In Situ Orientation of Linear Low Density Polyethylene Films Subjected to Mode I Fracture Load

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ABSTRACT: An *in situ* technique has been developed to study the deformation and orientation near a crack tip during Mode I fracture. The technique employs a pair of rotating crossed polar films positioned on either side of the sample. Images gained from transmitted light show kidney shaped process zones ahead of the crack tip that increase in size with deflection, primarily by isotropic expansion. Extinction bands, which are regions of either unoriented material or material oriented in the direction of one of the two polars, are observed as a function of the angular position of the polars with respect to the loading direction. A set of extinction bands at various crossed polar positions provides orientation direction information within the sample. Continuous flow of the molecules around the crack tip is observed at several stages of deformation and for all films tested. The orientation field around the crack tip evolves with increasing radius of curvature of the crack tip. A transition in orientation is observed when the cracks are coincident with the orientation direction of the film but not when they are normal to the orientation direction. The technique of rotating crossed polars is successfully used to determine the orientation direction in the vicinity of a crack tip for linear low density polyethylene during several stages of Mode I loading. The advantage of the technique is that *in situ* data may be collected quickly when compared to techniques such as X-ray scattering, which rely on data collection through scanning and not the parallel data collection utilized herein. The authors acknowledge that this technique is limited to material that transmits light. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 771–777, 2000

Key words: polyethylene; metallocene; birefringence; Mode I; thin films

INTRODUCTION

Large process zones may occur in front of a crack tip for many polymer systems during a Mode I fracture. This is especially true of thin, ductile polymer films subjected to plane stress loading.[1–3] The yield behavior in most polymer systems has been shown to follow a stress-induced, thermally activated flow process.[4,5] Hence, the deformation occurring at and beyond yield can be visualized as a *flow type* process. The stresses at the crack tip are much higher than the nominal stresses and therefore stress-induced plastic flow around the crack tip is expected, which in turn results in molecular orientation.

Extensive work has been done to investigate the molecular changes that occur during deformation in polymers using techniques such as X-ray scattering,[6–10] infrared (IR) spectroscopy,[11–15] and birefringence.[15,16] Birefringence using polarizing films has the advantage of providing molecular orientation information over a much larger area than is possible by techniques such as X-ray diffraction and FTIR. This is useful when charac-

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Table I Property Data for Metallocene and Ziegler–Natta Films

	Ziegler–Natta	Metallocene
Percent crystallinity	28.8	31.7
Melting point (°C)	126.1	116.0
Direction of orientation	Machine direction	Machine direction
Birefringence	1.75×10^{-4}	5.11×10^{-5}

terizing large areas of deformation and orientation, such as in the plastic zone ahead of a crack tip. Furthermore, birefringence data may be collected quickly, which makes it useful for measuring *in situ* morphological changes in materials that occur at a faster rate than the information can be obtained from other methods. For instance, X-ray diffraction may require several minutes of exposure depending on the experimental setup. Finally, birefringence measurements are safe and relatively easy to acquire. However, optical birefringence techniques are limited to materials that transmit visible light such as amorphous polymers or semicrystalline polymer films having small crystalline domains.

The purpose of this research is to evaluate an *in situ* characterization technique based on birefringence. Rotating crossed polar films are used to provide orientation direction information in the vicinity of a crack tip during Mode I loading of linear low density polyethylene (LLDPE) films. We also investigate the influence of initial orientation and chain microstructure on the deformation behavior of the film.

EXPERIMENTAL

Materials and Properties

Two different LLDPE blown films for this research were supplied by Exxon Chemical Company. One film was made from a Ziegler–Natta catalyst and the other from a metallocene catalyst. The metallocene based resin has well controlled branching, while the Ziegler–Natta based resin has branches that are much more randomly placed along the main chain. Both films are nominally 75 μm thick and are slightly oriented in the machine direction (MD), resulting from the blowing process used to produce the films. Several properties for the films are given in Table I. Optical microscopy was used to determine the birefringence and orientation direction of the films. The melting point and percent crystallinity were obtained using differential scanning calorimetry (DSC). Wide angle X-ray scattering was used to determine the crystal structure and also to confirm the percent crystallinity and direction of orientation from the previously mentioned techniques.

Mode I Testing

Rectangular test specimens were cut from the films and secured into grips as shown in Figure 1(a). The film was secured with bolts between a set of two T-shaped stainless steel grips at the top and bottom. A rubber strip was placed between the film and steel grip to ensure that no slipping occurred. The test dimensions of the films were 20 $\times$ 10 cm. A razor blade was used to create a 10-cm crack in the center of the sheet along the length of the film. Two specimens were prepared for each film such that the direction of the notch was in the MD for one specimen and in the transverse direction (TD) for the other. The films were loaded at a constant crosshead speed of 2 mm/min using an Instron 1123 mechanical testing machine. All tests were conducted at room temperature. Polarizing films were mounted on the shaft of an ac electric motor such that they were at an angle of 90° to each other and positioned on either side of the film as shown in Figure 1(b). The electric motor provided a maximum torque of 50 in-lb and rotated the crossed polar films together at a speed of 1.11 rpm. A Zeiss 2000-C stereomicroscope fitted with a color CCD camera was used to acquire images of the process zone at a rate of 2 images/s. Sets of 30 images were taken at periodic points along the load/deflection curve. Lighting was provided by a Fostec light source. The loading rate was sufficiently low so that the degree of deformation in the films changed insignificantly in the time it took to collect a set of images.

Zeiss Image Analysis software was used to create text files containing the red, green, and blue (RGB) values for each pixel in the digital image.

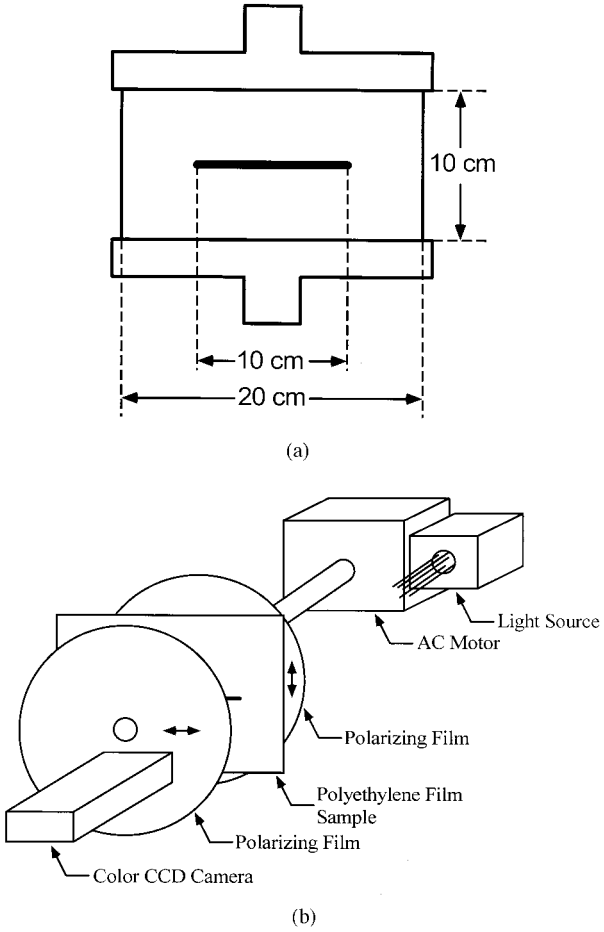

Figure 1 The schematics (a) Mode I test specimen and grips and (b) equipment used for obtaining *in situ* orientation information.

Thirty text files for a given film and deflection were imported into a Fortran program. Each text file contained the RGB pixel values for an image corresponding to a particular angular position of the crossed polars relative to the sample. The Fortran program analyzed the 30 text files and determined regions of extinction based on the RGB pixel values and a preset threshold value for extinction, which was arbitrarily but objectively prescribed. This was necessary because some ambiguity in the extinction band boundary existed. The program then wrote the x, y data pairs for those pixels that it regards as black to an output file. The data from the output files were then used to create orientation direction maps.

RESULTS

Polarizing films are used to characterize the plastic flow of LLDPE films in the vicinity of the crack tip under Mode I loading. Because PE has a polarizable dipole along the main chain, light transmitted through regions of the test sample in which these dipole segments are oriented parallel to either of the polars will be extinguished and consequently appear dark when viewed in transmission. Therefore, by rotating the pair of crossed polars through 45°, regions of oriented material for all directions of orientation may be identified. In this way it is possible to "map out" the orientation in the vicinity of the crack tip. Note that unoriented material always appears black when viewed through crossed polars. For convenience we adopt the following convention for identifying the films and loading conditions. Metallocene films with cracks in the MD and TD directions will be referred to as films A and B, respectively. Ziegler–Natta films with cracks in the MD and TD directions will be films C and D, respectively.

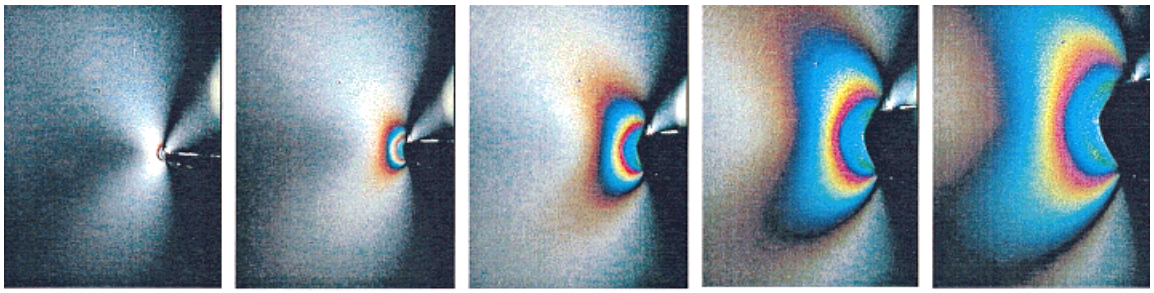

Figure 2 The process zone evolution in film A (metallocene film with crack propagating in MD) as observed through crossed polar films for various deflections. The polars are at 45° and −45° relative to the crack propagation direction.

These samples allow the effect of initial orientation and chain microstructure on the development of molecular orientation near the crack tip to both be investigated.

The process zone ahead of the crack tip is easily observed when viewed through crossed polar films. Figure 2 shows images of the process zone ahead of the crack tip at various deflections for film A. The plastic zone boundary appears to be fairly well defined. Also, the crack tip remains essentially stationary while the process zone increases in an almost self-similar fashion with deflection. Hence, isotropic expansion is the primary elementary motion associated with this damage evolution. A small increase in the height to width ratio of the process zone does increase with increasing deflection, which indicates that distortion also occurs to some extent. The load/deflection curves are given in Figure 3(a,b) for the metallocene and Ziegler–Natta films, respectively. Note that the points on the film A curve of Figure 3(a) corresponding to the images in Figure 2 are marked with solid circles. The similarity between the MD and TD load/deflection curves for both metallocene and Ziegler–Natta resins, as shown in Figure 3(a,b), indicates that the mechanical response of these materials is insensitive to the crack propagation direction. This is probably because the magnitude of the orientation induced during deformation is much greater than the initial orientation in the films. Hence, the weak initial orientation has little effect on the mechanical response of the films. However, note that the load/deflection curves are affected by the type of resin. Complete fracture occurs at a larger deflection with the Ziegler–Natta resin than with the metallocene resin. The area under the load/deflection curve represents the total work per film thickness required to completely tear the film ligaments. Although more formally evaluated tearing energies are planned in the future, initial measurements based on the energy to failure indicate the Ziegler–Natta resin is tougher than the metallocene resin for this mode of tearing.

Several images showing different extinction regions are shown in Figure 4 for film A. The extinction bands in each image correspond to different angular positions of the crossed polars relative to the loading direction. The directions of the polars are shown below each image. Two scenarios are possible to explain the existence of an extinction band. Either the material within the extinction band is unoriented with all surrounding material being oriented or the material inside the extinction band is aligned on average in the direction of one of the two polarizing films. Because extinction bands are observed at different locations within the process zone for different angular positions of the crossed polars, we conclude that the material within extinction bands is oriented. The orientation within the extinction band observed by this technique is a measure of the overall orientation direction, which is a sum of the crystalline and amorphous components of orientation.

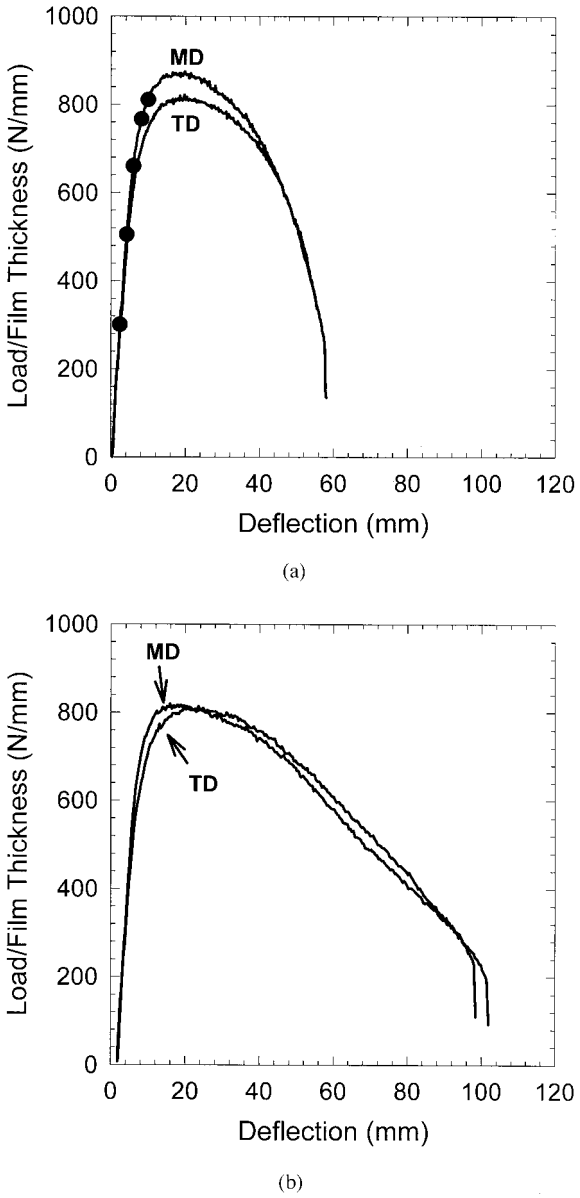

Figure 3 The load per film thickness versus deflection for (a) metallocene and (b) Ziegler–Natta. (●) The deflections at which images in Figure 2 were taken.

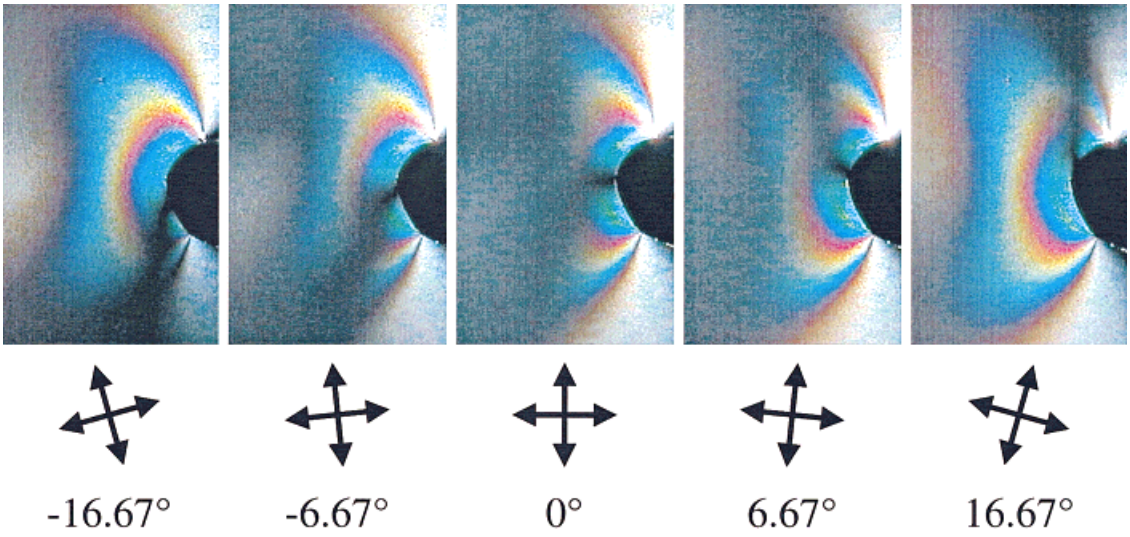

Figure 4 The process zones for film A (metallocene film with crack propagating in MD) showing extinction bands at various crossed polar angles and 8-mm deflection.

Plots were generated using the Fortran program as described in the Experimental section, which consisted of several extinction regions superimposed upon one another. Figure 5 shows these plots for Films A, B, C and D. Four plots are given for each film specimen corresponding to four different deflections (approximately 2, 4, 6, and 8 mm) with the exception of film B, because orientation could not yet be observed at a deflection of 2 mm. Each extinction band is plotted using a different color so that different extinction bands can be distinguished from each other. A color key given in Figure 5 provides the direction of orientation for each color. Therefore, each colored region in each plot in Figure 5 represents an area within which the material is oriented, on average, in one direction. Note that in Figure 5(A4), directional lines have been inserted to illustrate the flow of material around the crack tip.

To determine with which of the two polarizing films the material is aligned we start with the extinction band observed directly in front of the crack tip. This band occurs when the two polars are at 0° and 90° relative to the loading direction. It is expected that the material within this band is oriented in the direction of the applied stress rather than perpendicular to it, because the crack tip and surface are traction free. We then apply continuity across adjacent extinction bands. In other words, we do not expect a sharp discontinuity in orientation to occur between adjacent extinction regions. This analysis yields maps of the orientation direction around the crack tip, which are seen in Figure 5.

A development in the shape of the regions of orientation with respect to the deflection is evident in the plots in Figure 5 for all films. At low deflections the oriented regions are straight bands emanating from the crack tip, which shows material flowing around the crack tip. With increasing deflection the bands become more curved in shape. The crack tip at higher deflections becomes more blunt, resulting in a local stress field that is more influenced by the applied stress and less influenced by the crack tip. Hence, the bands change shape as the material adapts to the more uniaxial stress state. One can imagine that at even higher deflections, when the radius of curvature is quite large, the ligament resembles a rectangular test specimen that is subject to a nearly uniaxial stress state.

A change is also observed with increasing stress in the region in front of the crack tip at approximately between −45° and 45° with respect to the crack propagation direction [see Fig. 5(A1,C1)]. At low stages of deformation several colors exist within this region, indicating the region is unoriented. With increasing deflection the region becomes oriented with the chains predominantly aligned at 0° with respect to the loading direction. Note that this evolution is much more evident with films A and C than with films B and D [compare Fig. 5(A,C) with Fig. 5(B,D)]. This is because the molecules in films B and D are already aligned slightly in the MD, which is in the direction of the applied stress. Hence, the molecules do not have to change direction. Instead they simply become more oriented. However, with

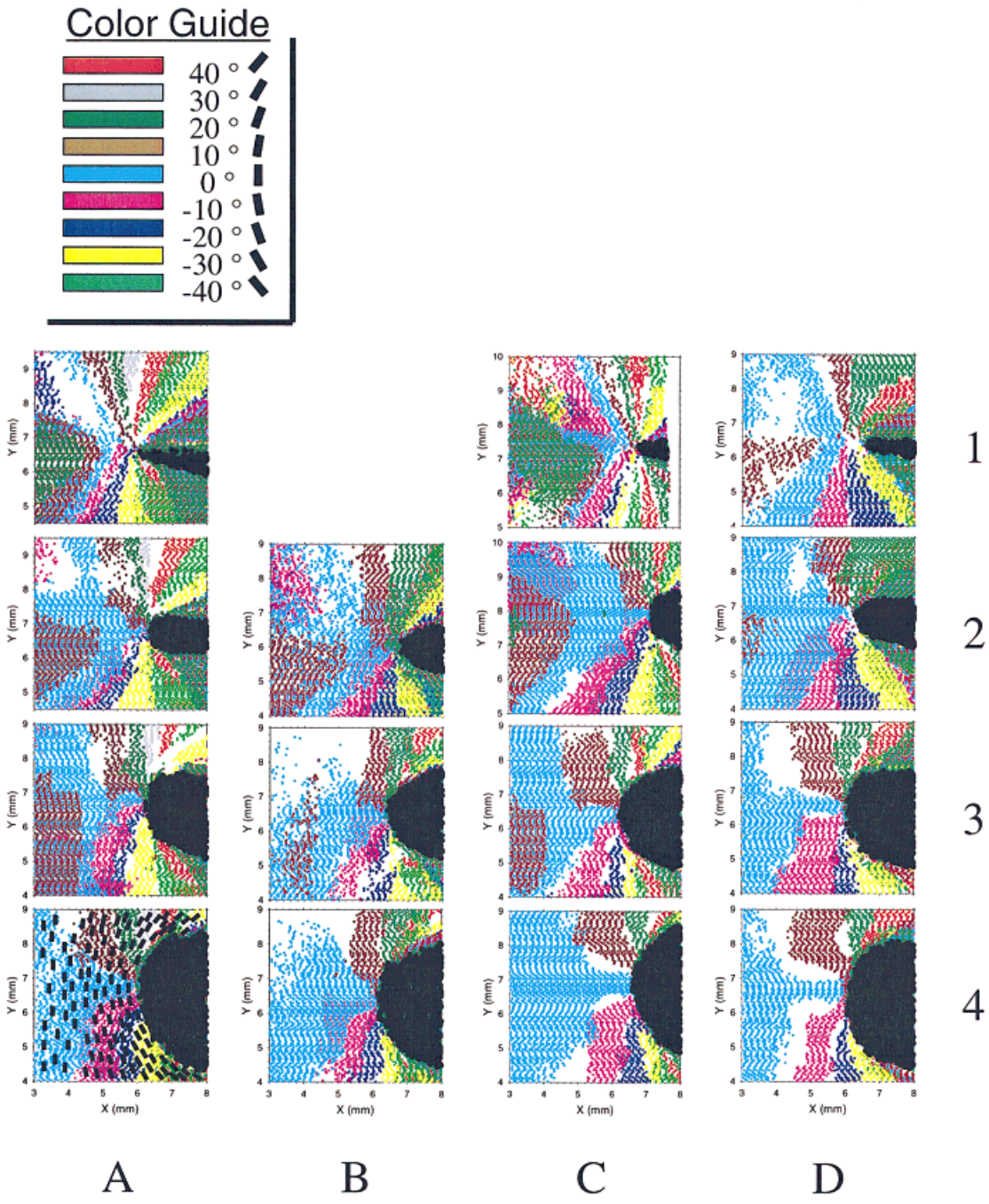

Figure 5 The orientation maps for films A, B, C, and D generated at various deflections. (A4) Directional field lines show molecular flow around the crack tip.

films A and C the molecules undergo a change in direction from being aligned in the MD to the TD, because the applied stress is in the TD. Therefore, a period exists when the molecules pass through an amorphous stage. At higher deflections the molecules realign with the applied stress and an amorphous region is not observed [see Fig. 5(A4,C4)]. Therefore, the initial orientation in the film does influence the deformation ahead of the crack tip up to a deflection of about 8 mm. However, no difference between the two resins is observed from the orientation maps at low stages at deformation. The load/deflection curves for the two resins also appear very similar at low defor-

mation. Only at higher stages of deformation, beyond the maximum in the load/deflection curve when the damage zone boundary has reached the edge of the film specimen, does a change in shape of the load/deflection curve occur, giving rise the increased toughness of the Ziegler–Natta film.

CONCLUSIONS

Kidney shaped process zones are observed ahead of the crack tip that increase with deflection primarily by isotropic expansion. A continuous flow of the molecules around the crack tip is observed at several deflections and for all films tested. Furthermore, the orientation field around the crack tip changes with increasing deflection. As the degree of deformation in the films increases, the orientation bands change from their original linear form to become more curved in shape. This is attributed to the increasing influence of the applied stress as the radius of curvature of the crack tip becomes greater.

An effect of initial film orientation on the orientation fields around the crack tip is observed for both metallocene and Ziegler–Natta films. A transitional region in front of the crack tip is observed for the films that are tested with the crack coincident with the machine direction of the film. The molecules, which are originally slightly oriented in the machine direction, eventually realign in the direction of applied stress. This transitional region is much less evident in the other films because the initial orientation is already in the direction of the applied stress, and hence little molecular reorganization is necessary. No chain microstructure effect on the deformation behavior is observed from the orientation maps at the low stages of deformation. At higher stages of deformation the load/deflection curves for the two resins changes. The Ziegler–Natta resin shows a higher strain to break than the metallocene resin, which suggests that the Ziegler–Natta is tougher for Mode I fracture.

The method of rotating crossed polarizing films is successfully used to generate orientation directional field maps in the vicinity of a crack tip during several stages of Mode I loading for LLDPE films. The use of rotating crossed polar films is not limited to simple Mode I tests. This technique can be used to investigate the *in situ* molecular orientation occurring during deformation under more complicated stress states. For instance, this method could be used to map out orientation fields for the case of several mixed Mode I and II cracks growing in close proximity such that their stress fields overlap.

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