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INFLUENCE OF THE STRETCHING IN THE CRYSTALLINITY OF BIAXIALLY ORIENTED POLYPROPYLENE (BOPP) FILMS

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The production of biaxially oriented polypropylene (BOPP) films, by tenter-frame technology in its different steps, was studied to find the crystalline morphology of these films. DMA, DSC, and WAXD measurements and tensile tests were carried out for the cast film, the mdo film (the produced film in the machine direction orienter unit) and BOPP film. The obtained results suggest that the stretchings lead to a strong alignment of the crystals, producing fibers oriented in the stretching direction. This fact can be proved by WAXD, DMA, and tensile tests, moreover the DSC technique is not sensitive to detect these changes.

Keywords: *films, isotactic polypropylene, orientation, stretching*

Introduction

Isotactic polypropylene (i-PP) is a semicrystalline polymer that it has been widely used since 1960. It was described by Natta and his coworkers in 1955. Natta himself and his coworkers determined, using the WAXD technology (Wide Angle X-ray Diffraction), the structure of i-PP as a monoclinic unit cell [1–3]. With this technique, they observed the following reflections for the called α-form: (110) at $2\theta\cong14°$, (040) at 17°, (130) at 18.5°, (111) at 21.4°, and (–131) at 21.8°.

In 1959, Keith *et al*. [4] found another crystalline morphology in polypropylene, with peaks at $2\theta\cong16°$ by the diffraction plane (300), and $2\theta\cong21°$ by the diffraction plane (301). A hexagonal structure for the unit cell was suggested. This crystalline morphology was called β-form, to distinguish it from the previous α-form. In the same year, Natta *et al*. [5] found out another form of polypropylene with two broad peaks. This form was described as smectic. Later, a new form (γ-form) was suggested by Addink and Beintema [6].

i-PP is a very light thermoplastic with excellent mechanical properties. Its chemical structure, based on C and H, gives it a good chemical resistance. This fact has given rise to important uses of the polypropylene.

Biaxially oriented polypropylene (BOPP) film is manufactured basically by two technologies: tubular process (double-bubble process) and tenter-frame process. In both cases, a wide distribution of molecular mass is required to assure the better rheological properties during the extrusion process. The orientation, by stretching, is specially important in these films, for an improvement in many of its mechanical, barrier and optic properties.

Recently, studies about crystallization of polypropylene [7, 8] and of BOPP films, industrially obtained, were carried out using thermal analysis techniques and WAXD methods by Yuksekkalayci *et al.* [9] and Elías *et al*. [10], who have studied the effect of a nucleating agent and of the conditions of processing on the properties of BOPP films.

The object of this paper is to study and characterize the crystalline morphology in the different steps of the production of three-layer BOPP films by tenter-frame technology. A good knowledge of the relationships between structure and properties in different steps of the production of BOPP films will be used as feedback to improve the parameters of production of these films.

Experimental

Material

The films of biaxially oriented polypropylene were manufactured by Polipropileno de Galicia, S.A. (POLIGAL), Narón, Spain. These co-extruded films were made with three layers. One central layer of homopolymer of polypropylene (i-PP) (95.5%), supplied by Repsol Química, S.A., ISPLEN PP 044W3F, and a slip agent, antistatic agents, and an antioxidant, in quantities less than 1000 ppm. The two external layers were manufactured using a random copolymer of poly-

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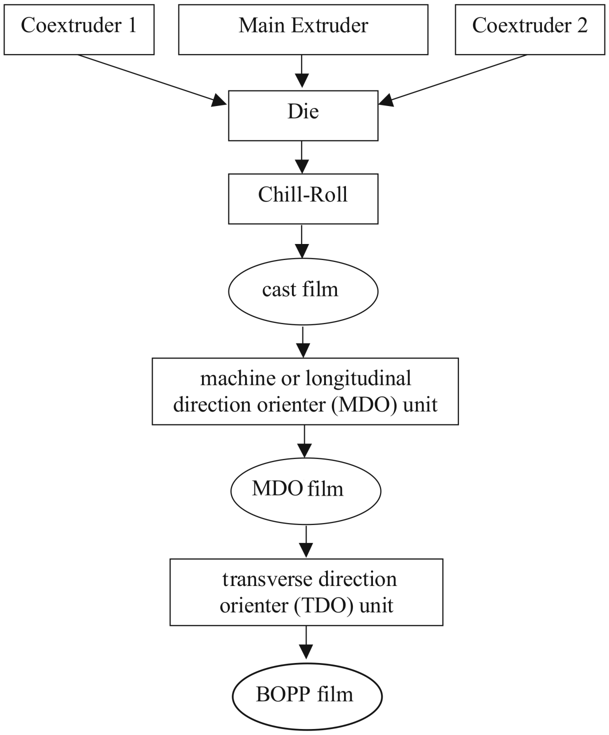

propylene and 3% of polyethylene-polybutylene as raw material. Some additives, as antiblocking and slip agents, were added in quantities less than 1000 ppm.

The core layer represents 90% and the skin layers 10% of the film. This compounding was confirmed by atomic force microscopy and micro thermal analysis [11].

The production line of the film is a BRÜCKNER BOPP tenter-frame line, of sequential stretching, nominal out-put 1200 kg h^{-1} and 6 m final width. The following scheme shows the different steps of the production line.

Both, extruder and coextruders use a monoscrew. As the raw materials are melted, the melt mass goes through a heated pipeline to a flat die at 523 K. The polymer is cooled very fast and melt mass goes down on a chill roll at the temperature of 301–303 K. Then, the crystallization is produced and this material is called cast film.

The cast film reaches the machine or longitudinal direction orienter (MDO) unit and passes by several steps: preheating up to the softening temperature of 393 K; stretching in the machine direction, this stretch is caused by a different speed ratio between the rolls in two zones and, finally, holding up 393 K.

After this, the mdo film is put into the transverse direction orienter (TDO) unit and it was preheated up to the softening temperature with a flow air at 443 K and stretched in the transversal direction. To stretch, the film is grabbed by a set of clips mounted on two chains by both sides of the TDO unit. Finally, the BOPP film was annealed.

The samples for the different measurements have been taken as follows: pellets of homopolymer and copolymer as they are supplied; cast film and mdo film, after a forced stop on the production line, to assure that the samples were obtained in the real conditions. The BOPP film was taken in the winder of the line.

Samples were stored under controlled conditions of temperature and humidity (296 K/50% r h) according to standard DIN 50014 for 45 days [12], with the aim to assure that the process of post-crystallization had finished.

Techniques

A dynamomechanical analyzer DMA-7 of PerkinElmer, equipped with an intracooler and supported by a PerkinElmer computer for data acquisition/analysis, was used to determine the dynamic storage modulus, E', and the loss factor or tanδ of the samples. A dry helium flow of 40 mL min^{-1} was used as purge gas. The temperature calibration of DMA was made using the melting point of pure indium. Other automatic routines allow to calibrate the height, furnace, temperature and force.

Isothermal tests by DMA at 298 K were carried out for the cast film, mdo film, and BOPP film in longitudinal and transverse directions to study their dynamic mechanical properties and the influence of the stretching on these properties. The tests have been made by the extension measuring system at the frequency of 1 Hz. The samples were of 6.5 mm length and 3 mm width. A static force of 900 mN and a dynamic force of 95 mN were applied for each test. Fifteen specimens were tested for each reported value, and the average value was used.

Tensile tests were conducted at room temperature with a Zwick 1425 Universal Testing Machine according to standard DIN 53457 [12]. Eight specimens for each measure of 150 mm length and 15 mm width were tested. The crosshead speed used was 1 mm min^{-1}.

A differential scanning calorimeter PerkinElmer DSC 7, equipped with an intracooler and supported by a PerkinElmer software for data acquisition/analysis was used. The calorimeter was calibrated with the heat of fusion and the melting point of pure indium. A dry nitrogen flow of 40 mL min^{-1} was used as purge gas. Three samples of about 10 mg were enclosed in aluminum DSC capsules and tested for each reported value. Dynamic heating experiments were carried out at a heating rate of 10 K min^{-1}.

The WAXD tests were done using a D5000 diffractometer manufactured by Siemens. The X-ray generator was operated at 30 mA and 40 kV using CuK_{α} radiation (0.1542 nm). The WAXD crystallinity measurements were made by subtracting the background

Table 1 Values of the parameters obtained by DMA and tensile tests

	cast film		MDO film		BOPP film	
	MD	TD	MD	TD	MD	TD
E' (Pa)	(9.80±0.07) E8	(9.60±0.05) E8	(17±2) E8	(9.1±0.8) E8	(17±1) E8	(31± 2) E8
tanδ	0.33±0.03	0.33±0.05	0.14±0.03	0.10±0.02	0.17±0.03	0.17±0.03
E (Pa)	(9.5±0.5) E8	(9.7±0.2) E8	(21.8±0.5) E8	(13.0±0.4) E8	(20.9±0.3) E8	(38.7±0.7) E8

and curve fitting the amorphous contribution to the crystalline peak intensities and using integrated areas for calculation. A peak-fit procedure, version 4.12 of Systat Software Inc., was used to deconvolute the peaks.

Results and discussion

DMA and tensile tests

The results of the tests made in DMA at 298 K of the specimens of the cast film, mdo film, and BOPP film in the longitudinal (MD) and transverse (TD) directions are shown in Table 1.

For the cast film, no difference was observed in the values of storage modulus, E', and loss factor or tanδ, for both directions. After the first stretching (mdo film), in the longitudinal direction an increase of the storage modulus, E', is produced, but in the transverse direction, the value for E' remains as for the cast film. The increase reached in the storage modulus in the longitudinal direction can be due to the alignment of the crystals caused by the stretching in this direction. Such conclusion is reinforced with the fact that the value of the loss factor or tanδ decreases from the cast film to the mdo film. The BOPP film, obtained after the second stretching, shows an increase of the storage modulus in the stretching direction. This increase is higher than the obtained for the first stretching due to the different stretching ratios.

The results obtained in tensile tests for the modulus, E, are also shown in Table 1. They agree well with the DMA results. The same trends are observed.

DSC and X-ray measurements

The melting heat of the pellets of homopolymer (core layer) and copolymer (external layers) were measured in a first scan made by DSC. Values of 81 J g^{-1} and 32 J g^{-1} were obtained, respectively.

Table 2 Measurement of the values by DSC and X-ray of homopolymer

ΔH_{f_1}/J g^{-1}	Crystallinity/% WAXD	$\Delta H^0_{f_1}$/J g^{-1}
97.4	55.1	177
92.0	51.0	180
85.6	49.0	175
78.8	46.8	168
	Average value	175±4

Table 3 Measurement of the values by DSC and X-ray of copolymer

ΔH_{f_2}/J g^{-1}	Crystallinity/% WAXD	$\Delta H^0_{f_2}$/J g^{-1}
34.8	35.6	98
35.8	35.1	102
43.4	40.2	108
	Average value	103 ± 4

Table 4 Melting heat by DSC of different films and pellets, and the crystallinity values obtained as much by DSC as by WAXD

Sample	Melting heat/J g^{-1} (DSC)	Crystallinity/% (DSC)	Crystallinity/% (WAXD)
cast film MD	71.5 ± 0.6	42.6	51.0
cast film TD			52.3
cast film b			44.0
MDO film MD	76.6 ± 0.6	45.6	59.3
MDO film TD			58.4
BOPP film MD	79.7 ± 0.6	47.4	72.0
BOPP film TD			74.2
homopolymer pellet	81 ± 2	46.3	44.5
copolymer pellet	32 ± 1	31.0	29.0

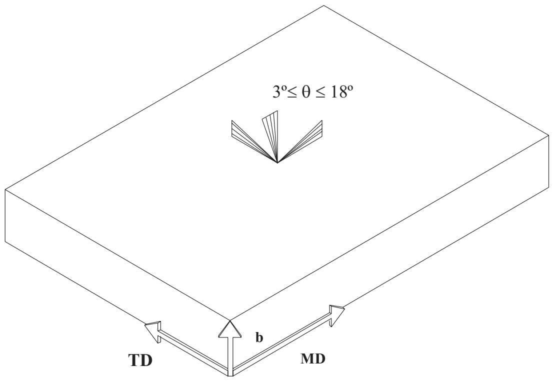

Fig. 1 MD, TD and b directions, and diffraction angles in these directions

With the purpose to obtain a value for the melting heat of the pellets with 100% crystallinity, ΔH_f^0 the melting heat of the homopolymer and copolymer pellets, ΔH_{f_1},ΔH_{f2} were determined by DSC. The thermal history of the samples was erased by mean of a process melting and different crystallizations were obtained when the samples were treated with different cooling rates [13]. Tables 2 and 3 show for the homopolymer and copolymer the obtained values, respectively, where ΔH_{f_1} and ΔH_{f_2} are the values of the melting peak measured by DSC. Also, in this table the values of crystallinity of these samples obtained by WAXD are displayed. The different values of $\Delta H_{f_1}^0$ and $\Delta H_{f_2}^0$ were obtained using these data. The average value of $\Delta H_{f_1}^0$, agree with other in literature [14].

Therefore, the melting heat for the BOPP film, with 100% crystallinity, can be taken as $\Delta H_f^0(\mathrm{J\ g^{-1}})=0.9\ \Delta H_{f_1}^0(\mathrm{J\ g^{-1}})+0.1\Delta H_{f_2}^0\ (\mathrm{J\ g^{-1}})=168\pm4\ \mathrm{J\ g^{-1}}$.

The melting heat for the all different samples were measured by DSC at a heating rate of 10 K min^{-1}. Table 4 shows the melting heat and the crystallinity values obtained by DSC and by WAXD.

The tests of the X-ray difraction in MD, TD and b directions (Fig. 1) for the different specimens are shown in the Fig. 2. It is deduced that, the i-PP crystallize in α-form. There is not β-form as it is proved by the absence of the peak corresponding to the plane (300) at 2θ≅16°. This peak is distinctly separated from all other α-crystal reflections and it is usually used as a marker for the β-crystals [15].

The cast film presents preferred directions as can be deduced from Fig. 2a and Table 4. These directions are not detected by DMA tests. The different values of crystallinity by WAXD obtained for MD, TD, and b directions could be due to the slight stretching in the machine direction produced by the speed of the chill roll on the melt and the air pressure used to assure a good contact between the melt and the chill roll. By other hand, the relative contribution of the symmetry planes is different. This fact is contradictory with a random spatial distribution of the crystals.

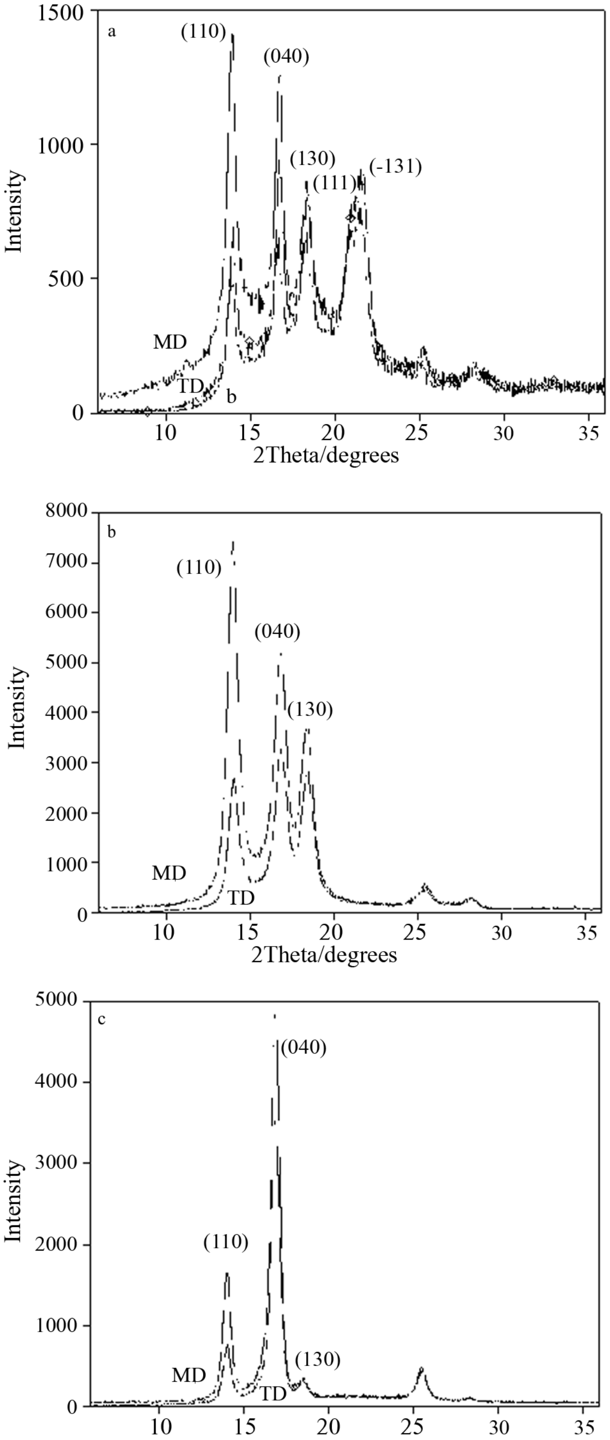

Fig. 2 WAXD pattern of a – cast film; b – MDO film, c – BOPP film, measured in machine direction MD and transversal direction TD (for the cast film also in b direction)

The relative contribution to the total crystallinity of the peak corresponding to the plane (040) is modified with the different stretchings.

When the cast film is analyzed in the b direction the crystallinity peak represents 5.1%, and if the analysis is carried out in the plane of the cast film, determined in MD and TD directions, this peak is 7.3%.

In the mdo film, the contribution of this crystallinity peak in the MD and TD directions is 14.3%, and it disappears in b direction.

In the BOPP film, the contribution of the crystallinity peak in the MD and TD directions is 45%. This high value could be that the stretching had produced an orientation of the majority of the crystallites orienting the plane (040) parallel to the plane of the film.

The stretching, in the machine and transverse directions, has produced a significant increase of order in the distribution of crystals, yielding an increase of the crystallinity determined by WAXD, and also it has produced a change in the contribution of the different symmetry planes to the crystallinity. The crystallinity determined by DSC increases slightly during the stretching, owing to the temperature at which the stretching carried out.

Conclusions

The crystallinity values obtained by WAXD suggest that the stretching leads to a strong alignment of the crystallites, producing fibers oriented in the stretching direction with preferred orientations. This fact can be connected with the values of the storage modulus, *E'*, obtained by DMA in the machine and transverse directions, and also by the values of the modulus, *E*, obtained in tensile tests. The disappearance of the peaks of the planes (111) and (–131) in the mdo film, and the relative decrease of the contribution of the peaks corresponding to the plane (130), in the BOPP film, obtained by WAXD, supports the conclusion of the alignment of the crystals. On the other hand, the tests carried out by DSC show that the different stretchings do not change significantly the values of the melting heat. The increase in the crystallinity by upon 10% stretching is due to annealing.

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