Macromolecules **2001,** *34,* 2015–2017

Characterization of Crystalline Texture of LLDPE Blown Films Using X-ray Pole Figures

Jianjun Lu and Hung-Jue Sue*

Polymer Technology Center, Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843-3123

Received June 13, 2000
Revised Manuscript Received December 14, 2000

Introduction

Polyethylene (PE) blown film is one of the most consumed polymeric materials today. In the film blowing process, polymer crystallization takes place under stress, causing the formation of row-nucleated structures along the extended polymer chains. The resultant film morphology is very different from that of the bulk material. The row-orientation model of Keller and Machin has been widely adopted in the literature to describe the structures of PE blown films.[1] According to this model, two major crystallization processes take place depending upon the magnitude of the stress in the melt, namely “low-stress” and “high-stress” crystallizations. Under low-stress conditions, the lamellae grow radially outward in the form of twisted ribbons, with the crystallographic *b*-axis parallel to their growth axis. As a result of this lamellar growth process, the *a*-axis of the crystal unit cell is oriented preferentially along the machine direction (MD) of the blown film. This texture is referred to as the Keller/Machin I morphology, or *a*-texture. Under high-stress conditions, the radially grown lamellae extend directly outward without twisting. The folded chains (*c*-axis) within the lamellae remain parallel to the extended microfibers, resulting in the *c*-axis being oriented preferentially along the MD. This is referred to as the Keller/Machin II morphology, or *c*-texture. Intermediate stresses will lead to an incomplete twisting of the ribbons. The Keller/Machin I morphology is the most commonly observed morphology in PE blown films.[2–11] The Keller/Machin II morphology has been observed only in HDPE blown films.[8,12,13]

As part of a larger effort to investigate the processing–structure–property relationships in PE blown films, the crystalline textures of two linear low-density polyethylene (LLDPE) blown films were investigated earlier.[14] These films were made from the same resin but under different processing conditions. One film (film A) was made by using a conventional bubble geometry for LLDPE (i.e., a nonstalk bubble configuration), while the other film (film B) was blown by using a stalk bubble configuration. The crystalline texture study was carried out using transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and infrared (IR) dichroism. Compared with the conventional nonstalk bubble geometry for LLDPE blown films, the stalk bubble configuration produces a much more random crystal orientation. For film A, the orientation distribution of crystal unit cells agrees with the typical Keller/Machin I morphology, but the shape and orientation of lamellae agree with the typical Keller/Machin II morphology. This crystalline texture feature is unique and has not been reported in the literature before. It has been speculated that the preferential *a*-axis orientation in the MD is due to the tilt of polymer chains relative to the lamellar normal, and lamellar twisting may not be necessary for the formation of the *a*-texture.[14] This speculation suggests that the row-orientation model of Keller and Machin may need modification. However, experimental evidence for chain tilt was not available then. Since then, the crystalline textures of the two films have been investigated further using X-ray pole figure analysis. Among the commonly utilized techniques for characterizing crystal orientation, X-ray pole figure analysis is most informative and accurate, especially for the characterization of biaxial crystal orientation. In this paper, the results from the X-ray pole figure analysis are presented and discussed, along with the previous experimental findings.

In the X-ray pole figure analysis, the data were collected on a Rigaku DMAX/rapid two-dimensional (2D) image plate system and a Bruker GADDS 2D detector system. Two layers of film were stacked together for the analysis. The (200) and (020) pole figures were obtained by collecting a total of 72 data “frames”. Each frame was collected at a different ϕ value, where ϕ is the rotation angle of the film about an axis along the MD of the film. All the data frames were then integrated for the peak of interest (i.e., *hkl* of interest) with an automatic background removal for each frame using the software developed by AMIA Laboratories (the Woodland, Texas).

Results and Discussion

Before discussing the X-ray pole figure analysis results, some results of other characterization methods[14] are reviewed first. The IR dichroism study showed that the *a*-axis of the crystal unit cell is preferentially oriented along the MD in both films, suggesting that their crystalline textures agree with the *a*-texture. It is also shown that film A has a higher degree of crystal orientation than film B. The SAXS experiments suggested that the long period lies along the MD in both films, and film A has a much higher degree of lamellar orientation.

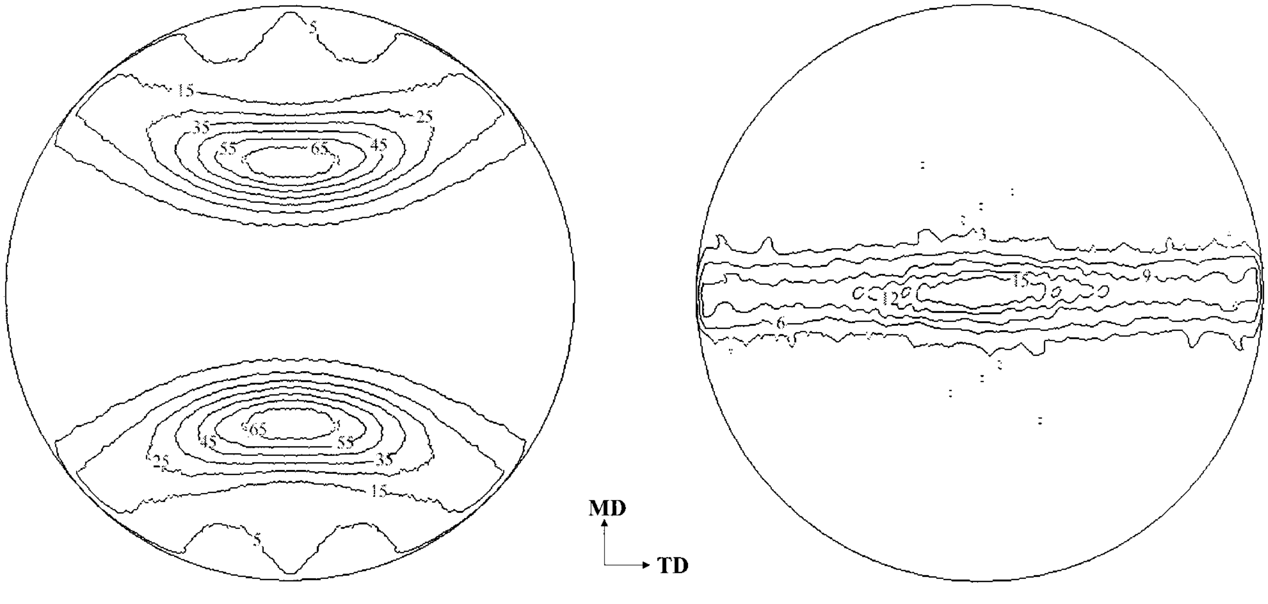
TEM micrographs revealed that the lamellae in film A are predominantly oriented perpendicular to the MD. No significant lamellar twisting can be observed in this film by TEM. On the other hand, TEM showed signs of lamellar twisting in film B. According to the row-nucleation model of Keller and Machin,[1] the preferential *a*-axis orientation along the MD in the Keller/Machin I morphology (or *a*-texture) is due to the twisting of lamellae along the lamellar growth direction, i.e., *b*-axis. However, the shape of the lamellae in film A is more close to that of the Keller/Machin II morphology (or *c*-texture). The crystalline texture in this LLDPE film agrees with neither Keller/Machin I nor Keller/Machin II morphology. Furthermore, based on the Keller/Machin model, film B should have a higher *a*-axis orientation than film A because of the lamellar twisting in film B, but IR dichroism results show the opposite.

To get more accurate information about the crystallographic axes orientations, X-ray pole figure analysis

---

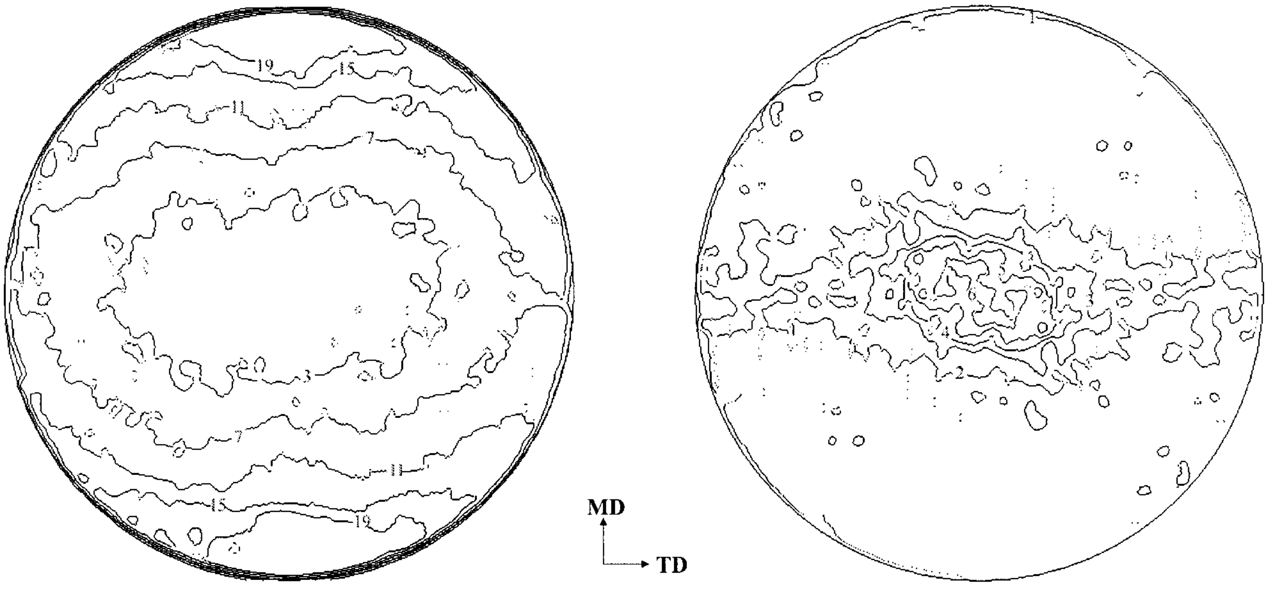
* To whom correspondence should be addressed. Tel (979) 845-5024, Fax (979) 862-3989, E-mail hjsu@acs.tamu.edu.

10.1021/ma001031h CCC: $20.00



(200) (020)

Figure 1. X-ray pole figures for (200) and (020) planes for film A.



(200) (020)

Figure 2. X-ray pole figures for (200) and (020) planes for film B.

of these films was performed. The pole figures of films A and B are given in Figures 1 and 2, respectively. Consistent with the results obtained earlier, the pole figures indicate that film A has a much higher crystal orientation than film B. For both films, the *b*-axis is distributed about the plane of the transverse direction (TD) and the normal direction (ND) and exhibits a maximum around the ND. However, there is an interesting difference in *a*-axis orientation between the two films. In film A, the maximum of the *a*-axis orientation is between the MD and ND and makes an angle of about 46° with the MD, based on the location of the (200) pole maximum. In film B, the *a*-axis distribution shows a maximum around the MD. This suggests that the two films have distinctly different types of crystalline texture.

Table 1. White−Spruiell Biaxial Orientation Factors of Films A and B

film ID	film A	film B	film ID	film A	film B
$f^{B}_{a,\mathrm{MD}}$	0.103	0.318	$f^{B}_{b,\mathrm{TD}}$	−0.165	−0.208
$f^{B}_{a,\mathrm{TD}}$	−0.173	0.122	$f^{B}_{c,\mathrm{MD}}$	0.290	−0.033
$f^{B}_{b,\mathrm{MD}}$	−0.393	−0.285	$f^{B}_{c,\mathrm{TD}}$	0.338	0.086

X-ray pole figure analysis is the only experimental method that allows quantitative analysis of the biaxial orientation of the crystalline phase in PE films. The White−Spruiell biaxial orientation factors[15] obtained from the X-ray pole figure analysis are listed in Table 1. In Figure 3, the biaxial orientation factors are plotted in the form of the White−Spruiell orientation triangle diagram.[15] The White−Spruiell orientation triangle diagram clearly shows that in film A the maximum *a*-,

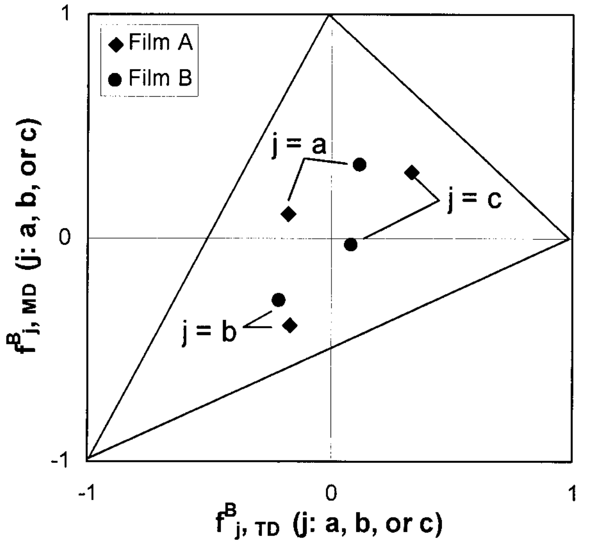


Figure 3. Biaxial orientation factors of the crystal unit cell axes in films A and B plotted in the form of the White−Spruiell orientation triangle diagram.

b-, and *c*-axes orientations are between the MD and ND, between the ND and TD (but closer to the ND), and between the MD and TD, respectively. In film B, the *a*-axis orientation maximum is close to the MD, the *b*-axis orientation maximum is along the ND, and the *c*-axis orientation is nearly random.

If the lamellae are perpendicular to the MD in a film and the polymer chains within the lamellae are perpendicular to the lamellar surface, then the crystal *a*- and *b*-axes will be oriented in the plane of lamella, thus perpendicular to the MD. In film A, the lamellae are flat and perpendicular to the MD, but the maximum *a*-axis orientation makes an angle of about 46° away from the MD. Since the *b*-axis must be oriented within the lamellar plane, the *c*-axis should be oriented at an angle to the lamellar surface. This finding supports our earlier speculation about the chain tilt in the lamellae of film A.

Note that the orientation functions determined by IR dichroism are uniaxial orientation functions. They only give the average orientation of the crystal unit cell axes with respect to a reference direction, in this case the MD. Since the lamellae grow radially from the MD-oriented, extended polymer chains, the direction of chain tilt is distributed around the MD. Thus, the overall result of the chain tilt will be that IR dichroism detects the preferential *a*- and *c*-axes orientations in the MD. Although the *a*-axis orientation maximum in film B coincides with the MD, the *a*-axis orientation function of film A obtained from IR dichroism is still higher than that of film B because of the much higher degree of lamellar orientation in film A.

In the earlier work of Keller and Machin,[1] lamellar twisting was observed directly by TEM. In later investigations of blown film morphology, crystalline texture characteristics were usually determined by other techniques, such as X-ray diffraction, IR dichroism, etc. The presence of *a*-texture is usually taken as an evidence for lamellar twisting (Keller/Machin I morphology). However, the findings in this study suggest that the presence of *a*-texture does not necessarily indicate lamellar twisting.

X-ray pole figures similar to those of film A were also obtained by Maddams and Preedy[7,8,12] for some of their PE films. They interpreted this kind of orientation as the combination of low-stress orientation (*a*-axis orientation) and high-stress orientation (*c*-axis orientation). However, since TEM was not performed on those films, there is no direct evidence to show the existence of two populations of lamellae, i.e., twisted lamellae and row-oriented planar lamellae. The chain-tilt concept provides an alternative way for interpreting the crystal orientation in those PE films. Other researchers also found that molecular chains can orient at an angle to the lamellar normal.[16−18] To experimentally determine the tilt angle of polymer chains, the amorphous regions must be removed using an acid treatment. The remaining crystal fragments can be examined in a transmission electron microscope using electron diffraction[16] or X-ray diffraction[18] techniques. However, these techniques cannot be easily applied to PE films.

In summary, the X-ray pole figure analysis has provided additional evidence to support our earlier speculation in the previous paper.[14] The two LLDPE blown films have distinctly different crystalline textures. Film B has a typical Keller/Machin I type morphology. In film A, the shape and orientation of the lamellae agree with the typical Keller/Machin II morphology. However, the polymer chains within the lamellae of film A tilt away from the lamellar normal, resulting in an apparent *a*-texture as determined by IR dichroism. This suggests that the detection of the *a*-texture does not necessarily imply lamellar twisting, thus the presence of the Keller/Machin I morphology.

Acknowledgment. The authors thank Polyolefins Films Consortium at Texas A&M University for financial support and technical input. Financial support from the National Science Foundation (Grant NSF/CTS-9705467) and the instrument funding from the South Texas Section of SPE are also greatly appreciated. Special thanks are given to Ms. D. Winter at AMIA Laboratories for performing X-ray pole figure analysis.

References and Notes

(1) Keller, A.; Machin, M. J. *J. Macromol. Sci.* **1967**, *B1*, 41.
(2) Desper, C. R. *J. Appl. Polym. Sci.* **1969**, *13*, 169.
(3) Kobayashi, K.; Nagasawa, T. *J. Polym. Sci., Part C* **1966**, *15*, 163.
(4) Haudin, J. M. *Ann. Chim. Fr.* **1980**, *5*, 513.
(5) Ashizawa, H.; Spruiell, J. E.; White, J. L. *Polym. Eng. Sci.* **1984**, *24*, 1035.
(6) Walenta, E.; Janke, A.; Hofmann, D.; Fanter, D.; Geiss, D. *Acta Polym.* **1986**, *37*, 557.
(7) Maddams, W.; Preedy, J. *J. Appl. Polym. Sci.* **1978**, *22*, 2721.
(8) Maddams, W.; Preedy, J. *J. Appl. Polym. Sci.* **1978**, *22*, 2739.
(9) Choi, K.; Spruiell, J. E.; White, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 27.
(10) Kwack, T. H.; Han, C. D.; Vickers, M. E. *J. Appl. Polym. Sci.* **1988**, *35*, 363.
(11) Pazur, R. J.; Prud'homme, R. E. *Macromolecules* **1996**, *29*, 119.
(12) Maddams, W.; Preedy, J. *J. Appl. Polym. Sci.* **1978**, *22*, 2751.
(13) Yu, T. H.; Wilkes, G. L. *Polymer* **1996**, *37*, 4675.
(14) Lu, J.; Sue, H.-J.; Rieker, T. P. *J. Mater. Sci.* **2000**, *35*, 5169.
(15) White, J. L.; Spruiell, J. E. *Polym. Eng. Sci.* **1981**, *21*, 859.
(16) Keller, A.; Sawada, S. *Macromol. Chem.* **1964**, *74*, 190.
(17) Khoury, F.; Bolz, L. H. In *38th Annual Proceedings of the Electron Microscopy Society of America, San Francisco, CA*; Baily, G. W., Ed.; Claitors: Baton Rouge, 1980; p 242.
(18) Varnell, W. D.; Ryba, E.; Harrison, I. R. *J. Macromol. Sci., Phys.* **1987**, *B26*, 135.

MA001031H