

Fibre formation in injection-moulded polyethylene-sodium lignosulphonate blends and its relationship to the morphological zones

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In injection-moulded parts, the degree of orientation (anisotropy) varies over the cross-section. Normally, such parts exhibit a layered structure, with a biaxially oriented surface layer (stretching of the flow front during mould filling), a highly oriented shear zone, and a core region with a relatively low orientation. This paper describes a novel method to show the different morphological zones by studying the occurrence and structure of fibres formed during injection moulding of certain incompatible blends, in the present case a mixture of high-density polyethylene and a technical lignosulphonate grade (Wanin S). The polyethylene fibres formed during processing of this composite were ribbon-shaped in the surface layer (biaxial orientation), while they had a normal appearance in the shear zone. Only relatively few fibres were found in the core region. A qualitative agreement was found when the fibre character in the various layers was compared with orientation data from thermal shrinkage measurements, as obtained with pure polyethylene samples (test bars).

1. Introduction

The strong influence of orientation, including both molecular and crystallite, on the mechanical and other properties of polymers is well-known [1]. Also known is the fact that conventional processing techniques, e.g. extrusion and injection moulding, produce parts with varying levels of orientation [2-6]. For injected-moulded parts, the degree of orientation is not constant, but varies over the cross-section. It also depends on the flow distance from the gate, and the processing conditions, such as mould and melt temperature. Such a variation makes it difficult to predict the performance of the end product.

The orientation results from the non-isothermal filling of the mould, which usually takes place under relatively high shear rates (10^3 to 10^4 sec^{-1}). Near the surface of the moulding, the degree of orientation in the flow direction may be rather high, but decreases somewhat with distance from the surface. A reversal of this trend manifests itself in a maximum at some distance from the surface.

After that, the degree of orientation decreases, more or less steadily, towards the centre. This variation of orientation is reflected, for instance, in the shrinkage behaviour [7] and the change in tensile modulus over the cross-sectional area [4]. It has been suggested that the orientation of the surface layers is due to biaxial stretching of the viscous flow front during the mould filling, while the orientation maximum somewhat under the surface is related to the maximum in shear rate at the boundary between the solidified surface layer and the flowing melt [7, 8]. Tadmor proposed a useful model for such an orientation profile, using concepts originally developed for dilute solutions [8]. The orientation resulting from the stretching of the flow front was ascribed to elongational flow effects, while the orientation effects beneath the surface layer were assumed to be induced by the shear flow field. The importance of elongational flow when describing the flow front movement has also been pointed out by others [9].

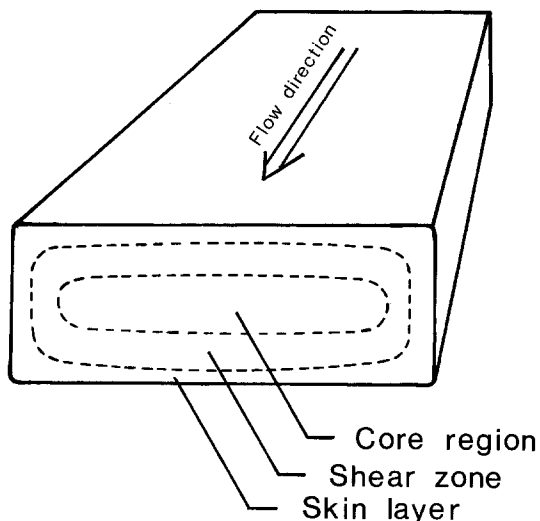


Figure 1 Laminate structure of an injection-moulded part.

Discussions of the orientation distribution have mainly been restricted to parts with a relatively simple geometry. Normally, such parts can be considered as a stratified composite, consisting of a skin layer, a shear zone where the orientation is high due to the high shear rate during mould filling and the gradual solidification, and a core region where the degree of orientation may be significantly lower than in the other two regions. A schematic picture of such a structure is shown in Fig. 1. It is important to note the fact that the origin of the orientation in the skin (elongational flow) is not the same as in the interior (shear induced).

The present paper describes a novel technique for showing the different morphological zones based on the formation of fibrous structures in incompatible polymer mixtures subjected to shear forces. The varying conditions of shear and extensional flow found in an injection-moulded part are reflected in the frequency with which the fibres occur, as well as in their shape. The model system chosen in the present case was high-density polyethylene (HDPE) as the fibre forming phase, together with an equal amount of a technical

grade of lignosulphonate (Wanin S, a water soluble substance).

It has earlier been found that injection moulding of this blend yields a composite partly consisting of polyethylene fibres in a matrix of Wanin S [10]. Similar findings have been made with polystyrene–Wanin S blends. Fibre formation has also been recorded in hydrostatic extrusion of HDPE–Wanin S blends [11].

The shape and diameter of fibres found in such incompatible blends depend on the flow conditions. Thus, the fibre geometry in the skin layer is different from that in the shear zone. This allows, for instance, a determination of the extent of the morphological zones in injection-moulded bars under varying processing conditions. This paper reports on an investigation of the polyethylene phase in the lignosulphonate matrix using scanning electron micrographs (SEM) of fracture surfaces. The micrographs are compared with the shrinkage behaviour of thin slices taken at various distances from the surface of unfilled HDPE mouldings produced under similar conditions (test bars). Even though such a comparison is somewhat difficult, an agreement has been found with regard to shrinkage data and the variation of SEM-pictures.

2. Experimental procedure

2.1. Materials

The high-density polyethylene grade used was Rigidex 50 (supplied by BP Chemicals Int. Ltd.) with a density of 0.962 g cm^{-3} and a melt flow index of 6 g per 10 min (BS 2782 Method 10S C). The average molecular weights were $\bar{M}_w = 101450$ and $\bar{M}_n = 6180$ [12].

Wanin S, a technical grade of sodium lignosulphonate, was supplied by Holmens Bruk, Vargön, Sweden. Its composition is given in Table I. The density of Wanin S was estimated to be 1.53 g cm^{-3} [11].

2.2. Processing

HDPE (50 wt%) and Wanin S (50 wt%) were blended in a mixing extruder (Co-Kneter, Buss AG,

TABLE I Typical composition of Wanin S

Component	Content (wt %)
High molecular weight sodium lignosulphonates	60
Salts of low molecular weight organic acids	10
Reducing matter calculated as glucose	25
Other substances	5

TABLE IIA Injection-moulding conditions chosen to produce a low degree of orientation *

Material	$T_M(^{\circ}C)†$	$P_i(\text{MPa})$	$P_h(\text{MPa})$	$V_s(\text{mm sec}^{-1})$
HDPE	60	45	20	2.2
HDPE–Wanin S	60	45	20	10

TABLE IIB Injection-moulding conditions chosen to produce a high degree of orientation

Material	$T_M(^{\circ}C)$	$P_i(\text{MPa})$	$P_h(\text{MPa})$	$V_s(\text{mm sec}^{-1})$
HDPE	20	135	135	14
HDPE–Wanin S	20	135	135	60

TABLE IIC Injection-moulding constants of the power law ($\tau = K\dot{\gamma}^n$) at 180° C

Material	$K(\text{MPa sec}^n)$	n
HDPE	9.1×10^3	0.44
HDPE–Wanin S	4.4×10^3	0.45

*The barrel temperature was in all cases 180° C.

† T_M = mould temperature, P_i = injection pressure, P_h = holding pressure and V_s = injection (screw) velocity

$L/D = 11$, $D = 46$ mm) at 180° C. The corresponding volume-fraction of HDPE in the composites is then about 60%. The homogenized blends were injection moulded with a conventional machine (Arburg Allrounder 221E/170R). The processing conditions are summarized in Table II. The injection moulded parts were rectangular bars with the dimensions of 55 mm × 8 mm × 3.5 mm. The flow direction of the melt was along the length of the bar.

The scanning electron micrographs of the fracture surface of the HDPE-Wanin S composites were compared with the shrinkage profile of unfilled HDPE, as it was not possible, due to inhomogeneous shrinkage, to determine the corresponding profiles of the blends with sufficient accuracy. To allow a meaningful comparison between the micrographs and the shrinkage profiles of the unfilled HDPE, the mould filling had to be performed in a similar way for both types of material. It was decided to fill the mould at approximately the same shear stress at the mould cavity wall during the filling stage. Assuming that both melts obey the power-law equation, the shear stress, τ , at the cavity wall is defined as

$$\tau = \left[V_s A_s \frac{2(2n+1)}{BH^2} \right]^n K, \quad (1)$$

where V_s is the injection velocity, A_s is the cross-sectional area of the plastification unit, B is the width and H is the height of the cavity and K and n are the constants of the power law ($\tau = K\dot{\gamma}^n$, $\dot{\gamma}$ = shear rate). When the parameters of the power-law equation (K , n) have been determined for both

systems, i.e. pure HDPE and HDPE–Wanin S, it is possible to choose V_s in such a way as to render the shear stress, τ , the same in both cases. The values of K , n , and V_s used in this approach are given in Table II.

The processing conditions have been chosen, as evident from Table II, to produce two extremes of orientation, one set of test bars with a low degree of orientation (low injection pressure, 45 MPa, and high mould temperature, 60° C) and the other set with a higher orientation (high injection pressure, 135 MPa, and low mould temperature, 20° C).

2.3. Testing

2.3.1. Shrinkage

Slices with a thickness of 100 μm were cut with a microtome from the surface and downwards from the unfilled HDPE bars. The slices were then immersed in silicone fluid ($138 \pm 1^{\circ}C$) for 10 min. The shrinkage in the flow, S_L , and transverse, S_T , directions was calculated from the equations [7]

$$S_L = 1 - \frac{1}{1 + \frac{l_u}{l_o} - \sqrt{1 - S_T}} \quad (2)$$

and

$$S_T = 1 - \frac{1}{1 + \frac{b_u}{b_o} - \sqrt{1 - S_L}}, \quad (3)$$

where l_u , b_u and l_o , b_o are the length and the width of the slices prior to and after the heat treatment. These shrinkage measures are used as

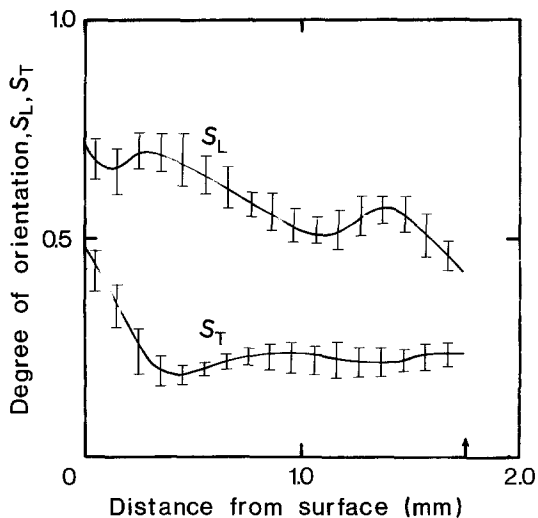


Figure 2 Variation of the shrinkage with the distance from the surface for the test bar produced at high mould temperature (60°C) and low injection pressure (45 MPa) (low overall orientation). The arrow indicates the centre of the cross-section.

an estimate of the degree of orientation. They may not give the same detailed information as methods like X-ray diffraction, but they are often used as a practical measure of the state of the moulding. As a rule, shrinkage data are more easily interpreted for amorphous than for crystalline polymers.

The S_L and S_T values given below are average values of 10 single determinations.

2.3.2. Scanning electron microscopy

The scanning electron micrographs were obtained from fracture surfaces with a JEOL JSM 35 microscope.

The test bars were fractured in the tensile mode at room temperature using a high-speed tensile tester (MTS 810). The drawing rate was >1000 mm sec⁻¹ in order to minimize the plastic deformation of the HDPE phase. The test bars fractured at low strains; in most cases less than 0.2% [11].

3. Results and discussion

3.1. Shrinkage profiles

In Fig. 2 the shrinkage measures, S_L and S_T , obtained from Equations 2 and 3 are shown as a function of the distance from the surface of the HDPE sample (test bar) moulded at a pressure level of 45 MPa and a mould temperature of 60°C, corresponding to a low degree of orientation. The variation of S_L exhibits all the characteristics

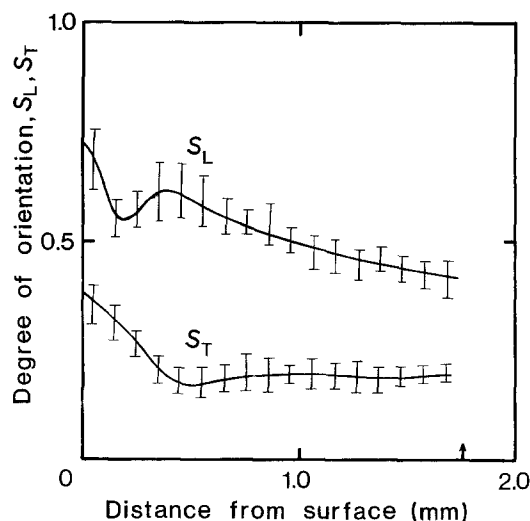


Figure 3 Shrinkage profiles (S_L and S_T) for the test bar produced at low mould temperature (20°C) and high injection pressure (135 MPa). The arrow indicates the centre of the cross-section.

stated above, i.e. a decrease in S_L from the surface, followed by a maximum and then a gradual decrease towards the centre of the moulding. The magnitude of S_L changes only little over the cross-section, which is rather typical of a crystalline polymer. The shrinkage in the transverse direction, S_T , decreases and acquires a rather constant value at approximately 0.3 mm from the surface. This distance approximately coincides with the shear-induced maximum of S_L . It also provides an estimate of the width of the flow-front affected region (skin), since the biaxial stretching of the flow front should manifest itself by a higher transverse shrinkage level [7].

Fig. 3 shows the shrinkage profiles for the test bar with a higher degree of orientation, moulded at a higher pressure (135 MPa) and a lower mould temperature (20°C). Basically, the variation of S_L and S_T is similar to that shown in Fig. 2. The initial decrease in S_L is somewhat less pronounced since the time allowed for molecular relaxation is shorter (lower mould temperature and higher pressure). The orientation in the flow direction, expressed through S_L , in the interior of the test bar is slightly higher than in Fig. 2. There is, however, a distinct second maximum in S_L closer to the centre of the moulding. This is likely to be associated with the higher holding pressure level in this case [7]. The region affected by the flow front (cf. the variation of S_T) appears to be about the same as that found for the test bar moulded



Figure 4 Scanning electron micrograph of the fracture surface of the test bar moulded at a high mould temperature (60° C) and low injection pressure (45 MPa) (lower overall orientation). Close to the surface the polyethylene “fibres” are ribbon-shaped, while at about 0.4 to 0.5 mm from the surface they change to a more circular cross-sectional area.

at a higher mould temperature (about 0.3 to 0.4 mm).

The major changes in the shrinkage profile, resulting from an increase in the pressure and a reduction in the mould temperature, are a higher longitudinal shrinkage, S_L , in the interior of the samples and the appearance of a maximum in S_L close to the centre of the moulding. As the S values are measures of the state of the orientation, the different processing conditions used here do not produce any significant changes in the orientation distribution of the samples.

3.2. Scanning electron microscopy

Fig. 4 is a SEM of the fracture surface of a sample of the 50/50 mixture of HDPE—Wanin S, moulded

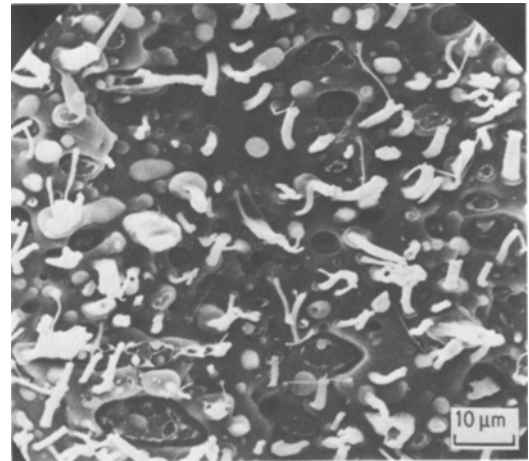


Figure 5 Scanning electron micrograph showing fibres with a circular cross-section in the shear zone of the test bar moulded at 45 MPa and 60° C (lower overall orientation).

at 45 MPa and 60° C in order to produce a relatively low overall orientation value. The polymer phase is apparent as fibres in a matrix of Wanin S. The fibres close to the surface (skin) are not cylindrical but pronouncedly ribbon-shaped. At some distance from the surface, corresponding approximately to the width of the flow-front affected region, the fibre area gradually assumes a circular shape, the fibres in the shear zone region being more regular and having the normal cylindrical appearance.

Fig. 5 is a close-up micrograph of the shear zone in the same bar as above (Fig. 4). The circular HDPE fibres are clearly distinguished. The fibre diameter is of the order of 2 to 5 μm. In the centre of the mouldings (core region) virtually no fibres are formed, as evident from Fig. 6. The formation of circular fibres thus can be associated with the level of the shear field during the mould filling. If the shear rate is not sufficiently high, as in the core region, the HDPE phase does not form any fibres.

The shape of the fibres in the samples moulded at a high pressure and low mould temperature, presumed to produce a higher overall orientation, follows the same pattern as described above. In Fig. 7 a close-up of the skin region of these composites is shown. The fibres have a rectangular, ribbon-like cross-section, which is likely to be associated with the biaxial stretching of the HDPE phase in the flow front. In the shear zone, normal fibres with a circular cross-section are observed.

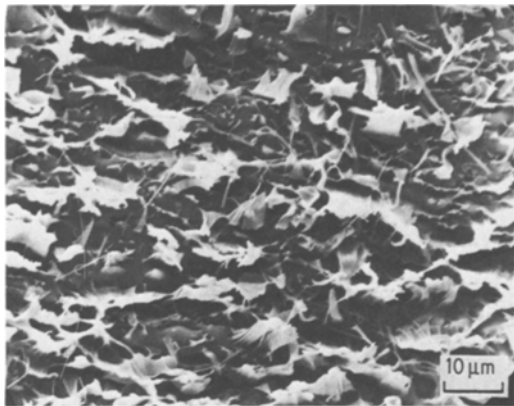


Figure 6 Scanning electron micrograph from the core region of the same test bar as in Fig. 4. Virtually no fibres are visible.

Fig. 8 is a scanning electron micrograph from a region close to the centre of a test bar with a higher orientation level (moulded at 135 MPa and 20°C). In contrast to what is observed in Fig. 6, some fibres are formed also in this region. This is probably due to the increased holding pressure level, which also produced a second maximum in the S_L curve in Fig. 3. This appears to illustrate the importance of melt movements (shear fields) during solidification for the formation of fibres.

4. Conclusions

It has been demonstrated that injection moulding of a 50/50 blend of HDPE and Wanin S, a technical grade of lignosulphonate, produces parts (test

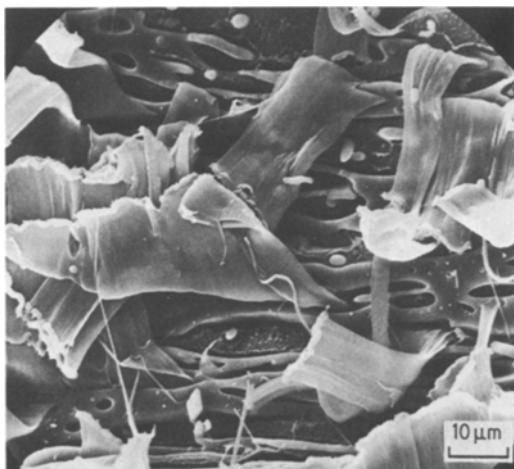


Figure 7 The ribbon-like appearance of the polyethylene phase in the skin layer of the test bar moulded at low mould temperature (20°C) and high injection pressure (135 MPa) (high overall orientation).

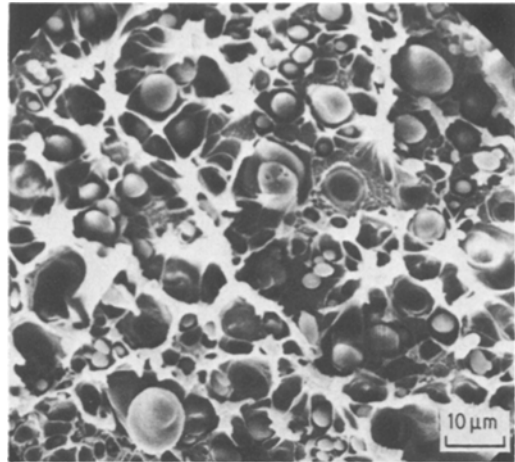


Figure 8 Fibre formation in the core region due to a high holding pressure. (Same test bar as in Fig. 7).

bars) having a stratified composite structure with the HDPE phase forming fibres in the skin and the shear zone of the part. In the centre region (core) the intensity of fibre formation is very low. The extent to which a fibrous phase is formed appears to be associated with the intensity of the forces acting on the melt during the mould filling stage. The character of the shear field is reflected in the shape of the fibres. In the surface layer (skin), where the flow field is dominated by biaxial stretching of the flow front during the filling of the mould cavity, the fibres are found to have a ribbon-like shape with a pronouncedly rectangular cross-section. In the shear zone, where the shear is basically uniaxial, the fibres assume their normal shape with a circular cross-section with a diameter of 2 to 5 µm. Due to the low shear normally encountered in the core region, virtually no fibres are formed there. If the holding pressure is sufficiently high, however, fibres are formed in the core region due to melt movements during the holding stage.

The method described above provides an independent way of studying the orientation distribution in injection-moulded parts and its dependence on processing variables. Qualitatively, it confirms the features of the mould filling process as found by measurements of shrinkage or bi-refringence. For practical purposes, it has the merit of being simple and rapid. Its qualitative character may at first sight be a disadvantage but, on the other hand, also the more sophisticated methods used at present normally do not produce more than comparatively crude pictures of the

orientation, especially in parts with complicated geometry.

Another aspect of this method is its possible value in short fibre production by processing incompatible polymer mixtures, as it identifies the optimum conditions under which fibres are being formed. In this connection it may be added, that the selection of Wanin S in the present case is purely arbitrary, a large number of other substances probably producing similar results.

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