Biaxial Orientation Characterization in PE and PP Using WAXD X-Ray Pole Figures, FTIR Spectroscopy, and Birefringence

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ABSTRACT: In this study, different polyethylene and polypropylene films (LDPE, LLDPE, HDPE, and PP) are produced using different processes (film blowing and biaxial orientation) and processing conditions. The orientation of the films is characterized in terms of their biaxial crystalline, amorphous, and global orientation factors using birefringence, Fourier transform infrared spectroscopy (FTIR) using a tilted incidence technique, and X-ray pole figures. The results indicate that FTIR overestimates the crystalline orientation factors, particularly for the crystalline *a*-axis. Significant discrepancies are also observed for the *b*-axis orientation, which may be due to an overlap of the amorphous contribution and/or saturation of FTIR bands. These differences are larger for films with low orientation, such as blown films. Amorphous phase orientation from FTIR depends on the band used and is not necessarily in agreement with that determined from the combination of X-ray and birefringence.

KEY WORDS: polyolefin films, biaxial orientation, X-ray diffraction, FTIR, birefringence, crystalline, amorphous.

INTRODUCTION

The production of oriented films from thermoplastic materials represents a large segment of the polymer industry. In fact,

*This paper was originally presented at the Films and Fibers 2004 Symposium of the National Research Council of Canada, which was held in Boucherville, Quebec, Canada in September 2004.
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8756-0879/05/02 0115–12 $10.00/0 DOI: 10.1177/8756087905056865

orientation of polymers enhances many of their properties [1–5], particularly mechanical, impact, barrier, and optical. Biaxial orientation has the added advantage of allowing this enhancement in both directions. One of the commonly used polymers in biaxial orientation processes is polyethylene (PE). The most widely used biaxial orientation processes for films are the standard film blowing process (such as for PE), tubular film blowing (such as for PP and LLDPE), and cast film biaxial orientation or tentering (PP, PS, PET, etc.).

The structure and orientation developed during these processes have a significant effect on the properties of the films. Different techniques can be used to determine the structure and orientation of the films. Microscopy gives an overall picture of the crystalline morphology (lamellar, spherulitic, etc.), X-ray pole figures yield details of crystalline phase orientation, Fourier transform infrared spectroscopy (FTIR) allows the determination of specific orientation factors for the crystalline and amorphous phases [6], and birefringence gives the average total orientation. For the particular case of PE, FTIR allows the determination of crystalline axes orientation as well. However, the accuracy and precise significance of the different orientation factors determined from these techniques are to be established, although some studies in the past addressed this issue partially [7–12]. In this study, we compare the results obtained for biaxial orientation factors of different PE films (both blown and biaxially oriented) using the FTIR, X-ray, and birefringence techniques.

EXPERIMENTAL

For blown films, polyethylenes (PEs) and polypropylenes (PPs) were used. For PEs, films from three resins were prepared: low-density polyethylene (LDPE, with a melt index of 0.75 g/10 min and a density of 0.92 g/cm^3), linear low-density polyethylene (LLDPE, with a melt index of 1.0 and a density of 0.918), and high-density polyethylene (HDPE, with a melt index of 0.34 and a density of 0.955). For PPs, three resins provided by Basell Company were used: a polypropylene homopolymer (homo-PP, Pro-fax PDC 1280 with a melt flow rate of 1.2 and a density of 0.902), a clarified PP random copolymer (Co-PP, Pro-fax-SR257M with a melt flow rate of 2.0 and density of 0.902) and a high melt strength PP designed for the blown film process (HMS-PP, Adflex KS353P with a melt flow rate of 0.45 and density of 0.882). The films were produced using an extrusion blown film line from Brampton Engineering (details of the equipment can be found in [6]). The extrusion

temperature profile ranged from 160 to 220°C. The extrusion blowing parameters used were a draw down ratio (DDR) of 12, a blow up ratio (BUR) of 2, a frost line height (FLH) of 70 cm, and an extrusion flow rate of 10 kg/h (the thickness of the resulting blown films was about 25 μm, the die diameter was 10 cm, and the gap used was 1.1 mm).

Initial samples for biaxial stretching were prepared by cast film extrusion for LLDPE and HDPE and by compression molding for LDPE. The initial thickness was in the range of 0.5–1 mm. The stretching conditions were a stretch rate of 10%/s simultaneous, an initial sample size of 10 × 10 cm, a stretch temperature of 106°C for LDPE, 120°C for LLDPE, and 127°C for HDPE. The final draw ratio was 4 × 4.

The morphology of the films was determined using a field emission scanning electron microscope (FE-SEM) with and without etching the films and a minimal coating on the surface (the details of the film preparation for SEM can be found in [6]). The global biaxial orientation factors were determined using birefringence. The absolute values of birefringence in the machine-normal and the transverse-normal planes were measured by an incident multi-wavelength double beam and photodiode array assembly, combined with an in-house developed software. Details of the technique can be found in [13,14]. The crystallinity was determined using a differential scanning calorimeter (DSC-7) at a heating rate of 20°C/min in the first scan.

The biaxial orientation factors used in this study are those of Hermans – $f_{j\mathrm{M}}$, $f_{j\mathrm{T}}$, and $f_{j\mathrm{N}}$ in the machine, transverse, and normal directions, respectively for the axis j. Relation can be developed between these orientation functions and other measurable quantities, such as birefringence. Assuming $\Delta^\circ = n_c - (n_a + n_b)/2$ (is about 0.058 for PE) and $\delta^\circ = n_a - n_b$ (is about −0.003 for PE), where n_a, n_b, and n_c are the refractive indices along the a-, b-, and c-axes of the crystalline lattice, the following equations for the crystalline phase have been obtained [14]:

$$(\Delta n_{\mathrm{MN}})_{\mathrm{C}} = \frac{2\Delta^\circ(f_{c\mathrm{M}} - f_{c\mathrm{N}})}{3} + \frac{\delta^\circ(f_{a\mathrm{M}} - f_{a\mathrm{N}} - f_{b\mathrm{M}} + f_{b\mathrm{N}})}{3} \tag{1}$$

$$(\Delta n_{\mathrm{TN}})_{\mathrm{C}} = \frac{2\Delta^\circ(f_{c\mathrm{T}} - f_{c\mathrm{N}})}{3} + \frac{\delta^\circ(f_{a\mathrm{T}} - f_{a\mathrm{N}} - f_{b\mathrm{T}} + f_{b\mathrm{N}})}{3} \tag{2}$$

The total birefringence is that due to both crystalline and amorphous phases, if ϕ is the crystalline birefringence, then, we can write:

$$\Delta n_{\mathrm{MN}} = \phi \cdot (\Delta n_{\mathrm{MN}})_{\mathrm{C}} + (1 - \phi) \cdot (\Delta n_{\mathrm{MN}})_{\mathrm{A}} \tag{3}$$

the indices A and C represent the amorphous and crystalline phases, respectively. It is then possible to determine the crystalline

phase birefringence from crystalline axes orientation, and amorphous phase birefringence by subtraction of the crystalline contribution from the total birefringence by using the above-mentioned equations (neglecting the form contribution).

The crystalline axes orientation factors were determined from wide angle X-ray diffraction pole figure measurements using Bruker equipment (model D8 Discover Gadds). They were also determined, in addition to those of the amorphous phase, from FTIR. The measurements were carried out on a Nicolet 170SX FTIR at a resolution of 4/cm with an accumulation of 128 scans. Polarization of the beam was performed using a zinc selenide wire grid polarizer from Spectra-Tech. The details on this method and the calculation procedure were reported in [6,15].

RESULTS AND DISCUSSION

Typical results from X-ray pole figures, FTIR, and SEM microscopy are shown in Figures 1–3 for blown films and in Figures 4 and 5 for biax films. The quantitative results obtained on orientation factors for crystalline axes as well as the amorphous phase for the polyethylenes are summarized in Tables 1–3.

We first compare the crystalline axes orientation determined from FTIR and X-ray pole figures for blown films. They all agree qualitatively, but in quantitative terms, significant differences are observed. In fact, for the crystalline a-axis for example, all the values confirm that it is oriented towards the machine direction (MD) for all the films with much higher values from FTIR; there are similar values for LDPE and HDPE and significantly lower values for LLDPE. A lamellar row nucleated structure has been obtained in all the cases, but with much less

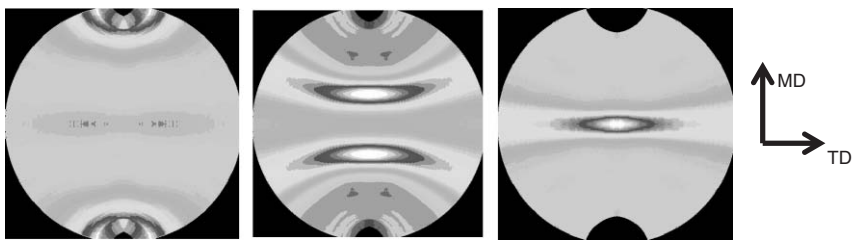


Figure 1. Typical pole figure for an LDPE blown film.

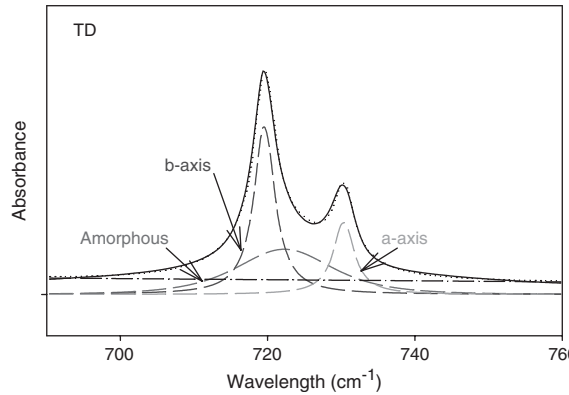
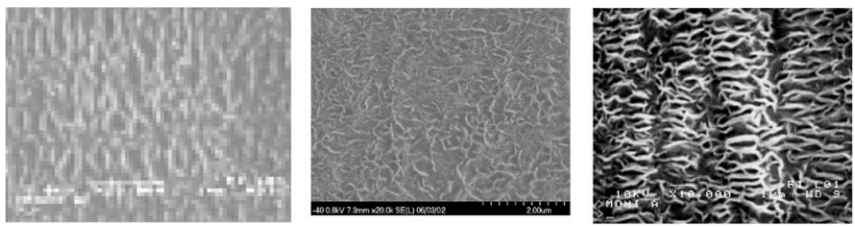
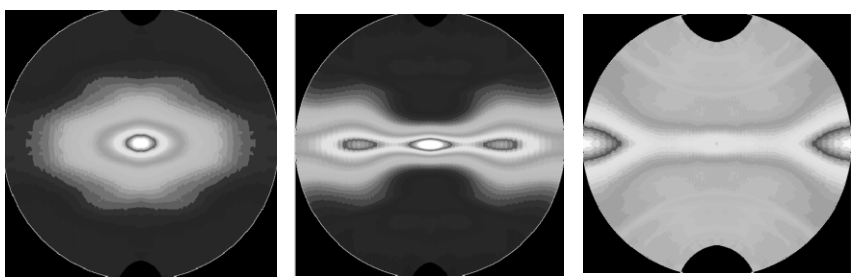


Figure 2. Typical infrared spectra (in TD) used for the calculations of the crystalline axes, amorphous phase, and global orientation factors for an LDPE film.



(LDPE) (LLDPE) (HDPE)

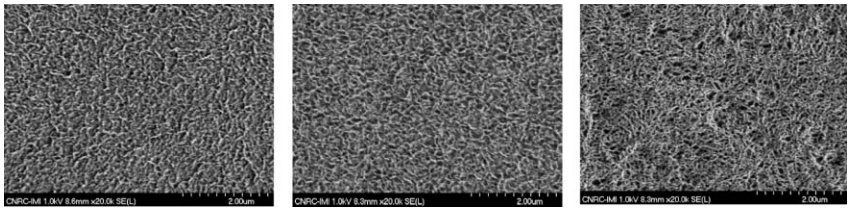
Figure 3. Typical micrographs of blown films.



(200) (110) (020)

Figure 4. Typical pole figure for an HDPE biax film.

row order for LLDPE as illustrated in Figure 3. The difference between the different materials is hence reproduced by the two techniques. The high values obtained from FTIR are mainly due to the intensity of the peak for the MD spectrum and possible overlap with the *b*-axis and



(LDPE) (LLDPE) (HDPE)

Figure 5. Typical micrographs of biax 4 × 4 films.

the amorphous phase peaks as clearly seen in Figure 2. For the transverse direction (TD) spectrum, the peak due to the *a*-axis is much weaker than that in MD, the values are generally low and the differences with those obtained from X-ray pole figures are less significant.

For the *b*-axis, the values indicate a preferential orientation in the TD–ND plane. It should be mentioned however that the results obtained for HDPE for the *b*- and consequently the *c*-axes orientation factors are not in agreement with those obtained for LDPE and LLDPE. This may be due to the fact that the *b*-axis band in the TD spectrum obtained for HDPE was saturated. For the *c*-axis, which was determined from the combination of the *a*- and *b*-axes orientations, the results indicate that it is slightly oriented in the MD (except for the FTIR results of HDPE, as mentioned above).

For biaxially oriented films (Table 2), the results obtained for the different orientation factors, measured total birefringence and calculated crystalline and amorphous phase birefringence for the three PEs showed also that the crystalline *a*-axis orientation determined from FTIR is higher in both the MD and TD directions, but with the same sign (negative), indicating that the *a*-axis is basically in the normal direction in all the cases. For the *b*-axis, it is a little more complex: FTIR indicate that it is in the MD–TD plane, except for HDPE, where it is basically in TD, whereas X-ray indicates that it is in the ND–TD plane, except for LDPE where it would be located basically in ND. For the *c*-axis, both the techniques indicate that it is located in the MD–TD plane, which is expected. This is in agreement also with the birefringence results. The numerical values are however quite different from both the techniques.

Using the equations mentioned previously, one can combine the crystalline axes orientation factors determined from both the techniques and measured birefringence to determine the birefringence of the crystalline and amorphous phases, as shown in Table 3. It is

Table 1. Crystalline orientation factors determined from the different techniques for the different blown PE films, DDR = 12 and BUR = 2.

Polymer	Technique	MD orientation factors			TD orientation factors			ND orientation factors		
		***a*-axis**	***b*-axis**	***c*-axis***	***a*-axis**	***b*-axis**	***c*-axis***	***a*-axis**	***b*-axis**	***c*-axis***
LDPE	FTIR	0.324	−0.361	0.037	−0.137	0.141	−0.004	−0.187	0.220	−0.033
	X-ray, BC, and AC	0.100	−0.117	0.017	−0.043	0.021	0.022	−0.058	0.096	−0.038
		–	−0.212**	0.112	–	0.071**	−0.028	–	0.157**	−0.099
LLDPE	FTIR	0.136	−0.185	0.049	−0.031	−0.012	0.043	−0.105	0.197	−0.092
	X-ray, BC, and AC	0.033	−0.138	0.105	0.016	0.024	−0.040	−0.049	0.114	−0.065
		–	−0.106**	0.073	–	0.027**	−0.043	–	0.094**	−0.045
HDPE	FTIR	0.341	−0.208	−0.133	−0.043	0.400	−0.357	−0.298	−0.192	0.490
	X-ray, BC	0.096	–	–	−0.011	–	–	−0.085	–	–
		–	−0.209**	−0.113	–	−0.095**	−0.084	–	−0.130**	−0.045

BC, background corrected; AC, absorption corrected.

*Indicates *c*-axis calculated from *a*-axis and *b*-axis; **indicates (020) calculated from (200) and (110).

Table 2. Crystalline orientation factors determined from the different techniques for the different biax PE films, 4 × 4.

Polymer	Technique	MD orientation factors			TD orientation factors			ND orientation factors		
		a-axis	*b*-axis	c-axis	*a*-axis	*b*-axis	c-axis	*a*-axis	*b*-axis	c-axis
LDPE	FTIR	−0.157	0.105	0.052	−0.168	0.059	0.109	0.325	−0.164	−0.161
	X-ray, NC	−0.117	−0.006	0.123	−0.109	−0.013	0.121	0.226	0.019	−0.245
LLDPE	FTIR	−0.204	0.081	0.123	−0.190	0.091	0.099	0.394	−0.172	−0.222
	X-ray, BC, and AC	−0.140	−0.080	0.220	−0.028	0.062	−0.034	0.168	0.018	−0.186
		–	−0.154*	0.294	–	0.100*	−0.072	–	0.069*	−0.237
HDPE	FTIR	−0.283	−0.128	0.331	−0.275	0.106	0.169	0.558	−0.057	−0.501
	X-ray, BC, and AC	−0.247	−0.113	0.360	−0.034	0.090	−0.056	0.281	0.024	−0.305
		–	−0.224*	0.471	–	0.147*	−0.113	–	0.093*	−0.374

BC, background corrected; AC, absorption corrected.

*Indicates *c*-axis calculated from *a*-axis and *b*-axis; **indicates (020) calculated from (200) and (110).

Table 3. Amorphous orientation factors determined from the combination of the different techniques for the different biax PE films, 4 × 4.

	Polymer	Crystallinity (%)	f_M	f_T	f_N
Amorphous orientation factors from FTIR	LDPE	46.0	0.131	0.076	−0.207
	LLDPE	48.1	0.116	0.049	−0.165
	HDPE	80.5	0.166	−0.420	0.254

Calculated orientation	Amorphous	f_M			f_T			f_N		
		XR1	XR2	FTS	XR1	XR2	FTS	XR1	XR2	FTS
Calculated amorphous orientation from X-Ray or FTIR and birefringence	LDPE	0.085	–	0.144	0.095	–	0.100	−0.180	–	−0.244
	LLDPE	0.215	0.142	0.303	0.031	0.062	−0.098	−0.246	−0.204	−0.205
	HDPE	0.553	0.087	0.671	−0.114	0.092	−1.075	−0.439	−0.179	−0.404

XR1 are X-ray results with background and absorption correction, *a*-axis determined from (200), *b*-axis determined from (020), and *c*-axis calculated from *a*- and *b*-axes. XR2 are X-ray results with background and absorption correction, *a*-axis determined from (200), *b*-axis determined from the combination of (200) and (110), and *c*-axis calculated from *a*- and *b*-axes. FTS are results from FTIR.

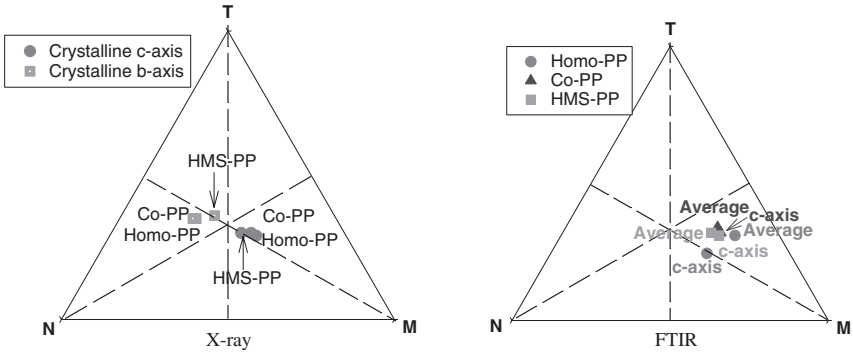


Figure 6. Triangular plots of orientation functions for different polypropylenes obtained using X-ray and FTIR.

clear that the results obtained for HDPE from FTIR are definitely not acceptable, whereas those obtained for LDPE and LLDPE from both the techniques seem reasonable. The amorphous orientation obtained from FTIR for LDPE indicates a higher orientation in MD than in TD, whereas that from X-ray and birefringence as well as the combination of FTIR and birefringence indicates the reverse, which indicate that the accuracy of the determination of amorphous orientation from FTIR is questionable.

For polypropylenes (three different resins), results obtained for the crystalline *c*-axis from both X-ray and FTIR are compared in triangular plots, shown in Figure 6. They clearly indicate the differences between the two techniques as well. In this case, crystalline *a*- and *b*-axes could not be obtained from FTIR and only the *c*-axis could be compared. For homo-PP, FTIR and X-ray results are close whereas for Co-PP and HMS-PP, clear differences are observed. This may be due to the higher level of orientation in homo-PP.

CONCLUSIONS

The determination of the biaxial orientation factors of polyethylenes and polypropylenes using different techniques can yield different results. FTIR may overestimate significantly *a*-axis orientation and in some cases, the results can be wrong. Amorphous orientation obtained from FTIR may also be questionable.

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BIOGRAPHIES

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Abdellah Ajji earned his MScA and PhD in Chemical Engineering from Ecole Polytechnique de Montreal and has worked in research and development on polymers, particularly orientation of polymer films, fibers and parts, rheology and polymer blends for the last 18 years. He is currently a Senior Research Officer at the Industrial Materials Institute of the National Research Council, Canada and has published over 75 papers in peer-reviewed scientific journals.

Saïd Elkoun

Saïd Elkoun got his PhD in Materials Science from the University of Science and Technology of Lille in France in 1998. Then, he taught polymer physics at the Ecole des Mines de Nancy in France from 1999 to 2001. From 2001 to 2004, he worked as a research associate at the Industrial Materials Institute of the National Research Council of Canada where his research activities focused on the characterization of orientation, structure development, and physical performances of polymer films. He recently joined the polymer group at Lille University.

Xiaomin Zhang

Xiaomin Zhang got his PhD from the Chinese Academy of Science. He has been working in the fields of polymer reactive blends, thermodynamics and polymer orientation. He worked as a research associate at the Industrial Materials Institute of the National Research Council, Canada from 2000 to 2003 and he is currently a research scientist at GE R&D labs in Shanghai.