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Orientation and Crystallinity Measurements in Film Casting Products

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Summary

Film casting experiments were carried out with iPP under processing conditions causing the crystallization process to occur under orienting flow. Draw ratio and cooling rates were changed by varying mass flow rates and die thickness. The effect of processing conditions on film crystallinity was investigated by combining WAXS and FT-IR transmission methods, while orientation of both phases was measured by IR dichroism (according to Fraser's method) and successfully compared to birefringence measurements on final films. Crystallinity appears to be almost insensitive to draw ratio and cooling rate. Moreover the crystallinity profile turned out to be also constant along the transverse film direction. Phases orientation were found relatively low and no dependence on draw ratio was detected.

Introduction

Measurement of polymer crystallinity and orientation is very important for transformation processes set-up and management, and, more generally, in the macromolecular research field. Structure-properties relationship can be indeed investigated only if reliable measurements of material properties are available.

Many different types of measurements are currently adopted to determine crystallinity [1-2] (density, WAXS, dilatometry) and orientation [3-4] (birefringence, dichroism, WAXS), but their applicability is still limited by two problems: the result of the measurement deeply depends on the method adopted, and the measurement is difficult to be performed during the process (*on-line*).

Aim of this work is to compare methods useful to measure crystallinity and orientation in iPP samples by FT-IR spectroscopy, by WAXS analysis and by birefringence, and to apply those techniques to the analysis of films obtained by film casting process.

Experimental

Material and sample preparation

The resin used along this work was a commercial iPP supplied by Montell (T30G, M_w = 481000, M_n = 75000, tacticity = 87.6%*mmmm*).

Oriented polymer film samples were produced by film casting. During film casting, if the path in air is long enough, crystallization takes place before chill rolls contact, i.e. while macromolecules are subject to flow, leading to oriented films.

Cast film extrusion was performed with a laboratory-scale extruder equipped with a take-up unit [5]. Tests were performed using two different rectangular dies (having the same width, L_0 = 0.20 m, and different thicknesses, S_0 = 0.0005 m and S_0 = 0.0003 m), and several values of both extrusion screw r.p.m. and take-up velocity. Extrusion temperature was kept constant for all experiments (220°C). The distance X between extrusion head and take-up rolls was also kept constant (X = 0.4 m). All runs and related measured parameters are reported in Table 1.

	Ω	$\dot{m}$	$v_x(x=0)$	$v_x(x=X)$	X	T_0	S_0	$DR=\frac{v_x(x=X)}{v_x(x=0)}$
#	rpm	$10^{-4}\cdot$kg$\cdot$s^{-1}	$10^{-3}\cdot$m$\cdot$s^{-1}	$10^{-3}\cdot$m$\cdot$s^{-1}	m	°C	μm	dimensionless
U1	20	1.33	2.97	71.8	0.4	220	300	24.1
U2	15	1.04	2.33	68.8	0.4	220	300	29.6
U3	12	0.76	1.70	69.7	0.4	220	300	41.1
V3	25	1.55	2.08	57.0	0.4	220	500	27.4
V1	20	1.30	1.75	57.0	0.4	220	500	32.6
V2	15	0.91	1.22	55.0	0.4	220	500	45.1

Table 1 – Operating conditions of the experimental runs

Mass flow rate $\dot{m}$ was measured by weighing the extrudate; extrusion velocity $v_x(x=0)$ was calculated from mass flow rate and melt density, evaluated at die temperature; take-up velocity $v_x(x=X)$ was simply evaluated from collected film length. Finally, draw ratio was drawn from these two velocity values [6].

FT-IR measurements

A modified M2000 FT-IR spectrometer (by Midac Co.) was adopted to collect IR spectra. The crystallinity index was determined through analysis of the FT-IR absorbance spectra by applying Lambert and Beer's law to selected peaks [1, 7]. Considering a crystalline peak and a peak insensitive to phase content, Lambert and Beer's law provides respectively:

$$A_{cr} = a_{cr} X_c S, \quad A_{av} = a_{av} S \qquad \textbf{(1, 2)}$$

Where A_{cr} and A_{av} are the absorbancies, a_{cr} and a_{av} are the absorptivity of crystalline fraction and of a peak insensitive to phase content respectively, X_c is the crystallinity index and S is the sample thickness. Eliminating S from (1) and (2):

$$X_c = \left(a_{av}/a_{cr}\right)\left(A_{cr}/A_{av}\right) \qquad \textbf{(3)}$$

It can be noticed that crystallinity evaluation requires only absorbancies measurements

(A_{cr} and A_{av}) if absorptivity ratio (a_{av}/a_{cr}) is known. As the absorbancy spectra are obtained by the superposition of single peaks due to molecular absorption, all the absorbancies were obtained by fitting the experimental spectra (using Gaussian/ Lorentzian peak functions) with a weighted combination of single peaks.

The absorbance peak at wavenumber 841 cm^{-1} was identified in literature and experimentally as a crystalline peak [8]. After preliminary investigations the absorbance peak at 973 cm^{-1} was used as *internal standard*, being a peak essentially insensitive to structure i.e. to amorphous/crystalline ratio [8-9]. The tuning procedure was carried out and details are reported elsewhere [9]. Numerical value of absorptivity ratio was found to be $a_{973}/a_{841} = 0.79$.

Orientation can be obtained from analysis of polarized FT-IR transmission spectra [3-4]. The IR beam was polarized with the polarization axis parallel and orthogonal to the draw direction. All the peaks related to the conformational zone of the spectrum (from 750 cm^{-1} to 1300 cm^{-1} for iPP) are dichroic (i.e. absorbancies are affected by the polarization plane of the source). Both crystalline phase (f_c) and average (f_{av}) Hermans orientation factors were determined by measuring the dichroic ratio $D_v = (A_\pi/A_\sigma)_v$, where A_π is the absorbance when polarization plane is parallel to draw direction and A_σ is the absorbance when polarization plane is orthogonal to draw direction. Hermans factor, if uniaxial orientation is assumed, is related to dichroic ratio at wavenumber v by [3]:

$$f = \left[\left(\frac{D-1}{D+2}\right)\left(\frac{D_0+2}{D_0-1}\right)\right]_v = K_v\left(\frac{D-1}{D+2}\right)_v \tag{4}$$

where $D_{0,v}$ is the dichroic ratio value when macromolecules are completely aligned. Denoting as f_c, f_{am} and f_{av} the Hermans factors for crystalline, amorphous phase and average content respectively, average orientation is related to crystalline content by:

$$f_{av} = f_c X_c + f_{am}(1 - X_c) \Rightarrow f_{am} = \frac{f_{av} - f_c X_c}{1 - X_c} \tag{5}$$

The same bands used for crystallinity (841 cm^{-1} and 973 cm^{-1}) were here adopted also for orientation measurements [9-10], because they are well isolated. For these bands, the dichroic ratio of completely aligned molecules gives rise to $K_{841} = K_{973} = 1$ [10].

WAXS measurements

Two different techniques were adopted to perform WAXS analysis:

a. X-ray diffraction patterns of oriented samples were recorded using a Philips PW 1830 X-ray generator (Ni-filtered Cu-Ka radiation). A Fujifilm MS 2025 imaging plate and a Fuji Bio-imaging Analyzer System, mod. BAS-1800, were used to acquire the diffraction patterns. The images, that are greyscale intensity measurements, were analysed to obtain crystallization indexes. In order to get crystallization index from imaging plate greyscale images, the data were averaged along the azimuthal angle β:

$$\bar{I}(2\theta) = \frac{1}{2\pi}\int_0^{2\pi} I(2\theta, \beta)\,d\beta \tag{6}$$

b. X-ray diffraction patterns of oriented samples were also recorded by using a Brucker D8 Advance X-ray generator, equipped with a Kristalloflex 760 generator (wavelength=0.154 nm) and a Goebel mirror to intensify and focus the X ray beam. For crystallinity measurements, "randomized" intensity vs. 2θ patterns were collected in transmission mode by rotating the sample along the azimuthal angle β. The rotation period was chosen as one half of the scattered signal collection time at a given 2θ angle.

In order to obtain phase contents, equation (7) [1] can be applied to averaged intensity (to the 2D patterns -eq. 6-, or to the patterns recorded on the rotating sample -as described in point b. above-):

$$X_{phase} = \frac{\int_{2\theta_1}^{2\theta_2} \bar{I}_{phase}(2\theta)d(2\theta)}{\int_{2\theta_1}^{2\theta_2} \bar{I}_{overall}(2\theta)d(2\theta)} \tag{7}$$

In equation (7) [$2\theta_1$, $2\theta_2$] is the range of significant scattering, *phase* can be crystalline alpha, mesomorphic or amorphous, while *overall* is the overall scattering signal. Partial contributions of different phases to the overall scattering signal were separated by fitting the experimental spectra with a weighted combination of single peaks, due to different phases scattering, located at known Braggs' angle. Figure 1 shows a typical example of WAXS imaging plate greyscale image and corresponding averaged signal together with appropriate fitting.

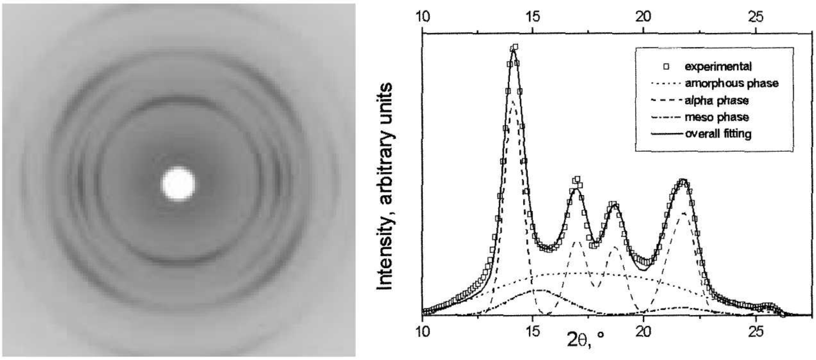

Figure 1 – WAXS image (left side) and intensity vs. Bragg angle graph (right side) for a film casting product

Birefringence measurements

Birefringence was measured by using a polarized microscope (AUS Jena) and a compensator, to determine the phase difference (optical retardation) of a filtered (green, λ = 551 nm) beam of light. Birefringence represents a measure of average orientation. It can be related to phase content and orientation level by:

$$\Delta n = \Delta_c f_c X_c + \Delta_{am} f_{am}(1 - X_c) \tag{8}$$

neglecting the very low form birefringence contribution. Samuels [3] reports Δ_c = 0.030 and Δ_{am} = 0.060 for iPP.

Results and Discussion

Figure 2 shows phase contents versus film draw ratio for six different samples corresponding to six different film casting experiments (see table 1). For every film the central area was used for analysis (WAXS, FT-IR). In figure 2 open symbols indicate phase percentages drawn from WAXS analysis by means of the analytical average (eq. 6, 2D pattern measurements, noted as SA) whereas open symbols with a superimposed cross are drawn from the WAXS analysis obtained by rotating the sample (noted as PA) while collecting the scattered X-ray intensities. While WAXS analysis discriminates between different ordered phases (alpha and mesomorphic), FT-IR is not able to do so, because "crystallinity" peaks are sensitive to the molecular order characteristic of both alpha and mesomorphic phase. A comparison between WAXS and FT-IR, however, can be made on the basis of amorphous content, i.e. total crystallinity content. Therefore, in figure 2 amorphous percentages drawn from FT-IR are also reported as small full symbols.

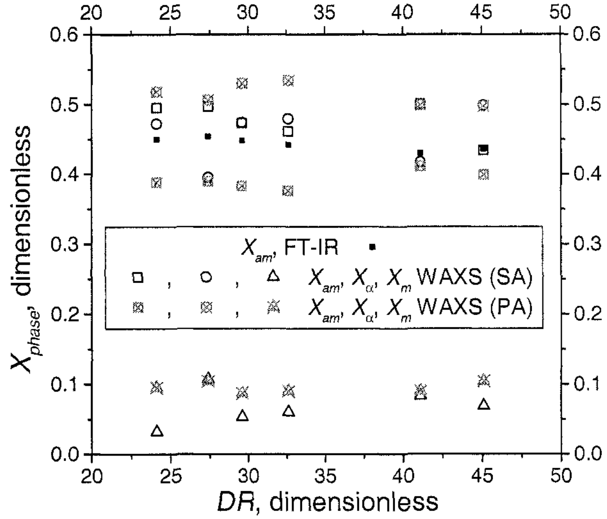

Figure 2 – Phase content of film cast samples, as revealed by FT-IR and WAXS analysis

Irrespectively to the method adopted, phase content appears to be almost insensitive to draw ratio. The two WAXS techniques lead to small differences of phase content, the same phase distribution is however obtained: cast film products, in the range of operating conditions applied, show a low meso-phase level (PA results exhibit a level slightly higher than SA results), and comparable levels of amorphous and alpha phase contents (PA results show a larger alpha content and a lower amorphous content, while SA result show identical values for both phases). FT-IR method provides amorphous values in between SA and PA measurements (around 45%).

It should be reminded that higher draw ratios lead to higher cooling rates, and it is expected that increased cooling rate gives rise to iPP resins with higher meso-phase percentage (while alpha content decreases). On the other hand, the increase of flow (that should increase with draw ratio) leads to an increase of alpha phase content. The opposite effects (as *DR* increases, cooling rate and stress level increase too) probably cause the observed almost constant phase contents. A clarification of the simultaneous effects of cooling rate and flow on final phase content deserves, however, further investigations to understand the results thoroughly.

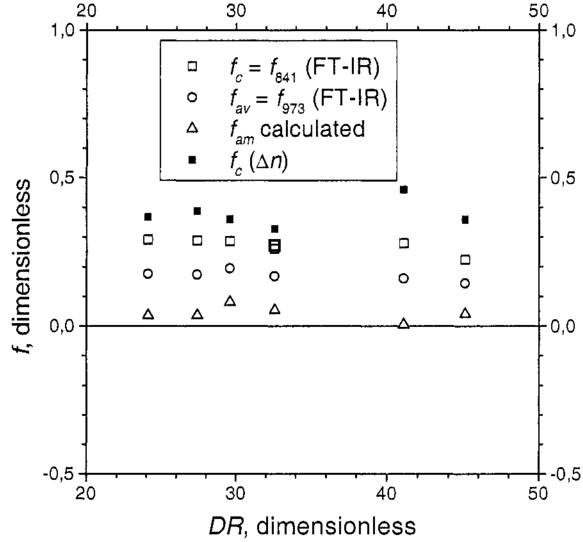

Figure 3 – Orientation factors obtained from IR dichroism and birefringence analysis

The IR dichroic analysis described in the experimental section was applied to the same samples subjected to the crystallinity measurements reported in figure 2. Crystalline and average orientation factors were obtained by applying equation 4. Amorphous phase orientation factors were obtained by equation 5. All FT-IR orientation factors are reported in figure 3 as open symbols. With the aim of comparison, birefringence measurements have been performed on the same samples. From equation 8, neglecting amorphous orientation and using crystallinity values from FT-IR reported in figure 2, the birefringence crystalline orientation factor values were calculated and reported in figure 3 (filled symbols).

Figure 3 clearly shows that all the calculated orientation factors appear to be almost insensitive to draw ratio. Dichroism measurements provide a moderate orientation of crystals (f_c = 0.25÷0.30) and a level of average orientation (f_{av} = 0.15÷0.20) compatible with a very low level of amorphous orientation (f_{am} = 0.00÷0.05). The slightly higher level of crystal orientation obtained by birefringence can be explained on the basis of the neglected amorphous orientation, that is low but not zero.

As stated above, the crystalline orientation level calculated from birefringence has been obtained from equation 8 neglecting the amorphous orientation, and they resulted higher than the one obtained by dichroism. These orientation factors obtained from birefringence would better agree with the ones obtained by dichroism, if amorphous orientation were accounted for in equation 8.

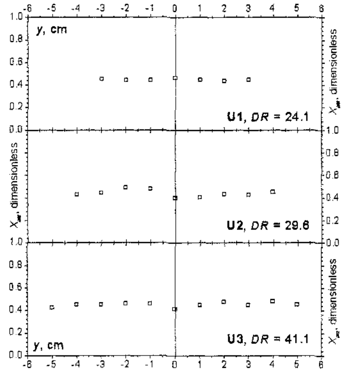

Figure 4 – Distributions of amorphous content (X_{am}) in transverse direction in series U runs

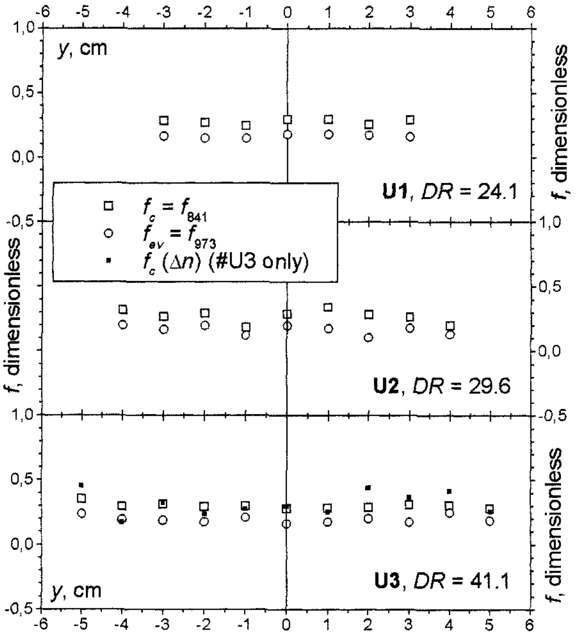

Figure 5 – Distributions of orientation factors (f_c, f_{av}) in transverse direction in series U runs

The orientation level observed, coupled to optical observations by polarized microscopy that confirms the spherulitical morphology of the samples, leads to the following considerations:

1. The stress level achieved does not allow row structures to form, but it induces some kind of orientation in the samples (according to Keller and Kolnaar orientation could arise from the presence of completely extended chains mixed with random structures like spherulites [11]),
2. The orientation is essentially confined to the crystalline phase (amorphous orientation is very low).

In figures 4 and 5 crystallinity and orientation distribution along the transverse direction (*y* axis) of films (series U) was reported respectively. Crystallinity was calculated by FT-IR analysis, while orientation factors were obtained by dichroism. For comparison, crystalline orientation factors of the U3 run were also measured by birefringence and reported as full symbols in figure 5.

Crystallinity and orientation factors were found to be constant along the transverse direction, at the same levels as reported in figures 2 and 3. Birefringence measurements of f_c agree with dichroic measurements, within the experimental error of measurements.

Conclusions

Several experimental techniques (FT-IR, WAXS, birefringence) were adopted in this work to determine and compare crystallinity and orientation factors for oriented iPP samples produced by film casting.

The overall crystallinity was measured by a simple FT-IR method. Analysis of WAXS spectra, known as to be the only reliable method to discriminate phase contributions in un-oriented samples, was successfully applied to partially oriented samples too, by carrying out both "analytical" (SA method) and "physical" (PA method) averaging. Both aforementioned WAXS-based methods gave satisfactory results when compared with values drawn from FT-IR technique.

FT-IR dichroic orientation results satisfactory agree with birefringence results. Cast film samples show constant values of crystallinity and orientation along the transverse direction.

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