the surface of the film.
- Presence of impurities and voids in the bulk and or the surface of the films.
- Presence of macro-scale structures on the surface.
- Extrusion defects like flow-lines formed on the surface of the film during extrusion.

Thus the aim of this study was to determine the reason for light scattering in ZN. The surface of the films was studied using optical microscopy and small angle light scattering (SALS). To study the nature of the crystal texture in the films, small angle x-ray scattering (SAXS) was used. Small angle x-ray scattering gave us data on a nano-scale while; small angle light scattering gave us data on a micro-scale. The nano-scale orientation (orientation of lamellae) was studied using SAXS while; SALS was used to study micron-scale orientation.

2.2 Material

Figure 3. DSC curves for a) STAR α and b) ZN

Films designated as ZN and STAR α , blown under similar conditions at Equistar Technology Center, Cincinnati, OH were studied. Two films with identical degree of crystallinity [63% by differential scanning calorimetry (DSC)] are reported here. The DSC curves for both the films are shown in Figure 3. The ZN film was manufactured from HDPE synthesized with a Ziegler-Natta third generation titanium complex catalyst on an inorganic support (ZN), while the STAR α film was manufactured from HDPE synthesized with a single-site catalyst. The Ziegler-Natta catalyst gives HDPE with a broader molecular weight distribution as compared to that obtained from a single-site catalyst [24]. This is clearly seen from the GPC curves (Figure 4) for both the films. The molecular weight of the polymers is presented in Table 2.

Figure 4. GPC curves for a) STAR α and b) ZN.

SAMPLE	Mn	Mw	MWD
STAR α	10,780	46,090	4.28
ZN	12,400	176,560	14.24

Table 2. A molecular weight characteristic of the polyethylene's used in this study.

The film processing conditions are presented in Table 3. The ZN film was cloudy, while the STAR α film was transparent. Single sheets of these blown films were immersed in benzyl alcohol, an index matching liquid, to remove surface scattering. In the absence of index matching solvent the STAR α film was clear while; ZN film was too turbid for light to pass through it as seen in figure 5.a. The films become of comparable

clarity when immersed in benzyl alcohol as seen in Figure 5.b. This showed that the film ZN had certain features on its surface, which scattered light and made it turbid.

Blow up ratio	Die Gap (mil)	Die (inch)	Air Ring	Frost Line Height (inch)	Lay Flat Width (inch)	Output (lb/hr)	Screen Pack	Gauge (mil)
2.5:1	60	4	Standard	9-14	14	75	Standard	1.25

Table 3. Film extrusion conditions.

(a)

(b)

Figure 5. STAR α (left) and ZN (right) are placed in a cell in both (a) and (b). The cell is at a height of 1.5cm for better clarity. In (b) films are immersed in benzyl alcohol while in (a) they are held in air.

2.3 Small angle x-ray scattering (SAXS)

2.3.1 Introduction

When any form of electro-magnetic radiation interacts with matter, it is scattered if domains with sufficient contrast, and of a size associated with the wavelength of the radiation exist. The manner in which this scattering occurs depends on the internal distribution of “scattering entities”, i.e., heterogeneities, their size, shape, composition and the wavelength of the incident radiation.

Ordinarily the wavelength is kept constant during a scattering measurement and the scattered intensity is monitored, as a function of scattering angle. This gives the scattering curve the shape of which is associated with the morphology of the scattering system. In fact, every point of the scattering curve is indicative in some way of the features of the system’s morphology, i.e. whether there is random or an ordered arrangement, whether the system is isotropic or has preferred orientation (texture), whether the heterogeneities are micro or macro on an average, the degree of heterogeneity or homogeneity.

The scattering of x-rays by matter is the result of fluctuations in the electron density of the material. If a material was completely homogeneous in its electron density, no scattering would occur. All materials have some kind of heterogeneity in electron density. If heterogeneities occur on a nano-scale, i.e., 50Å to 5000Å, SAXS can be used to investigate the fluctuations and the corresponding morphology. Typical systems studied by SAXS are those composed of discrete particles such as colloidal suspensions;

dilute solutions of macromolecules; and phase separated systems such as polymer blends, semi-crystalline polymers, nanostructured ceramics (catalysts, membranes).

Small angle x-ray scattering (SAXS) can be used to characterize the nanometer-scale structures in semi-crystalline polymers. SAXS is a study of x-ray scattering in reciprocal space at angles very close to the beam, typically $2\theta < 5^\circ$, where θ is half the scattering angle. SAXS depends on the large-scale periodic heterogeneity in the structure. Strong diffraction peaks result from constructive interference of x-rays scattered from well-ordered structures (e.g. lamellae) in a polymer. These ordered structures scatter incident x-rays at various angles. Much can be learned from the angular distribution of scattered intensities at low angles. SAXS measures the distance between lamella centers, which is in the range of hundreds of angstrom units. The peaks in the SAXS patterns correspond to the periodic arrangement (long periods) of the crystalline lamellae along the chain axis. Bragg's law gives the long period L , of the crystalline lamellae.

$$L = 2\pi / q^*_N \quad (2)$$

q^*_N is $|q|$ for the peak scattering intensity in the lamellar normal direction. q is the scattering vector and is defined as

$$q = 4\pi \sin \theta / \lambda \quad (3)$$

Where θ is the scattering angle and λ is the wavelength of x-rays.

SAXS can also be used to obtain the thickness of these structures (lamellae). The long period of the lamellae stacks produce a maximum in the scattering intensity, and the

sharpness and angular distribution of these peaks reflect the regularity of the variation in electron density along different directions.

Different microstructures of the stacked lamellar crystalline structures will produce different scattering patterns. Typical scattering patterns obtained are shown in Figure 6.

Figure 6. X-ray scattering patterns (left) for different microstructures of a stacked lamellae crystalline structure (right).

The topmost pattern resembles the one obtained for a polymer with random orientation of the lamellar stacks. A ring is obtained for such spherically symmetric systems having isotropic lamellar stacks. The middle pattern is the one obtained for slightly deformed samples in which, some lamellar structures orient perpendicular to the direction of stress while some lamellar are at an angle to the direction of stress. The

pattern at the bottom is the one for a highly deformed sample in which most of the crystalline structures align perpendicular to the direction of stress.

2.3.2 Apparatus

The apparatus used for measuring small angle scattering generally employs transmission geometry, as it is difficult to measure the intensity near the beam in the reflection geometry. The most important requirement of the measurement is a fine x-ray beam so that the direct beam can be intercepted without blocking much of the range of scattered intensity. Monochromatic radiation is required so a crystal monochromator is used between the x-ray source and the sample. Three successful approaches to data collection are slit collimation, pinhole collimation and crystal monochromator collimation.

A typical experimental setup is shown below in Figure 7.

Figure 7. Scattering geometry showing 2θ the scattering angle.

2.3.3 SAXS measurement

Small angle x-ray scattering (SAXS) measurements were conducted on a 2-meter pinhole camera with focusing optics and a 2-dimensional detector as described in earlier publications [16]. Data was corrected for dark current, empty cell and sensitivity. The 2-D measurements are useful in determining both lamellar nanostructure and orientation.

Since the films are very thin (50 μm); around 25-40 films are stacked over one another. Care is taken that the films are stacked in a manner that all the films in a stack have their machine direction (MD), transverse direction (TD) and normal direction (ND) aligned. Stacks of around 1.25-1.50 mm thickness were prepared from the 50 μm thick films.

As stated earlier, crystalline domains in the film could scatter light if they were of sizes comparable to the wavelength of light. Thus determining the nature i.e. size, shape and arrangement (orientation) of these micron-scale structures was important to predict the cause of haze in the ZN film. Small angle x-ray scattering (SAXS) is an extensive technique for determining the lamellar size and orientation. The lamellae in blown films, which are 100 to 300 $\text{\AA}$ thick, fall in the q range of SAXS measurements, viz. 0.002 to 0.4 $\text{\AA}^{-1}$. Due to this reason SAXS was used.

Although the major component of the lamellar normal orientation is along the MD, they do have some degree of orientation along both the film TD and the ND. Determination of the degree of orientation in all the three directions is equally important.

It is difficult to measure the component of orientation in the normal direction i.e. along the thickness of the film. This would require passing the x-ray beam in the plane of the film. We have developed a simple approach using out of plane (M-T) tilts of ϕ_{Tilt} to access 3-D orientation. This technique gives components of the degree of orientation in the machine direction (MD), the transverse direction (TD) and in the normal direction (ND). Figure 6 shows the three sample orientations used for the SAXS measurement.

a) Orientation M-T: The sample is placed with MD horizontal and TD vertical with the beam in the ND. (Figure 8.a)

b) Orientation M-NT: The sample as in 8.a. is rotated about the MD by 45^0 so that the orientation vector along the vertical axis is a combination of orientation vectors in the MD and the ND. Thus the orientation vector along the ND contributes to scattering. (Figure 8.b)

c) Orientation TMN: The sample as in 8.a. is now flipped so that the TD is horizontal and MD is vertical. Now it is rotated about the TD by 45^0 so that the orientation vector along the vertical axis is a combination of the orientation vector along the MD and the ND. (Figure 8.c)

Figure 8. a) Orientation M-T. b) Orientation M-NT. c) Orientation T-MN. Prime coordinates are after tilting, unprimed are the original arrangement with the x-ray beam in the normal direction. Also shown are simple sketches of the orientation used in Figure 5 and the acronyms used in the text.

For the M-T projection an azimuthal average yields the radial plot of Figure 9 showing Intensity versus $q = 4\pi (\sin (\theta/2))/\lambda$ where θ is the scattering angle and λ is the wavelength. The scattering intensity depends on the deviation from the mean and not on the absolute value of the scattering length density, which in turn depends on the lamellar thickness. The lamellar thickness may not be constant and so there could be deviation in scattering intensity from lamellae to lamellae. Thus an expression or technique is required which relates the scattering intensity to the lamellae thickness distribution. Hoseman and Bagachi [40-44] derived such expression and put forward the Hoseman-Bagachi function. Least square fits using the Hoseman-Bagachi function [40, 44] (shown

in Figure 9) indicate similar lamellar thickness and correlation distance for the films. Thus the main difference on a nano-scale is orientation as seen in Figures 10 and 11. Azimuthal averages of M-NT and T-MN are essentially identical to Figure 9.

Figure 9. SAXS Intensity (a. u) versus $q \text{ (}\text{\AA}^{-1}\text{)}$ for STAR α and ZN sample in M-T orientation (Figure 6.a). Fits are the Hosemann-Bachi function [40, 44]

2.3.4 SAXS analysis of 2-d orientation

The SAXS measurements were conducted with the sample orientations as shown in Figure 8 and using the nomenclature M-T, M-NT and T-MN.

Corrected 2D SAXS patterns are shown in Figure 10 for the three different orientations of the samples STAR α and ZN. The sample orientation is designated below each image

with reference to Figure 8. The observed orientation in the SAXS pattern is normal to the material orientation since it reflects a Fourier transform of real space. For instance the sharp orientation of the SAXS pattern for ZN in 10.b along the MD indicates preferred lamellar orientation in the TD. The SAXS orientation describes the lamellar normal orientation in the indicated plane of projection.

Quantitatively Figures 10.a and 10.b (M-T), as well as 10.c and 10.d (M-NT) show that ZN has a higher degree of lamellar normal orientation along the MD than STAR α . In 10.b and 10.d a faint 2nd order peak can be seen at intermediate angle (distance from the center).

10.e and 10.f are the 2-D plots for STAR α and ZN respectively when placed in orientation T-MN as shown in Figure 8.c. In this case both the samples quantitatively show much weaker orientation. This weak orientation for the T-MN projection can be explained by the 3-d analysis presented below.

The box in Figure 10.a indicates the left and right position for a radial average about an azimuthal angle from top dead center (TDC) around the center of the 2D data set that produces a plot of intensity (averaged radially from the center and over the box) as a function of the azimuthal angle about the center of the pattern, rotating clockwise from 0 to 360 degrees from TDC. The azimuthal plot is used to calculate $\langle \cos^2(\phi) \rangle$ for the projection through the calculation of the average cosine square of the azimuthal angle weighted by the scattered intensity [16].

Figure 10. 2D SAXS patterns for the 2 samples in 3 different orientations. Line pointing to lower right corner is transmission monitor/Beam top wire.

Figure 11. Azimuthal plot for the 2 samples in 3 orientations of Figure 2, 4. Intensities are relative for a given sample since the same sample was used for different orientations.

The azimuthal plots for the 3 positions of the samples are shown in Figure 11. Since the peak in the SAXS pattern (Figure 9) is related to the long period [40, 44] and is associated with the lamellar normal direction, the azimuthal plots (Figure 11) can be used to calculate the averaged cosine square of the normal to the lamellae. This can be calculated under the assumption that either, the normal displays a uniaxial orientation [16] i.e. the orientation is symmetric about a selected axis of the sample, such as in a fiber pattern, as done in a previous publication [16, 45, 46] or, by considering 2 projections of the lamellar normal vector and calculating the 3-d orientation as described here.

If it is assumed that the sample shows uniaxial orientation the average cosine square of the angle ϕ between the lamellar normal in projection and the chosen axis (MD) of uniaxial symmetry is calculated by integration and normalization of $I(\phi)\cos^2(\phi)\sin(\phi)$ where ϕ is the azimuthal angle in Figure 11 [16]. The $\sin(\phi)$ term is used to reflect uniaxial symmetry (fiber symmetry). That is, as the azimuthal angle from the axis of orientation increases, the intensity from the observed plane must be multiplied by $\sin(\phi)$ to account for the increasing fraction of lamellae that do not fall in the plane of observation for SAXS.

If uniaxial orientation is not assumed then the lamellar normal projected on the plane of observation i.e. the M-T planar projection of the 3-dimensional orientation, $\langle \cos^2(\phi_{MT}) \rangle$, can be calculated by integration of $I(\phi_{MT}) \cos^2(\phi_{MT})$, with no $\sin(\phi_{MT})$ term [16]. Therefore,

$$\langle \cos^2(\phi_{MT}) \rangle = \int_0^{360} I(\phi_{MT}) \cos^2(\phi_{MT}) d\phi_{MT} / \int_0^{360} I(\phi_{MT}) d\phi_{MT} \quad (4)$$

$\langle \cos^2(\phi_{MT}) \rangle$ represents the M-T planar projection of the average normal to the lamellar plane in the MD direction. (In Figure 7, MD is at 90° for the M-T projection so $\phi_{MT} = 0$ at 90° .)

$\langle \cos^2(\phi_{MT}) \rangle$ can be used together with another planar projection such as $\langle \cos^2(\phi_{M-NT}) \rangle$ or $\langle \cos^2(\phi_{T-MN}) \rangle$ to determine the 3-dimensional orientation of the

lamellar normal to the MD, TD and ND represented by the angles ϕ_M , ϕ_T and ϕ_N respectively.

2.3.5 SAXS calculations

The scattering vector $\mathbf{q}$ can be represented in three dimensions as shown in Figure 12. $\mathbf{q}$ reflects the direction associated with an observed intensity. The direction of $\mathbf{q}$ at the maximum of a 2-d scattering pattern is the same as the preferred direction of the lamellar normals in a 2-d projection on the plane of observation.

Figure 12. 3-d view of the resultant scattering vector [40].

From the calculations shown below it is seen that, to determine the average angle of tilt of the lamellar normal with the MD, TD and ND (ϕ_M , ϕ_T and ϕ_N) only 2 of the 3 orientations are needed. Two of these combinations are discussed below.

Figure 13 schematically shows the three observed projections and the orientation angles obtained from Figure 11 using equation (4). The two calculations of ϕ_M ; ϕ_T ; ϕ_N are described below.

Figure 13. Direction of the intensity vector in the 3 different orientations. Φ_{MT} is the angle made by the scattering vector q with the horizontal (MD) when projected on the M-T plane. Φ_{M-NT} is the angle made by the scattering vector q with the horizontal (TD) when projected on the T-MN plane.

Case 1) M-T and M-NT orientation. Using Figure 12 and Figure 13.a,

$$q_M = q_{MT} \cos \phi_{MT} \quad (5)$$

$$q_T = q_{MT} \sin \phi_{MT} \quad (6)$$

From (4) and (5),

$$q_T / q_M = \tan \phi_{MT} \quad (7)$$

For M-NT orientation (Figure 13.b) the sample is tilted across MD by an angle ϕ_{Tilt} (in our case $\phi_{Tilt} = 45^\circ$) and so the scattering vector in the vertical direction will have a component of orientation along the TD and a component of orientation along the ND.

Using Figure 12 and Figure 13.b,

$$-q_N \sin\phi_{\text{Tilt}} + q_T \cos\phi_{\text{Tilt}} = q_{\text{M-NT}} \sin\phi_{\text{M-NT}}. \quad (8)$$

$$q_M = q_{\text{M-NT}} \cos\phi_{\text{M-NT}} \quad (9)$$

Using equations (4), (5) and (6),

$$q_N / q_M = [(\tan\phi_{\text{MT}} / \tan\phi_{\text{Tilt}}) - (\tan\phi_{\text{M-NT}} / \sin\phi_{\text{Tilt}})] \quad (10)$$

$$q_N / q_T = [1/\tan\phi_{\text{MT}}] / [(\tan\phi_{\text{MT}}/\tan\phi_{\text{Tilt}}) - (\tan\phi_{\text{M-NT}}/\sin\phi_{\text{Tilt}})] \quad (11)$$

From Figure 12,

$$\cos^2\phi_M = q_M^2/q^2 = q_M^2 / (q_M^2 + q_T^2 + q_N^2) \quad (12)$$

$$\cos^2\phi_T = q_T^2/q^2 = q_T^2 / (q_M^2 + q_T^2 + q_N^2) \quad (13)$$

$$\cos^2\phi_N = q_N^2/q^2 = q_N^2 / (q_M^2 + q_T^2 + q_N^2) \quad (14)$$

Substituting equations (7), (10) and (11) in equations (12), (13) and (14) and substituting

$A = (\tan\phi_{\text{MT}})$ and

$B = [(\tan\phi_{\text{MT}} / \tan\phi_{\text{Tilt}}) - (\tan\phi_{\text{M-NT}} / \sin\phi_{\text{Tilt}})]$ we get,

$$\cos^2\phi_M = 1 / \{1 + A^2 + B^2\} \quad (15)$$

$$\cos^2\phi_T = A^2 / \{1 + A^2 + B^2\} \quad (16)$$

$$\cos^2\phi_N = B^2 / \{1 + A^2 + B^2\} \quad (17)$$

Values of $\phi_{\text{M-NT}}$ and ϕ_{MT} , obtained from Figure 11, on substitution in (15), (16) and (17)

give the values of $\langle\cos^2\phi_M\rangle$, $\langle\cos^2\phi_T\rangle$ and $\langle\cos^2\phi_N\rangle$ reported in Table 3.

From Figure 13 it is clear that

$$\langle\cos^2\phi_M\rangle + \langle\cos^2\phi_N\rangle + \langle\cos^2\phi_T\rangle = 1 \quad (18)$$

Eqn.15 can be used to cross check the values (Table 4).

Case 2) M-T and TMN orientation. For M-NT orientation (Figure 13.c) the sample is tilted across TD by an angle ϕ_{Tilt} (in our case $\phi_{\text{Tilt}} = 45^\circ$) and so the scattering vector in the vertical direction will have a component of orientation along the MD and a component of orientation along the ND.

Using Figure 12 and Figure 13.c,

$$q_N / q_M = 1 / \tan \phi_{\text{Tilt}} - (\tan \phi_{\text{MN-T}}) (\tan \phi_{\text{MT}}) / (\sin \phi_{\text{Tilt}}) \quad (19)$$

$$q_N / q_T = [1 / \tan \phi_{\text{MT}}] [1 / \tan \phi_{\text{Tilt}} - (\tan \phi_{\text{MN-T}}) (\tan \phi_{\text{MT}}) / (\sin \phi_{\text{Tilt}})] \quad (20)$$

Substituting (7), (19) and (20) in (12), (13), (14) and

$$A = (\tan \phi_{\text{(MT)}}) \text{ and}$$

$$C = [1 / \tan \phi_{\text{Tilt}} - (\tan \phi_{\text{MN-T}}) (\tan \phi_{\text{(MT)}}) / (\sin \phi_{\text{Tilt}})],$$

$$\cos^2 \phi_M = 1 / (1 + A^2 + C^2) \quad (21)$$

$$\cos^2 \phi_T = A^2 / (1 + A^2 + C^2) \quad (22)$$

$$\cos^2 \phi_N = C^2 / (1 + A^2 + C^2) \quad (23)$$

Values of $\phi_{\text{MN-T}}$ and $\phi_{\text{(MT)}}$, obtained from Figure 11, on substitution in (21), (22) and (23) give the values of $\langle \cos^2 \phi_M \rangle$, $\langle \cos^2 \phi_T \rangle$ and $\langle \cos^2 \phi_N \rangle$ reported in Table 4 (bracket values). The results from Case 2 can be used to crosscheck those obtained from Case 1.

SAMPLE		STAR a	ZN
Calculated projections. Case 1 (Case 2)	$\langle \cos^2 \phi_M \rangle$	0.596(0.610)	0.773(0.756)
	$\langle \cos^2 \phi_T \rangle$	0.379(0.388)	0.207(0.202)
	$\langle \cos^2 \phi_N \rangle$	0.025(0.002)	0.020(0.045)
	SUM	1.000(1.000)	1.000(1.003)
Observed projections. SAXS (SALS) data.	$\langle \cos^2 \phi_{TM} \rangle$	0.611(0.540)	0.789(0.600)
	$\langle \cos^2 \phi_M (NT) \rangle$	0.666	0.813
	$\langle \cos^2 \phi_T (MN) \rangle$	0.534	0.477

Table 4. Values of cosine square of angles made by the scattering vector with the MD, TD and ND

2.3.6 Results from biaxial orientation calculations

(b)

Figure 14. (a) Wilchinsky triangle [38, 39, 47] for average lamellar normal orientation of completely random oriented (central dot), and the 2 samples examined here. ZN has stronger lamellar normal orientation in the MD. (b) Measured projections as seen on Wilchinsky triangle planar projections showing close to random orientation for T-MN (as seen in Figure 10) and higher orientation for M-TN than MT. Line bisecting the M-N plane is the T-MN plane while, line bisecting the N-T plane is the M-NT plane. Arrows indicate the direction of projections on the T-MN and the M-NT plane.

The results in Table 4 show that both cases give similar results. The sum of $\langle \cos^2 \phi \rangle$ is also shown, which is close to 1. The average cosine square projection of the lamellar normals from the 'i' axis, $\langle \cos^2 \phi_i \rangle$, can be used in a Wilchinsky triangle [38, 39, 47] construction for the average lamellar normal orientation (Figure 14). This ternary plot seems the simplest to display the direction of the lamellar orientation for these samples.

The Wilchinsky triangle [38, 39, 47] is constructed by counting from the opposite side of a direction 'i' the value of $\langle \cos^2 \phi_i \rangle$ and making a point where the three $\langle \cos^2 \phi_i \rangle$ values intersect (according to Eqn.18). For a randomly oriented sample $\langle \cos^2 \phi_M \rangle = \langle \cos^2 \phi_N \rangle = \langle \cos^2 \phi_T \rangle = 1/3$ and a point in the center of the Wilchinsky triangle results. For perfect orientation in MD, a point at the MD corner results. Orientation of the lamellar normals in the M-T plane occurs for a point on the bottom axis [38, 39, 47].

The Wilchinsky plot shows that the lamellae lie with normal basically in the MT plane with stronger orientation in the MD direction. The lamellae are essentially perpendicular to the film surface in both the cases. ZN has a higher lamellar normal orientation in the MD.

The T-MN projection in Figure 10 shows little orientation (bottom 2 patterns). This can be understood in the context of the Wilchinsky diagram by drawing a line from the TD to the middle of the ND-MD axis, through the random point. Projecting the ZN and STAR α point along a line parallel to the ND-MD line shows close to random orientation for the TMN projection as observed. A similar construction for M-NT shows a strong deviation from the random point consistent with Figure 10.

2.4 Optical microscopy

2.4.1 Industrial films

Industrial films of polyethylene are manufactured for a wide range of applications. Accordingly, the morphology of these materials is studied to determine structure-property relationships, to understand how to improve properties and also control the quality of commercial products. The major topic of interest relating to film structure is the effect of crystallinity on the deformation mechanism.

2.4.2 Apparatus

In the conventional optical microscope (OM) an object is illuminated and the light that it transmits (Transmission optical microscope) is collected by a system of lenses to form an image. The image can reveal fine details in the specimen at a range of magnification from 2x to 2000x. Resolution of about 0.5 μ m is possible, limited by the nature of the specimen, the objective lens and the wavelength of light. The data obtained from OM is generally concerned with the size, shape and the relative arrangement of visible features.

2.4.3 Polarized light microscopy

Since the biaxially oriented blown HDPE films studied were birefringent and optically anisotropic, polarized light microscopy was used. Polarizing microscopy is the study of the microstructure of objects using their interactions with polarized light. A polarizing microscope is a transmitted light microscope that has, besides all the basic

features, a rotatable stage, a polarizer in the illumination system and an analyzer between objective and eyepiece. One or both of the polarizer and analyzer must be rotatable. The polarizer and analyzer are both polarizers, that is, device that selectively transmit light polarized in one specific plane. By far the most common arrangement in the polarizing microscope is crossed polars. 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. With no specimen or with an isotropic specimen, the field of view will be dark in crossed polars. Optically anisotropic, birefringent materials may appear bright between crossed polars. Optical anisotropy in semi-crystalline polymers of the type studied here is associated with crystalline domains.

2.4.4 Transmission optical microscopy analysis

Transmission optical micrographs are shown in Figure 15. The image was dominated especially for the ZN film, by surface features when observed in air. When the same film is immersed in an index matching fluid the bulk structure can be observed as shown in Figure 4. Benzyl alcohol ($n \sim 1.52$) has refractive index almost same as that of PE ($n \sim 1.49-1.51$) as seen in Figure 5 (b). Under crossed-polars in the optical micrographs of Figure 15, birefringent regions are white. We associate these birefringent regions with micron-scale, crystalline domains, while the dark regions reflect amorphous regions. The ZN film shows well-organized linear structures in both surface and bulk micrographs. The linear structures for the ZN film are in the MD. STAR α shows disorganized domains in both micrographs with a few rod-like structures of unknown origin at an angle to MD in the bulk micrograph.

Figure 15. Magnification 400x (under crossed-polars): (a) STAR α : in air. (Surface) (b) STAR α : immersed in benzyl alcohol. (Bulk) (c) ZN: in air. (Surface) (d) ZN: immersed in benzyl alcohol. (Bulk)

The optical micrographs support micron-scale orientation as the main difference between the two films.

2.5 Small angle light scattering

2.5.1 Introduction

Small angle light scattering is a very handy and convenient technique to study heterogeneities in the range of 0.5 to 50 microns. It is mainly used to study systems having, two or three-dimensional spherulities, two or three-dimensional rod structures, oriented and unoriented systems, etc. The general theoretical framework of SALS is essentially the same as that of SAXS [48-50] in the sense that while SAXS is sensitive to local changes in electron densities, SALS is sensitive to changes in polarizability, i.e., fluctuation in composition as well as anisotropy on a micron scale.

Polymers scatter light because they contain heterogeneous entities of dimensions comparable to the wavelength of light. As in SAXS, the angular dependence of scattered light is characteristic of the size, shape and distribution of the scattering particles.

In semicrystalline polymer films, two sources of heterogeneities could occur, 1) density fluctuation due to crystallinity; 2) orientation fluctuation due to anisotropy. By selecting the proper mode of polarization, one can discriminate between the various fluctuations.

2.5.2 Apparatus

The SALS technique as shown in Figure 16. consists of a laser light source and a camera. The laser provides an intense, coherent and monochromatic source of radiation,

which, impinges on the sample. The camera then captures the scattered radiation. Since the laser beam is very fine (small diameter) one does not need a very large sample area.

Figure 16. Schematic of a small angle light scattering setup.

2.5.3 Experimental procedure

Single sheets of blown films were immersed in benzyl alcohol, an index matching liquid, to remove surface scattering. In the absence of index matching solvent the ZN film was too turbid for the laser beam to pass through making light scattering from the film

impossible. The films become of comparable clarity when immersed in benzyl alcohol as seen in Figure 5.b. Light scattering measurements were conducted using a helium neon laser with $0.6328\mu\text{m}$ wavelength and pinhole optics. The small angle light scattering (SALS) pattern was projected onto a screen and imaged with a CCD camera equipped with a macro lens as previously reported [51]. Scattering was corrected for a benzyl alcohol background, dark current and sensitivity of the detector. All scattering was run with no polarizers other than the inherent polarization of the laser source. The MD direction of the samples is roughly in the horizontal direction of the SALS pattern in Figure 17 with the bright peaks in Figure 17 oriented normal to MD consistent with the optical micrographs.

The 2-dimensional patterns display different degree of orientation in SALS with the ZN sample showing stronger orientation in the MD direction (bright peaks normal to MD). The difference in orientation parallels that seen in the SAXS pattern despite roughly 3 orders difference in size between SALS and SAXS. The SAXS M-T orientation, Figure 10.a, is orthogonal to the SALS orientation shown in Figure 17. The SAXS, SALS and optical microscopy indicate that lamellae stacked within the rod-like structures of Figure 15 are normal to the fiber axis.

Figure 17. 2-dimensional corrected SALS patterns for STAR α (left) and ZN (right) films. A correlation peak associated with regular spacing of linear birefringent regions appears as a ring in the patterns. The machine direction (MD) is roughly in the horizontal plane with the bright lobes normal to MD.

The corrected SALS patterns shown in Figure 16 were averaged about the beam center resulting in the 1-dimensional radial scattering patterns shown in Figure 18. The SALS 1-dimensional patterns show a correlation peak associated with the ring seen in Figure 17. The correlation size, $2\pi/q^*$, is about $1.5 \mu\text{m}$ with the ZN film showing a slightly larger spacing. A Guinier fit is done on the curves at the weak knee seen at high- q resulting in a radius of gyration that is converted to the width of the lines seen in the optical micrographs by $W = 2R_g$. The region lower in q than the weak knee is consistent with 1-dimensional objects as indicated by a superimposed power-law decay of about -1

slope in the log-log plot of Figure 18. At high- q a Porod regime of -4 slope is seen indicating sharp interfaces to the linear domains.

Figure 18. Averaged 1-dimensional intensity versus scattering vector $q=4\pi/(\lambda \sin (\theta/2))$.

The peak in the pattern corresponds with the ring seen in Figure13.

Correlation distances and line width are noted as described in the text.

The average cosine squared for the SALS patterns can be obtained in a similar fashion to SAXS for the M-T planar projection. The radial plot of intensity near the peak

is shown in Figure 19. From this plot the average cosine squared for the M-T projection can be calculated, ZN: 0.609 and STAR α : 0.546, which is consistent, although of lower value, with the values reported for SAXS for the lamellar structure in the M-T plane (Table 3). This supports a hierarchal structure to the rod-like structures seen in the optical micrographs (Figure 15) with orientation stronger on the nanoscale and becoming more disorganized at larger scale.

Figure 19. Radial plot of intensity versus radial angle for the two films. The average cosine squared for the M-T planar projection is shown in the inset.

3. DISCUSSION

3.1 Molecular Weight Distribution (MWD) and orientation

The ZN film was manufactured from HDPE synthesized using a Ziegler-Natta (ZN) catalyst, while the STAR α film was manufactured from HDPE synthesized using a single-site catalyst. Ziegler-Natta catalysts give HDPE with a broader molecular weight distribution as compared to that obtained from a single-site catalysts [24] (Table 2). From the SAXS and SALS analysis it can be seen that the ZN film has a higher degree of orientation than the STAR α film. This variation in orientation could be related to the molecular weight distribution (MWD). A broader distribution contains more high molecular weight chains. The presence of long chains increases the number of chain entanglements. Hence ZN is expected to display a longer relaxation time and higher orientation due to chain entanglements. Thus the ZN film, with broader MWD, should show more oriented lamellae structures with maximum chain orientation in the direction of stress i.e. the MD. Since the chains pack in the direction of the lamellar normal, this indicates lamellar normal orientation in MD also. The results obtained from the SAXS and SALS analysis are consistent with this model.

5.2 Relation between micron and nano-scale orientation

The micron-scale orientation of linear domains seen in Figures 15, 17 and 19 is normal to the lamellar orientation seen in Figures 9 and 10. The size of the lamellar domains, from SAXS is about 120Å in thickness with a long period spacing of about 170Å. The linear domains are about 1.5 μm (15,000Å) in width and spaced regularly at about 5 μm (50,000Å) from SALS. The SALS results bring up two main questions: 1)

What governs the regularity of the linear domain spacing? and 2) Why are the linear domains orthogonal to the lamellar domains? The second question might be answered by considering the possibility of stacked lamellae or cylindrite structures within the linear domains seen in light scattering and optical microscopy. These cylindrite structures have been observed in blown and oriented HDPE films, and are composed of around 3 to 10 lamella stacked together in blocks with blocks distributed along the fiber [14, 52]. The lamellae in these cylindrite structures are typically oriented with the basal planes almost perpendicular to the MD-TD plane and their surface normals parallel to the MD.

Figure 20. Schematic of the morphological features observed for the ZN film.

Such cylindrite structures are shown in the schematic diagram in Figure 20 and depicted as composing the primary units of the linear structures observed in the optical data. The structure in Figure 20 would explain the orthogonal relationship between the lamellae observed in the SAXS data and the linear structures observed in the SALS data. The ratio in size between the lamella thickness and the linear width is about 2 orders. Then one should consider the linear domains are composed of many cylindrite structures across their width, rather than a single linear domain being associated with a single cylindrite structures.

The regularity in lateral spacing of the linear domains is a far more puzzling question. A high degree of order is necessary to produce the correlation peak seen in Figures 18 and 19. Such order is often due to a balance between thermodynamics and kinetics such as in case of spinodal decomposition. Keith and Padden [13] have considered a possible relationship between transport of impurities or non-crystallizable chains and the lamellar growth rate as an explanation for coarsening in spherulitic crystallites through the del-parameter, $d = D/G$, where D is the diffusion coefficient for non-crystallizable chains or species and G is, in this case, the lateral growth rate for lamellae in the linear structures. The origin of the regularly spaced linear structure observed in the optical data, therefore could be explained by build-up of non-crystallizable species in the regions between the crystalline material. The material with higher impurities i.e. low molecular weight PE or branched chains is likely to show a stronger tendency to form ordered fibrillar structure under this line of reasoning. This could explain the ZN sample showing strong streaks.

A second potential explanation is the spinodal mode of crystallization such as discussed by Strobl [53]. In this model phase separation of species differing in molecular weight or branch content precedes crystallization under the stresses of film blowing operation. Some evidence for the spinodal mode exists from SAXS studies made by Schultz et al. [54] on melt crystallized polypropylene films. The observed micron scale correlation is consistent with sizes expected from spinodal decomposition in polymers.

3.3 Film clarity

The ZN film was cloudy while the STAR α film was transparent and glossy. Both the films were blown under similar conditions. These films had the same degree of crystallinity and almost identical lamellar structure and size. The primary structural factor that varied between the films was the degree of orientation at both the nano and micron scales. Wilkes [24] has indicated that surface roughness is associated with haze in HDPE films. We have verified this using index matching and optical microscopy. In the blown films discussed here the surface structure and the bulk structure are parallel as shown in Figure 15. The rod-like structures of Figure 15 appear to be intimately related to the bulk crystalline morphology on the nano to micron scales. Our data indicates that this structure is consistent with a stacked lamellae or cylindrite morphology [14]. Figure 20 shows a schematic of the regular arrangement of the rod-like structures associated with surface roughness and haze.

From the SALS, SAXS and optical microscopy measurements the surface irregularities and the bulk orientation on the micron scale appear to be linked. Then

surface haze is tied to a hierarchical structure composed of nano-scale oriented lamellae in cylindrite morphologies that cluster into oriented micron-scale streaks governed by Keith and Padden transport/ growth rate laws or spinodal mode morphological development. These oriented, correlated micron scale domains lead to surface roughness in highly oriented systems.

4. CONCLUSION

Two blown films were studied in this work. A ZN film manufactured from HDPE synthesized with a Ziegler-Natta catalyst and a STAR α film manufactured from HDPE synthesized with a single-site catalyst. The ZN film exhibited high haze, while the STAR α film was relatively clear. Both films ZN and STAR α had similar degree of crystallinity and it was found that both films had similar lamellar structures. The primary difference between the films was the degree of orientation i.e. the orientation of the lamellar structures on a nanometer scale.

The lamellar structure and their orientation are important factors in determining the structure-property relations in blown films. The lamellar orientation was determined by SAXS. Although there are prior studies in the literature where lamellar orientation, as determined by small angle x-ray scattering, has been correlated to micro properties such as permeability and tear strength, no such study was found which correlated this lamellar orientation to the macro-scale orientation in the films which in turn affected the optical properties of the film.

The ZN film had lamellae regularly arranged and oriented with normals along the film MD. The film ZN also exhibited micron-scale rod-like structures on the surface, oriented along the film MD. The micron-scale characteristics were determined by SALS and optical microcopy. The lamellar orientation was linked with the formation of micron-scale rod-like structures, which produce roughness on surface of the film. These surface irregularities scatter light and are the cause for the haze observed in the ZN film. The

STAR α film exhibited very similar lamellar structure and size compared to the ZN film but with lower orientation. The STAR α film exhibited much less surface roughness, compared to the ZN film, and was relatively clear due to lower lamellar and associated micron-scale orientation

A new approach to the analysis of 3-d lamellar orientation from SAXS was also presented. The approach takes advantage of the Wilchinsky construction to simplify the comparison of bulk orientation.

5. FUTURE WORK

Transmission Electron Microscope (TEM) study

Although an optical microscopic evidence for the presence of the rod-like crystalline structures on the surface of the ZN film has been presented in this thesis, a more thorough study using a Transmission Electron Microscope (TEM) would be highly advantageous.

Orientation in Polymer-layered Silicate (PLS) nanocomposites

Polymer-layered Silicate (PLS) nanocomposites exhibit outstanding properties that are synergistically derived from the organic and the inorganic component. PLS nanocomposites exhibit superior mechanical properties, [56] reduced gas permeability, [57] and improved solvent resistance [58]. Such hybrids are also believed to offer unique opportunities for understanding the influence of confined polymers on the properties of macroscopic systems. Various other publications [59-65] have studied different techniques for synthesizing PLS nanocomposites. Although the above studies involve either synthesizing PLS nanocomposites or studying the affect of addition of clay on the final properties of the PLS nanocomposites, no study has been made which talks on how these clay layers enhance the final properties. We believe that it is the orientation of these clay layers, which play an important role in determining the final properties. Thus orientation of these clay layers is a issue where much has to be learned.

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