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Electron microscopy studies of α- and β-form spherulites in weld lines of injection moulded polypropylene parts

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The crystal morphology of the weld lines in injection moulded polypropylene parts has been investigated by X-ray scattering and transmission electron microscopy. Wide angle X-ray scattering curves reveal two crystal modifications in the samples: the monoclinic α-modification and the hexagonal β-modification. The fraction of the crystallinity which is due to the β-modification is lower in the vicinity of the weld line and increases with the distance from the weld line.

Transmission electron micrographs reveal that in the weld line no crystallization of β-spherulites occurs.

1. Introduction

When a polymer melt is injected into a mould through separate gates, a weld line is formed which leads to mechanical weakening of the injection moulded part [1–17]. This unfavourable behaviour originates from the morphological properties of the weld line and its immediate vicinity.

It is generally assumed that the morphology of the weld line is determined by the nature of the melt flow [2–4]. In order to fill the mould, the melt has to flow behind the front radially from the centre to the walls. As a result, shear forces should occur when the two flow fronts meet to form the weld line. Bands of transcrystalline growth nucleated on highly ordered material running along the weld line [3] seem to support this model.

Indeed, as a result of melt flow and temperature profile several layers of different nucleation densities appear on alternate sides of the material at the site of the weld line.

The molecular orientation in the weld line has been investigated by a number of authors. It seems, however, that final agreement about the orientation has not yet been achieved, for example Hagerman [2] assumes that the skin material is oriented in the direction of flow while the molecules in the weld line are oriented perpendicular to the flow direction. In contradiction hereto, Bell *et al.* [8] observed a random distribution of glass fibres in the weld region.

Leaving the problem of molecular orientation unsolved, it is clear from all investigations that the weld line represents an area with a high morphological gradient. This structural inhomogeneity is the reason for the mechanical weakening of the sample. In the preceding paper [9] we investigated the morphology of low molecular polypropylene injection moulded samples containing a weld line using X-ray, light scattering, and polarization microscopy. A strong inhomogeneity of the spherulitic structure in the vicinity of the weld line has been found. Spherulites of both monoclinic α-modification and (pseudo)-hexagonal β-modification can be detected in the polarization microscope. The β-form spherulites cluster together and form aggregates which increase in size when approaching the weld line. Wide-angle X-ray investigations reveal a lower crystallinity of the β-modification in the vicinity of the weld line and increasing β-crystallinity with increasing distance from the weld line. The absolute values of the β-crystallinities are dependent on the temperature of the mould. The sizes of the sample segments cut out for X-ray and microscopic investigations exceed by far the lateral extension of the weld line, thus it was not possible to investigate the crystal morphology in the weld line. Such an investigation is presented in this paper.

The inner spherulitic structure and the crystal modification in the weld line are investigated by electron microscopy. X-ray methods are used to measure the crystal modification as a function of distance from the weld line.

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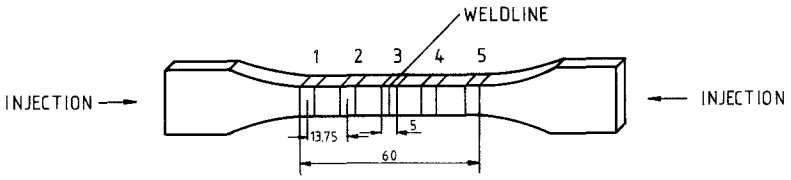

Figure 1 Injection moulded tensile test bar (sizes in mm) and positions of sample segments cut out of the bar.

2. Experimental procedure

Isotactic polypropylene with a molecular weight M_v = 223 000 (Novolen 1100 HX of BASF) was used to produce injection moulded standard tensile bars by injecting through two gates at both ends of the mould under the following processing parameters

melt temperature	$T_s = 240 \pm 2°C$
form-filling pressure	$P_e = (3 \times 10^7 \pm 5 \times 10^5)$Pa
mould filling time	$t_f = 270$ msec
holding time	$t_h = 4.0$ sec
holding pressure	$P_h = (6 \times 10^6 \pm 5 \times 10^5)$Pa
mould temperature	$T_w = 40°C, 60°C, 80°C, 100°C, 110°C, 120°C$

The standard tensile test bars had sizes as given in Fig. 1 (DIN 53455). To investigate morphological changes as a function of distance from the weld line, sample segments were cut out of the bars. The positions of the segments in the bar are also given in Fig. 1.

For transmission electron microscopy (TEM) investigations samples were prepared as follows. To enhance the image contrast, the samples were exposed to ruthenium tetroxide (RuO_4) used as staining agent. For the preparation of RuO_4 we used ruthenium trichloride ($RuCl_3$) and sodium hyperchloride. To yield a 15% concentration of RuO_4 we added 10 ml NaOCl to 0.2 g $RuCl_3$. Specimens of dimensions 5 × 5 × 3 mm^3 were exposed to the RuO_4 solution for 16 h. Then, samples of smaller thickness (40 to 50 nm) were cut out of the stained specimens by use of a microtome. The electron microscope used was a Zeiss EM 902. To measure the crystallinity of the samples, a Philips PW 1380 goniometer was used.

3. Results and discussion

In Fig. 2 a wide angle X-ray scattering curve (sample at T_w = 120° C, sample segment 1), is displayed which is typical for all investigated samples. From these curves, the crystallinities can be determined by separating the fraction of the curve due to amorphous scattering (Halo) from the total scattering [10, 11]. The result is shown in Fig. 3. We find that the crystallinity is increasing with the mould temperature and that X_c assumes a minimum in the sample segment containing the weld line.

As we see in Fig. 2, a strong (200)-peak, which is due to the β-modification appears in the curve. This allows the determination of that fraction of the crystallinity which can be attributed to the β-modification [12]. Fig. 4 displays the β-crystallinity as a function of sample segment. The figure reveals that $X_{c,\beta}$ is strongly dependent on the distance from the weld line and on the mould temperature. The β-crystallinity is minimal in the sample segment containing the weld line, for mould temperatures below 100° C $X_{c,\beta}$ is zero in this segment. It is clear that this behaviour of the crystallinity represents a strong structural inhomogeneity which certainly contributes to the mechanical weakening of the moulded parts. This inhomogeneity seems less pronounced for mould temperatures $T_w > 80°C$.

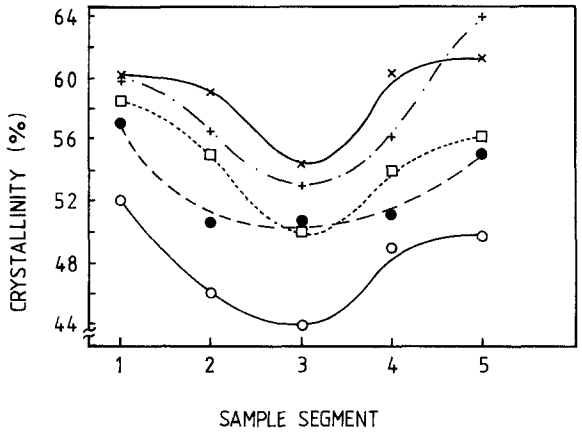

Figure 3 Total crystallinity (α- and β-modification) as a function of mould temperature. (○ T_w = 40° C, ● T_w = 60° C, □ T_w = 80° C, × T_w = 100° C, + T_w = 120° C).

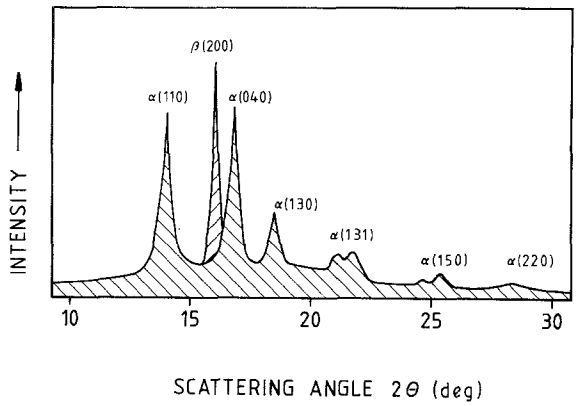

Figure 2 Wide angle X-ray scattering curve of a sample injection moulded at T_w = 120° C (sample segment 1).

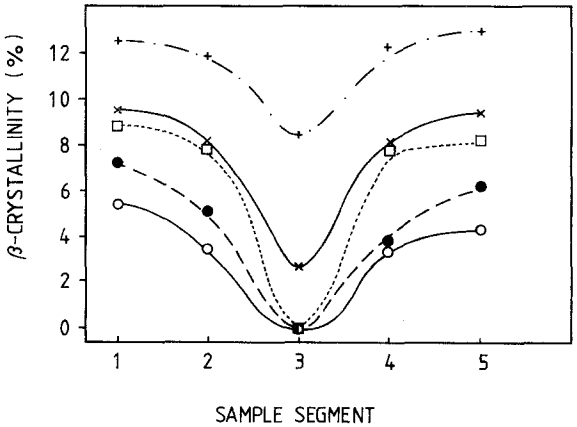

Figure 4 Crystallinity of the β-modification (β-crystallinity). (Symbols as in Fig. 3.)

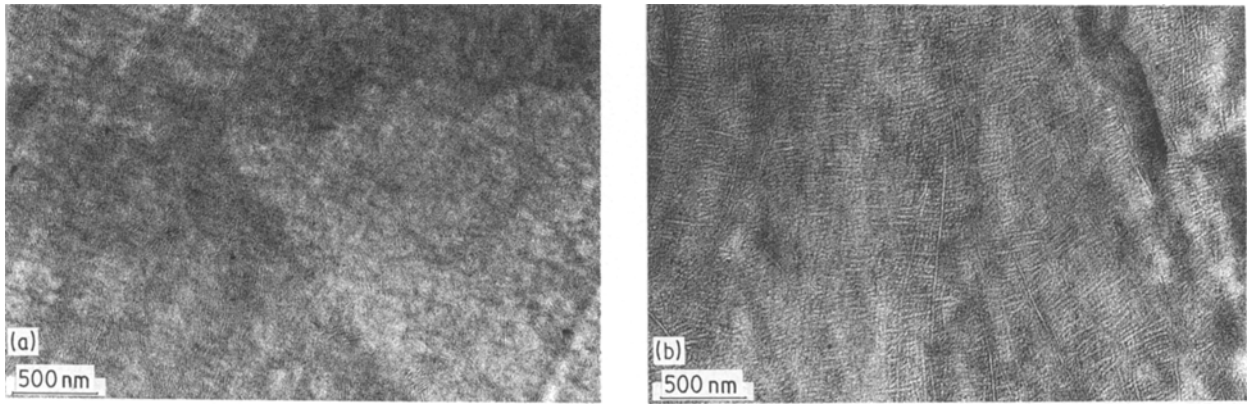

Figure 5 Transmission electron micrographs of spherulites in the weld line segment at (a) $T_w = 40°C$ and (b) $T_w = 120°C$. In (a) the edge of the spherulite is seen. The lamellar morphology is typical for epitaxial growth of lamellae on each other (cross-hatched structure). Also some lamellar bridging between spherulites can be detected.

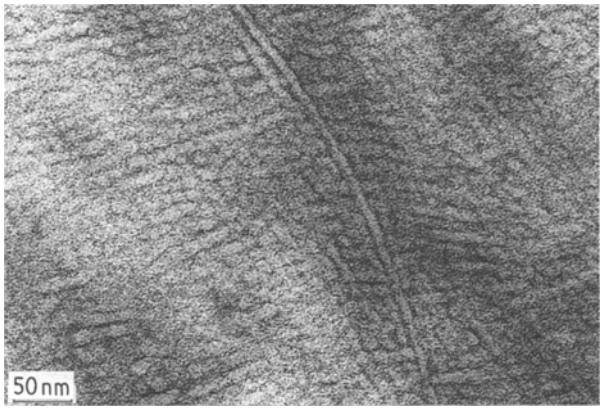

Figure 6 Electron micrograph of a section of a spherulite in the weld line at $T_w = 40°C$.

We cannot, however, determine the β-crystallinity in the weld line from the X-ray investigations alone because the thickness of the sample segment (segment 3) exceeds the lateral dimension of the weld line by far.

Such information, however, can be obtained from electron microscopic investigations made on microtome cuts. α- and β-crystals, crystallized under certain conditions can be distinguished by their different superstructural formation: α-crystals grow preferentially epitaxially on each other [13] which is not observed with β-crystals. Fig. 5 shows the electron micrograph of a weld line segment in relatively low magnification. In this figure, for two different mould temperatures the edges of two spherulites can be seen.

We know from the X-ray experiments, that at $T_w = 40°C$ no β-crystals occur but that at $T_w = 120°C$ the β-crystallinity is at its maximum. Both micrographs in Fig. 5 display the same type of morphology and already at this magnification on some spots epitaxial overgrowth is detected which can be concluded from the orientation of the lamellar crystals [13].

Fig. 6 shows a section of a spherulite in the weld line segment at $T_w = 40°C$ in higher magnification. The typical cross-hatched structure of epitaxial overgrowth is seen in the entire picture. This could be expected due to the absence of any fraction of β-crystals. A different pattern we could only expect for mould temperatures $T_w = 100°C$ and $T_w = 120°C$ where β-crystallization occurs. As the micrographs in Fig. 7 reveal, however, at these mould temperatures only epitaxial overgrowth is found. The micrographs thus demonstrate that in the weld line and its immediate vicinity no crystallization of β-modification occurs.

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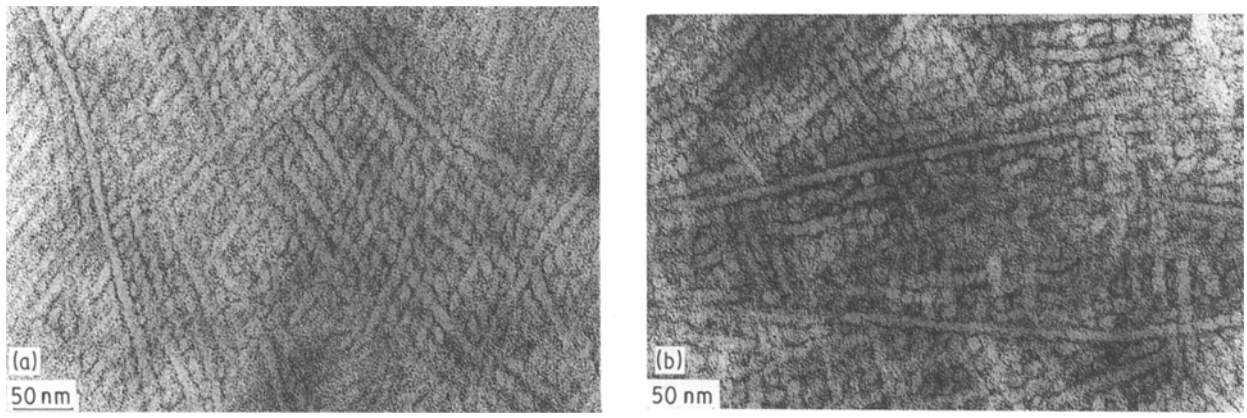

Figure 7 Electron micrographs of spherulite sections in the weld line at (a) $T_w = 100°C$ and (b) $T_w = 120°C$.

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