γ Phase in injection moulded isotactic polypropylene

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Wide angle X-ray diffraction has been used to investigate polymorphism in isotactic polypropylene (IPP) mouldings produced by conventional injection moulding and by shear controlled orientation injection moulding (SCORIM). γ Phase was found to form in highly oriented IPP produced by SCORIM, with a marked enhancement of the preferred orientation of the α phase and percentage crystallinity when compared with conventionally moulded IPP.

(Keywords: polypropylene; molecular orientation; crystallinity)

INTRODUCTION

Shear controlled orientation injection moulding (SCORIM) provides a route for producing strongly preferred molecular orientation by the controlled application of shear forces to a solidifying melt[1–3]. It is also possible to obtain oriented polymer by die-drawing[4], and Prox and Ehrenstein[5] recently reported on self-reinforcement in isotactic polypropylene (IPP) resulting principally from the application of very high injection pressures and injection rates, and the use of low melt temperatures during injection moulding. In all three processes a two- to three-fold increase in the Young's modulus is attainable.

The occurrence of γ phase[6,7] in injection moulded IPP is not mentioned in published literature, nor is there evidence for the existence of γ phase in the published diffraction patterns gained from injection mouldings[8]. The γ phase is observed in small proportions in association with the α phase[6], and can also be obtained as the major constituent or in pure form by crystallization of the whole polymer under elevated pressure or by crystallization of low molecular weight material from the bulk[6,7,9]. The crystal structure and the unit cell geometry of the γ phase are controversial, but they have close resemblances to those of the α phase[6,10]. The triclinic cell geometry of the γ phase, which is the widely accepted unit cell geometry proposed by Morrow and Newman[7], has been adopted for indexing of X-ray reflections in the work reported in this paper. The α phase monoclinic unit cell has the dimensions $a = 6.66$, $b = 20.78$, $c = 6.495$ Å and $\beta = 99.6°$, as reported by Turner Jones *et al.*[11], representing a small change in lattice parameters from those originally reported by Natta and Corradini[12]. The lattice cell dimensions of the γ phase[7] are $a = 6.54$, $b = 21.40$, $c = 6.50$ Å and $\alpha = 89°$, $\beta = 99.6°$, $\gamma = 99°$, although the crystallography of the γ phase remains a topic of discussion[13].

This paper reports the evidence for the occurrence of the γ phase in moulded IPP.

EXPERIMENTAL

Material

The material investigated is an IPP supplied by Shell (Louvain-la-Neuve, Belgium). The grade is KF 6100 with a melt flow index of 3.1 ± 0.05 g/10 min, density 0.905 g ml^{-1}, weight average molecular weight (M_w) 352 000 and number average molecular weight (M_n) 45 000.

Injection moulding and tensile testing

Round tensile test specimens with a diameter of 5 mm and gauge length of 40 mm were produced by both conventional injection moulding (sample CM-A) and SCORIM (sample SCORIM-A).

An Instron 4206 machine was used for tensile testing. Young's moduli were measured with a clip strain gauge; the crosshead speed was 0.05 mm min^{-1} at 24°C.

Wide angle X-ray diffraction

CuKα radiation was used for both X-ray diffractometry and Debye patterns. The Debye patterns were used to record preferred orientation. The samples used for Debye patterns were 1.5 mm thick and were cut parallel to the injection direction. A camera with a 100 μm diameter defining aperture was used.

For diffractometer studies the X-rays were incident on a longitudinal section. Diffraction profiles were recorded at a scanning rate of 0.02° 2θ s^{-1} over an angular range $7° < 2\theta < 47°$. The β phase and α phase orientation indices and the crystallinity index were calculated as described in detail by Trotignon *et al.*[14]. This quantitative method of estimating the relative proportions of α and β forms was first suggested by Turner Jones *et al.*[11] and extended by Trotignon *et al.*[14]. The crystallinities of the samples were also determined from the diffractometer profiles.

RESULTS AND DISCUSSION

Tables 1 and *2* summarize measurements of 2θ angles, d-spacings, d^* $(= \lambda/d)$, the relative intensities of the

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Table 1 X-ray data for CM-A

2θ (deg)	d-Spacing (Å)	d^* ($=\lambda/d$)	Miller indices, (hkl)	Crystal phase	Relative intensity (%)
14.06	6.301	0.245	1 1 0	α	70
16.07	5.514	0.280	3 0 0	β	38
16.85	5.262	0.293	0 4 0	α	100
18.51	4.794	0.322	1 3 0	α	59
21.24	4.183	0.369	1 1 1	α	65
21.72	4.091	0.377	0 4 1	α	66
25.35	3.513	0.439	0 6 0	α	21
28.42	3.140	0.491	2 2 0	α	14
33.31	2.689	0.573	$\bar{2}41$	α	7
42.57	2.123	0.726	$\bar{1}13$	α	18

Table 2 X-ray data for SCORIM-A

2θ (deg)	d-Spacing (Å)	d^* ($=\lambda/d$)	Miller indices, (hkl)	Crystal phase	Relative intensity (%)
14.10	6.282	0.245	1 1 0	$\alpha(+\gamma)$	71
16.85	5.262	0.293	0 4 0	$\alpha(+\gamma)$	100
18.57	4.778	0.323	1 3 0	α	46
20.06	4.426	0.348	$1\bar{2}0$	γ	21
21.20	4.192	0.368	1 1 1	$\alpha(+\gamma)$	10
21.87	4.064	0.379	0 4 1	$\alpha(+\gamma)$	9
25.33	3.516	0.439	0 6 0	α	19
27.14	3.286	0.469	2 0 0	α	4
28.52	3.129	0.493	2 2 0	α	12
42.47	2.128	0.725	$\bar{1}13$	α	6

diffraction peaks, crystal phase, and the Miller indices associated with the reflections recorded from conventionally moulded and SCORIM samples, respectively. *Figure 1* shows the X-ray diffraction profiles obtained from CM-A and SCORIM-A mouldings. CM-A shows α and β phases whereas SCORIM-A shows α and γ phases. The occurrence of the γ phase and non-occurrence of the β phase is the most prominent finding, since the γ phase has not been reported to occur in injection mouldings. The β and γ peaks that are not coincident with α peaks were recorded at 2θ values of 16.07° and 20.06°, respectively, and the Miller indices of the reflecting planes are $\{300\}_\beta$ and $\{1\bar{2}0\}_\gamma$, respectively.

Turner Jones *et al.*[11] stated that the γ phase is characterized by five strong X-ray reflections of d-spacings at 6.37, 5.29, 4.415, 4.19 and 4.05 Å, four of which lie close to four of the five strong reflections of the α phase at 6.26, 5.19, 4.77, 4.19 and 4.04 Å. The reflection at 4.77 Å of the α phase is completely absent in the γ phase[11]. The presence of a reflection at a d-spacing of 4.426 Å in SCORIM-A indicates the presence of the γ phase.

The crystallinity index C, β phase index B, α phase orientation index A, and the crystallinities of CM-A and SCORIM-A are summarized in *Table 3*. The calculation of A and C is based on the contribution of β and γ phase peaks to the corresponding α phase peaks. In essence, A and C are measures of the preferred orientation and crystallinity of the crystalline phases, which are attributed predominantly to the α phase. The orientation index A of SCORIM-A is greater than that of CM-A. The crystallinity index C and the crystallinity of SCORIM-A are also substantially greater than those of CM-A. The β phase index B of SCORIM-A is zero whereas that of CM-A is 0.22.

The tensile test measurements show SCORIM-A has substantially greater stiffness than CM-A. The Young's modulus of SCORIM-A is 3.3 GPa, whereas that of CM-A is 1.2 GPa.

Figures 2a and *b* show the Debye patterns obtained from SCORIM-A and CM-A at the same relative position along the flow path length, and *Figure 2c* shows the schematic representation of the Debye pattern from SCORIM-A. The diffraction pattern in *Figure 2a* is consistent with the patterns reported by Mencik and Fitchmun[8], which represent an $(a+c)$ axis oriented texture and in which the $[001]_{\alpha,\gamma}$ zone axes are parallel to the injection direction in moulded polypropylene. SCORIM-A exhibits a substantially more pronounced preferred orientation of the crystalline phases than the conventional moulding. It is also apparent that the $\{1\bar{2}0\}$ γ phase reflection appears in the Debye pattern from SCORIM-A. The ring corresponding to $\{1\bar{2}0\}_\gamma$ ($2\theta = 20.06°$) is absent from *Figure 2b*.

The relative orientations of the observed reflections are consistent with the preferred orientations of the planes

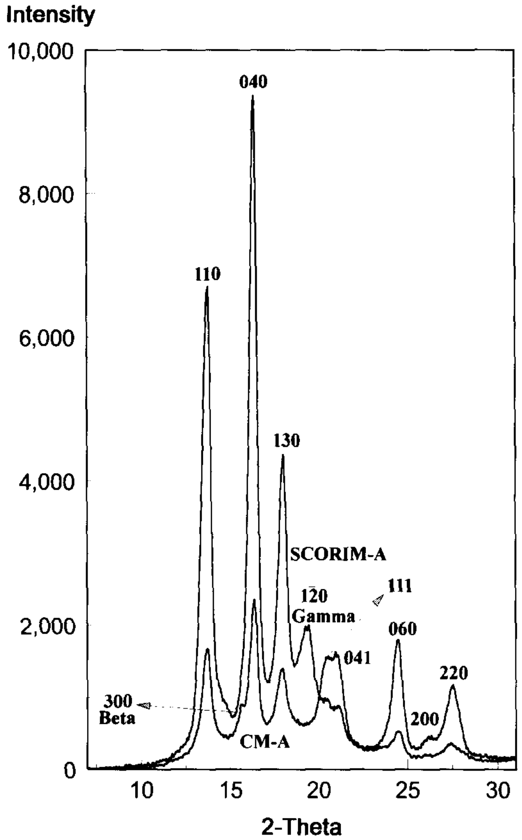

Figure 1 X-ray diffraction profiles from CM-A and SCORIM-A

Table 3 α-Phase orientation index A, β phase index B, crystallinity index C, and crystallinities of the conventional and the SCORIM mouldings

	CM-A	SCORIM-A
A	0.56	0.97
B	0.22	0
C	1.65	2.58
Crystallinity (%)	38.63	52.57

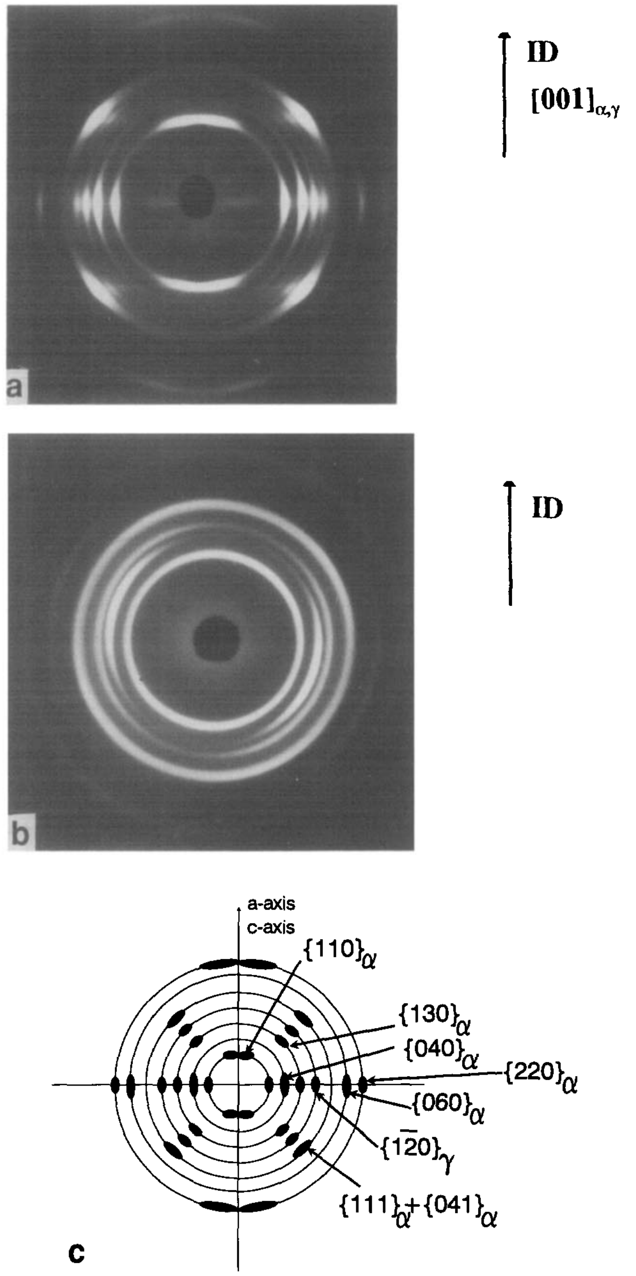

Figure 2 X-ray diffraction pattern from (a) SCORIM-A and (b) CM-A. (c) Schematic representation of the X-ray diffraction pattern from SCORIM-A

$(1\,1\,0)_\alpha$, $(0\,4\,0)_\alpha$, $(1\,3\,0)_\alpha$ and $(1\,\bar{2}\,0)_\gamma$ being parallel, and representative of $[0\,0\,1]_\alpha$ and $[0\,0\,1]_\gamma$ being parallel to the process direction in moulding and the direction in which a macroscopic shear is applied during solidification.

The occurrence of pronounced $\{1\,\bar{2}\,0\}_\gamma$ and $\{2\,0\,0\}_\alpha$ reflections in the SCORIM-A X-ray diffraction profiles is attributed to the high level of preferred orientation that results from the application of macroscopic shears during solidification. These reflections may not be apparent, although the γ phase may be present, because of the relatively low level of preferred orientation in conventional injection mouldings.

CONCLUDING REMARKS

This paper reports the occurrence of the γ phase in IPP moulding produced using SCORIM. The reasons for this occurrence, together with the non-occurrence of the β phase, will be considered in a more extensive treatment[15] that reports on the relationships between the mechanical properties, micromorphology and processing conditions in mouldings produced by conventional injection moulding and SCORIM. In the work reported here, SCORIM is found to produce highly oriented IPP mouldings, with substantially enhanced Young's modulus.

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