The Influence of Flow-Induced Crystallization on the Impact Toughness of High-Density Polyethylene

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Summary: The relation between the impact toughness and flow-induced crystalline orientation of high-density polyethylene (HDPE) was investigated. Flow-induced crystalline orientation was created in the samples via injection moulding and the amount of orientation was controlled through variation of processing conditions (injection temperature) and sample thickness. The impact toughness behaviour was found to be strongly dependent on the amount of crystalline orientation, whereas the loading direction also had a strong influence, e.g. giving highest impact properties in flow direction. Subsequently, injection moulded samples of HDPE modified with calcium carbonate filler particles were tested. In this case a similar relation between crystalline orientation and loading direction was found, whereas the total amount of flow-induced crystallization was observed to be strongly influenced by the presence of the filler particles.

Introduction

Most semi-crystalline polymers, like polyethylene (PE), are known to behave ductile under normal testing conditions. However, at high deformation rates and triaxial stress states, like in a notched Izod impact test, they start to show brittle behaviour. It is generally known that the impact toughness of semi-crystalline polymers can be increased via the addition of a well-dispersed rubbery phase. This has been studied extensively in the past and an important toughening criterion was first presented by Wu [1,2], who showed that the brittle to tough transition in rubber modified nylon (PA 6,6) was related to the average interparticle ligament thickness. Since this single parameter is directly related to both, rubber concentration and average particle size, it is a practical criterion, however a clear explanation for its existence was not evident. A morphological explanation was later proposed by Muratoglu et al.[3,4]. Their observation of a preferential oriented crystalline structure between the rubber inclusions, was coupled to the local anisotropic mechanical behaviour of this heterogeneous system. Below a critical interparticle distance the anisotropic behaviour of the orientated interface causes large shear deformation to percolate throughout the structure and, since matrix yielding is a significant source of energy dissipation, toughness is enhanced. This

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toughening mechanism was also considered by Bartczak et al. [5,6], who found that for HDPE an increase in toughness was not only achieved for rubber modification but also with the addition of dispersed calcium carbonate particles. Effective toughening was found not to depend on the two types of fillers used (soft: different rubbers, hard: calcium carbonate) and was controlled by the average critical ligament thickness, apparently being the only controlling parameter in the onset of toughening semi-crystalline polymers. The change in morphology was introduced by a heterogeneous nucleation effect originating from the particle surface[7]. Their results, however, showed some striking differences in the level of toughness increase. Specimens were prepared via injection moulding a long flexural bar, which was divided into two impact test specimens (close end and far end, indicating the position of the specimen being, respectively, close to and far from the injection gate). For the calcium carbonate filled systems, the close end specimens showed an increase in impact properties that was twice as high as for the far end specimens. In their explanation for this result, only the effect of particle orientation due to flow, combined with the particle surface orientation was discussed briefly, and the effect of flow-induced nucleation and crystallization of the polymer was not taken into account.

Studies on injection moulding of semi-crystalline polymers show that the inner structure of injection moulded parts are highly inhomogeneous [8-10,15]. Since molecular chains have experienced a shear stress, or are even crystallized under stress, 'skin layers' of oriented crystallites are formed. The thickness of these 'skin layers' varies with polymer melt properties and moulding conditions, but also over the distance of the moulded parts in flow direction. Zuidema[8,9] studied the dimensional stability of injection moulded polypropylene and found by experiments and numerical modelling that the thickness of the oriented layer decreases with increasing distance from the injection gate, see also Peters et al.[10].

First of all, this study will focus on the relation between flow induced crystalline structure and the impact toughness behaviour of injection moulded HDPE. This is done by changing the relative amount of orientation in the samples by variation of the moulding conditions and sample thickness. The second part of this study is concerned with the close and far end toughness increase in calcium carbonate filled HDPE as studied by Bartczak[6] and aims at a better understanding of the combined effect of filler particles and flow on the structure development and the related impact toughness.

Experimental

Materials

The high-density polyethylene used in this study was Stamylan HDPE 9089s, supplied by DSM, The Netherlands. It has a density of 0.963 g/cm^2 at room temperature, a melt flow index of 8 dg/min, a weight-average molecular weight (M_w) of 70.000 g/mol, and a number-average molecular weight (M_n) of 11.000 g/mol. The calcium carbonate filler used was Super-Pflex 200, supplied by Specialty Minerals Inc., USA. This precipitated calcium carbonate has a density of 2.7 g/cm^2, an average particle diameter of 0.7 μm, a very narrow particle size distribution and a 2% stearic acid surface coating to improve dispersion.

Extrusion mixing

Different volume fractions (5%, 10%, 15% and 20%) of calcium carbonate particles were mixed in the HDPE with a 25 mm Werner and Pfleiderer corotating twin-screw extruder, ZSK 25. The temperature of the extruder was in the range of 175-180^{o}C, the rotation speed of the screws was 150 rpm and the length of the screws was 1050 mm. The calcium carbonate powder was fed to the polymer melt by a side feeder situated directly after the melting zone. The polymer pellets and the calcium carbonate powder were fed with the desired weight fractions (calculated from the volume fractions and densities of HDPE and $CaCO_3$) by two K-Tron Soder gravimetric material feeders (type K-CL-KQX2 and K-CL-KT20). The material flux was optimized to get the highest torque of the extruder in order to achieve a proper particle dispersion.

Injection moulding

For the first part of the study, plates of unfilled polyethylene with a dimension of 70 × 70 mm and thickness of 1, 2, 3 and 4 mm were moulded on a Arburg 320S / Allrounder 500-150 injection moulding machine. Injection moulding temperatures of the material of 150^{o}C and 250^{o}C were applied and the mould was kept at 20^{o}C. The injection speed was equivalent to a feed rate of 10 cc/s and holding pressure was 450/350/200 bar for 6/4/2 sec respectively. Izod bars with dimensions of 60 × 12.7 mm were machined out of these plates, in flow direction and perpendicular to flow direction. These samples were notched with a notching machine, according to the dimensions of the ASTM D-256 protocol and marked accordingly as FLOW (in flow direction) and PERP (perpendicular to flow direction) as shown in figure 1(a). To investigate separately the geometrical effect of reducing the thickness of the plates, Izod bars with a different thickness (0.9 to 4 mm) were also prepared via compression moulding. This was done by melting the material pellets in a mould in a hot press at 200°C and a pressure of 500 kPa. The mould was cooled to room temperature by placing it in a water cooled press at 20°C. Izod bars, marked as CM (compression moulded), were cut out of the plates and notched.

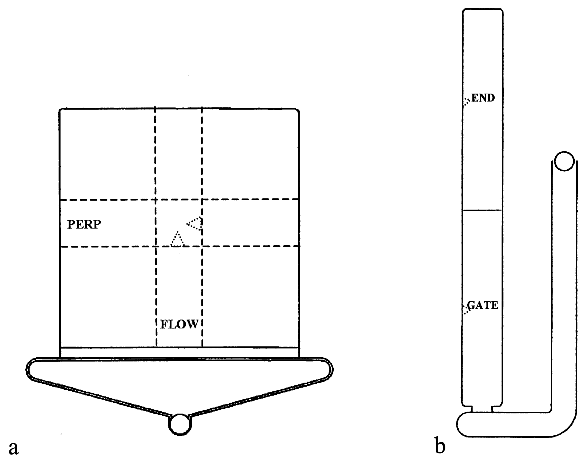

Figure 1. Schematic drawing of (a) injection moulded plate, with a 4 mm nozzle gate and an ISO 294 film gating with a 1 × 70 mm entrance gate, and (b) flexural bar, with a 4 mm nozzle gate and a Z-shaped ASTM D3641 gating with a 6 × 3.2 mm entrance. For both geometries the cutting procedure for FLOW and PERP and GATE and END type of specimens are indicated.

For the second part of this study, where we first try to reproduce the results of Bartczak[6], the extruded blends were pelletized and flexural test bars (ASTM D-790 127 × 12.7 × 3.2 mm, Axxicon Iso Manufactured (AIM)) were injection moulded with an injection temperature of 250°C, a mould temperature of 20°C and an injection speed equivalent to feed rate of 10 cc/s and 88 cc/s. Two Izod bars were cut out of the flexural bars, notched and marked as GATE and END, being respectively the sample cut out of the bar at the injection gate and the one at the end of the bar as indicated in figure 1(b). To clarify the flow effect for the filled system, also compression moulded Izod bars of the filled HDPE with a thickness of 3 mm were prepared with the compression moulding process described above. Because it is not possible to show an anisotropy effect with the flexural bars, for an intermediate filler volume fraction (15%) FLOW and

PERP type of samples were manufactured from plates with similar dimensions and processing conditions as described for the unfilled system. Moreover, from these specimens the influence of the thickness was studied for the filled system as well.

Mechanical behaviour

Impact tensile tests, at a tensile speed of 1 m/s, were performed at room temperature using a Zwick Rel hydraulic tensile machine. The impact energy was calculated by integration of the measured force-displacement curve, divided by the fracture surface area. For each sample thickness and sample processing condition, at least five specimens were tested, to determine the reproducibility.

Microscopy

Cross-sections of approximately 3-7 μm were prepared with a rotary microtome and, using an Axioplan imaging microscope combined with an Axio Cam camera, pictures were made for a comparison of the thickness of the oriented layers in the different samples.

Crystalline orientation

To measure the orientation in the injection moulded samples, small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) patterns were taken using the synchrotron radiation at the ESRF (European Synchrotron Radiation Facilities, Grenoble, France). The measurements were performed at beamlines ID2 and ID11, for SAXS and WAXD respectively, using a X-ray wavelength of 1.5 Å and a sample-to-detector distance of 10 m and 0.32 m, respectively. The size of the beam was 0.3 × 0.3 mm at both beamlines. For all plate samples, SAXS and WAXD patterns were recorded with a 2D-CCD detector with the beam normal to the plates, collecting a qualitative image of the overall morphology in the plates. From the flexural bars cross-sectional layers of 1 mm thickness were cut out at the position of the notch close to the injection gate. With the beam going through these cross-sectional layers, WAXD patterns were recorded with the X-ray beam scanning over the complete thickness of the sample with steps of 0.1 mm. For a comparison of the crystalline orientation in the samples, the 2-dimensional 110 and the 200 crystal patterns were isolated, intensities were normalised with the total intensity of the diffraction ring and plotted as a function of the azimuth angle ($0^\circ - 90^\circ$).

Results and Discussion

Unfilled HDPE

Figure 2 shows the impact tensile test results as a function of the specimen thickness for the compression moulded samples and for the FLOW and PERP type injection moulded samples cut out of the plates. The level of toughness is approximately the same for all processing conditions above a sample thickness of 1 mm (~ 8 kJ/m^2). At a sample thickness of 1 mm a strong anisotropic behaviour is present between the FLOW and PERP type of samples. The injection moulded samples taken from flow direction show a large increase in impact toughness, where the highest impact toughness (~40 times the standard level!) was reached for an applied injection temperature of 150°C. Testing perpendicular to flow direction resulted in an impact value at the level of compression moulded samples. The sample moulded at 150°C showed highest anisotropic behaviour. The PERP type of this sample even showed a decrease (~ 50 %) in impact toughness compared to the level of the thick samples.

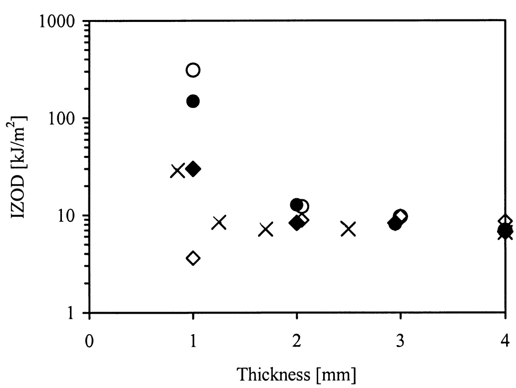

Figure 2. Impact toughness (logarithmic) of HDPE as a function of sample thickness for different sample types: FLOW at T_{inj} = 250°C (●), PERP at T_{inj} = 250°C (◆), FLOW at T_{inj} = 150°C (○), PERP at T_{inj} = 150°C (◇), and CM (×).

Examination of the samples after testing gives an idea of the anisotropy effect in the deformation zone behind the notch (figure 3). A stress-whitened zone of almost 3 mm in depth below the crack flanks is observed for the 1 mm FLOW samples, whereas all the low impact toughness samples show a brittle fracture surface. The increase in toughness, observed for the 1 mm thick CM and PERP (at 250°C) type of samples, are to be

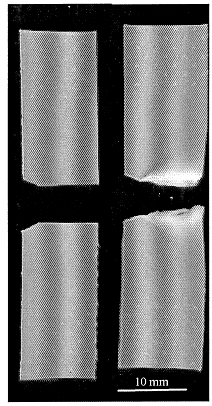

Figure 3. Images of tested samples (T_{inj} = 150°C, left: PERP, right: FLOW).

accounted for two phenomena. The first is related to a transition in stress conditions for reduced sample thickness, going from plain strain to plane stress, where the latter favours plastic deformation.[11]. The second is the relatively higher cooling rate at the surface of the samples, resulting in a lower crystallinity and a smaller lamellae thickness, also decreasing the yield stress of the material[12]. For thinner samples the contribution of this type of crystalline morphology is larger. For both effects the lower yield stress accounts for an increase in impact toughness, since localisation of deformation is lowered for decreasing yield and increasing strain hardening as shown by Smit.[13] These effects are beyond the scope of this study and will be studied in future work.

To clarify the observed impact toughness differences between the 2-4 mm and 1 mm samples and the moulding conditions applied, the flow-induced structure is studied. Figure 4 shows microscopic images of half of the cross-sections of the 1 mm thick injection moulded plates. For both injection temperatures applied, an orientated layer is found near the surface of the sample. This layer consists of a small ‘skin layer’ (A), a ‘transition layer’ (B) a ‘shear layer’ (C) and a ‘fine grained layer’ (D). The total thickness of these layers is largest for the low injection temperature, where also the shear layer is more pronounced. In the core of the samples an isotropic spherulitical structure is observed, similar to the structure formed in the quiescent conditions of compression moulding.

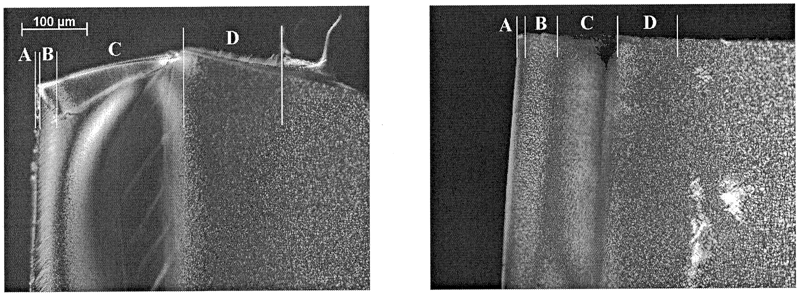

Figure 4. Microscopic structure of cross-section near surface (left side of cross section) of 1 mm plate injection moulded at 150°C (left) and 250°C (right). Showing the 'skin layers' (A), 'transition layer' (B), 'shear layer' (C) and 'fine grained layer' (D).

The crystalline orientation in the orientated layer, taking all layers into account, can be interpreted from the SAXS and WAXD patterns presented in figure 5. Since the X-ray beam was transmitted through the complete sample thickness (horizontally in plane direction in sample image of figure 4), no distinction between the different orientated layers and the isotropic core can be made. The SAXS pattern of a 1 mm thick sample (figure 5a) shows the features of a typical shish-kebab structure; the small intensity streak in horizontal direction and large intensity spots, in flow direction, on the scattering halo of the lamellae of the spherulites in the isotropic core. The additional WAXD patterns (figures 5b, c) show a crystal orientation which is typical for a twisted lamellae structure (similar to a row structure[14]) as shown schematically in figure 6. Since a row structure is known to be of anisotropic nature, it can be accounted for the anisotropic impact behaviour, giving high impact toughness if the lamellae are orientated perpendicular to the loading direction and losing impact toughness when loading in lamellae direction. In both the SAXS and WAXD patterns, respectively, an isotropic lamellae halo and isotropic crystal planes of the unorientated core are also present. This isotropic core dominates even more in the 2 mm thick injection moulded samples (figures 5d, e, f), since in these samples the oriented layer thickness is approximately the same. This allows the isotropic core to dominate the structure and the impact toughness to fall down to isotropic behaviour.

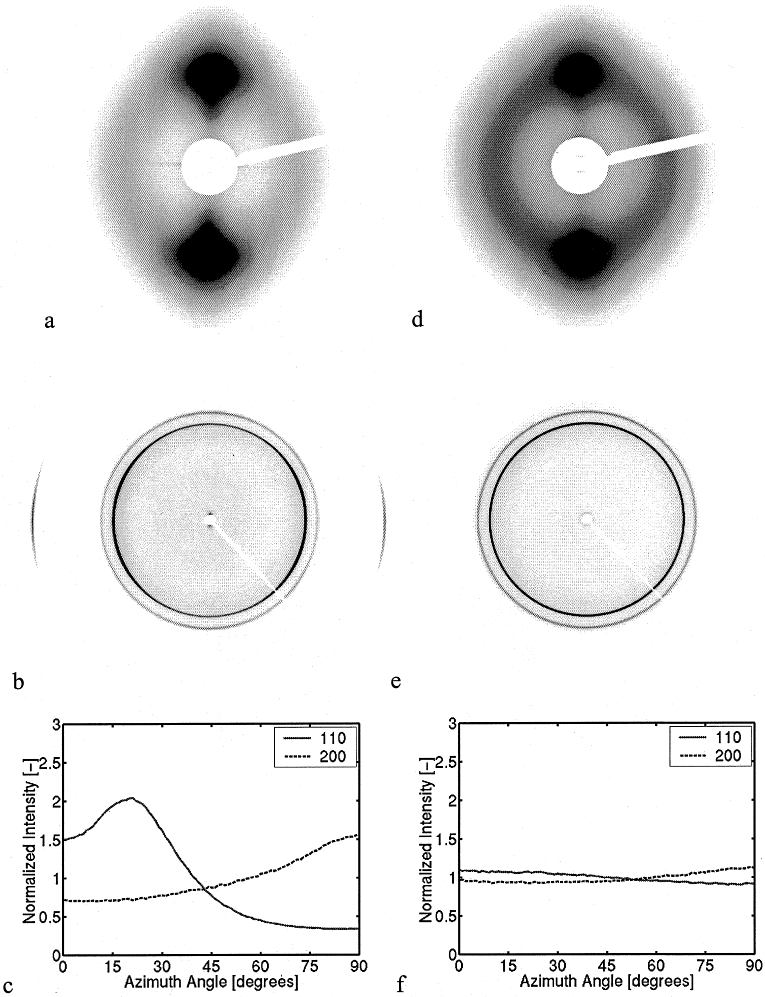

Figure 5. Measurement of overall orientation of injection moulded (at 150°C) plates of 1 and 2 mm thickness; SAXS pattern (a,d), WAXD pattern (b,e) and normalised (110) and (200) plane azimuthal scan curves (c,f). Flow direction vertical.

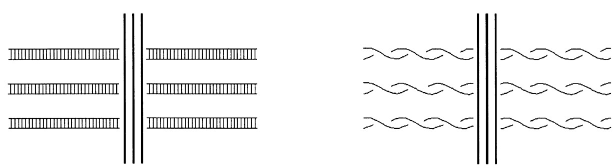

Figure 6. Schematic drawing of a shish-kebab, with untwisted (left) and twisted (right) lamellae according to Keller[14].

Filled HDPE

Figure 7 shows the impact tensile test results as a function of blend composition for the compression moulded samples (CM) and for the samples cut out of the injection moulded (at 88 cc/s) flexural bars (GATE & END). An increase in toughness is seen at a volume concentration of approximately 5 % calcium carbonate, but the level of increase differs quite a lot for the different manufacturing conditions of the samples. The toughness enhancement of the compression moulded samples is much lower than that of the injection moulded samples, which show a much higher increase in toughness. Similar to the results reported by Bartczak[6], a difference is observed for the GATE and END type of specimens. Hanging on to the concept that crystal orientation is related to the impact toughness, both the difference between the compression and injection moulding conditions, as well as the difference between GATE and END type of specimens, can be rationalized by the presence of flow-induced crystalline orientation. No influence of the distance to the injection gate is observed for the unfilled flexural bars, which is in accordance with the results shown before in figure 2, since for 3.2 mm thick flexural bars the isotropic core dominates the impact toughness.

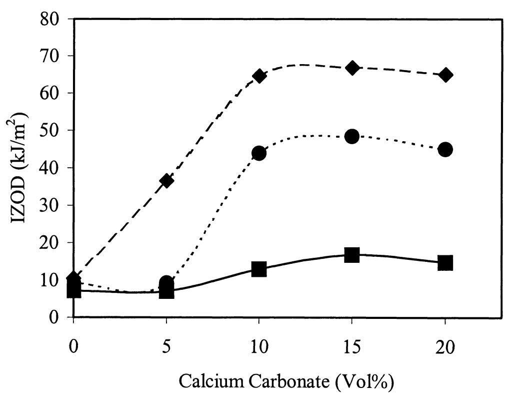

Figure 7. Impact toughness as function of volume % calcium carbonate (CC) for different sample types: GATE (◆), END (●), and CM (■).

Considering the relation between flow-induced orientation and impact toughness, as found for the neat HDPE, the orientation in the filled samples is studied. WAXD patterns with the X-ray beam transmitting through the complete thickness, taking all layers into account, were recorded to obtain an insight in the overall orientation. Figure

8 shows the azimuthal orientation scans of the crystal planes for the 10 % filled HDPE samples (CM, END, GATE). In the injection moulded samples an integrated crystalline orientation is observed, having highest orientation in the GATE sample. As expected, no orientation is observed in the compression moulded (CM) sample. Although, less twisting of the lamellae is observed than with the unfilled samples, the amount of orientation seems to be related to the impact toughness.

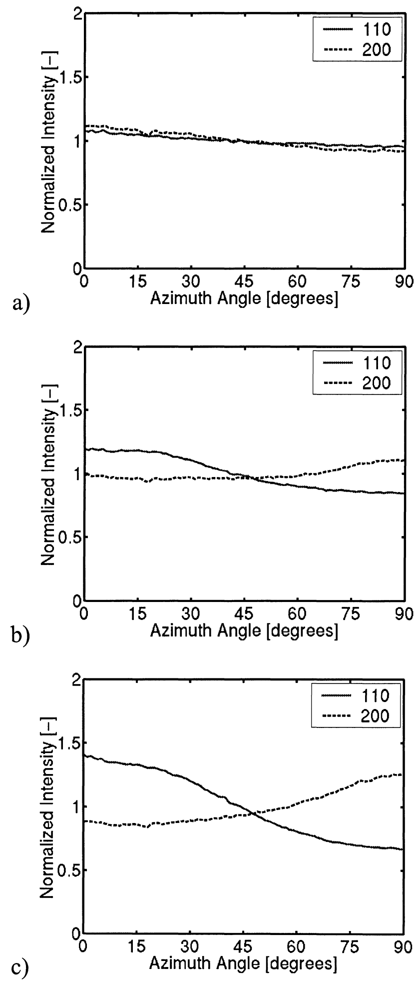

Figure 8. WAXD measurement of overall orientation in 10 % filled HDPE samples; normalised azimuthal scans curves of (110) and (200) crystal plane of CM (a), END (b) and GATE (c) type of samples.

To obtain more information about the crystal orientation over the specimen thickness, WAXD patterns with the x-ray transmitting through a cross-sectional layer of the flexural bar were recorded. In figure 9, WAXD intensity plots of the 110 and 200 crystal planes of HDPE of an unfilled flexural bar (GATE type) are given. The normalised intensity is plotted as a function of the azimuth angle (0^{o} – 360^{o}) of the 2-D WAXD patterns and as a function of the sample thickness. The 'skin-core' effect of injection moulding is clearly present: at the edges of the sample an orientated 'layer' is observed and the core shows no orientation. Although again no distinction between the different orientated layers can be made, since the size of the x-ray beam is 0.3 × 0.3 mm, the average size of the 'total skin layer' is found to be approximately 0.3 mm, so the isotropic core dominates the impact behaviour.

If we now look at the same orientation plots of a 15 % calcium carbonate filled sample

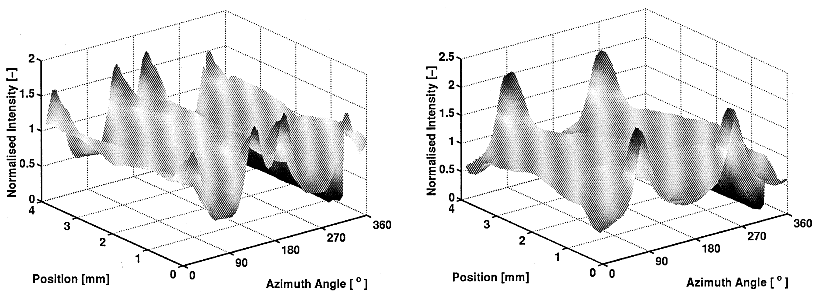

Figure 9. Normalised 110 (left) and 200 (right) plane azimuthal scan curves plotted over the thickness of an unfilled GATE sample.

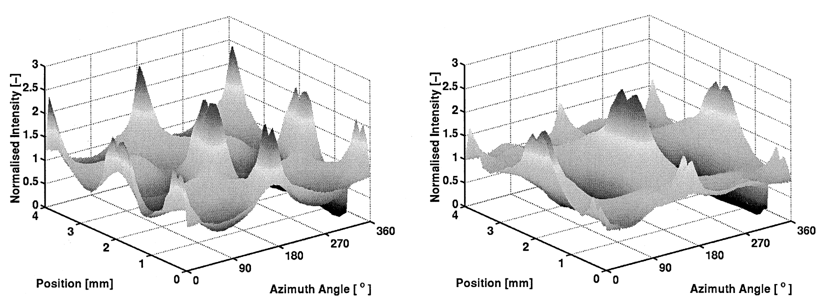

Figure 10. Normalised 110 (left) and 200 (right) plane azimuthal scan curves plotted over the thickness of a 15 % calcium carbonate filled GATE sample.

(GATE type) in figure 10, a completely different orientation is found. Most striking is the fact that a high orientation is present in the core. At the present time, the origin of this orientation is not clear. The effect of (extensional) flow between hard filler particles in a shear flow is considered to be of relevance for flow-induced crystallization. Also 'unwanted' additional effects of the injection moulding process, originating from the injection extruder towards the nozzle and runners in the mould, should not be underestimated[15]. Nevertheless, for the increase in toughness of filled HDPE, the orientation observed in the core seems to be of equally importance as the orientation in the skin. This is also confirmed by the impact toughness behaviour of 15 % filled HDPE injection moulded plates as shown in figure 11. Here the drastic difference in toughening between samples of 1 mm thickness and the others, like in the unfilled HDPE (figure 2), is not observed. For the filled plates samples an approximately linear relation is present between the impact toughness and sample thickness. This decrease in toughness for increasing thickness is expected to be a result of a decreasing shear rate, since the volumetric injection feed rate is kept constant, whereas the cross section of the mould cavity increases, resulting in a lower shear stress. The impact toughness of the 15% GATE sample is largest (also plotted in figure 11) and has no relation with the plate samples. This can be explained by the fact that the cross section of the flexural bar mould cavity is significantly smaller than that of the plate mould cavity, resulting in a larger shear stress. Apparently, the impact toughness for filled HDPE is related to the shear stress during flow, and the effect of particulate fillers on the deformation field in a polymer flow should be considered.

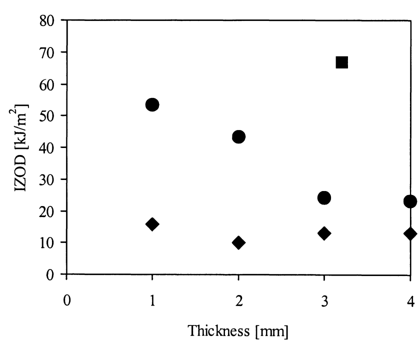

Figure 11. Impact toughness of 15% filled HDPE as function of sample thickness for sample types: plate FLOW (●), plate PERP (◆), and flexural bar GATE (■).

Conclusions

The results, reported in this study, show that the toughness of high-density polyethylene can be related to flow-induced crystalline orientation. If the thickness of an injection moulded sample is reduced and moulding conditions are in favour of a large oriented 'skin layer', the impact toughness behaviour is dominated by the anisotropic nature of this oriented material. Although different types of layers are observed in this 'skin layer', the primarily orientation is a twisted lamellae row structure. The impact toughness of this structure in flow direction (lamellae orientation perpendicular to flow) is at such a high level, that in case of an orientation of more than 50 % over the thickness of a sample the toughness increases with a factor of 40. The anisotropy causes the toughness to decrease upon loading perpendicular to the flow direction.

If a particulate filler is added to the polymer, an extra flow-induced orientation is created with injection moulding. Although the origin of this orientation is not known yet and the rheological behaviour of this system as well as additional effects of the injection moulding process should be considered to be of relevance, the increase in impact toughness as an effect of this orientation seems to be clear.

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