Influence of high injection moulding pressures on the engineering properties of linear polyethylene

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Two grades of high density polyethylene, one injection moulding grade and another with a substantially higher molecular weight (melt index 0.1 g/10 min) were injection moulded at pressures ranging from 100 to 500 MPa using a modified conventional injection moulding machine. For the high molecular weight grade, improvements were observed in the elastic modulus, the tensile strength at rupture measured in the flow direction, and the unnotched impact strength. These improvements were accompanied by a second high temperature (137°C) melting peak in d.s.c. diagrams. For both grades it was also found that the mould shrinkage decreased and the crystallinity increased with injection pressure.

INTRODUCTION

The effect of processing conditions on the morphology and properties of crystalline polymers has been the subject of several recent investigations dealing for instance with extruded and blown films[1,2], injection moulded parts[3,4] and spun fibres[5], to mention only a few examples. After injection moulding at normal pressures (100–200 MPa) a layered structure of the moulded specimens has been found[3,4,6–8]. The outer layer, formed during the rapid solidification of the polymer at the cavity walls, has a comparatively low degree of orientation. In contrast, the layer underneath, a transition layer (shear zone), is often highly oriented in the flow direction, while the interior contains unoriented spherulites[7,8].

Previously, we have found two d.s.c. melting peaks in high density polyethylene samples with high molecular weights[9] (melt index, *MI*, 0.1 g/10 min). The intensity of the peak corresponding to the higher melting point structure (137°C) increased with the injection pressure. The existence of a higher melting point structure of polyethylene in injection moulded specimens is supported by results reported in the literature[7,8].

The present work, which is the first of two studies dealing with the properties and morphology of high pressure injection moulded samples, concerns some basic engineering properties of injection moulded samples of polyethylene with injection pressure and the molecular weight as the main variables.

It is shown that an increase in injection pressure and molecular weight is accompanied by a substantial increase in tensile modulus and strength in the flow direction. The maximum pressure used is 500 MPa, which should be compared with the maximum pressures of 100–200 MPa used in normal applications. For normal injection moulding grades, having a comparatively low molecular weight (*MI* about 7 g/10 min), the effects due to increasing injection pressure are not so pronounced. In addition to the parameters of the stress–strain curves, the creep behaviour and impact strength for varying injection pressures are reported here. Using wide-angle X-ray diffraction it was found that the orientation of the surface layer (skin) differs from that of the transition layer and the core for the high molecular weight polyethylene.

EXPERIMENTAL

Injection moulding

Injection pressures up to 500 MPa were attained using a modified machine of conventional type (Engel 250/500 AS). At one end the screw was equipped with a plunger having a centrally placed bore with a non-return valve preventing the melt from flowing back during the moulding cycle. Details of the machine and the moulding conditions are given in ref 10. During the moulding cycle the mould pressure was measured with a transducer (Colortronic 407) via a dummy ejection pin. Two types of specimens were injection moulded: a tensile test bar with a gauge length of 25 mm, width 5 mm, and thickness 1.5 mm and a square plate with the dimensions 34 x 34 x 5 mm. For the tensile test samples the flow direction was along the gauge length, while the plates were moulded using a centrally placed sprue.

Materials used and moulding conditions

The following grades of high density polyethylene were used: HDPE (normal injection moulding grade), Hostalen GC 7260, Hoechst, density 0.960 g/cm^3, melt index 7 g/10 min (MFI 190/2); HMWPE (high molecular weight grade), DMDS-2215, Unifos Kemi AB, density 0.953 g/cm^3, melt index 0.1 g/10 min (MFI 190/2). The moulding conditions are given in *Table 1.*

The general appearance of the mould pressure *versus* time curves for PE during the injection moulding cycle showed no deviation from that registered at normal pressures[9,11]. The maximum pressure (in this context referred to as the injection pressure), p, was maintained for a relatively short period of time (~¼ of the total cycle).

Table 1 Moulding conditions

	HDPE	HMWPE
Melt temperature (°C)	200–240	250–280
Mould temperature (°C)	30	30
Injection time (sec)	10	6
Holding time (sec)	5	15
Cooling time (sec)	8	5

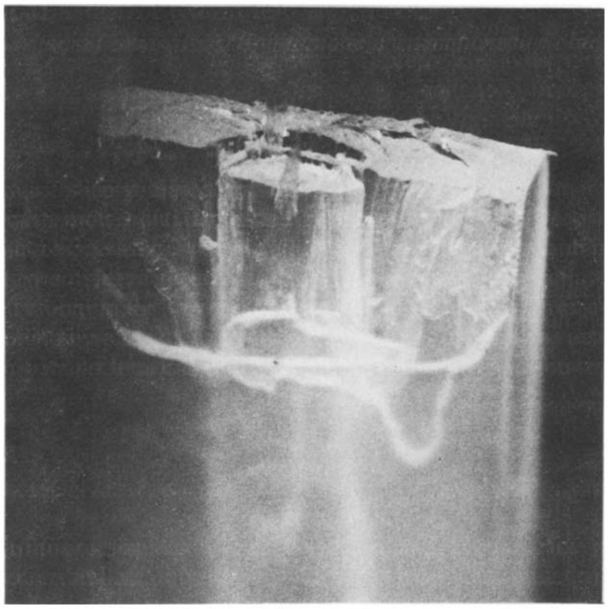

Figure 1 Optical micrograph of a fractured tensile test sample (HMWPE) moulded with an injection pressure of 500 MPa. A core region in the centre of the sample is clearly visible. Original magnification: 10 X

Scanning electron micrographs

Scanning electron micrographs of gold-coated fracture surfaces were obtained with JSM/U3, JEOL.

Tensile tests

The mechanical properties of the tensile test samples, i.e. Young's modulus (E), determined as the tangent modulus at the origin, tensile strength at rupture (σ_B) and yield (σ_y) were determined with a conventional tensile tester (Instron model 1193) according to ASTM D638 at a temperature of 25° ± 0.5°C. The strain rate ($\dot{\epsilon}$) was 1.3×10^{-2} sec^{-1}.

Creep experiments

The creep measurements were performed on the tensile test bars, measuring the strain with differential transformers. The temperature was 30° ± 0.5°C.

Impact strength

The unnotched impact strength (Charpy) was determined perpendicular to the flow direction for tensile test samples cooled with liquid nitrogen.

Differential scanning calorimeter measurements

Thin slices (30 μm) of the tensile test bars, cut with a microtome, were measured in a Perkin–Elmer DSC 2 instrument. The slices were cut at different depths from the surfaces of the samples. The accuracy of the temperature measurements was ± 2°C and the heating rates 5, 10 and 20 K/min.

Wide-angle X-ray scattering (WAXS)

The WAXS photographs were taken at room temperature using a pinhole camera and nickel-filtered CuKα radiation. Thin slices (30 μm) were taken at different distances from the surface of the tensile test samples and mounted with their planes and flow directions perpendicular to the incident X-ray beam.

Crystallinity

The density of the samples was determined with a density column (isopropanol and water). The corresponding amount of crystallinity was calculated using the following specific volume values of the amorphous and crystalline components: $v_a = 1.175$ cm^3/g and $v_c = 1.000$ cm^3/g.

Mould shrinkage

The mould shrinkage was expressed as a percentage of the dimensions of the mould cavity, the mouldings being quadratic plates (34 x 34 x 5 mm).

RESULTS

Optical and scanning electron micrographs

An optical micrograph of a fractured HMWPE tensile test bar, injection pressure 500 MPa, is shown in *Figure 1.* A core region in the centre can clearly be distinguished. For injection pressures lower than 300 MPa no core region was observed. For HDPE no core of this kind was found.

Scanning electron micrograph from the core of fractured HMWPE specimens, moulded at 300–500 MPa, have a fibrous appearance (*Figure 2*), the direction of the fibres coinciding with the flow direction. Near the surface or at lower pressures fracture surfaces of this kind were not observed. The same applies for HDPE samples through the entire pressure region.

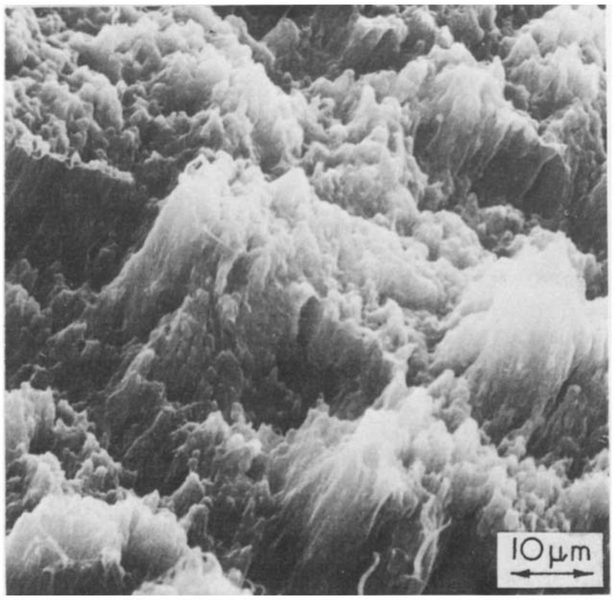

Figure 2 Scanning electron micrograph taken from the core region of the sample shown in *Figure 1.* Note the fibrous appearance of the core

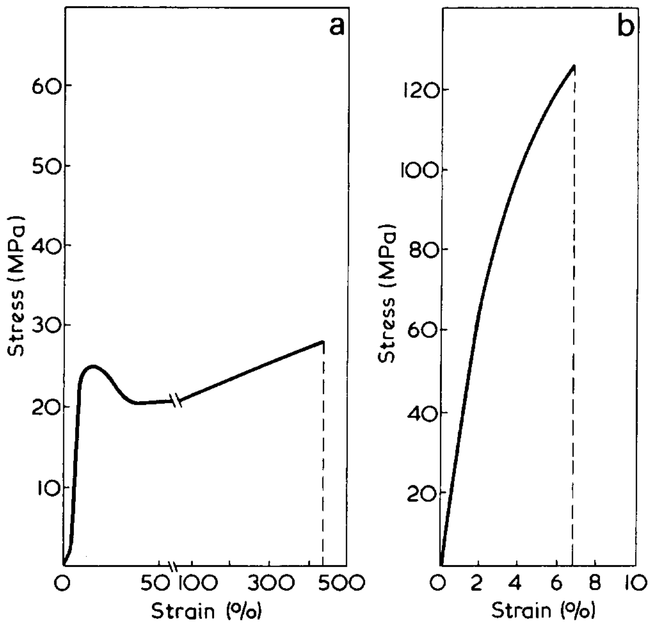

Figure 3 Stress–strain curves (nominal values) for HDPE (a) and HMWPE (b) tensile test samples moulded at 500 MPa

Stress–strain behaviour

In *Figure 3* nominal stress–strain curves in the flow direction for the low and high molecular weight materials, injection moulded at 500 MPa, are shown. Evidently their deformation behaviours differ significantly. The HMWPE samples broke in a brittle manner, while the low molecular weight grade exhibited normal necking followed by a cold drawing state. The tensile modulus measured in the flow direction is shown together with the tensile strength in *Figure 4*. For HDPE the modulus was practically unaffected by the maximum pressure in the mould during the injection, while for HMWPE it increased from 1.1 GPa at 100 MPa to 3.4 GPa at 500 MPa. The latter value is comparable with modulus values of common engineering plastics (dry polyamide, polyoxymethylene, etc.). The variation of the tensile strength with increasing pressure followed a similar pattern. The tensile strength at rupture and yield of the normal *MI* grade HDPE was hardly affected by the pressure while the high molecular weight grade showed tensile strength values increasing from 60 to 130 MPa.

From *Figure 5* it can be seen that the elongation at yield (ϵ_y) for HDPE was not influenced by the injection pressure, while the elongation at rupture (ϵ_B) after cold drawing decreased from about 800 to 400% with increasing *p*. The same behaviour was also found for ϵ_B for HMWPE even though it was about two orders of magnitude lower than that for HDPE.

These results show that the stress–strain behaviour of HDPE remains practically unchanged by the injection pressure when the molecular weight lies within the range normally used for injection moulding. With the high molecular weight grade a substantial improvement is observed in the modulus and the tensile strength, accompanied by a decrease in the elongation at rupture.

Creep behaviour

Figure 6 shows the creep curves for HDPE and HMWPE samples moulded at 100 and 500 MPa. For all samples the nominal tensile stress was about the same (20 MPa). The resulting strain was in all cases lower for the high molecular weight material. The difference was especially pronounced for the samples produced at the lower moulding pressures (*Figure 6*). For both HDPE and HMWPE the creep resistance was improved when the specimens were moulded at higher pressures. The normal injection moulding grade showed the largest reduction in creep rate when the injection pressure increased from 100 to 500 MPa.

Impact strength

The impact strength of the tensile test bars perpendicular to the flow direction varied with the injection pressure in a

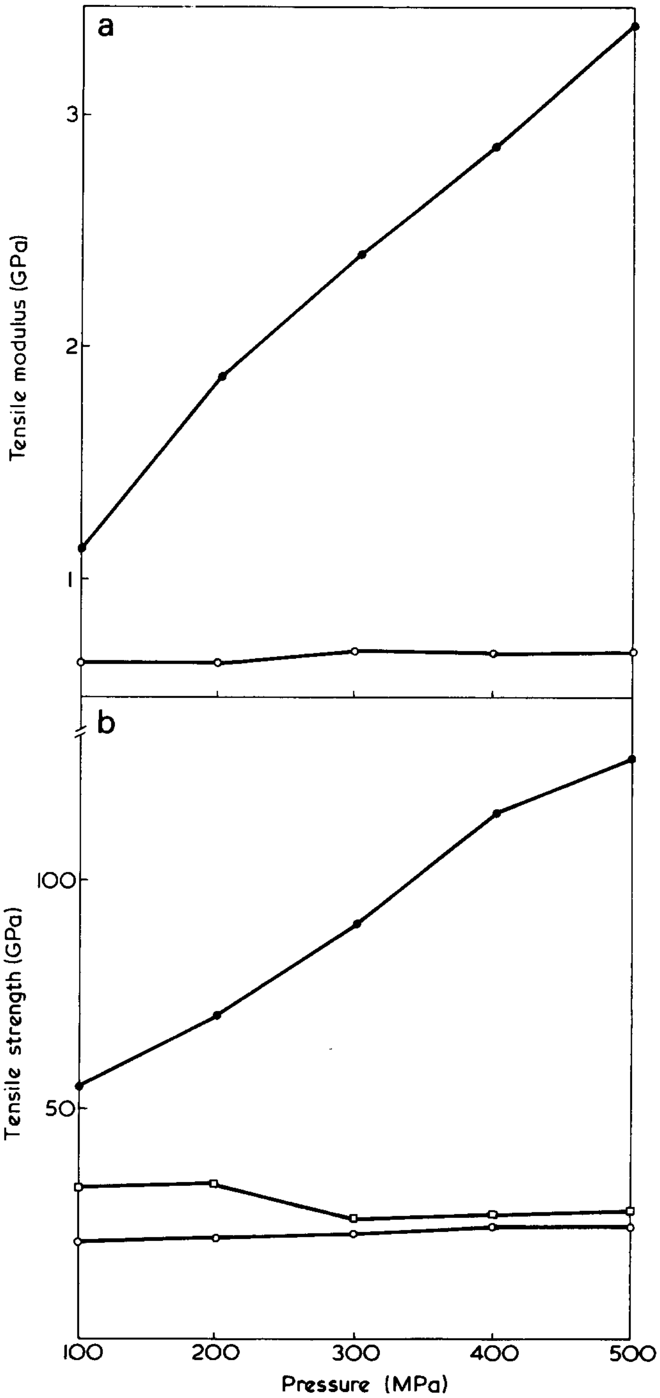

Figure 4 Tensile modulus (*E*) *versus* maximum mould pressure for (○) HDPE and (●) HMWPE (a); and the pressure dependence of tensile strength at yield (○) and at rupture (□) for HDPE, and at rupture (●) for HMWPE (b) [Reproduced from Djurner, K., Kubát, J. and Rigdahl, M. *J. Appl. Polym. Sci.* 1977, **21**, 295 by permission of John Wiley and Sons Inc., New York ©]

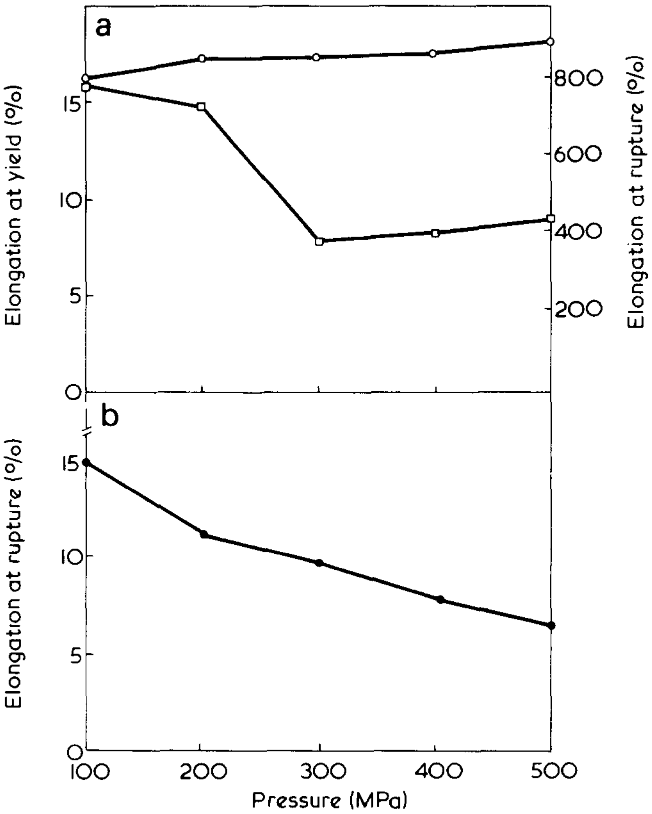

Figure 5 Elongation at yield (○) and rupture (□) for HDPE (a) and at rupture (●) for HMWPE (b) as a function of the maximum mould pressure

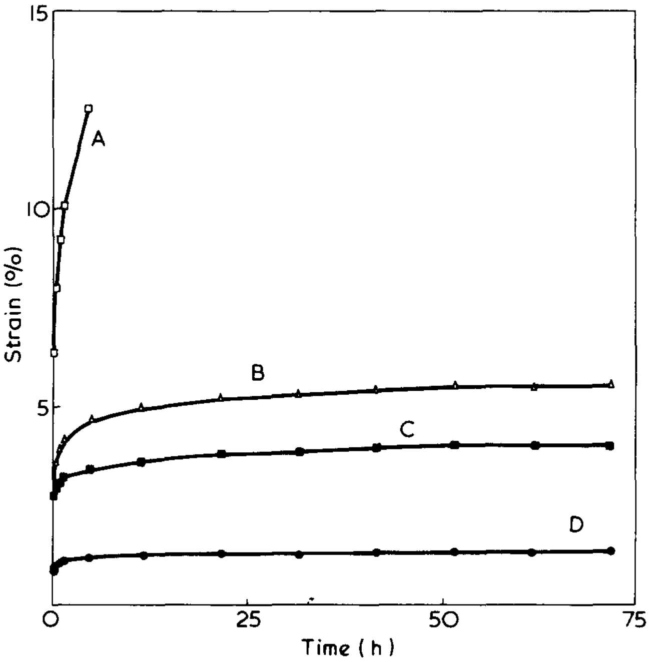

Figure 6 Creep curves for (□,△) HDPE and (■,●) HMWPE, moulded with different injection pressures. The applied stress was about 20 MPa for all samples. The creep experiment for the 100 MPa HDPE sample had to be stopped after about 5 h, since the maximum measurable strain was 12.5% for the experimental set up used. A, HDPE, 100 MPa; B, HDPE, 500 MPa; C, HMWPE, 100 MPa; D, HMWPE, 500 MPa

way similar to the tensile modulus and strength. For HDPE no influence of the pressure was found, while for HMWPE the impact strength increased from 5.2 J/cm^2 for lower pressures to 8 J/cm^2 at 500 MPa (*Figure 7*). However, for pressures in the range of 100–200 MPa the impact strength was almost constant.

D.s.c. measurements

The results of the d.s.c. measurements on HMWPE can be summarized as follows: the curves shown in *Figure 8* relate to samples taken 50, 350 and 600μm from the surface of the tensile test bars, i.e. from the skin, from the edge of the core and from the core interior respectively. The mould pressures were 100, 300 and 490 MPa. The curve of the 350 μm sample from the bar produced at 100 MPa has a barely discernible shoulder (indicated by an arrow) above the normal melting peak at T_m = 128°C. Increasing the cavity pressure to 300 and 490 MPa results in a new, clearly developed melting peak at 137° ± 1°C. The intensity of this peak increases with pressure. Varying the heating rate (5, 10 and 20 K/min) did not significantly change the location of the melting peaks.

For the normal grade HDPE only a single peak corresponding to the melting point of chain-folded lamellae was recorded, independent of the maximum mould pressure.

WAXS

WAXS photographs for the bulk sample, the skin layer, the transition region and the core of the high molecular weight material moulded at 500 MPa are given in *Figure 9*. The diffraction pattern for the skin shows that this layer is only slightly oriented while the photographs for the transition layer and the core indicate an appreciable degree of orientation of the crystalline component in the flow direction. For samples moulded in the pressure range 300–500 MPa there was also a faint diffraction ring resulting from a small amount of monoclinic material. The significance of this reflection will be discussed in a forthcoming paper dealing with the structure of high pressure injection moulded specimens[12]. A similar observation of this structure in samples obtained by capillary extrusion has been reported by Porter *et al.*[13].

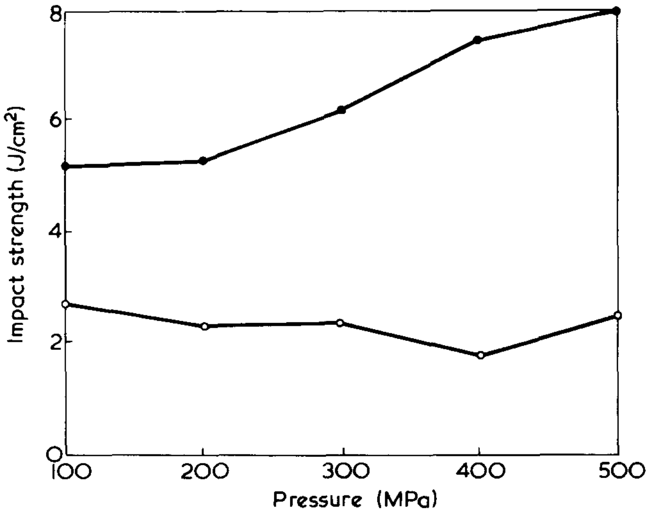

Figure 7 Impact strength perpendicular to the flow direction *versus* maximum mould pressure for (○) HDPE and (●) HMWPE tensile test samples (length 25 mm, width 5 mm and thickness 1.5 mm) which had been cooled for 15 min with liquid nitrogen

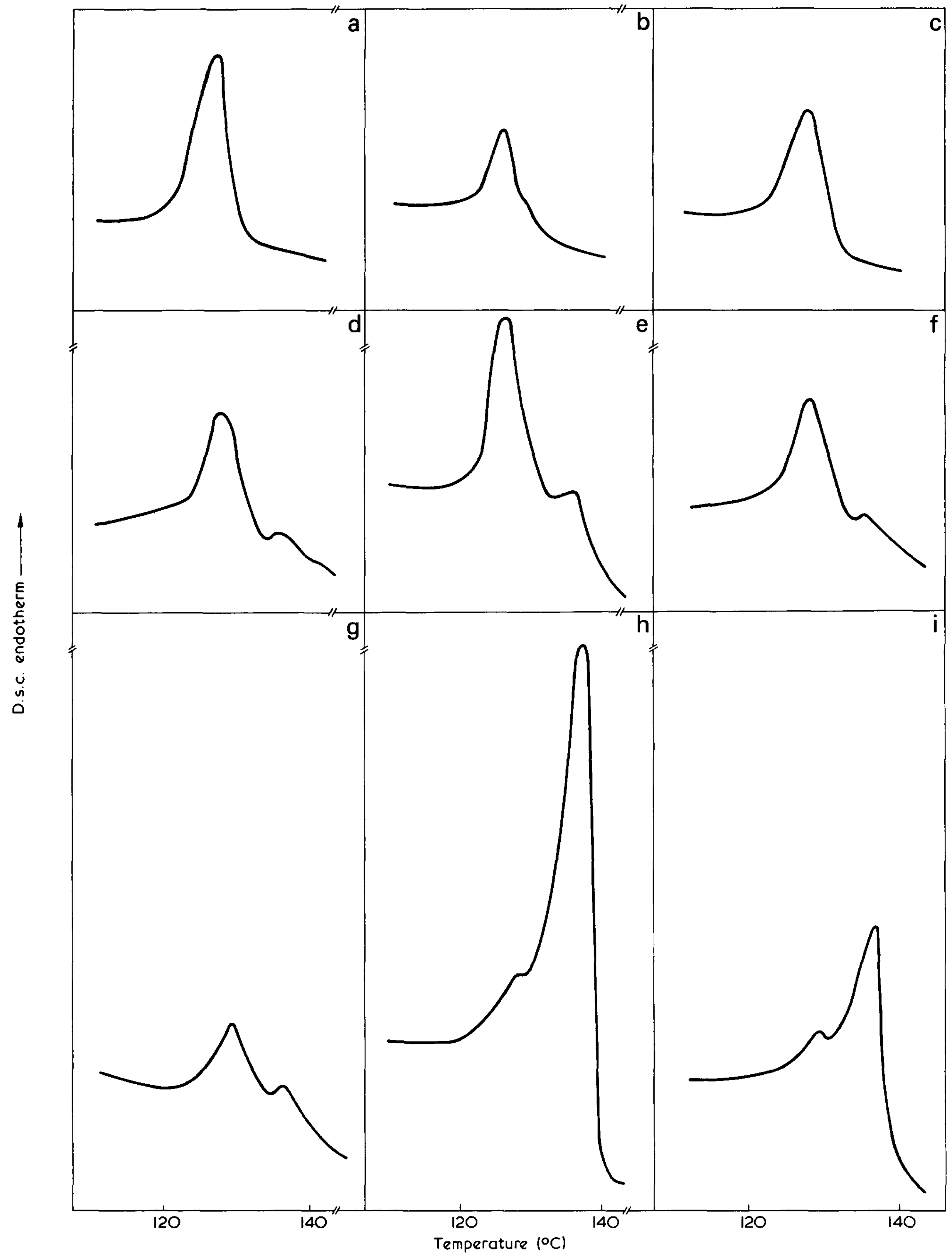

Figure 8 D.s.c. endotherms (arbitrary units) for thin specimens of HMWPE taken at various depths from the Surface. Heating rate 10 K/min (a) ~50µm, 100 MPa; (b) ~350µm, 100 MPa; (c) ~600µm, 100 MPa; (d) ~50µm, 300 MPa; (e) ~350µm, 300 MPa; (f)~600µm, 300 MPa; (g) ~50µm, 490 MPa; (h) ~350µm, 490 MPa; (i) ~600µm, 490 MPa [Reproduced from Djurner, K., Kubát, J. and Rigdahl, M. *J. Appl. Polym. Sci.* 1977, **21**, 295 by permission of John Wiley and Sons Inc., New York ©]

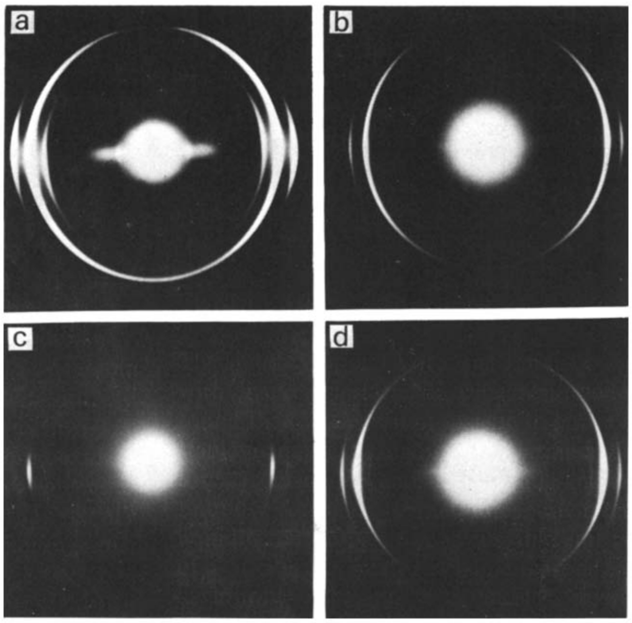

Figure 9 **Wide-angle X-ray diffraction patterns for HMWPE samples moulded at 500 MPa. (a) refers to the bulk sample. (b) (c) and (d) refer to the skin layer: ≈50 μm from the surface (b), the transition layer, ≈250 μm (c) and the core, ≈ 650 μm (d)**

Crystallinity

The influence of the injection pressure on the crystallinity of the tensile test specimens is given in *Figure 10.* For HDPE only a very small increase in crystallinity with pressure was observed, while for HMWPE it increased from 66 to almost 75%.

Mould shrinkage

The mould shrinkage varied with the maximum mould pressure in a similar way for both grades (*Figure 11*). At 100 MPa it was about 1% and it decreased to zero for pressures in the region 200–300 MPa. A further increase in pressure caused expansion. The mould shrinkage was always lower for the high molecular weight material.

DISCUSSION

The use of high pressures when injection moulding high molecular weight polyethylene produces a material with mechanical properties that are comparable with those of engineering plastics.

The double peaks of the d.s.c. endotherms can either be a result of supercooling of the material in the mould or due to crystalline structures which are similar to those obtained from either crystallization[14] or annealing[15] at pressures in the range of 200–500 MPa (extended chain crystals), from flow or strain-induced crystallization (shish-kebabs)[16,17], or from capillary extrusion at high pressures[13,18]. In the present study the mechanical properties and the fibrous appearance of the fracture surface indicate that the crystalline structures are the more likely explanation. In a forthcoming work[12] the existence of extended chain crystals in these samples will be demonstrated using transmission electron microscopy. Supercooling effects do not adequately account for the fact that the intensity of the second melting peak is stronger for slices taken at a depth of 350 μm than that of those taken at 600 μm (*Figure 8*). It may also be noted that non-quenched samples and samples that had been melted, cooled and then re-examined with the d.s.c. displayed a single peak in the d.s.c. endotherms corresponding to a melting temperature of ~130°C. In the paper to follow[12] results of detailed WAXS experiments will be presented, showing that the orientation changes only slightly when the injection pressure is raised and that this effect cannot fully explain the improvement in mechanical behaviour.

Samples from which the skin and the transition layer had been removed showed higher modulus and strength values than bulk samples. Thus the improved mechanical properties appear to be associated with high strength structures in the cores. However, the core is rather brittle and the high impact strength must be due to the more ductile, less oriented skin. The thickness of the skin increased somewhat with injection pressure, this probably being due to less undercooling at high pressures. To some extent this would explain why the impact strength increases with pressures. Thus, the mechanical behaviour of the high molecular weight material can be regarded as that of a composite with ductile surface layers and a brittle core.

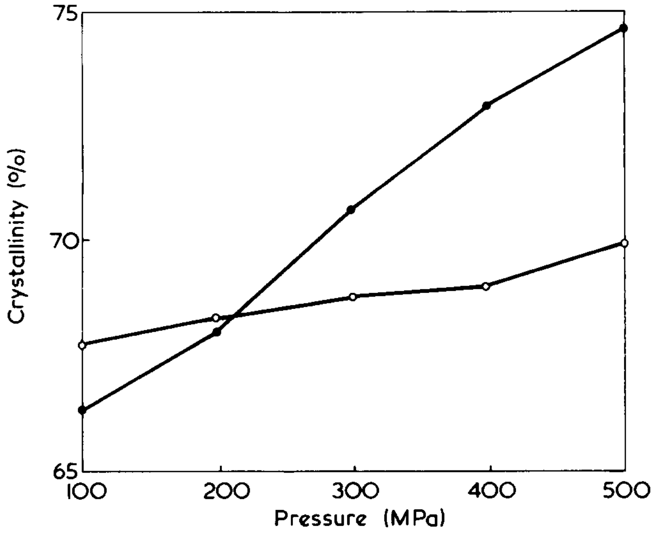

Figure 10 **Crystallinity of bulk tensile test samples as a function of maximum mould pressure for (○) HDPE and (●) HMWPE**

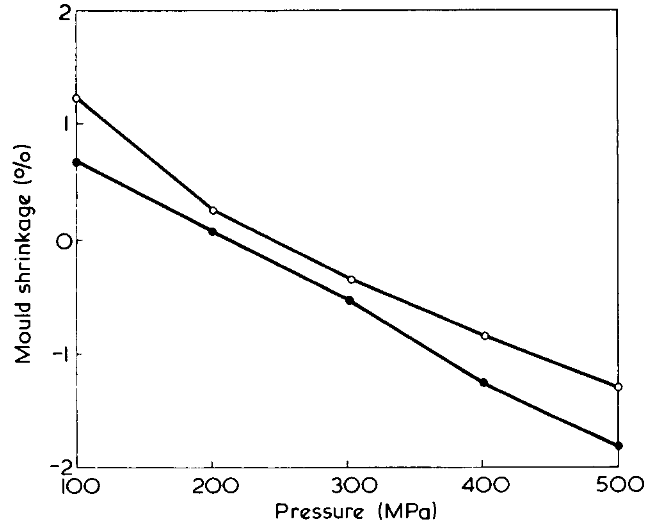

Figure 11 Mould shrinkage of square plates *versus* maximum mould pressure for (○) HDPE and (●) HMWPE

The reason for not obtaining high strength structures with the normal injection moulding grade could be that such structures are more difficult to form if the molecular weight is lower[19,20]. Further, from capillary extrusion work it is known that the processing conditions for obtaining high strength structures of a given material cannot be chosen within too broad limits. The moulding conditions used for HDPE may not have been chosen properly in this respect.

The improved creep resistance of samples moulded at high pressures seems to be due partly to the high strength of the core and partly to a decrease in the average internal stress level (σ_i). The creep rate is determined by the effective stress given by the difference between the applied and internal stress. The internal stresses determining the flow rate of injection moulded samples are normally negative (compression stresses). A decrease of the absolute value of σ_i thus lowers the creep rate. The internal stresses were determined using a stress relaxation method. For HDPE and HWMPE it was found that the absolute value of σ_i decreased from about 4 and 6 MPa, respectively, for samples moulded at 100 MPa, to a level close to zero for samples moulded at pressures in the range of 400–500 MPa. The decrease in the internal stress level at higher pressures is probably due to an increase in the melting point with the pressure. Since the σ_i level is determined primarily by the temperature gradients when the sample solidifies, these stresses should be reduced if the entire content of the mould is solidified simultaneously. A sufficiently high injection pressure appears to have such an effect. A detailed discussion of internal stresses in high pressure injection moulded specimens can be found in ref 21.

The relatively large increase in crystallinity of HMWPE compared with HDPE is in agreement with the appearance of the high strength structures mentioned above.

The mould shrinkage is often a parameter of great technological importance. The observation in the present work that the degree of shrinkage can be controlled by adjusting the pressure level could therefore be of some value, particularly with regard to precision moulding.

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