An HDPE-Phase Melting at 137° C Formed During Injection Molding at Pressures in the 100–500 MPa Range

INTRODUCTION

It is known that the injection molding of crystallizable polymers produces a layered structure at the surface of the molded part.[1-3] First, there is the rapidly solidified outer layer (skin) next to the wall of the mold cavity. Underneath, one finds a transition layer, with a comparatively high degree of orientation. It is believed that the higher level of molecular order is due to the shear forces between the solidified material next to the cavity wall and the flowing melt. The interior of the specimen is found to contain unoriented spherulites. It has been suggested that, in the case of polyethylene, the second layer acquires a somewhat "anomalous" structure. For instance, Heckman and Johnson[3] found small irregularities in the DSC diagrams of samples taken at the depth of that layer, indicating the possible occurrence of a phase with a higher melting point. Their results were interpreted in terms of the row-structure model proposed by Keller,[4] showing certain similarities with the structure of shish kebabs.[5]

In this note, we report on DSC measurements on samples injection molded at pressures varying from 100 to 490 MPa. It will be shown that the barely discernible shoulder in the DSC curves occurring above the normal melting point can be converted into a distinct maximum which, at the highest pressures, markedly exceeds the height of the normal T_m peak. The DSC specimens were cut from moldings, having the shape of small tensile testing samples. It will further be shown that the increase in the amount of the higher melting phase is accompanied by marked changes in the mechanical parameters of the moldings. It appears plausible to assume that the phase with the higher T_m value, i.e., 137°C, is associated with the occurrence of extended chains or similar structure. Further comments on this will be given below.

EXPERIMENTAL

High-density polyethylene (HDPE, DMDS-2215, supplied by Unifos Kemi AB, density 0.953 g/cm³, 7 g/10 min MI_{21}) was injection molded, using a modified injection molding machine (Engel 250/500 AS). (The relatively low density of this grade is perhaps more consistent with a medium-density polyethylene, but we have chosen to follow the classification of the producer, Unifos Kemi AB.) One feature of the machine was that the plunger, attached to the screw, had a centrally placed channel equipped with a nonreturn valve, preventing the melt from flowing back during the injection process which is described in detail in reference 6. The molding conditions are given in Table I.

The injection-molded specimens were small, tensile test bars with a gauge length of 25 mm and thickness of 1.5 mm (see also ref. 6). During the cycle, the hydraulic pressure and the pressure within the mold were recorded. The mold pressure was measured with a pressure transducer (Colortronic 407) via a dummy ejection pin.

Thin slices (30 μm) of the specimens, cut with a microtome, were measured in a differential scanning calorimeter (Perkin-Elmer, DSC 2). The slices were cut at different distances from the surface of the samples. The accuracy of the DSC measurements was ±2°C.

The mechanical properties of the tensile test samples were determined using a conventional tensile tester (Instron model 1193). The strain rate was 20 mm/min (1.3×10^{-2} s⁻¹). The tangent modulus

TABLE I
Molding conditions

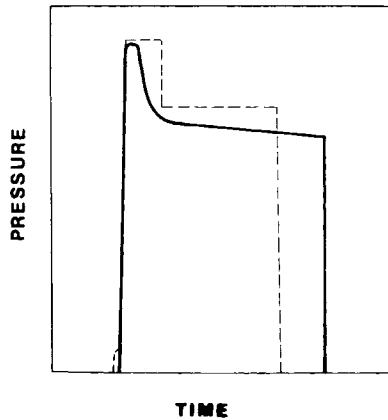|	
Melt temperature, ° C	250–280
Mold temperature, ° C	30
Injection time, sec	6
Holding time, sec	15
Cooling time, sec	5

Fig. 1. Pressure in the mold cavity (—) and hydraulic pressure (- - -) as a function of time. The difference between the maximum values is small (ca. 10 MPa). The maximum value of the pressure within the mold, shown above, is 490 MPa, and the cycle time is 26 sec.

(E), tensile strength at break (σ_u), and elongation at rupture (ϵ_u) were determined according to ASTM D638.

RESULTS

As there appears to be no reference in the available literature to injection molding in a conventional machine at pressures in the 500 MPa range, we show in Figure 1 the time dependence of the pressure during a molding cycle. It can be seen that the agreement between the maximum hydraulic p value in the nozzle and that in the mold is rather good. The maximum value of p in the mold is maintained for a relatively short time period; the general appearance of the p–time curves shows no deviation from that registered at normal pressures.[7]

The results of the DSC measurements are summarized in Figure 2. The curves shown relate to a maximum cavity pressure of 100, 300, and 490 MPa, respectively, for samples taken at varying distance from the surface of the molding. As can be seen, the curves for the 100 MPa samples have the normal appearance, indicating a T_m value at 128°C. Only the sample taken 350 μm from the surface exhibited a small shoulder at $T > T_m$ (indicated by an arrow in Fig. 2).

An increase of the maximum p value in the mold to 300 MPa results in a new, clearly developed melting peak for all the samples investigated and particularly for the sample taken 350 μm under the surface. At 490 MPa, a further increase in the intensity of this new peak can be seen. Again, the 350-μm sample peak is markedly higher when compared with samples cut at 50 and 600 μm from the surface, respectively. At the 350 μm depth, the bulk of the melting now seems concentrated to the 137°C level; but even at 600 μm, the higher melting peak is more intense than at 50 μm.

When the samples were heated to 150°C, slowly cooled and examined once more in the DSC equipment, only the normal 128°C melting was recorded (Fig. 3). For compression-molded samples, which had been annealed for 12 h at 124°C and thereafter slowly cooled, a single peak at 131°C was obtained.

MECHANICAL PROPERTIES

As already mentioned, the occurrence of a high-pressure phase, melting at 137°C, was associated with rather marked changes in the mechanical properties of the moldings. Figure 4 shows the tensile modulus and the tensile strenth σ_u and elongation at rupture ϵ_u as a function of the maximum cavity pressure. Both the modulus and σ_u increase markedly with this pressure. At 490 MPa, the value of σ_u reaches the notably high level of ca. 120 MPa. Parallel with this increase, ϵ_u falls from 15% at 100 MPa to 5% at the highest pressure. The samples showed no tendency to cold drawing, independent of the pressure.

The internal stress level of the samples, measured using a stress relaxation technique,[8] decreased sharply with increasing pressure. This is in agreement with results from earlier measurements on HDPE with a lower molecular weight.[8]
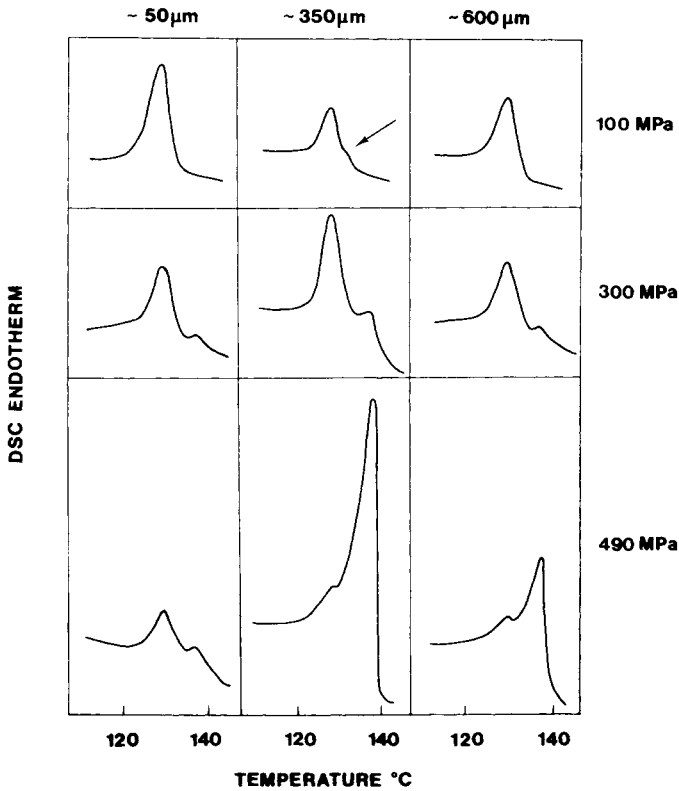
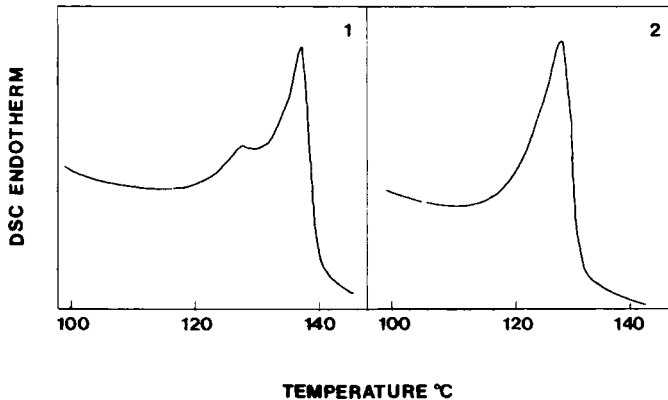Fig. 2. DSC endotherms (arbitrary units) for thin specimens taken at different depths from the surface (heating rate 10°K/min).

Fig. 3. DSC endotherms for a specimen taken at ca. 600 μm from the surface of a sample injection molded at 490 MPa. The left curve corresponds to the original recording. The sample was thereafter cooled down, and a second DSC curve was recorded with the same sample (right) (heating rate 10°K/min).

FINAL REMARKS

The results presented here show that increasing the molding pressure above 300 MPa is associated with the appearance of a new PE phase showing a DSC melting peak at 137°C. This phase appears to be concentrated to the well-known second layer of injection-molded parts.[1-3] During the filling
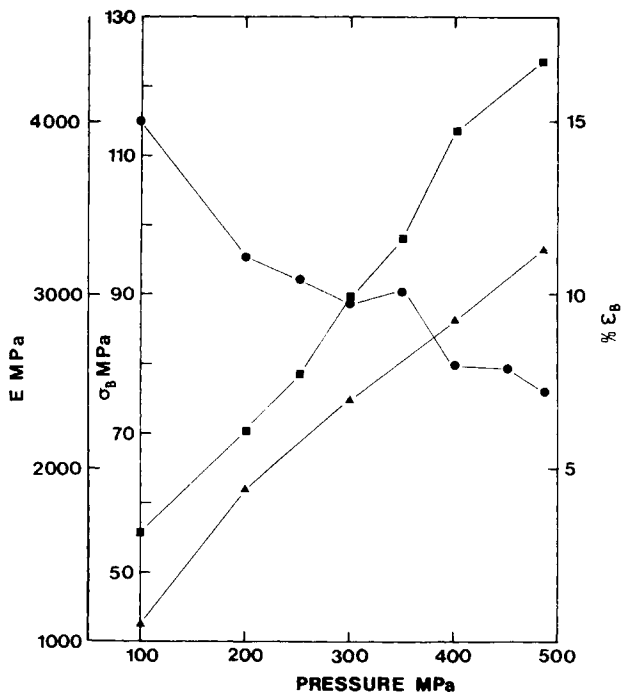
Fig. 4. Modulus E (▲), tensile strength at break σ_u (■), and elongation at rupture ϵ_u (●) as a function of the maximum pressure within the mold.

of the mold, relatively high shearing forces occur. This effect is due to an increasing melt viscosity with pressure. The reason behind this is partly a reduction of the free volume, partly a substantial increase in the melting point (ca. 20°C/100 MPa). It can be supposed that the shearing forces are especially intense close to the first solidified layer at the cavity walls. This could, in turn, be related to the excessive occurrence of the new oriented phase in the second layer. In this connection, the formation of extended chains during capillary extrusion of HDPE, as reported by Porter,[9] may also be mentioned. Even though there is limited direct evidence for this, it seems plausible to suppose that this second melting peak is associated with the occurrence of extended chain-like structures in the moldings—among other things, the T_m value agrees with literature data;[10-13] and it has also been suggested that extended chains are formed when PE crystallizes at pressures above 200 MPa.[14,15] However, it is not possible, at this stage, to determine whether this new structure consists of pure extended chain crystals, which are formed at high pressures, or to shear-induced shish kebabs. The small shoulder in the DSC curve exhibited by the sample molded at 100 MPa, taken from 350 μm depth, could be due to formation of less perfect extended chain-like crystals having a lower melting point than the more perfect ones. DSC endotherms have been recorded at the heating rates 5, 10, and 20°K/min. In no cases did the melting points of the two phases change significantly with the heating rate. However, this is described in more detail in a forthcoming publication together with a closer study of the orientation in the samples with x-ray techniques.

Substantial changes in the properties of injection molded HDPE parts may thus be obtained by increasing the cavity pressure above 300 MPa. Experiments with other polymers, such as polypropylene, polyoxymethylene, and poly(ethylene terephthalate),[6,16] gave similar results, although their properties did not change to the extent demonstrated here. It is not unlikely that the present results are tied to the relatively high molecular weight (low melt index) of the HDPE grade used. In experiments with HDPE (Hoechst, Hostalen GC 7260, density 0.960 g/cm³, melt index 7 g/10 min MFI 190/2), no indication of a 137°C melting peak was obtained with DSC. Also, the changes in mechanical properties of the moldings were substantially smaller.

It is evidently not possible to draw further conclusions from the above findings. A closer analysis, to be published later, will have to consider the layered structure of the samples, their orientation, a detailed study of the influence of the DSC heating rate and the role played by the molecular weight.

For the moment, it may suffice to say that the effects attributed to the occurrence of a high-pressure modification of HDPE can be obtained under conditions of normal injection molding by substantially increasing the molding pressure.

References

1. W. Heckmann and U. Johnsen, *Coll. Polym. Sci.,* **252,** 826 (1974).

2. M. R. Kantz, *Int. J. Polym. Mater.,* **3,** 245 (1974).

3. E. S. Clark and G. A. Garber, *Int. J. Polym. Mater.,* **1,** 31 (1971).

4. A. Keller and M. J. Mackin, *J. Macromol. Sci.,* **B1,** 41 (1967).

5. A. J. Pennings, J. M. A. A. van der Mark, and A. M. Keil, *Kolloid-Z. Z. Polym.,* **237,** 3361 (1970).

6. H. Aasa, K. Djurner, and J. Kubát, *Plaste und Kautschuk,* **23,** 448 (1976).

7. J. M. McKelvey, *Polymer Processing,* Wiley, New York, 1962, p. 346.

8. J. Kubát and M. Rigdahl, *Polymer,* **16,** 925 (1975).

9. T. Niikuni and R. S. Porter, *J. Mater. Sci.,* **9,** 389 (1974).

10. D. C. Bassett, B. A. Khalifa, and B. Turner, *Nature Phys. Sci.,* **239,** 106 (1972).

11. P. D. Calvert and D. R. Uhlmann, *Polym. Lett.,* **8,** 165 (1970).

12. Y. Maeda and H. Kanetsuna, *J. Polym. Sci., Phys. Ed.,* **12,** 2551 (1974).

13. V. Tan and C. G. Gogos, *Soc. Plast. Eng. 33rd Annu. Techn. Conf.,* (Atlanta, Georgia) 1975, p. 346.

14. J. L. Kardos, H.-M. Li, and K. A. Huckshold, *J. Polym. Sci. A-2,* **9,** 2061 (1971).

15. Y. Maeda and H. Kanetsuna, *J. Polym. Sci, Phys. Ed.,* **12,** 2551 (1974).

16. K. Djurner and J. Kubát, *Kunststoffe 66,* **9,** 511 (1976).

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