

Morphological Analysis of Linear Low Density Polyethylene Films by Atomic Force Microscopy

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ABSTRACT: Atomic force microscopy has been used to investigate the morphology of hexene linear low density polyethylene (LLDPE) blown film in the undrawn and drawn states. The morphology of the undrawn film, which is biaxially oriented due to the nature of the extrusion process, is composed of crystallites, which consist of aggregates of lamellae. Elongation of the film caused these crystallites to undergo deformation, resulting in the gradual formation of a fibrillar structure in the draw direction. The transformation of these crystallites into fibrils corresponded with an initial increase in the surface roughness, until 250% elongation. Further extension of the film to 450% caused the surface roughness to reach a plateau. The changes observed in the surface roughness and morphology indicate that drawing of the film caused the crystallites to tilt and slip, rupturing crystalline blocks, which then develop into a fibrillar structure. Further extension of these initial fibrillar structures resulted in a more oriented fibrillar morphology. Wide-angle x-ray scattering clearly showed the orientation of the crystals with respect to the draw direction throughout the film. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 777–784, 2002

Key words: linear low density polyethylene; blown film; atomic force microscopy; morphology; tensile properties

INTRODUCTION

Films made from polyethylene for the packaging industry are commonly prepared using the blown film extrusion process. Films produced by this process undergo biaxial orientation, as a consequence of the tubular bubble of film being stretched in the longitudinal direction by the extrusion process, and in the transverse direction due to expansion of the bubble. The bubble of film is cooled by air blown onto the outside of the film. The degree of molecular orientation in the blown film is dependent on a number of factors, includ-

ing the extent of elongation, in both the machine and transverse directions, as well as the rate at which the material is cooled.

Generally, as well as displaying adequate mechanical properties, packaging films must exhibit excellent optical properties, such as high surface gloss and low haze. The principal contributor to haze in both linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) films is surface crystallization, which refers to the formation and subsequent aggregation of the crystallites at the film's surface.^{1,2} Both the inherent properties of the polyethylene, such as molecular weight distribution and branch type, along with the subsequent film blowing process, strongly influences the size of the crystallites.

The development of the atomic force microscope (AFM) now enables profiling of dimensions

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X and Y with a height of Z, providing a direct measurement of the surface roughness. Several reviews on atomic force microscopy and its application to polymer surfaces have been published.^{3,4} Of interest to this study are the number of AFM studies that have focused on the microstructure of polyethylene in various forms, including solution-grown crystals and gel-drawn films.^{5–18} AFM images of dendritic polyethylene crystals have confirmed many of the lamellar morphological features previously observed by electron microscopy, but with enhanced resolution. In particular, Magonov and co-workers¹⁰ have examined the development of fibrillar structures from lamellae, for gel-drawn polyethylene films with draw ratios between 10 and 70 using the AFM. Images of these uniaxial drawn films showed a fibrillar morphology. These fibrils were observed to be composed of a number of units; beginning with the polyethylene chains, the nanofibril is formed as the primary unit, which in turn forms the microfibril, which subsequently group together. These observations are consistent with Peterlin's model for plastic deformation.^{19,20} While many of these atomic force microscopy studies have used forms of polyethylene that due to the nature of preparation are already drawn to a high ratio,^{6–12,16} little research has focused on forms of polyethylene that are not already drawn, such as blown film. Those studies that have used the AFM to probe the surface of blown films have shown that insight into the topography and the influence of the extrusion process, such as the effect of both oxidation¹⁷ and the cooling rate of the film,¹⁸ can be attained.

Typically in application, these blown films are placed under stress ultimately leading to elongation. In this study, the AFM was used to investigate the effect of this deformation process on the morphology and calculated surface roughness from the unstrained state of the film through varying extension until just before fracture. To complement the data obtained from the AFM, wide angle X-ray scattering (WAXS) was used to examine the orientation of the crystalline features.

EXPERIMENTAL

Polymeric Materials

An experimental grade of hexene copolymerized LLDPE supplied by Orica Pty Ltd. was used in

this study. This LLDPE polymerized using a Ziegler–Natta catalyst had a melt flow index of 1.0 and a density of 917 m^{-3} .

Blown Film Processing

Films of the hexene LLDPE resins were prepared by the tubular blown film process, on an Axon AB 35 mm extruder, with a die diameter of 100 mm and a 1 mm die gap. A screw speed of 100 rpm was used. The temperature profile of the extruder was set between 200 and 220°C in the feeding, compression, and metering zones, and between 210 and 230°C at the die. The films were made with a thickness of 22 μm .

Tensile Measurements

Film samples, of 35 mm width, were drawn under ambient conditions using an Instron tensile test instrument (Model 4465). A 100 mm grip distance was used, at a crosshead speed of 500 mm min^{-1} giving a strain rate of 5 min^{-1} . A relatively high strain rate was used to approach that of commercial packaging machines. Films once drawn were left under tension for a period of approximately 18 h to relieve stress.

Atomic Force Microscopy

Sections taken from the midpoint of the stretched films were mounted on a microscope slide, then rinsed with AR grade ethanol followed by Millipore "Milli-Q" water and dried by blowing a steady stream of nitrogen gas onto the sample immediately prior to imaging. This cleaning process aided in the removal of surface debris, such as dust and dirt. Atomic force microscopy measurements were performed using a Nanoscope IIIa controller and a 3100 microscope (Digital Instruments, Inc.). Images of the surfaces of the films were acquired in air under ambient conditions with the AFM operating in tapping mode,²¹ using a Nanoprobe SPM silicon cantilever tip (DNP-100). Tapping mode is the preferred mode for soft polymers, as the lateral shear forces present in contact mode are eliminated, thus minimizing damage to the sample. In tapping mode atomic force microscopy, the cantilever is oscillated close to its resonance frequency. The surface profile of the sample is imaged by monitoring the change in the root mean squared oscillation amplitude of the cantilever during intermittent contact with the surface.

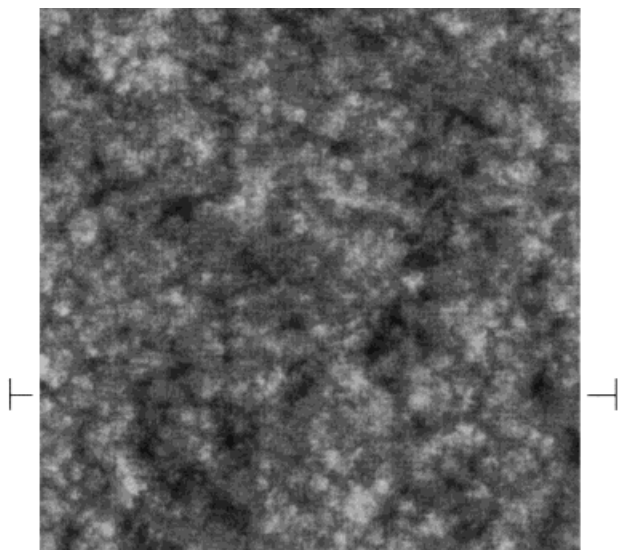


Figure 1 AFM Images of unstretched blown film of hexene LLDPE. Image dimensions are 20 by 20 μm .

WAXS Measurements

The films used in this study were packed to form a block with a sample thickness of 2–3 mm. WAXS data was obtained using a thick block of films to improve the signal intensity. A Rigaku Geigerflex generator was used with a wide angle goniometer. A 30 kV accelerating voltage and 30 mA current was applied using Ni filtered Cu-K α radiation. WAXS intensities were collected between a scattering angle (2θ) of 3° and 50° by transmission. A scanning rate of 2° min^{-1} and a $\Delta 2\theta$ step of 0.05° were applied.

RESULTS AND DISCUSSION

An atomic force microscopy image of the unstrained hexene LLDPE blown film is shown in Figure 1. Images of the blown films were collected of the inner side of the film only. The surface topography did not show any significant difference between the inner and outer sides of the film.

The image reveals that the surface of the blown film is composed of aggregates of crystallites (as indicated by the light regions of the image). The crystallites are approximately 0.5–0.8 μm in size. The shape and dimensions of the crystallites are in accordance with those previously reported for blown hexene LLDPE film, as determined by scanning electron microscopy.¹ The crystallites shown in the image have no distinct orientation in the unstretched state.

Typically, in AFM measurements the surface roughness of the sample is calculated as a root mean squared or RMS roughness, R_{RMS} . R_{RMS} is the geometric standard deviation of the height dimension, Z , within a specified area referenced to a mean plane. The R_{RMS} of the hexene LLDPE film in the unstretched state is $13 \pm 1 \text{ nm}$, indicating that the surface of the film is reasonably smooth.

Figure 2 shows a typical tensile curve for hexene LLDPE blown film, following elongation to 450%, parallel to the machine direction, at ambient temperature. Images were recorded of film stretched to varying extensions, as indicated by arrows on the tensile curve. These extensions cover the region of constant stress following yielding, at both the start and midpoints, as well as the region where the stress rises sharply just before fracture, often referred to as “strain hardening.”

A series of AFM images illustrating the effect of increasing extension, at a constant rate, on the surface morphology of hexene LLDPE blown film, is shown in Figure 3. The images clearly show that extension of the film from 0 through to 450% caused orientation in the surface profiles, with the direction of drawing. The crystallites observed at 0% have transformed to pronounced fibrillar structures by 450%. Transitional morphological features were observed for films drawn at intermediate extensions between 0 and 450%. By an extension of 125%, permanent deformation of the crystallites was observed, with elongation of the crystallites occurring in the draw direction. Extension of the film to 250% led to further elongation of the crystallites. Some transformation of

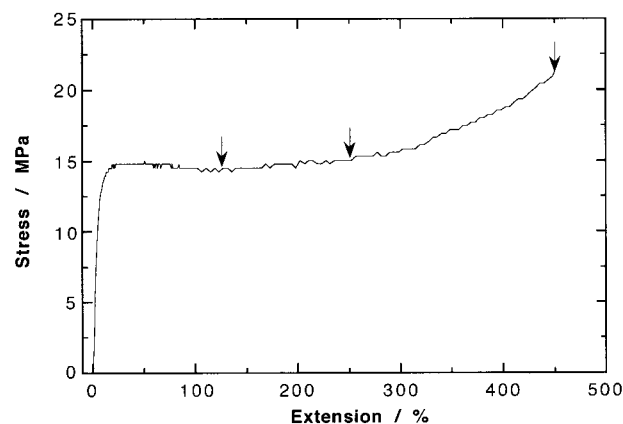


Figure 2 Tensile measurement of hexene LLDPE film recorded under ambient conditions for a cross-head speed of 500 mm min^{-1} .

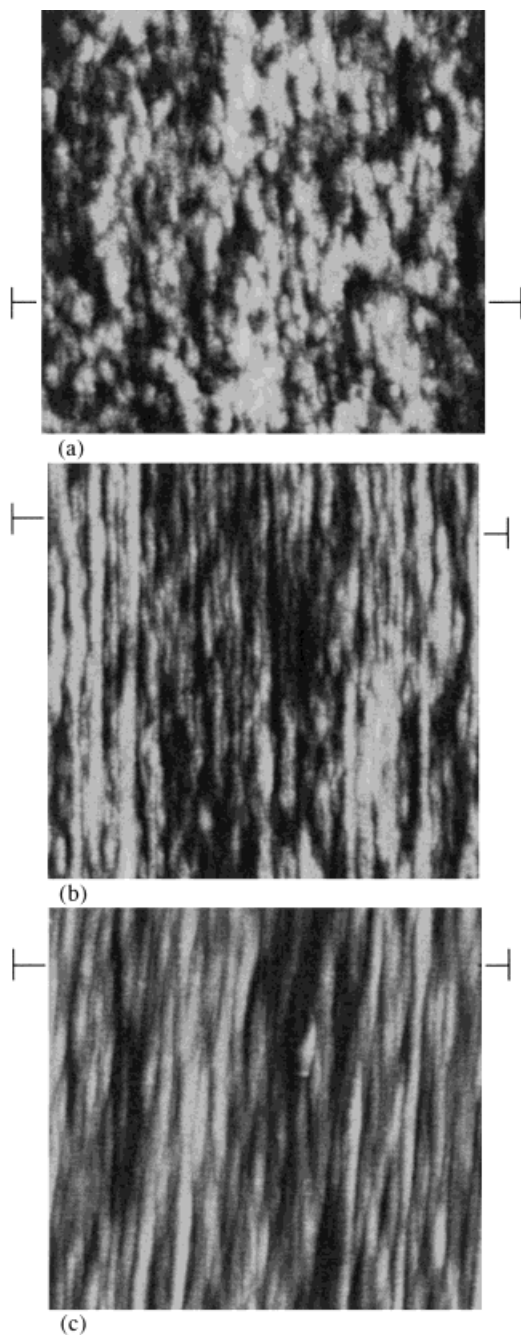


Figure 3 AFM images showing the topographical changes that occur when the hexene LLDPE film is placed under stress ultimately leading to extensions of (a) 125%, (b) 250%, and (c) 450%. Image dimensions are 20 by 20 μm . The draw direction is vertical.

the crystallites into fibrillar structures took place during cold drawing in the region between 125 and 250% elongation. Extension of the film to 450% caused additional extension of both the elongated crystallites and the fibrillar structures,

forming a well-defined fibrillar structure, with no resemblance of the initial crystallites of the undrawn film observed in Figure 1 remaining for the same resolution. The images indicate that the fibrillar structures are composed of material from a number of crystallites.

The orientation of the surface features with the draw direction between 0 and 250% elongation corresponded to an increase in the R_{RMS} from 13 ± 1 nm at 0%, 48 ± 5 nm at 125% to 63 ± 5 nm at 250%. Further elongation of the film to 450% produced a decrease in the R_{RMS} to 53 ± 6 nm.

Cross-section profiles of the hexene LLDPE films of varying extensions were calculated perpendicular to the draw direction. In Figure 4 the deviations in height of the topographical features as recorded by the cross-section profiles are shown. Markers on the AFM images in Figures 1 and 3 show the topographical features that the calculated cross-section profiles incorporate. Initially in the undrawn state the surface topography is flat, with little deviation in the height profile of the surface features. The section profiles illustrate that the initial extension to 125% causes significant disruption to the surface topography, resulting in the production of a number of peaks and troughs in the Z direction. Subsequent extension to 250% leads to a continued increase in intensity, as well as frequency of the topographical features. Comparison of the cross-section profile with the corresponding topographical features of the AFM image indicates that the occurrence of either an elongated crystallite or an individual crystalline fibril corresponds to a steep increase in the height of the topography. The width of the individual fibrils at 450% is typically between 0.7 and 1.2 μm and the frequency of the fibrils is approximately $1 \mu\text{m}^{-1}$. The increase in surface roughness stems from the difference in height between the nonfibrillar regions and fibrillar regions of the extended film, as the height profile indicates that the individual fibrils are relatively smooth.

Further magnification of the extended (450%) LLDPE film highlights that although the surface is smooth, the surface features of the individual fibrils are quite detailed, with the appearance of ridges on the surface as shown in Figure 5. These surface features are of varying shape, size, and orientation, and are on the molecular scale. The fibrils appear to consist of small crystallites or blocks of molecules of 100–300 nm in size with slightly different orientation. In a study of gel-drawn ultrahigh molecular weight polyethylene,

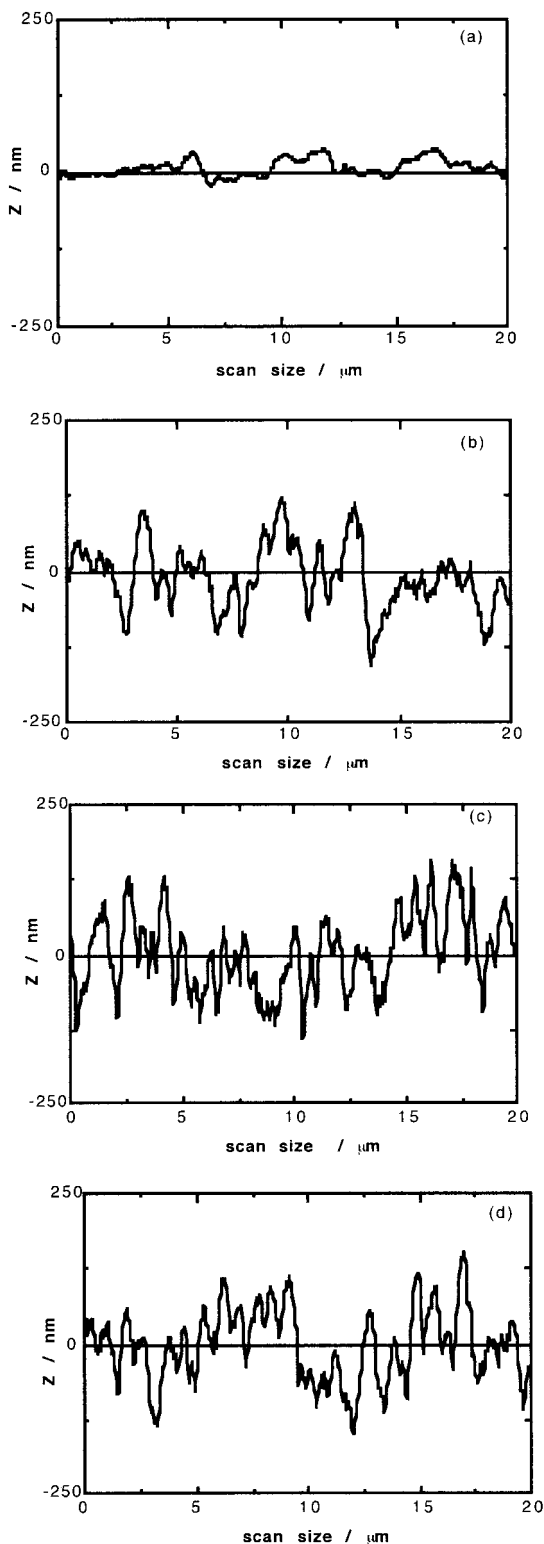


Figure 4 Cross-section profiles of the hexene LLDPE film for (a) the unstretched states, (b) 125%, (c) 250% and (d) 450% extensions.

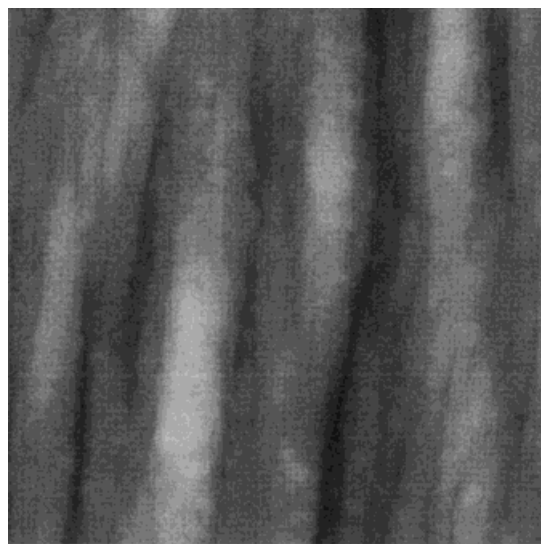


Figure 5 An AFM image of hexene LLDPE film extended to 450%. The image dimensions are 4.2 by 4.2 μm . Draw direction is vertical.

Maganov et al.¹⁰ also observed similar “block-like” features of approximately 100 nm in size composing the “microfibrils” (0.2–1.2 μm), although not well defined. These features, referred to as “nanofibrils,” were thought to be fragments of lamellae.

The orientation of the polyethylene crystals was examined by WAXS, both parallel and transverse to the draw direction, as shown in Figures 6(a) and (b) respectively. In a nonoriented form of crystalline polyethylene, the intensity of the [110] line is approximately 5 times larger than that of the [200] line. In this study, the intensity ratio of the unstrained blown film was reversed, as shown in Figure 6(a), indicating that most of the [110] planes were not in a diffracting position parallel with the machine direction. The low intensity of the [110] diffraction peak indicates that the crystals have a preferred orientation, with the crystallographic a axes oriented mainly parallel with the machine direction. The diffraction lines corresponding to [020] ($2\theta = 35.9^\circ$) were only present for the WAXS recorded in the transverse direction.

Elongation of the LLDPE film resulted in an increase in the intensity of the [110] and [200] peaks in the transverse direction and a decrease in intensity of the peaks in the direction parallel to the draw direction. The size of the crystals perpendicular to the fiber axis can be estimated from the line width. Using the Scherrer equation,²² a maximum diameter of the crystal size

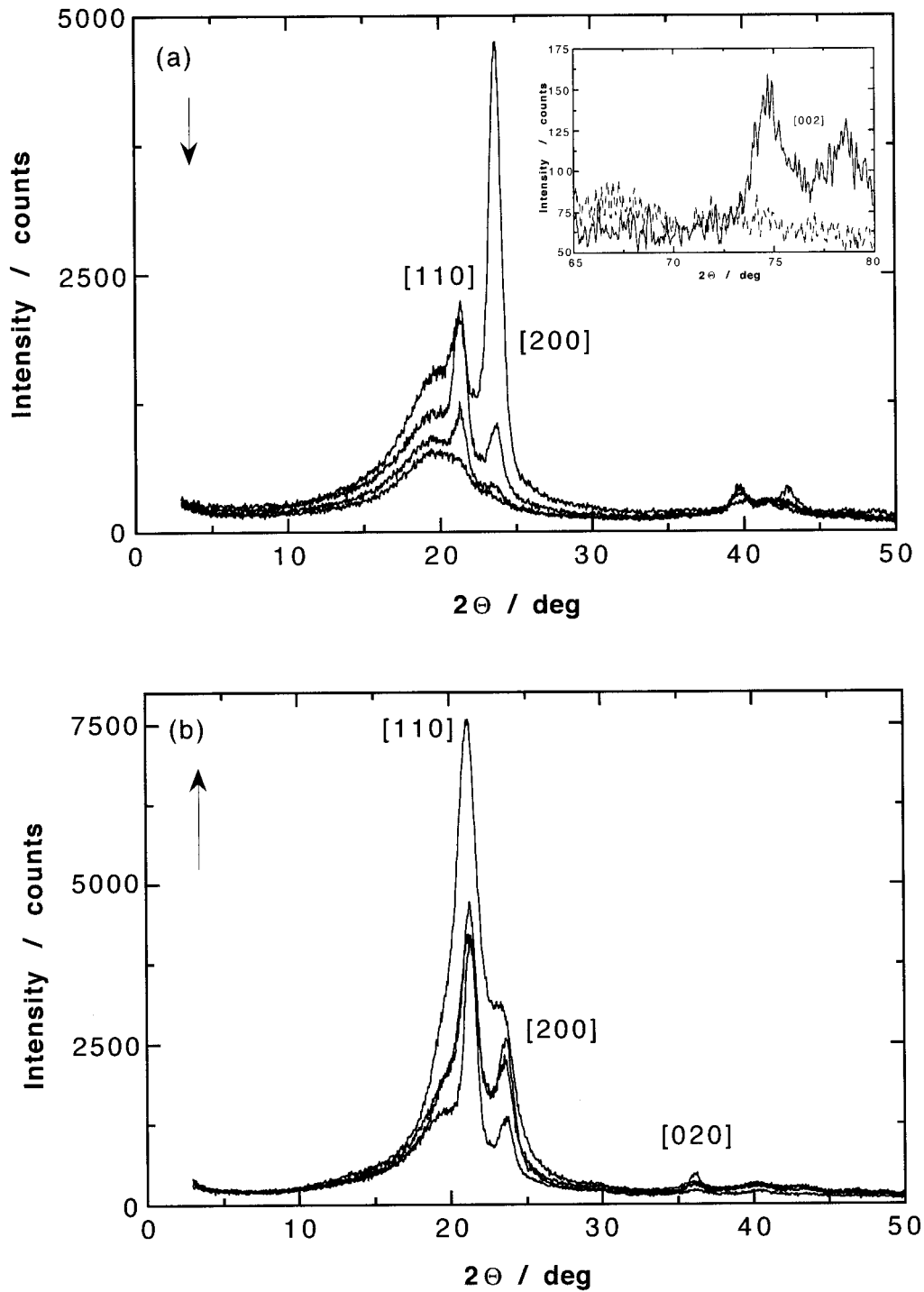


Figure 6 WAXS of LLDPE film of varying extension, taken (a) parallel to the draw direction and (b) perpendicular to the draw direction. The arrows represent an increase in stretching from 0, 125, 250, to 450% extensions. Also shown as an inset in (a) is the data between 65° and 80° recorded parallel (—) and transverse (---) to the draw direction.

was estimated from the line width of the [110] (0.0264 rad) diffraction peak of the unstrained LLDPE film to be 130 and 99 \AA for the film ex-

tended to 450%. Intensities of the peak [002] between a scattering angle of 74° and 78° , shown as an inset in Figure 6(a), increased significantly for

the data taken in the parallel direction, while they are reduced to zero in the transverse direction, indicating that the crystallographic *c* axis is oriented parallel with the draw direction. The crystallographic *c* axis corresponds to the chain axis of the macromolecules, which also means that the molecules are oriented mainly parallel with the direction of the stretch. By 450%, there is complete fiber orientation of the polyethylene molecules parallel with the draw direction. These observations confirm that the morphology observed by AFM at 450% is representative of the bulk properties of the film.

The complexities of molecular orientation in crystalline polymers and the mechanism for the plastic deformation of these polymers have been examined in a number of reviews spanning several decades.^{23–25} The model proposed by Peterlin in the 1960s for the deformation of polyethylene^{19,20} is still the most widely accepted. In this model, it is proposed that drawing of polyethylene leads to permanent deformation of the lamellae causing the lamellae to tilt and slip, thereby rupturing into crystalline blocks. Ultimately, the blocks of chains are incorporated into a fibrillar structure. This model holds for a number of different forms of polyethylene, including crystals (on which the model was originally proposed) and melt drawn films.^{19,20} To date, research examining the effect of plastic deformation on the morphology of blown polyethylene films is less detailed. One of the earliest studies was that by Kobayashi, who proposed that the polymer chains from the tilted lamellae simply unfold in the necking region during drawing of the film, to ultimately form fibrils.²⁶ A study on the morphology of blown high density polyethylene (HDPE) film in relation to tensile properties showed that the lamellae become highly oriented with the draw direction by 400–500%, forming microfibrils of 10 nm in size.²⁷ A small angle X-ray scattering and transmission electron microscopy study of the deformation of blown LLDPE film suggested that the lamellae “rotate and slide” upon yielding. However, no significant change to the morphology was noted until 230% extension, where the lamellae were proposed to rotate causing a reduction in the thickness of the lamellae. It was suggested that drawing of the film caused the amorphous material to undergo orientation leading to secondary crystallization,²⁸ although thermal studies have revealed there to be only a slight increase in the degree of crystallization with elongation.²⁴

In this study it has been shown that deformation occurs by orientation of the crystallites with the draw direction, causing significant disturbance to the topography and surface roughness of the LLDPE film. Transitional morphological features (such as discontinuous elongated crystallites) were observed before the onset of long fibrillar structures. These observations are consistent with the molecular rearrangement of the crystallites, whereby the crystallites tilt and slide, relative to one another. During this process, the elongated crystallites undergo fragmentation to form the fibrillar morphology. The atomic force microscopy images indicate that these fibrillar structures are composed of small crystallites that are reconstructed from a number of different crystallites, although the small crystallites are not highly oriented. WAXS measurements indicate that the molecules are aligned with the draw direction. The plateau in surface roughness with the onset of a well-defined fibrillar morphology indicates that formation of the fibrillar structures are followed by drawing of the individual fibrils. Before this final stage, both fibrillar structures and the drawn crystallite structures coexist.

CONCLUSION

The use of the atomic force microscope to study the topography of blown film of linear low density polyethylene has provided insight into the deformation of the surface topography that occurs when the film undergoes extension. Initial extension of the film caused the crystallites to orientate with the draw direction, resulting in significant disturbance to the surface topography of the film. Even before the onset of “strain hardening” fibrillar structures were observed. Further drawing of the film, to an extension within the “strain hardening” region, produced a more well-defined fibrillar structure. Section profiles taken across the AFM images of the elongated film indicated that the appearance of the fibrils corresponds to an increase in the height of the surface features. Wide angle X-ray scattering confirmed the clear transformation of the original semicrystalline structure to a completely fiber oriented one.

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