

The occurrence of the γ -phase in injection moulded polypropylene in relation to the processing conditions

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Wide-angle X-ray diffraction has been used to characterize different grades of conventionally injection moulded and shear-controlled-orientation injection moulded isotactic polypropylene. The occurrence of the γ -phase in injection mouldings was discussed in particular. A newly defined γ -phase index is used as a criterion for the characterization of mouldings. The γ -phase was shown to be associated with pronounced molecular orientation while the β -phase is indicative of low modulus. Shear-controlled-orientation injection moulding (SCORIM) provided for a good control on the final properties of the mouldings. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

In previous papers^{1,2}, evidence for the occurrence of the γ -phase in injection moulded isotactic polypropylene (IPP) was reported. This paper extends the analysis with the presentation of further evidence for the occurrence of the γ -phase and its dependence on the grade of polypropylene, and the interpretation of diffraction data based on the structure of the γ -phase reported recently by Brückner and Meille^{3–5}.

It is well known that isotactic polypropylene exhibits three different crystal phases apart from the smectic phase^{6,7}, which is a phase of intermediate order between the amorphous and the crystalline phase⁵. These three crystal phases are monoclinic (α), hexagonal (β), and orthorhombic (γ)^{3,4} which was previously accepted to be triclinic^{8,9}. The lattice cell dimensions of the α -phase are $a = 6.666$, $b = 20.78$, $c = 6.495$ Å and $\beta = 99.6^\circ$, as reported by Turner-Jones *et al.*⁸ and represent a small change from those originally reported by Natta and Corradini¹⁰. The crystal unit cell for the β -phase and its dimensions are controversial but the most probable dimensions for a hexagonal lattice are accepted to be $a = 22.03$ and $c = 6.49$ Å¹¹.

The triclinic cell geometry of the γ -phase, which has been widely accepted with the unit cell as proposed by Morrow and Newman⁹, has the lattice cell dimensions $a = 6.54$, $b = 21.40$, $c = 6.50$ Å and $\alpha = 89^\circ$, $\beta = 99.6^\circ$, $\gamma = 99^\circ$. However, Brückner and co-workers^{3,4} discussed the consistency of the crystallographic data and suggested an orthorhombic crystal structure, which was also supported by electron diffraction studies^{12,13}. Brückner and Meille³ initially determined the crystal structure by using the Rietveld method of analysis of X-ray powder

diffraction data, and later confirmed the proposed structure by following a packing-energy analysis that compared the internal energies of the α - and γ -phases⁵. The proposed^{3,4} face-centred orthorhombic lattice cell dimensions are $a = 8.54$, $b = 9.93$ and $c = 42.41$ Å.

In the α -phase all of the chains are parallel, and the adjacent bilayers contact each other through layers of helices of opposite chirality, whereas in the γ -phase the interaction between the bilayers occurs through helices of the same chirality⁵ (see Figure 1 of ref. 5). Packing of iso-chiral helices results in an 80° rotation of the chain axis and consequently non-parallelism of the chains^{5,12}. In the α -phase the iso-chiral packing is occasional and results in lamellar branching^{12,14}. The γ -phase is known to grow epitaxially on α crystals and the crystallographic relationship between the two phases is established very satisfactorily by Lotz and co-workers^{12–14}. A γ lath grows on an α parent lamellae, making an angle of 40° with the latter¹². The crystal morphology of γ -IPP is closely related to that of α -IPP since epitaxial growth of γ on α lamellae is one of the most common routes to obtain γ -IPP¹⁴.

The $\gamma \rightarrow \alpha$ transformation has also been debated in the literature^{9,15–20}. The $\gamma \rightarrow \alpha$ transformation was earlier considered to be a solid-state transformation^{9,15,18,20} which occurs when α -phase polypropylene is subjected to mechanical deformation⁸ or to appropriate thermal treatment^{9,15–17,19}. Kardos *et al.*¹⁵ reported that the $\gamma \rightarrow \alpha$ transformation at 1 atm occurs at a temperature only slightly below the γ -phase melting point and is very sensitive to the concentration of defects in the crystalline polymer. Pae¹⁶ found that the rate of conversion from γ to α is a function of time and temperature and tends to approach a constant value with increasing time. Sauer and Pae¹⁷ reported that the γ -phase may be stable or metastable depending upon the crystallization conditions.

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For high values of supercooling (ΔT) the γ -phase shows a partial conversion to the α -phase under elevated temperature annealing, whereas for low values of ΔT the γ -phase does not convert to the α form even at elevated temperatures¹⁷. The γ -phase is thermodynamically the most stable for chain-extended polypropylene, or for polypropylene of a large-fold period grown in a high-pressure environment, whereas the α -phase appears to be the preferred form of folded-chain polypropylene grown in the absence of severe restraints¹⁷. Morrow¹⁸ also showed that under particularly-high-pressure crystallization conditions a stable γ -phase can be produced which does not transform to the α form either by thermal or mechanical treatment. The $\gamma \rightarrow \alpha$ solid-solid transformation was accepted to be martensitic in nature^{9,19,20}, and Morrow and Newman⁹ reported that this solid-solid transformation involves relative motion between the (040) planes which are invariant in the γ and α -phases. However, Brückner and co-workers^{3,4} ruled out the possibility of solid-solid transformation on the basis of the very different crystal lattices that were defined for the α - and γ -phases. Moreover, they have recently reported⁵ the packing energies for the α - and γ -phases which indicated that the γ -phase structure is at least as stable as the α -phase structure.

It is also interesting to note that the γ -phase also occurs in random copolymers of propylene with minor proportions of ethylene or butene^{21,22} and that the proportion of the γ -phase increases with the comonomer content.

In this present study both conventional injection moulding and shear-controlled-orientation injection moulding (SCORIM), where the latter provides a route for producing strongly preferred molecular orientation by the controlled application of shear forces to a solidifying melt²³⁻²⁵, were used for the production of mouldings. The two injection moulding techniques were applied to several grades of polypropylene, and by drawing in retrospect on the mouldings produced in two separate investigations, it was possible to draw useful conclusions relating to the crystallinities of the mouldings. Because the moulding conditions used were not closely coordinated it was not possible to gain insight into the key factors controlling the enhancement of physical properties. However, a detailed investigation of crystal phases influencing the morphology and mechanical properties such as impact and tensile properties has been carried out and will be reported in a subsequent paper²⁶.

EXPERIMENTAL

Materials

Two grades of polypropylene were used in this study. The grade KF6100 homopolymer with a melt flow index of 3.1 g per 10 min was supplied by Shell (Louvain-la-Neuve, Belgium). The other polypropylene was the grade GYM43 homopolymer with a melt flow index of 10.5 g per 10 min, which was obtained from ICI. Further GYM43 was also compounded with the addition of 0.15% Geniset nucleating agent, which is a mixture of the isomers of dimethylbenzylidene sorbitol, and used for moulding and characterization.

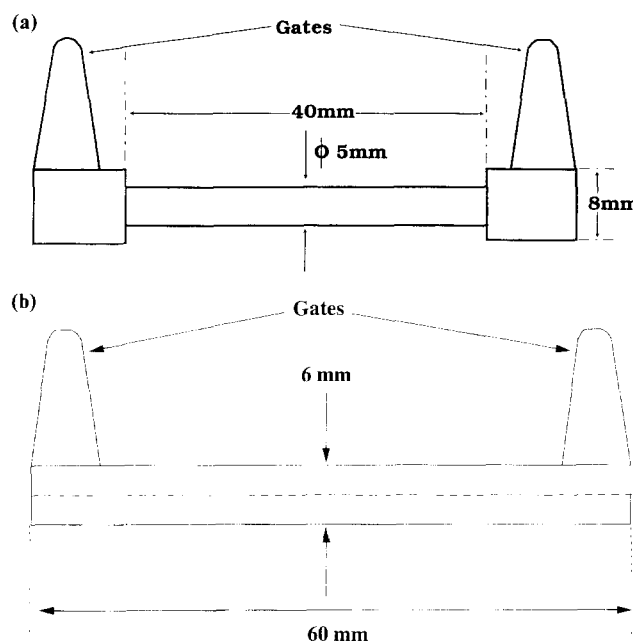


Figure 1 Schematic representations of (a) the cylindrical tensile test bar and (b) the square-cross-section bar

Injection moulding

Mouldings. Both conventional injection moulding and shear-controlled-orientation injection moulding were applied in the processing of the three polypropylene compounds. Round tensile test bars with a diameter of 5 mm and a gauge length of 40 mm, and mouldings with a square cross-section of 36 mm² and a length of 60 mm, were produced with the KF6100 and GYM43 grades, respectively. Figures 1a and 1b show schematic diagrams of the moulded bars used in the work. A Demag 150 injection moulding machine with a double live-feed moulding device²³ was used for the production of the bars.

The processing conditions used for moulding the KF6100 grade. Details of the moulding conditions for KF6100 are given below.

(1) Conventional injection mouldings. Four sets of mouldings were made, which can be briefly described as:

- (i) CM-A high injection speed and low melt temperature;
- (ii) CM-B low injection speed and low melt temperature;
- (iii) CM-C high injection speed and high melt temperature;
- (iv) CM-D low injection speed and high melt temperature.

The conventional injection moulding conditions are summarized in Table 1. The cavity pressure was measured by a transducer located at the centre of the bar. For all of the mouldings the cavity was filled from one of the gates shown in Figure 1a.

(2) SCORIM mouldings. The general moulding conditions for the SCORIM samples were the same as those used for the conventional mouldings and are summarized in Table 2. Three sets of mouldings were prepared, which can be described as:

- (i) SCORIM-A, high injection speed and low melt temperature;

Table 1 The processing conditions used for the production of conventional mouldings

Parameter	Processing condition							
	A	B	C	D	1A	1B	2A	2B
Injection time (s)	0.48	1.76	0.48	1.76	2	2	2	2
Holding pressure (bar) ^a	38	38	38	38	120	120	120	120
Holding pressure time (s)	45	45	45	45	67	97	67	97
Mould temperature (°C)	60	60	60	60	70	70	70	70
Melt temperature (°C)	195	195	230	230	230	280	230	280
Cavity pressure (bar) ^a	774	427	966	450	1715	1715	1687	1637

^a 1 bar = 10⁵ Pa**Table 2** The processing conditions used for the production of SCORIM mouldings

Parameter	Processing condition							
	A	B	C	1A	1B	1C	1D	
Injection time (s)	0.48	0.92	0.48	2	2	2	2	
Holding pressure bar ^a	38	38	38	120	120	120	120	
Holding pressure time (s)	86	86	86	75	69	67	135	
Mould temperature (°C)	60	60	60	30	70	70	70	
Melt temperature (°C)	195	195	230	220	230	230	280	
Average cavity pressure (bar) ^a	1393	1282	1460	1678	1678	1602	3033	

^a 1 bar = 10⁵ Pa**Table 3** The processing sequence in SCORIM for SCORIM-A, -B and -C samples

Stage	Duration (s)	Move time (s)	Compression pressure (bar) ^a
SO	4	2	55
S1	12	2	41
S2	12	2	28
S3	18	3	21
S4	40	5	14

^a 1 bar = 10⁵ Pa

- (ii) SCORIM-B, low injection speed and low melt temperature;
- (iii) SCORIM-C, high injection speed and high melt temperature.

When the mould had been initially filled with the melt from one of the gates the same SCORIM profile of conditions was applied to all of the mouldings. This profile only utilized the Mode A of operation of the process previously described²⁴. The SCORIM pistons were caused to reciprocate in their respective chambers with a phase difference of 180°. This action ensured that the remaining melt in the cavity was being constantly sheared during solidification.

The details of the SCORIM profile are shown in Table 3. Five stages of conditions were set and they were activated during the cycle in the order SO → S4. It can be seen that the piston pressure used to drive the material through the mould (compression pressure) was systematically reduced from one stage to the next. This was done in order to ensure that the complete section solidified during the shearing action from the SCORIM piston. For all three moulding conditions the cavity pressure transducer indicated that solidification was completed during stage S4 of the SCORIM profile.

The processing conditions used for the mouldings of the GYM43 and the GYM43 + 0.15% Geniset. Details of the moulding conditions for GYM43 and GYM43 filled with 0.15% Geniset nucleating agent are summarized below. The numbers 1 and 2 following the abbreviations CM and SCORIM stand for GYM43 and GYM43 + 0.15% Geniset, respectively.

(1) Conventional mouldings. Two sets of mouldings were made both with GYM43 and GYM43 + 0.15% Geniset and can be described as:

- (i) CM-1A and CM-2A, short holding pressure time and low melt temperature;
- (ii) CM-1B and CM-2B, long holding pressure time and high melt temperature.

The conventional injection moulding conditions for these mouldings are also summarized in Table 1. The cavity melt pressures were also measured by a transducer located at the center of the bar. The values given in Table 1 are the cavity pressure recorded at the start of the hold pressure time in the moulding cycle.

(2) SCORIM mouldings. The general moulding conditions are summarized in Table 2. The average cavity pressure value was taken from the cavity pressure traces which were printed from the graphics data on the machine control. The set conditions for the SCORIM2 mouldings were the same as those in Table 2. The resulting average cavity pressures however, only deviated slightly from the SCORIM1 values shown.

Four different sets of mouldings were made from each of the GYM43 (series SCORIM1) and that GYM43 + 0.15% Geniset (series SCORIM2). For all of the SCORIM mouldings the initial volume displacement of the SCORIM piston was 5 cm³ for each piston movement and the time for one movement was 2 s. The SCORIM action was maintained during the solidification

of the moulded section as determined by the pressure transducer. In all cases the moulded section had solidified before the holding pressure time (shown in Table 2) had elapsed. The SCORIM profiles were adjusted for each set of moulding conditions to give a controlled shearing/solidification curve as indicated by the cavity pressure transducer response.

Tensile testing

An Instron 4206 tensile testing machine was used for the tensile testing. Stress-strain curves were determined using crosshead speeds of 25 and 50 mm min⁻¹ for the KF6100 and GYM43 mouldings, respectively. Values for the Young's modulus were determined with a clip strain gauge, with crosshead speeds of 0.05 and 0.1 mm min⁻¹ for the KF6100 and the GYM43 mouldings, respectively.

Wide-angle X-ray diffraction

CuK α radiation was used for both X-ray diffractometry and measurement of Debye patterns. The Debye patterns were used to record any preferred orientation. The samples used for these were 1.5 mm thick and cut parallel to the injection direction. A 100 μ m diameter aperture was used to define the position and cross-section of the incident X-ray beam.

For the diffractometer studies the X-rays were incident on a longitudinal section. Diffraction profiles were recorded by scanning at a rate of 0.02° 2 θ s⁻¹ over the angular range 8° < 2 θ < 32°. The β -phase and α -phase orientation indices, and the crystallinity index were calculated as described in detail by Trotignon *et al.*²⁷. This quantitative method of estimating the relative proportions of the α and β forms was first suggested by Turner Jones *et al.*⁸, and extended by Trotignon *et al.*²⁷. Additionally, the crystallinities of the samples were also determined from the diffractometer profiles. In this present paper, a new γ -phase index^{28,29}, G , is used as a criterion for the γ -phase and is defined as follows:

$$G = \frac{h\gamma}{h\alpha_1 + h\alpha_2 + h\alpha_3 + h\alpha_4} \quad (1)$$

where $h\alpha_1$, $h\alpha_2$, $h\alpha_3$, and $h\gamma$ are the heights of the crystalline peaks corresponding to 2 θ angles of 14.1, 16.9, 18.5 and 20.05°, and $h\alpha_4$ is the average height of the peaks corresponding to 2 θ angles of 21.2, 21.7 and 21.8°. In two previous papers the method described by Turner-Jones *et al.*⁸ was adopted for the indexing of the γ peaks but the new orthorhombic cell indexing⁴ will be used for the γ -phase in this present paper. Therefore the 20.05° γ -phase reflection is assigned the Miller indices (117).

An estimation of the γ -phase content relative to the α -phase is also made from the peak heights of the 130 α and 117 γ reflections. Turner-Jones²¹ estimated the percentage γ -phase for IPP samples containing both α - and γ -phases. The γ -phase crystallinity was plotted against the ratio $h\gamma/(h\gamma + h\alpha_3)$ ²¹, and this ratio was calculated for the mouldings and the corresponding percentage γ -phase is read from Figure 2 of ref. 21. It is worth emphasizing that although this calculation holds true for samples which do not exhibit a β -phase, it is an approximation, and must be seen as a comparative figure for those injection mouldings exhibiting the β -phase.

Table 4 The tensile test results obtained from conventional mouldings^a

Sample	Stress at peak (MPa)	Stress at 0.2% yield (MPa)	E (MPa)
CM-A	31.6 (0.6)	18.55 (0.6)	1195 (113)
CM-B	32.2 (0.4)	18.44 (0.7)	1887 (401)
CM-C	32.0 (0.3)	18.31 (0.7)	1629 (188)
CM-D	31.7 (0.5)	18.23 (0.2)	1910 (430)
CM-1A	40.6 (1.5)	23.2 (1.3)	1540 (90)
CM-!B	31.7 (1.0)	14.5 (0.6)	1860 (140)
CM-2A	35.0 (2.3)	17.5 (2.6)	1630 (280)
CM-2B	31.5 (0.8)	14.0 (0.7)	1770 (130)

^a Standard deviations given in parentheses

Table 5 The tensile test results obtained from SCORIM mouldings^a

Sample	Stress at peak (MPa)	Stress at 0.2% yield (MPa)	E (MPa)
SCORIM-A	51.2 (0.5)	25.14 (1.0)	3334 (965)
SCORIM-B	51.6 (0.2)	25.39 (0.8)	2787 (713)
SCORIM-C	50.0 (1.1)	25.39 (1.1)	2312 (460)
SCORIM-1A	57.4 (1.4)	19.89 (6.0)	3910 (340)
SCORIM-1B	54.8 (1.7)	22.50 (6.4)	2620 (320)
SCORIM-1C	56.0 (1.9)	27.8 (3.2)	2630 (180)
SCORIM-1D	48.6 (0.2)	19.0 (0.8)	2350 (230)
SCORIM-2A	50.0 (1.9)	20.4 (1.4)	2420 (140)
SCORIM-2B	51.1 (1.8)	18.1 (3.1)	2800 (340)
SCORIM-2C	53.3 (1.1)	21.6 (1.9)	2980 (270)
SCORIM-2D	47.5 (0.5)	18.8 (1.3)	2850 (550)

^a Standard deviations given in parentheses

RESULTS AND DISCUSSION

Tensile test results

Tables 4 and 5 summarize the tensile test results for the conventional and the SCORIM mouldings, respectively.

For the conventional mouldings of the KF6100 grade IPP, the highest Young's modulus is achieved for processing conditions B and D for which the injection speed is lower than that of A and C. Table 4 shows the tensile test results for the conventional mouldings. The decrease in modulus at higher injection speeds is attributed to the higher shear heating. Kubát and Rigdahl³⁰ reported that the stiffness of the mouldings increases up to a certain limit and then decreases beyond this limit as the injection speed increases. The stress at the peak and at 0.2% yield show almost the same values (within the experimental error) for all processing conditions. It is also found that the two different processing temperatures applied, namely 195 and 230°C, show considerable differences in the stiffness of the mouldings but not in other tensile properties. Samples fail in a ductile manner in tensile testing.

The conventional mouldings of the GYM43 and the GYM43 + 0.15% Geniset behave in a similar manner in tensile testing. Yield stress decreases when a high Young's modulus is achieved, following the application of long holding pressure times and a high melt temperature. Conversely, when a high yield strength is achieved following short holding pressure times and a low melt temperature the Young's modulus decreases. The addition of 0.15% Geniset nucleating agent does not cause a significant change in the mechanical behaviour of the GYM43 polypropylene in conventional injection moulding.

When using SCORIM for the production of mouldings of the KF6100 grade polypropylene, the highest

Table 6 X-ray diffraction data obtained for the CM-1A moulding

2θ (deg)	d (Å)	d^{*a}	Miller indices (hkl)	Crystal phase	Relative intensity (%)
13.96	6.336	0.243	110	$\alpha(+\gamma)$	80
16.10	5.499	0.280	300	β	92
16.80	5.270	0.292	040	$\alpha(+\gamma)$	100
18.51	4.764	0.323	130	α	44
20.01	4.432	0.347	117	γ	34
21.19	4.187	0.368	111	$\alpha(+\gamma)$	59
21.72	4.087	0.377	041	$\alpha(+\gamma)$	51
25.31	3.515	0.438	060	α	13
28.50	3.128	0.492	220	α	6

$$^a = \lambda/d$$

Young's modulus is then achieved with processing conditions A in which a high injection speed was applied. The use of a lower injection speed results in a decrease in modulus, which is clearly indicated by the results obtained for processing conditions B. An increase in melt temperature also causes a decrease in modulus. The melt temperature is caused to increase by the use of processing conditions C and the SCORIM-C mouldings exhibit the lowest Young's modulus. The use of high melt temperatures tends to cause sheared and oriented molecules to relax before the completion of solidification. The tensile strengths of the SCORIM mouldings, as also found for the conventional mouldings, show no dependent on the processing conditions that have been applied. However, when the ultimate tensile strength of the SCORIM mouldings is compared to that of conventional mouldings a 60% increase is recorded for the SCORIM mouldings. An increase of 75% in Young's modulus occurs as a consequence of the SCORIM processing and SCORIM samples exhibit brittle failure in tensile testing.

For the SCORIM mouldings of the GYM43 grade polypropylene, the highest Young's modulus, i.e. 3.91 GPa, is achieved for the SCORIM-1A sample, which was produced using the lowest melt and mould temperatures. This represents a greater than two-fold increase in the Young's modulus for the GYM43 grade polypropylene with SCORIM. SCORIM-1D conditions produced the lowest Young's modulus, i.e. 2.35 GPa, when compared with the other GYM43 grade IPP SCORIM mouldings. The SCORIM profile A gives the highest stiffness for the GYM43 material. The SCORIM profile D, which results in twice the cavity pressure that is achieved with the SCORIM profile A, also leads to the lowest yield strength mouldings for GYM43. There is an increase of more than 45% in the 0.2% yield strength with the application of the SCORIM profile C, in comparison to profile D. The holding pressure time for profile D is very long, and the melt temperature is the highest. The two stages for this profile have a very long duration, during which very high cavity pressures are achieved. Therefore, mechanical degradation of the polypropylene may have occurred. A very high percentage of the γ -phase and a lower overall crystallinity (see Table 8, below) were recorded for profile D mouldings, compared with other mouldings of the same grade, and suggests degradation of the polymer resulting from the processing conditions.

The tensile test results for the SCORIM mouldings produced from GYM43 filled with 0.15% Geniset nucleating agent exhibit a different behaviour. The highest Young's modulus is achieved for SCORIM-2C which has a low melt temperature; SCORIM-2B exhibits a slightly lower Young's modulus than SCORIM-2C. The SCORIM profile D for the GYM43+0.15% Geniset gives a lower yield strength and Young's modulus than those recorded for the profile C, although it does not result in the lowest mechanical response, with this being recorded for the GYM43 without the addition of Geniset. SCORIM-2A mouldings exhibit the lowest Young's modulus.

Wide-angle X-ray diffraction results

Tables 6 and 7 summarize the measurements made of 2θ angles, d -spacings, d^* ($= \lambda/d$), relative intensities of the diffraction peaks, crystal phase, and the Miller indices associated with the reflections recorded from CM-1A and SCORIM-2C, respectively. These two samples exhibit all three of the crystalline phases α , β and γ .

The CM-A and CM-B data are similar, whereas CM-C and CM-D, for which a higher melt temperature in processing (than CM-A and CM-B) was applied, show no peaks at a 2θ of 16.07° which is the 300 β -phase reflection. CM-A, -B, -C, and -D do not show any γ -phase reflections. CM-1A and CM-1B exhibit γ -phase reflections which are identified with the peak at a 2θ of 20.06° . The γ -phase peak for CM-1B is more intense than the corresponding peak for CM-1A. While CM-1A exhibits a 300 β -phase reflection the mouldings CM-1B do not exhibit any β -phase peaks. Another important difference between CM-1A and CM-1B is the intensity of the doublet which comprises the 111_α and 041_α reflections. CM-1B shows a higher intensity for this doublet than CM-1A. CM-2A and CM-2B exhibit similar behaviours to CM-1A and CM-1B. Both exhibit a 117 γ -phase reflection, but this reflection is more intense for CM-2B than CM-2A. A 300 β -phase reflection is observed for CM-2A but it is not observed for CM-2B. Again, the intensity of the doublet corresponding to the 111_α and 041_α reflections are more intense for CM-2B than for CM-2A.

SCORIM-A, -B and -C mouldings exhibit 117 γ -phase reflections, but they do not exhibit a 300 β -phase reflection. This is the major difference between the conventional and SCORIM mouldings of the KF6100

Table 7 X-ray diffraction data obtained for the SCORIM-2C moulding

2θ (deg)	d (Å)	d^{*a}	Miller indices (hkl)	Crystal phase	Relative intensity (%)
13.83	6.396	0.241	110	$\alpha(+\gamma)$	80
14.98	5.907	0.261	113	γ	14
16.10	5.499	0.280	300	β	71
16.78	5.277	0.292	040	$\alpha(+\gamma)$	100
18.52	4.785	0.322	130	α	28
19.97	4.441	0.347	117	γ	36
21.20	4.192	0.368	111	$\alpha(+\gamma)$	7
21.80	4.072	0.378	041	$\alpha(+g)$	5
25.26	3.522	0.437	060	α	14
27.10	3.286	0.469	220	α	1
28.57	3.121	0.493	220	α	8

$$^a = \lambda/d$$

grade polypropylene. As Turner-Jones⁸ stated, the presence of reflections with a d -spacing of 4.426 Å indicates the presence of the γ -phase, which is in fact the case for the SCORIM mouldings of both grades of polypropylene under investigation here. SCORIM-A, -B and -C mouldings exhibit a 200_α reflection whereas this reflection is not present in the conventional mouldings. The SCORIM mouldings of the GYM43 grade polypropylene exhibits two γ -phase peaks at 2θ angles of 14.98 and 20.06°, which correspond to 113 and 117, respectively, whereas the SCORIM mouldings of the KF6100 grade exhibits only a 117_γ reflection, except for SCORIM-C which also exhibits a 113_γ reflection. Of the four SCORIM1 mouldings, only SCORIM-1B exhibits a 300_β -phase reflection. The intensity of the doublet of the 111_α and 041_α reflections is more pronounced for SCORIM-1D than the other three SCORIM1 mouldings. The main characteristic of the SCORIM2 mouldings is the presence of the β -phase reflection 300. Only SCORIM-2D does not show this reflection. The presence of more β -phase in the SCORIM2 mouldings than in the SCORIM1 mouldings may be attributed to the Geniset nucleating agent. As with the SCORIM1 mouldings, all of the SCORIM2 mouldings exhibit 113 and 117 γ -phase reflections. SCORIM-2A shows a weak reflection at a 2θ angle of 28.24°, corresponding to a d -spacing of 3.156 Å, which appears as a shoulder on the 220_α reflection. This reflection may be identified as 411_β . As with the SCORIM mouldings of the KF6100 grade IPP, the SCORIM-2C mouldings also exhibit a 200_α reflection at a 2θ angle of 27.10°. The intensity of the $111_\alpha + 041_\alpha$ doublet is higher for SCORIM-2D than for the other three SCORIM2 mouldings.

The α -phase orientation index, β -phase index, γ -phase index, crystallinity index and percentage γ were calculated for all of the conventional and SCORIM mouldings. The relative orientations of the section of the mouldings used for X-ray Debye pattern measurements and X-ray diffractometry were the same for all samples, thereby providing for the standardization of the technique for mouldings exhibiting different textures and anisotropy of physical properties. The crystallinities of each sample were calculated. All of the results are shown in Table 8. Figure 2 shows the X-ray diffraction profiles gained from the CM-A and SCORIM-A mouldings.

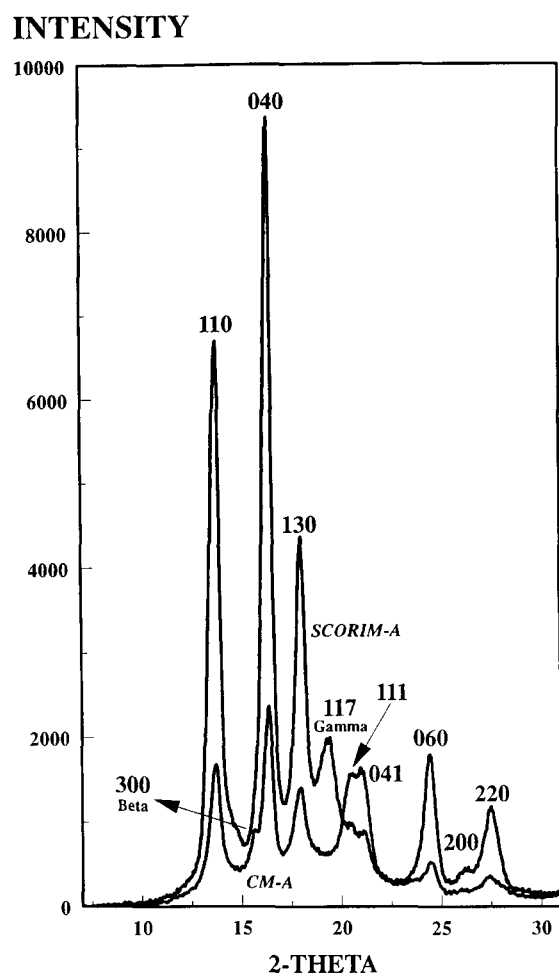
Figures 3 and 4 show the X-ray diffraction profiles obtained for various samples of the GYM43 and GYM43 + 0.15% Geniset systems, respectively.

The α -phase orientation indices of all of the SCORIM mouldings are considerably higher than those of the conventional mouldings. The crystallinity indices and the crystallinities of all of the SCORIM mouldings are also higher than those of the conventional mouldings. The SCORIM mouldings of the KF6100 grade polypropylene have a β -index value of zero, with the β -phase indices of the samples CM-C and -D, CM-1B, CM-2B, SCORIM-1C and -1D, and SCORIM-2D also being zero. All of the conventional mouldings of KF6100 have a zero γ -phase index, and all of the conventional mouldings of the GYM43 and the GYM43 + 0.15% Geniset have a lower γ -phase index than the SCORIM mouldings of the corresponding grades. These results are consistent with the differences in the Young's moduli of the mouldings. The results concerning the γ -phase also confirm the association of the γ -phase with the chain-extended morphology. In SCORIM mouldings the high shear applied to the melt during processing creates a high molecular alignment which is revealed as a chain-extended-like micromorphology², and all of the SCORIM mouldings exhibit a high proportion of the γ -phase, as is evident from the γ -phase index for SCORIM mouldings. The percentage γ for the mouldings are also consistent with the γ -phase indices. Both the SCORIM1 and the SCORIM2 mouldings exhibit high proportions of the γ -phase. The percentages of γ for these mouldings are three- to four-fold higher than that recorded for the SCORIM mouldings of the KF6100 grade polypropylene. The γ -phase in injection mouldings can be seen as a sign of enhanced mechanical properties, although since it is also associated with low-molecular-weight polypropylene, as a single parameter it does not have too much of a significance²⁶. However, the presence of a high γ -phase content is certainly consistent with high molecular alignment and consequently high mechanical performance²⁶ when compared with injection mouldings that do not exhibit a pronounced degradation.

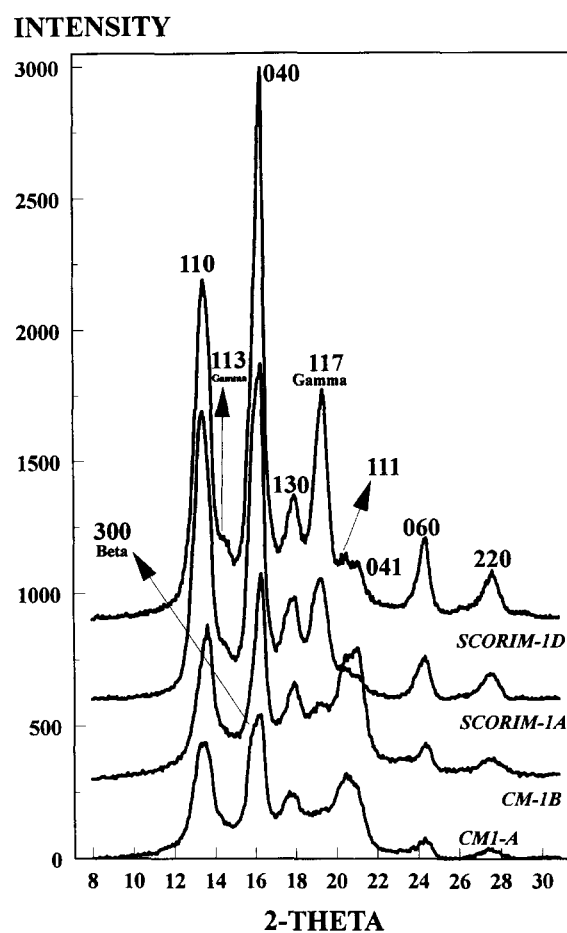
SCORIM-A mouldings exhibit a high Young's modulus and a zero β -phase index. The β -phase is associated with low modulus and tensile yield strength values². CM-D has the highest Young's modulus of those mouldings

Table 8 The α -phase orientation index A , β -phase index B , γ -phase index G , crystallinity index C , percentage γ , and percentage crystallinities of the conventional and SCORIM mouldings

Sample	A	B	G	C	γ content (%)	Crystallinity (%)
CM-A	0.561	0.216	0	1.650	0	38.63
CM-B	0.561	0.223	0	1.691	0	40.42
CM-C	0.583	0	0	1.778	0	41.48
CM-D	0.582	0	0	1.858	0	43.66
CM-1A	0.643	0.358	0.049	1.733	29.55	49.13
CM-1B	0.599	0	0.047	1.348	25.32	42.04
CM-2A	0.572	0.231	0.041	1.729	25.00	48.61
CM-2B	0.602	0	0.065	1.429	34.94	44.44
SCORIM-A	0.971	0	0.045	2.577	14.94	52.57
SCORIM-B	0.971	0	0.040	2.573	13.64	52.39
SCORIM-C	0.962	0	0.039	2.710	14.94	54.88
SCORIM-1A	0.976	0	0.124	2.262	48.05	62.91
SCORIM-1B	0.969	0.378	0.132	2.976	53.25	61.02
SCORIM-1C	0.976	0	0.136	2.459	47.21	64.88
SCORIM-1D	0.941	0	0.190	2.353	64.74	59.00
SCORIM-2A	0.965	0.370	0.125	2.291	55.58	57.17
SCORIM-2B	0.957	0.420	0.139	2.704	54.55	64.70
SCORIM-2C	0.974	0.357	0.138	3.174	53.25	66.94
SCORIM-2D	0.894	0	0.185	1.968	64.74	54.40

**Figure 2** X-ray diffraction profiles obtained from CM-A and SCORIM-A mouldings

prepared from the same grade polypropylene, which is consistent with the relatively low level of β -phase and the high crystallinity. CM-1A and CM-2A mouldings exhibit a β -phase which is identified by the β -phase

**Figure 3** X-ray diffraction profiles obtained from the CM-1A, CM-1B, SCORIM-1A and SCORIM-1D mouldings

indices, while CM-1B and CM-2B mouldings do not exhibit any β -phase reflections. As shown above, CM-1A and CM-2A mouldings exhibit lower Young's moduli than CM-1B and CM-2B mouldings, respectively. SCORIM-1A has the highest Young's modulus of the

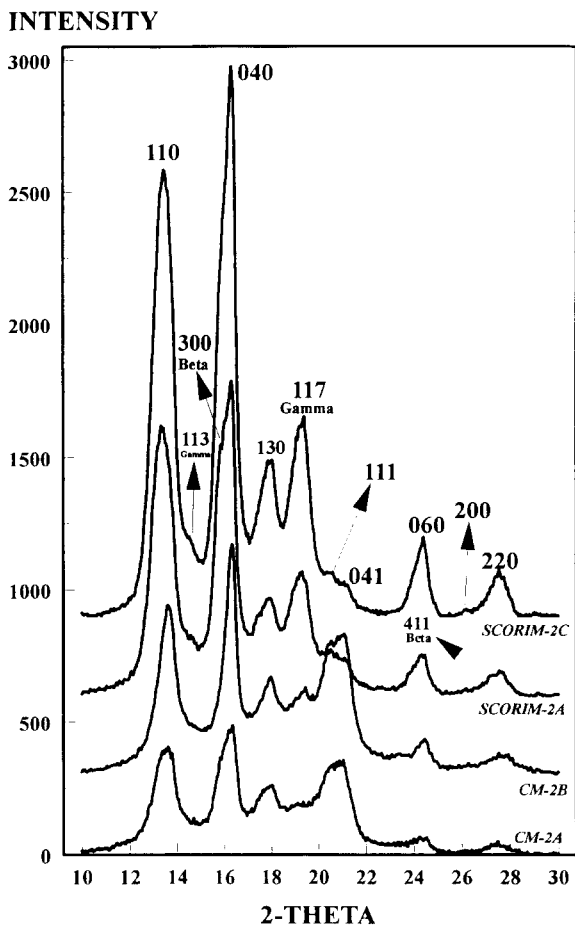


Figure 4 X-ray diffraction profiles obtained from the CM-2A, CM-2B, SCORIM-2A and SCORIM-2C mouldings

SCORIM1 mouldings, which is consistent with the high α -phase orientation index and high crystallinity, although the γ -phase index is relatively low compared with those of mouldings SCORIM-1B -1C and -1D. SCORIM-1D has the lowest Young's modulus of the SCORIM1 mouldings and this is also consistent with its relatively low α -phase index and low crystallinity, although it has a high γ -phase index. The Young's modulus values of SCORIM-A, -B and -C can be described by their γ -phase indices. SCORIM-A has the highest Young's modulus and γ -phase index of all of the samples, whereas SCORIM-C has the lowest values for these parameters. When the SCORIM mouldings of the GYM43+0.15% Geniset are considered, similar relationships are apparent. For example, SCORIM-2A has a low crystallinity, and a low γ -phase index, and exhibits the β -phase, with all of these being associated with a low Young's modulus. Similarly, SCORIM-2C has the highest Young's modulus of the SCORIM2 mouldings and has a relatively high α -phase orientation index, a low β -phase index, a high γ -phase index and high crystallinity. As Table 8 shows, all of the parameters are interdependent, and also clearly indicate the complex relationship between the mechanical properties and the occurrence of specific crystalline phases.

Figures 5 and 6 show the Debye patterns obtained from the CM-1B and SCORIM-1C mouldings, respectively, with Figure 7 showing a schematic representation of the Debye pattern from SCORIM-1C. The Debye

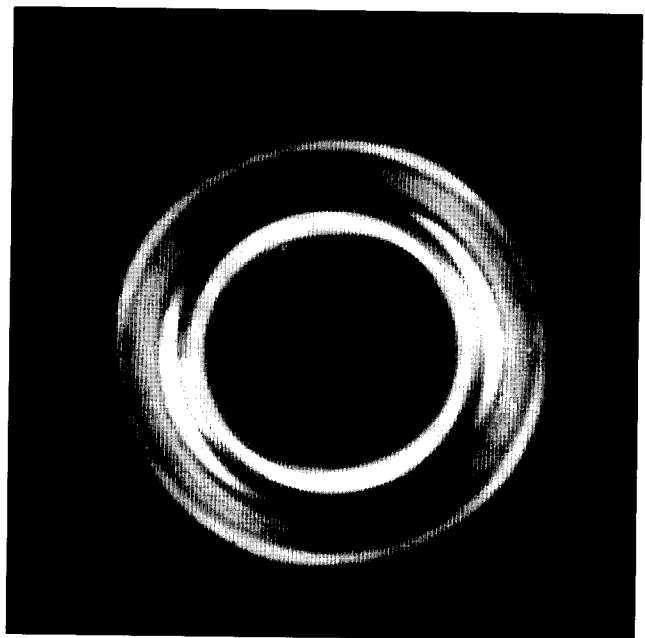


Figure 5 Debye pattern obtained from the CM-1B moulding

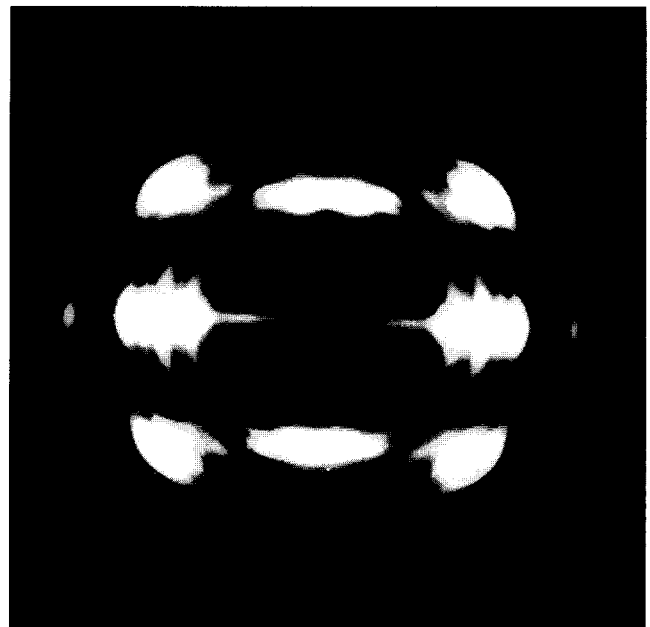


Figure 6 Debye pattern obtained from the SCORIM-1C moulding

patterns are also consistent with the pronounced orientation in the SCORIM mouldings. For CM-1B nine Debye rings are observed. The rings are, from the inner to the outer ring, an unidentified ring at $2\theta = 12.63^\circ$, associated with a d -spacing of 7.000 Å, 110_α , 113_γ , 040_α , 130_α , 117_γ , $111_\alpha + 041_\alpha$, 060_α , and 220_α . Principally, 040_α , 130_α , and 060_α represent a low level of preferred orientation, which is readily apparent from the arcing of these reflections. For SCORIM-1C, ten Debye rings are observed, which are shown schematically in Figure 7. All of the rings show a preferred orientation and they are, from the inner to the outer ring, an unidentified ring at $2\theta = 12.63^\circ$ as above, 110_α , 113_g , 040_α , 130_α , 117_γ , $111_\alpha + 041_\alpha$, 131_α , 060_α , and 220_α . The most prominent feature is the occurrence of the ring with a d -spacing of 7 Å, apart from the

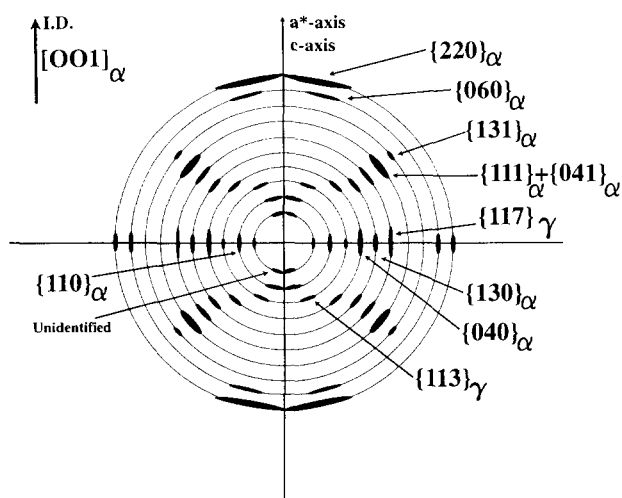


Figure 7 Schematic representation of the Debye pattern from the SCORIM-1C moulding

occurrence of the two γ -phase rings. The Debye pattern for SCORIM-2C shows an $(a^* + c)$ -axis oriented texture where the $[001]_{\alpha}$ zone axis is parallel to the injection direction. This characteristic was discussed in a previous article¹. As reported earlier¹ the Debye pattern for the SCORIM-A moulding shows seven rings, while 030_{α} , 110_{γ} , and 131_{α} , which are observed for SCORIM-2C, are not observed. Additionally, the 040_{α} and 060_{α} rings exhibit only two arcs for SCORIM-A, whereas they exhibit six arcs for SCORIM-2C; the latter may be attributed to twinning.

The observations that are reported above are based on the interpretation of Debye patterns. A more comprehensive interpretation of the pronounced textural characteristics should result from the pole figure studies that are currently in progress.

CONCLUSIONS

The conclusions drawn from the results presented above may be summarized as follows:

- (A) Shear-controlled-orientation injection mouldings exhibit higher molecular orientation than conventional injection mouldings, which is consistent with a substantial increase in the Young's modulus of mouldings produced by the SCORIM technique. A two-fold increase in Young's modulus of the GYM43 grade polypropylene and a 75% increase in Young's modulus of the KF6100 grade polypropylene are reported for SCORIM mouldings when compared with their conventional counterparts.
- (B) The presence of the β -phase in injection moulded IPP samples is indicative of a decrease in the Young's modulus.
- (C) The γ -phase is associated with pronounced molecular orientation for a range of polypropylene grades, and the γ -phase index serves as a useful criterion in the complete characterization of IPP.

Further studies, based on higher-molecular-weight grades of polypropylene, and the use of conventional and SCORIM moulding, have been carried out for the purpose of exploring the influence of molecular weight on the micromorphology and physical properties of moulded IPP. These results will be reported in subsequent publications, which will particularly refer to chain-extended morphologies and the simultaneous enhancement of impact properties and modulus that can be realized through the use of SCORIM moulding.

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