Orientation and Crystallinity Measurements in Injection Moulded Products

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Summary

Orientation and crystallinity of isotactic polypropylene moulded products have been investigated by means of infrared microscopy. The experimental techniques are described elsewhere [1-3]. The previous application to film casting products and the application in this work to injection-moulded products confirms their usefulness in polymer science. Orientation and crystallinity distributions obtained for different samples are reported and briefly discussed.

Introduction

Final properties of a plastic product are determined by its morphology that, in turn, will be developed as a consequence of molecular composition and of processing conditions. Therefore, full knowledge of the morphology plays a key role, both in product understanding properties, and in managing processing conditions.

Important properties for semi-crystalline polymers are crystallinity and orientation and therefore many experimental methods are currently adopted to determine these properties in polymeric products. It is desirable that these measurements techniques are simple, fast and inexpensive. FT-IR and FT-IR dichroism meet all these needs, as was explained already in recent papers [1-3] in which crystallinity and orientation were determined in iPP film casting products [1-2] and during the film casting process [2-3]. A further advantage of methods based on the FT-IR technique in combination with infrared microscopy is that properties of a sample can be investigated on a local scale and in a non-destructive way.

The morphology of samples obtained by injection moulding process is an important topic that is little investigated until today due to difficulties in analysing small sample areas. Only recent work reports birefringence measurements along thickness direction in injection-moulded parts [4-5], whereas WAXS analysis was reported in [6]. Birefringence accounts for crystallinity and orientation, being unable to discriminate their contributions. Despite its ability to provide data for crystallinity and crystal orientation, the WAXS analysis in [6] were only used to give crystallinity distributions. Birefringence and IR dichroism measurements have been performed in

injection-moulded [7]. However, in that work, measurements require a cumbersome cutting procedure.

Aim of this work is to test the reliability of simple and fast techniques, based on FT-IR microscopy, already proposed and applied in analysis of iPP film casting products, for the analysis of iPP injection-moulded products. To this purpose the analysis procedures were applied to some samples obtained by cutting two injection-moulded products.

Experimental

Material and Injection Mouldings Conditions

The material used in this study was a commercially isotactic polypropylene (StamylanP 15M10, $M_w = 354.000$, $M_n = 64.000$, tacticity $= 0.962$), supplied by DSM, the Netherlands.

Plates of rectangular shape (70 x 70 x 1 mm^3) were injection moulded on an Arburg 320S / Allrounder 500-150 injection moulding machine. The mould had a V-shaped runner and no reduction in cross-section at the entrance (70 x 1 mm^2) and was specially manufactured by Axxicon Moulds B.V., the Netherlands. The amount of flow induced orientation was varied by applying two extremes in injection moulding temperature (260°C & 185°C) and flow rates (10 $cm^3 \cdot s^{-1}$ & 25 $cm^3 \cdot s^{-1}$). Mould cavity temperature was kept constant (20°C). Filling and packing time were obtained from the measured pressure profile in the nozzle. Table 1 gives all injection moulding conditions for the two samples produced.

Table 1. Injection mouldings conditions

	Product "A"	Product "B"
Melt temperature, °C	260	185
Cavity temperature, °C	20	20
Filling time, s	1.6	0.6
Packing time, s	8	8
Packing pressure, MPa	30	30
Nominal flow rate, $cm^3 \cdot s^{-1}$	10	25

FT-IR analysis

Polarized and not polarized spectra were collected working from thin slices, cut with a microtome, using a FT-IR Spectrometer BIO-RAD FTS 6000 connected to a FT-IR Microscope BIO-RAD UMA 500. Spectra have been collected along the thickness direction for sample areas of about 30 $\mu m \times 30$ μm adopting a motorized stage (PRIOR CS152DP), connected by a digital camera Sony CCD-IRIS (model DXC-107AP with Camera Adaptor CMA-D2) and managed by the BIO-RAD WIN-IR Pro 30 software (shadow subprogram). For each sample, the average of 32 scans was used, working at a resolution of 2 cm^{-1}. The range of the collected spectrum was 4000-650 cm^{-1}.

Orientation evaluation

The orientation can be obtained from analysis of polarized FT-IR transmission spectra [1]. The IR beam is polarized with the polarization axis parallel and orthogonal to draw direction. Both the crystalline phase (f_c) and the average Hermans orientation factor (f_{av}) can be determined by measuring the dichroic ratio $D_\nu = (A_\pi/A_\sigma)_\nu$, where A_π is the absorbance for the plane parallel to the draw direction and A_σ the absorbance for the polarization plane orthogonal to the draw direction. The Hermans factor, assuming uniaxial orientation, is related to dichroic ratio at wave-number ν by [1]:

$$f = \left[\left(\frac{D-1}{D+2}\right)\left(\frac{D_0+2}{D_0-1}\right)\right]_\nu = K_\nu \left(\frac{D-1}{D+2}\right)_\nu \tag{1}$$

where $D_{0,\nu}$ is the dichroic ratio value when macromolecules are completely aligned and K_ν is an auxiliary variable. The absorption bands at 841 cm^{-1} and at 973 cm^{-1} were, respectively, adopted here for crystal phase and for average orientation measurements [1-2]. For these bands, the completely aligned dichroic ratio gives rise to $K_{841} = K_{973} = 1$ [8]. Because they are well isolated and definite, the usual fitting procedure [1] can be avoided, and the absorbencies have been let equal to peak heights.

Crystallinity evaluation

Starting from Lambert and Beer's law and considering a crystalline peak (*cr*) and a peak insensitive to phase content (*av*), the crystalline content can be evaluated as follows

$$X_c = \left(a_{av}/a_{cr}\right)\left(A_{cr}/A_{av}\right) \tag{2}$$

by simply carring out absorbancies measurements (A_{cr} and A_{av}) and the absorptivity ratio (a_{av}/a_{cr}) is known. For isotactic polypropylene, the absorption band at $\nu = 841$ cm^{-1} has been assigned to the crystalline phase content and the band at $\nu = 973$ cm^{-1} was reported as insensitive to crystalline phase [1, 9]. For these two bands the absorptivity ratio a_{av}/a_{cr} was found to be 0.79 [1]. It should be noted that FT-IR does not discriminates between different ordered phases (alpha and mesomorphic) and, as a consequence, the "crystallinity" obtained from IR analysis has to be considered as an overall measure of both the ordered phases.

Absorbancies A_{841} and A_{973} can be obtained from non-polarized spectra analysis or by the suitable averaging of the polarized values, as suggested by Stein [10]:

$$\langle A \rangle = \left(A_\parallel + 2A_\perp\right)/3 \tag{3}$$

Using values obtained by analysis polarized spectra allows for a smaller number of spectra to be collected: two polarized spectra instead of three (two polarized + one not polarized). In this work both procedures have been followed, with the purpose of mutual confirmation.

Results and discussions

Figures 1 and 2 show the shape and dimensions of the injection moulded slabs and the positions at which samples were cut. For each sample, two graphs are reported: on the

right hand sides the crystallinity distributions and on the left hand sides the orientation distributions.

Crystallinity distributions

Except for sample S5, for which experimental data are scattered (probably due to sample heterogeneity), the two measuring methods; direct measurement of A_{841} and A_{973} from not polarized spectra and evaluation of these absorbancies starting from polarized spectra and using Eq. (3). Results from both methods are in good agreement. Crystallinity is almost everywhere the same along the whole thickness for all the samples examined.

The contact between the polymer melt and the cold mould surface gives rise to extremely high cooling rates (in the order of thousand degrees per second), which for quiescent crystallization conditions cause a limited crystallization level [1]. The nearly constant crystallinity found, instead, can be explained in term of the enhancement of nucleation and crystallization kinetics due to the strong shear flow that the molecules experience close to the wall. In the cases presented, the flow effects seem to be strong enough to cause the crystallization to achieve the maximum value (about 60%), for all the conditions under investigation, close to surface. The data points corresponding to the surface have been left out from the graph because of their poor reliability (the IR beam travels partially in air, and therefore the collected spectra are strongly disturbed).

Orientation distributions

For each sample crystalline phase orientation factors (solid lines) and average orientation factors (dashed line) are reported.

Sample S3 (low flow rate, high melt temperature, close to the gate). The sample is almost un-oriented.

Sample S4 (low flow rate, high melt temperature, far from the gate). The sample shows the well known bi-modal distribution of orientation, in which a zone close to sample surface shows an orientation maximum due to the shear flow occurring during the filling step, and a layer intermediate between surface and sample core shows another orientation maximum due to packing flow. Although the conditions are the same as in sample S3, a clear orientation is found because the material far from the gate is cooled during the flow through the mould, causing the effect of flow gradients to be much larger. Literature reports comparable maxima for PS [4], whereas for iPP the external maximum is always higher than the internal one [5, 7].

Sample S5 (high flow rate, low melt temperature, close to the gate). Despite the scattering of data, the sample is almost fully oriented at the same, high level ($f_c \cong 0.5$). The melt entering and passing through the gate is subjected to an elongational flow that is very effective in causing molecular orientation.

Sample S6 (high flow rate, low melt temperature, far from the gate). The sample shows a trace of the bi-modal orientation, even if the orientation level is somewhat low. Full understanding of such orientation patterns, caused by a competition between high shear rate, relatively low total shear and short cooling times, can only be obtained by means of numerical simulation of such process [4].
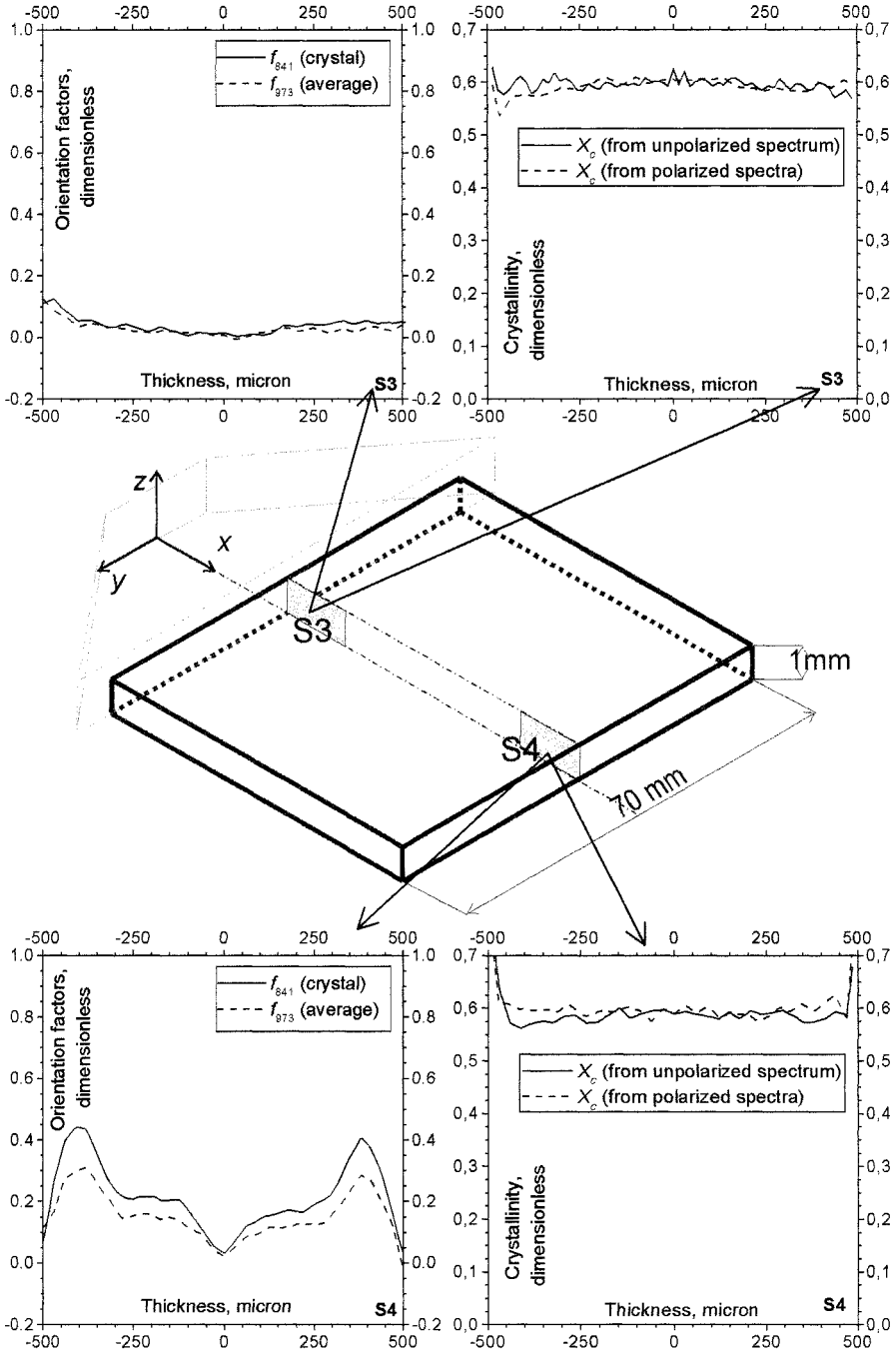
Figure 1 – Orientation factors and crystallinity distributions along thickness direction in two samples cut from the injection-moulded part noted as "A" (see table 1).
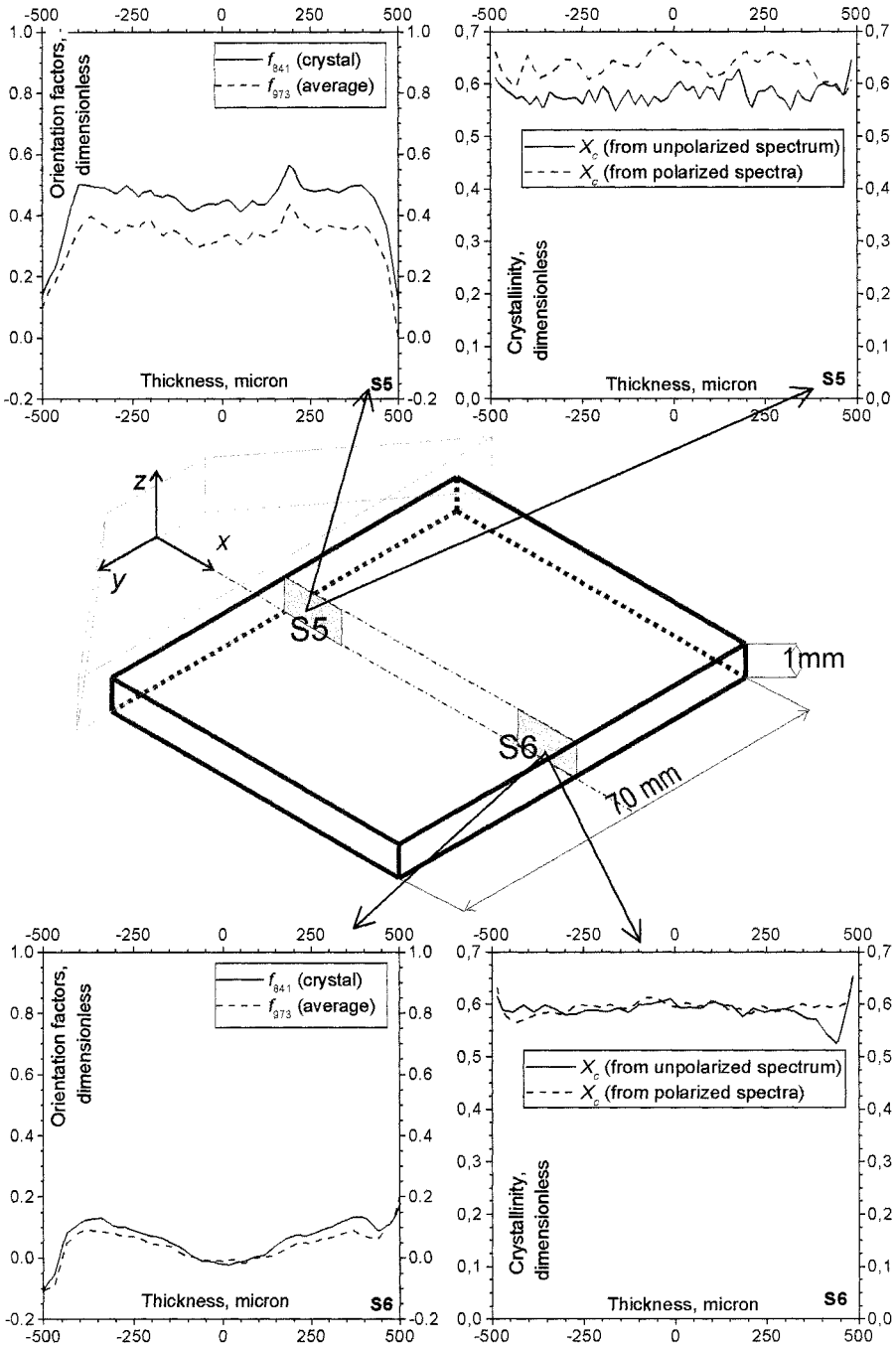
Figure 2 – Orientation factors and crystallinity distributions along thickness direction in two samples cut from the injection-moulded part noted as "B" (see table 2).

Conclusions

In this work orientation and crystallinity measurements techniques, previously applied to cast polypropylene film [2], have been applied to cut samples obtained from injection-moulded products.

By means of an automated infrared microscope spectra were collected along the thickness direction for various positions in the flow direction. Analysis of these spectra according to the mentioned procedures [1], reveal the expected, complicated orientation and crystallinity distributions.

Measured crystallinity and orientation distributions along the thickness in the injection-moulded samples, despite their relevance for structure-property studies, are not very common in literature. The (relatively cheap) set-up and the simple and fast procedures proposed make such measurements much more accessible. Therefore, a considerable impact on process management and optimisation can be expected.

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