Influence of Mold Filling Rate and Gate Geometry on the Modulus of High Pressure Injection-Molded Polyethylene

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Synopsis

High pressure injection molding of HDPE with relatively high molecular weight is known to give products with significantly increased modulus and strength. The extent of this improvement is reduced when the thickness of the molded sample increases. The present paper is an account of experiments with varying mold filling rates and gate geometries. After choosing proper gating and then optimizing the filling rate, thick samples with tensile moduli previously characteristic of thinner samples have been obtained. The modulus data are supplemented by measurements of the melting point of the normal and high-strength HDPE structures at different locations in the molded test bars. Corresponding crystallinity data are also included. The structure of the samples appears to provide some guidance in interpreting the observed modulus variations.

INTRODUCTION

Today there exist several techniques for producing high strength and high modulus linear polyethylene including hydrostatic, ram, and capillary extrusion, tensile drawing, and solution crystallization methods (see, for example, Ref. 1). Values of the tensile modulus and strength as high as 100 and 4 GPa, respectively, have been reported for such specimens. At our laboratory efforts have been made to produce high strength/high modulus linear polyethylene using high pressure injection molding.[2-4] The nominal molding pressure used in these investigations was 500 MPa, which substantially exceeds the maximum pressure levels used in practice (100–150 MPa).

With high pressure injection molding the values obtained for the tensile modulus and strength are significantly lower than the results obtained with the methods mentioned above. One of the reasons for this can be traced to the nonhomogeneous character of injection molded specimens.[5-7] The amount and perfection of the structures responsible for the improvement in mechanical properties of polyethylene (PE) are not evenly distributed over the cross section of the injection-molded part and they vary also with the flow length of the melt when it fills the mold cavity.[4] Earlier work[3,4] has indicated that the improvement in high pressure injection-molded linear polyethylene is due to formation of structural elements differing from the normal spherulitic structure. Tie molecules (or similar elements) interconnecting the crystallites, which may be of the extended type, or shish kebab structures can account for the observed behavior. The nature of these elements is thus similar to that observed in other types of high performance polyethylene specimens such as

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specimens obtained with hydrostatic extrusion, shear-induced crystallization, or crystallization under elevated pressures.

The appearance of the nonspherulitic structures and the resulting improvement in the mechanical properties are related to the flow-induced crystallization taking place during the high pressure injection molding cycle.[3,4] It also follows that the specimens are highly oriented, which can be assessed by shrinkage measurements, wide angle X-ray scattering, and far-infrared birefringence measurements.[8,9] The mechanical properties are related to the degree of orientation (both of the crystallites and the amorphous phase) of the specimens.[9]

In earlier work[3,4] it has been shown that injection molding of HDPE with a relatively high molecular weight at nominal pressures up to 500 MPa produces specimens with a tensile modulus of 12 GPa and a tensile strength of 260 MPa in the flow (orientation) direction. This should be compared with the values obtained at a more conventional pressure level (100 MPa), 1 GPa and 50 MPa, respectively.[2] However, high values were obtained only for thin specimens with a thickness of 1 mm. When the thickness was increased, the modulus and the strength decreased substantially.[4] It is known that the processing conditions have a significant effect on the properties and the structure of injection molded parts.[5,6,10,11] This is also the case with high pressure injection molding.[3,4] In Ref. 4 it was noted that the flow conditions during mold filling had a strong influence on the mechanical properties of high pressure injection-molded linear polyethylene. The aim of the present work is to optimize the tensile modulus of the molded polyethylene samples by analyzing the effect of the mold filling rate (injection speed) and the gate design on the modulus. Of special interest is to investigate if the decrease in the modulus with increasing thickness of the molded part could be prevented, at least to some extent.

The results presented below show that a modulus maximum can be obtained by changing the mold filling rate. The optimal mold filling rate refers to a specific gating. Furthermore, the gate geometry has a significant influence on the modulus of the samples. By choosing proper gating and adjusting the injection rate, one can obtain thick samples with a modulus previously only found for thinner ones.

EXPERIMENTAL

Material

The material used was a high density polyethylene (HDPE) grade with a high molecular weight (DMDS 2215, Unifos Kemi AB, Sweden). This is the same HDPE-grade as was used in Refs. 3 and 4. Its density was 0.953 g/cm^3 and the melt flow index was 0.1 g/10 min (MFI 190/2). The average molecular weights were $\bar{M}_w$ = 286,000 and $\bar{M}_n$ = 22,000.

Injection Molding of the Specimens

The injection molding machine was a modified version of a conventional machine (Sund-Åkesson AB, Helsingborg, Sweden) with a clamping force of 250 Mp. This machine is described in detail in Ref. 7. The nominal pressure was kept at 500 MPa throughout the injection molding cycle. The corresponding maximum cavity pressure, measured inside the mold, was about 300 MPa.[4]

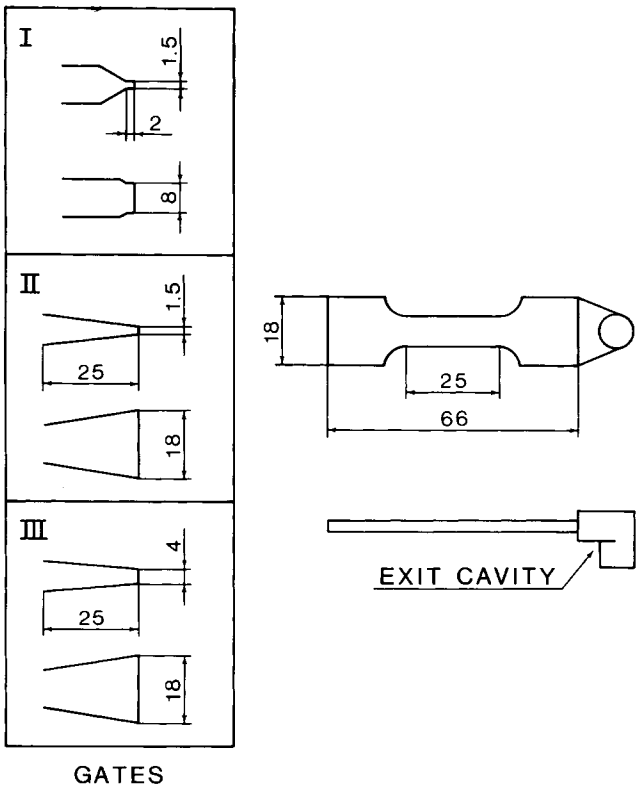

Fig. 1. The dimensions (mm) of the different gates, and a schematic picture of the test bar with the exit cavity.

The melt (barrel) temperature was 190°C, and that of the mold 30°C. The dimensions of the test bars are shown in Figure 1; their thickness could be varied between 1 and 6 mm. The bars were produced using a mold equipped with an exit cavity. This cavity gave an improvement in the mechanical properties of the bars[4] since it allowed greater material movement during the molding cycle, an effect beneficial with regard to the development of the high modulus structures in polyethylene (see also Ref. 12).

In Ref. 4 an account of the influence of the gate geometry on the mechanical properties of high pressure injection-molded HDPE was presented. It was observed that a gate with a rectangular cross section produced test bars with the highest modulus and strength. In view of this, such gates were used in the present work. Three different gate geometries, denoted I, II, and III, respectively, were designed (see Fig. 1). Although somewhat unusual in their appearance, gates II and III possess some advantageous features:

- An elongational flow can be produced during the mold filling stage. This refers mainly to gate II.
- Longer holding pressure times, that is, longer sealing times are achieved. The sealing times for gates I, II, and III are 1.5, 2.5, and 5 s, respectively, for a test bar with a thickness of 4 mm.
- The gates also provide a more gradual change in velocity distribution when the melt flows from the runners to the mold cavity.

The sealing time was determined from pressure–time recordings at varying pressure holding times obtained with a pressure sensor in the mold. It was defined as the shortest holding time necessary to prevent a drop in cavity pressure after release of the holding pressure. The maximum error in the sealing time values was about ± 0.5 s.

Tensile Tests

The tensile modulus in the flow direction at room temperature was determined with an Instron tensile tester (Model 1193) according to ASTM D638. The tester was equipped with an extensometer (Instron G51-15MA). The strain rate was 0.2 min^{-1}.

Thermal Analysis

The melting point (T_m) and the heat of fusion (ΔH_f) were determined with a DTA-device (Mettler 2000TC) for thin slices taken from the central portion of the test bar (along the length of the bar). The slices, 100 μm thick, were taken at different distances from the surface of the bars. The planar area of the slices was about 5×5 mm^2, their weight was approximately 1 mg. The crystallinity of the slices was evaluated from the heat of fusion using $\Delta H_f = 293$ J/g for crystalline HDPE.[13] The T_m values were corrected for the influence of the heating rate (10°C/min).

RESULTS

Tensile Modulus

The modulus exhibited a pronounced dependence on both the main variables of this investigation, that is, the thickness of the test bars and the mold filling rate (injection speed). Figure 2 shows this for samples molded using gate II (cf. Fig. 1). As can be seen, the filling rate has a significant influence on the modulus values of the thinner samples, 2–3 mm thick, a maximum being found at a rate of about 17 cm^3/s. For the samples with a thickness of 4 mm, the modulus changes with the rate relatively little, although the basic features of the variation noted with the other samples can also be found in this case. Decreasing the thickness from 4 to 2 mm produces an overall increase in the modulus level, at the same time as the maximum in the modulus value becomes more pronounced. These effects are also evident from a plot of the modulus value vs. the linear filling rate, that is, the volume filling rate divided by the sample thickness. From such a plot, not shown here, it can be seen that the modulus-rate maximum is shifted towards lower rates when the thickness of the samples increased. It may be noted that corresponding maxima in the degree of orientation of similar samples have been found earlier by measurements of far-infrared birefringence and wide angle X-ray scattering.[9]

The decrease in the modulus at higher filling rates may be due to flow instabilities during filling of the mold cavity or to higher heat dissipation. The reduction of the modulus value in the thicker samples appears to be caused by the lower flow rates (shear and/or elongational flow) in the mold cavity and by longer cooling times. Both these effects appear to produce fewer or less

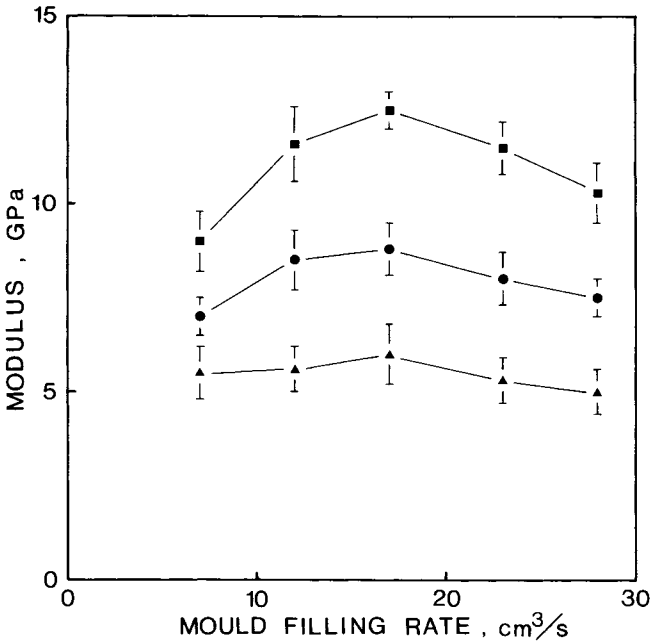

Fig. 2. The tensile modulus vs. the mold filling rate for HDPE test bars produced with gate II. The thicknesses (mm) of the test bars were: (■) 2; (●) 3; (▲) 4. The standard deviations of the moduli were less than 1 GPa.

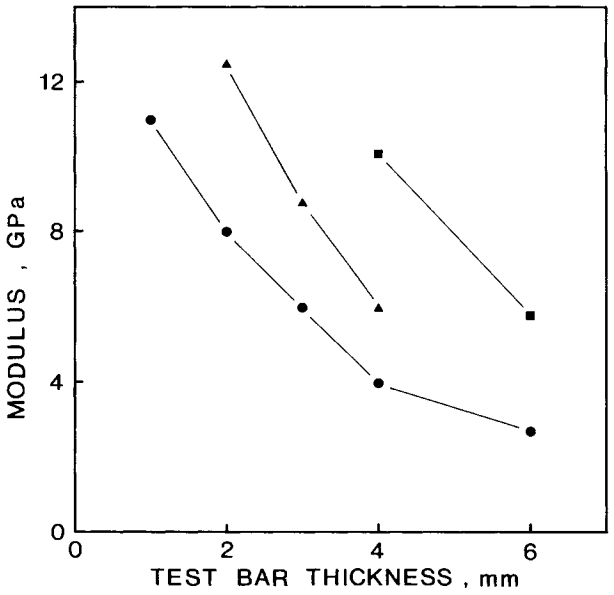

Fig. 3. The tensile modulus vs. the thickness of the HDPE-bars produced with: (●) gate I; (▲) gate II; (■) gate III. The standard deviations of the moduli were less than 1 GPa.

stretched interconnecting structural elements between the crystallites.[3,4] It is therefore natural to expect that the influence of the injection rate will be less marked for thicker samples.

Effects similar to those discussed above were also observed with the other gates. This applies to the maxima in the modulus–rate curves. For instance, gates I and III produced such maxima at volume flow rates of 23 and 12 cm^3/s, respectively. Obviously, shorter sealing times require higher injection speeds to obtain optimal modulus values.

The effect of the gate geometry on the modulus of test bars with different thickness is shown in Figure 3. For each type of gate the mold filling rate was chosen to produce the optimum stiffness. For all test bars, an increase in the thickness results in a lower modulus. This is in agreement with earlier results and is to be expected.[3,4] However, the gate geometry has a significant effect on the modulus. For instance, at a thickness of 4 mm, test bars produced with gate I have a modulus of about 4 GPa while gate III yields specimens with a stiffness of more than 10 GPa. From the data shown in Figure 3 it can be concluded that a longer sealing time produces test bars with higher stiffness values. The longer sealing times may allow for greater material movement under high pressure cycles which results in a higher modulus.[4,12] The longer sealing times also counteract relaxation of the interconnecting structural elements, such as tie molecules, during the cooling period of the molding cycle. It is thus to be expected that the effect of the prolonged sealing time will be more pronounced for thicker specimens.

Thermal Analysis

The endotherms of high pressure injection-molded HDPE often exhibit two melting peaks, the lower corresponding to the melting of the normal melt crystallized material and the higher to the crystalline structures partly related to the improved mechanical properties.[3,4] Figure 4 shows the two corresponding melting points as a function of the distance from the surface of test bars

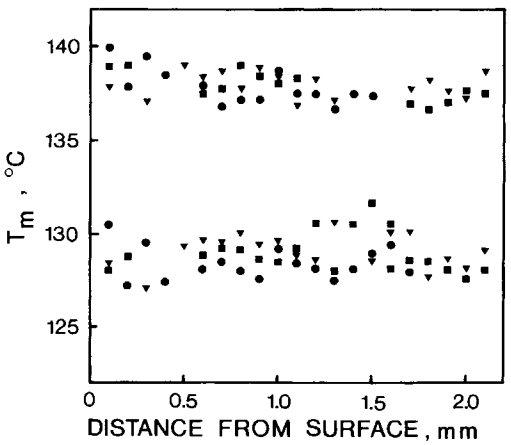

Fig. 4. The variations of the two melting peak temperatures T_m over the cross section of a 3 mm thick sample molded with gate II. The test bars were produced at different mold filling rates (cm^3/s): (▼) 12; (●) 17; (■) 23.

produced with gate II and with three different volume filling rates, 12, 17, and 23 cm^3/s, respectively. The thickness of the test bars was 3 mm and the thin slices used for this thermal analysis were microtomed from the central part of the bars (about 30 mm from the gate). In this case, the two melting points were 129 and 138 ± 2°C over the cross section. The T_m values did not vary appreciably with the distance from the surface of the bars, nor did the mold filling rate have any marked influence on these values. It may be mentioned that some data points are missing in Figure 4, which is due to experimental difficulties in obtaining thin slices of acceptable quality in some regions of the test bars. However, this has no effect on the conclusions.

Figure 5 shows the variation of the total crystallinity C_T over the cross section of the same test bars (discussed in connection with Fig. 4). The crystallinity varies between about 50 and 75%. It seems to be higher in the interior parts of the bars (about 0.5–1.4 mm from the surface). Figure 5 also shows the variation of the crystallinity associated with the crystalline structures melting at the higher temperature, C_H, over the cross section of the same test bars. This graph depends on a method for separating the two partly overlapping melting endotherms. The details of this method may appear somewhat arbitrary, but do not have any significant effect on the results. The method used here is largely similar to the one described in Ref. 14.

As can be seen the C_H value exhibits a maximum between the surface and the center of the sample. This is especially pronounced for the samples molded at 17 and 23 cm^3/s injection rates. For the third sample, molded at 12 cm^3/s,

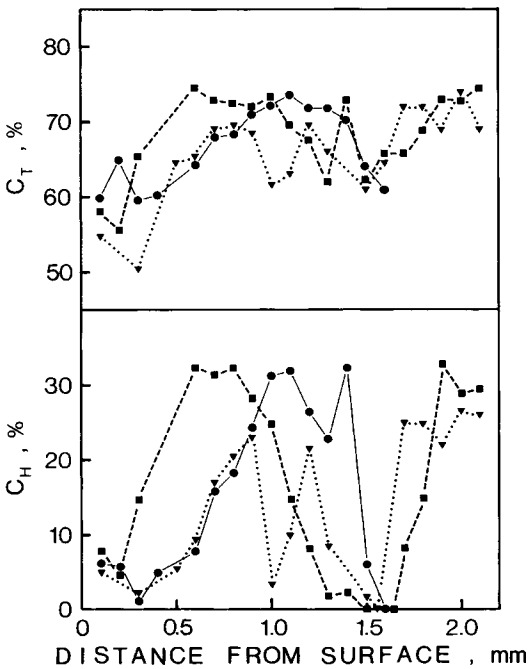

Fig. 5. The variation of the total crystallinity C_T and the crystallinity associated with the high temperature melting structure C_H over the cross sections of the same samples as in Figure 4, symbols as in Figure 4.

this effect is less pronounced, C_H showing two smaller maxima. In the latter case, the total amount of the C_H structures is also significantly lower. Close to the center of the test bars there is a narrow zone where the HT structures (associated with C_H) are virtually absent. The orientation varies over the cross section in a similar way,[9] which shows that the appearance of this structure is closely related to the orientation of the samples.

According to Figure 5 the total fraction of high temperature melting structure (C_H) was equally large for samples molded at 17 and 23 cm^3/s. The stiffness is determined by the orientation state, in addition to C_H.[3] X-ray measurements show that the orientation in the sample molded at 17 cm^3/s is greater than that molded at 23 cm^3/s,[9] which explains the difference in modulus for the samples in Figure 3.

DISCUSSION

It has been shown that the tensile modulus of high pressure injection-molded HDPE for thicker specimens can be enhanced if the proper injection rate and adequate gate geometry are used (Fig. 3). With these precautions, 4 mm thick bars with a stiffness of 10 GPa can be produced. The important factor with regard to the gate geometry appears to be the sealing time. Increasing this time may partially prevent the structural elements related to the high modulus structures from relaxing during the cooling stage of the moulding cycle. The longer sealing time may also result in a larger fraction of crystalline or noncrystalline polyethylene structures contributing to the mechanical properties as outlined in the previous section. Both these effects will have a positive effect on the magnitude of the modulus and the strength.

It is also likely that the appearance of the high modulus structures in HDPE is associated with the high degree of orientation encountered in high pressure injection molding (see also Ref. 9). However, it is important to recognize that it is necessary to use high pressures to obtain these structures, that is, a high orientation in itself will not yield these structures nor give an improvement in mechanical properties of the magnitude reported here. Using an injection pressure of 100 MPa the same degree of orientation, as revealed by wide angle X-ray scattering, can be produced as in high pressure injection-molded HDPE, but the high modulus structures do not appear and no significant improvement in strength and modulus is obtained.[15] In agreement with earlier works,[3,4] it was noted here that the high pressure injection-molded bars contained an appreciable amount of a crystalline structure melting at a higher temperature. These HT structures probably contribute appreciably to the mechanical properties, but it should be understood that also the interconnecting (noncrystalline) elements between these crystallites are of significance with regard to stiffness and strength.[3]

High pressure injection-molded HDPE is highly oriented and any products produced with this technique should be designed with this in mind. Thus, from this point of view, the situation is very similar to that encountered when injection molding liquid crystallizable (LC) polymers. The development in mechanical properties in LC polymers is also dependent on the degree of orientation. It is certainly interesting to note that high pressure injection-

molded HDPE has approximately the same mechanical performance as the more sophisticated injection-molded LC polymers.[16,17]

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