Phase transition in high molecular weight polyethylene during capillary extrusion: the reversibility of the temperature window

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We present results confirming the existence of discontinuity in extrusion pressure, with temperature, within a very narrow temperature window (150–152°C) during the extrusion of high molecular weight polyethylene melts. This pressure minimum effect, the appearance of which is critical in both molecular weight (M_w) and shear rate ($\dot{\gamma}$), is now found to be reversible with temperature. Further, our work shows, in a quantitatively documented manner, that die swell is much reduced in the temperature window, corroborating the previously proposed interpretation that the effect is associated with a new phase with liquid crystal characteristics, which is the mobile hexagonal phase. Finally, we report on a structure-related memory effect, observed during the cooling cycle, which is interpreted in terms of structures created during the preceding heating cycle adhering to the flow vessel and persisting in the melt regime up to 180°C.

(Keywords: phase transition; extrusion; memory)

INTRODUCTION

Anomalous melt flow behaviour of polyethylene (PE) has been reported in a previous paper[1] and in a concurrent work[2] from this laboratory. To sum up the previous works, the effect in question was discovered in the course of capillary extrusion experiments of high molecular weight material ($M_w \geqslant 10^5$). The anomalous feature is a sharply defined minimum of extrusion pressure with temperature within a narrow temperature window (150–152°C), as opposed to the expected slight steady decrease with increasing temperature for a given piston velocity (or shear rate, $\dot{\gamma}$).

At temperatures below the minimum, the pressure is high due to onset of flow-induced crystallization which, if close enough to the melting point, can lead to blockage of flow. Above the minimum, the pressure rises steeply to a value characteristic of the melt in conventional melt flow experiments at those temperatures. (For high molecular weight materials and sufficiently high flow rates the latter may also encompass spurting flow.)

Within the temperature window of the pressure minimum there was comparatively little die swell, and the extrudate had a smooth surface finish. This is in contrast to the substantial die swell on extrusion outside the window. At higher temperatures, beyond the window in particular, the extrudate could become rough, and when spurting occurred (which is mostly the case at the higher temperature side) the extrudate became grossly uneven and 'gnarled'. The latter is the usual experience with very high M_w materials, making them, in practical terms, unprocessable. With the new findings they should, in fact, be processable within a specific 1–2°C temperature window, with anomalously low flow resistance (viscosity).

The existence of the window was found to be critically dependent (within a factor of two) on molecular weight, setting in between $M_w = 2 \times 10^5$ and 4×10^5 for the piston speeds (hence corresponding $\dot{\gamma}$ for the particular die dimension and geometry) examined so far. Further, for a given M_w it was found to set in only above a critical piston speed; below this speed the melt displayed normal flow behaviour. Criticality in both M_w and $\dot{\gamma}$ are characteristics of elongational flow-induced chain extension, as predicted theoretically[3,4] and established experimentally in this laboratory in the case of solutions, using well characterized extensional flow fields[5]. In the present die geometry we expect a strong elongational component in the flow field due to convergence at the die entrance.

By traditional rheological considerations one would not expect a sharp discontinuity with temperature within a homogeneous true melt. The fact that such is observed indicates an abrupt change in the nature of the melt itself. This we can only attribute to structure formation. In the first publication[1], phase transformation due to flow-induced chain extension was postulated, with the new phase being a highly mobile mesophase which, in the case of PE, is the hexagonal 'crystal' phase. Here the liquid crystal character should be responsible for lowered viscosity and much reduced die swell. The findings in the subsequent work[2] provide further support for this proposition, also linking it with previous experiences[6,7].

The main objectives of the present work are three-fold: (1) to confirm that the effects described above are general to PEs with the appropriate molecular weights and that they are material structure related; (2) to investigate the temperature reversibility of the pressure minimum effect and associated features; (3) to assess the contributions of elastic stresses to the occurrence of the pressure minimum effects. All these objectives have been achieved. In addition a new effect was recognized in the course of pursuing objective (2); this was the memory of previous

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Table 1 PE samples used and their corresponding molecular weights

Designation	M_w	Source
HIZEX-145	10^6	Mitsui
PE(R)	4.4×10^5	BP Chemicals
LAHD01	4.4×10^5	BP Chemicals (Grangemouth)
MK536	3.5×10^5	DSM

flow history, presumably through the structures it creates, persisting well into the melt regime. This feature is itself of interest and awareness of the effect is essential for securing reproducibility of the results.

EXPERIMENTAL

General procedure

Following the procedure first adopted by Waddon and Keller[1], the rheometer barrel was first heated to 180°C and kept at this temperature for up to 1 h before cooling to the temperature at which extrusion was to proceed. As described in ref. 1, this latter temperature was as close as possible to the lowest temperature where subsequent extrusion was still possible without the familiar capillary blocking setting in. This lower temperature limit depended on molecular weight and was 146°C for the lowest and 148°C for the highest M_w material used here. Having attained this limiting lower temperature, extrusion commenced and pressure was recorded at constant piston speed. First, the temperature was held constant until a steady pressure was reached, after which the temperature was raised at 0.5–1°C min^{-1} while extruding and the pressure (P) *versus* temperature (T) trace recorded, usually up to about 172°C. In addition to these experiments on heating, cooling runs were also carried out. As a standard procedure, cooling was started immediately, with the piston kept moving and hence material extruding, by reversing the heating to cooling. Departures from this practice will be mentioned in the appropriate section.

The method of recording used previously[1,2] was improved upon: point by point readings have been replaced by continuous recording of both P and T with an x–y plotter.

Materials

We used four linear PE materials all giving rise to the pressure anomaly which was the subject of these investigations. The materials are described in *Table 1*.

PE(R) and HIZEX-145 have been examined in the preceding works. In this work two further materials were studied, at the low molecular weight end of the range; due to lower self-blocking temperatures this gave a wider scope for the recording of P *versus* T traces than the ultra-high molecular weight PE.

RESULTS

Figure 1a is a confirmatory result of the features first reported in the preceding work[1], for PE(R). To reiterate the previous findings, the pressure *versus* temperature trace displays a sharply defined minimum at 150–152°C. Above this temperature window the pressure oscillates initially (larger error bars) with the melt emerging from the die in spurts, until around 164°C. Above 164°C both the amplitude of pressure oscillations and the spurting effects decay to more or less a constant level. The nature of the extrudate corresponding to *Figure 1a* also agrees with the earlier description, namely, that it shows a maximum die swell in the region preceding the pressure minimum, a smooth surface texture in the narrow temperature window followed by varying degrees of melt fracture which begins from around 152°C.

Figure 1b shows the pressure *versus* temperature plots for the cooling process, the exact reverse of the results in *Figure 1a*. We see that the features in this figure also appear in the reverse order, thus demonstrating the reversibility of the pressure minimum effects. (Such P *versus* T traces on cooling were not reported in the previous work. This was due to lack of reproducibility on which the rest of the present work will throw some light.)

Figures 2–4 show pairs of pressure *versus* temperature plots (heating and cooling) for the remaining three samples listed in *Table 1*. Although these samples come from three different sources, they all produce the pressure minimum effects with the associated features within an identical temperature range.

We also examined the hysteresis of our results in order

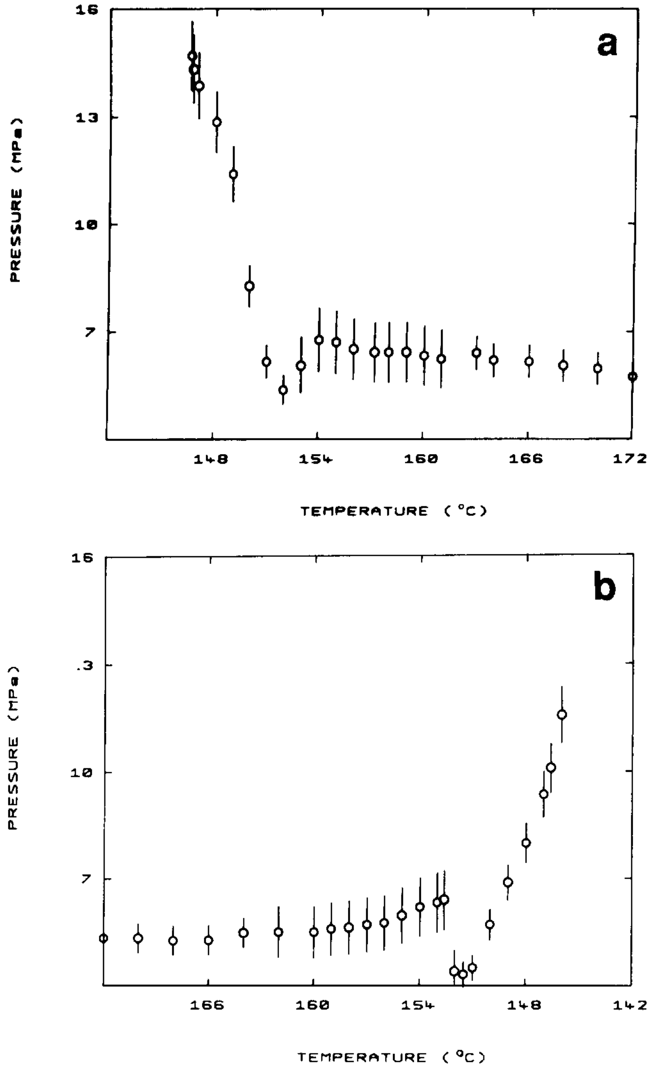

Figure 1 Plot of pressure *versus* temperature for heating (a) and cooling (b) during extrusion of PE(R). Piston speed, 0.15 cm min^{-1} ($\dot{\gamma} = 2.5\ \mathrm{s}^{-1}$); die diameter, 2 mm

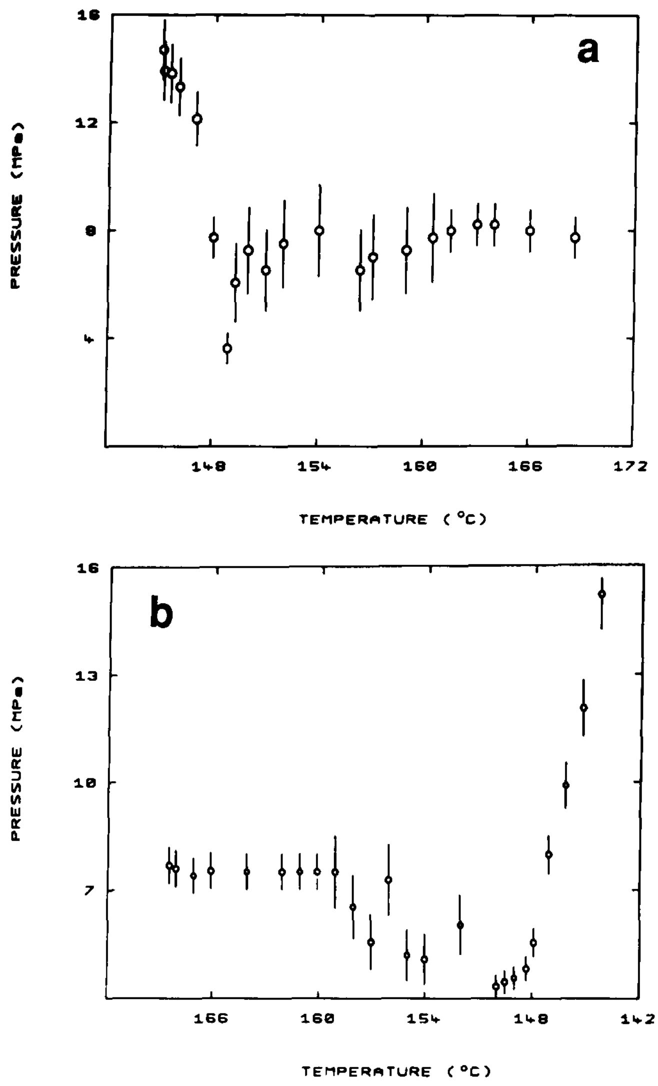

Figure 2 Plot of pressure *versus* temperature for heating (a) and cooling (b) during extrusion of LAHD01. Piston speed, 0.125 cm min^{-1} ($\dot{\gamma} = 2.08\ \mathrm{s}^{-1}$); die diameter, 2 mm

to eliminate any degradation effects. We would expect any thermal degradation resulting from the long exposure to high temperatures to lead to chain scission predominantly at the high M_w tail[8]. The consequence of this would be a reduction in the melt viscosity or the extrusion pressure. A simple test used for the degradation mechanism was to subject the extrusion process through a heating–cooling–heating cycle a number of times. The results for one such test are plotted in *Figure 5* and show that no significant degradation has occurred during a run such as could be of consequence for the effects under investigation.

The criticality of the flow rate (or piston speed) in producing the features shown in *Figures 1–4* was also examined. The results for this are plotted in *Figure 6*, which also suggests that no pressure minimum is produced below a piston speed of 0.075 cm min^{-1} (die diameter = 2 mm). This is equivalent to a die wall shear rate of 1.25 s^{-1}. In fact, after a series of runs we found the critical piston speed to be around 0.05 cm min^{-1} ($\dot{\gamma} = 0.83\ \mathrm{s}^{-1}$) although the corresponding value for the ultra-high molecular weight PE sample is much lower ($\sim$0.025 cm min^{-1}; $\dot{\gamma} \approx 0.42\ \mathrm{s}^{-1}$). These results confirm the previous findings[2], with numerical agreements between the two works, and supplement it with some additional traces.

From results such as those in *Figure 6* we were also able to assess the influence of elastic stresses on the pressure minimum effects. In this respect, die swell was used as a rough measure of the stresses in the melt inside the die, prior to its emergence into the atmosphere. In *Figure 7* are plotted the swelling ratio (extrudate diameter/die diameter) at temperatures below ($T = 145$°C) and above ($T = 151$°C) the pressure minimum as a function of the shear rate. In the region preceding the pressure minimum the material displays a typical die swell behaviour[9], the swelling ratio rising steeply with shear rate (shown by crosses). It is also clear from this figure that die swell is smallest in the temperature window containing the pressure minimum and that this remains more or less constant within the temperature window, for all the shear rates used. These results, we believe, represent another manifestation of the extrudability of the melt in the temperature window, and provide evidence for the postulated liquid crystalline nature of the melt in that window. (Liquid crystal polymers show little, if any, die swell, which is a favourable characteristic for chain extension behaviour.)

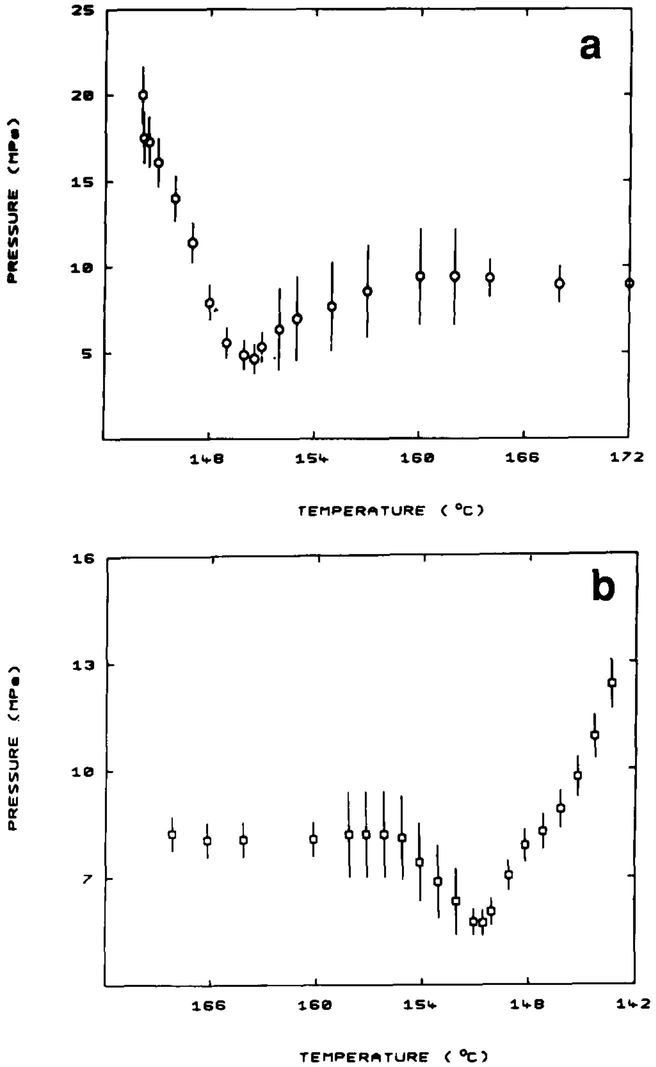

Figure 3 (a) Plot of pressure *versus* temperature for heating (a) and cooling (b) during extrusion of HIZEX-145. Piston speed, 0.05 cm min^{-1} ($\dot{\gamma} = 0.83\ \mathrm{s}^{-1}$); die diameter, 2 mm

Conditions for temperature reversibility: memory effects

Most high polymers display 'memory' effects of the previous processing history, which may appear in various forms during the laboratory experimental manipulation of the sample. However, memory effects can generally be eliminated by heating and holding the sample at an elevated temperature before cooling to the experimental temperature as seen in some earlier works in solution[10]. Nonetheless, in the present work we did observe some persistent features in our measurements which warranted

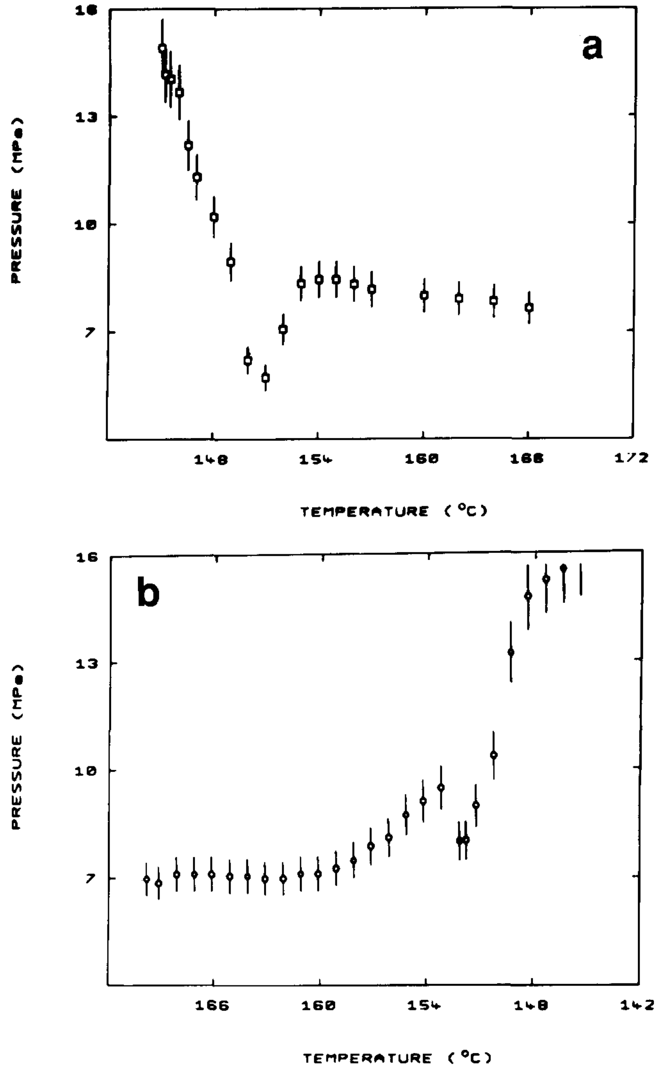

Figure 4 Plot of pressure *versus* temperature for heating (a) and cooling (b) during extrusion of MK536. Piston speed, 0.15 cm min^{-1} ($\dot{\gamma} = 2.5\ \mathrm{s}^{-1}$); die diameter, 2 mm

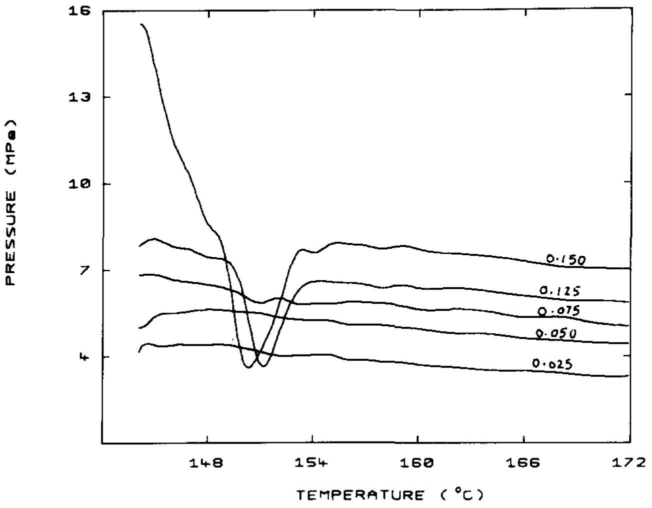

Figure 6 Examination of the criticality of the piston speed (or die wall shear rate) in producing the pressure minima. Plot of pressure *versus* temperature for a series of piston speeds. Figures on the curves are the piston speeds in centimetres per minute. Die diameter, 2 mm

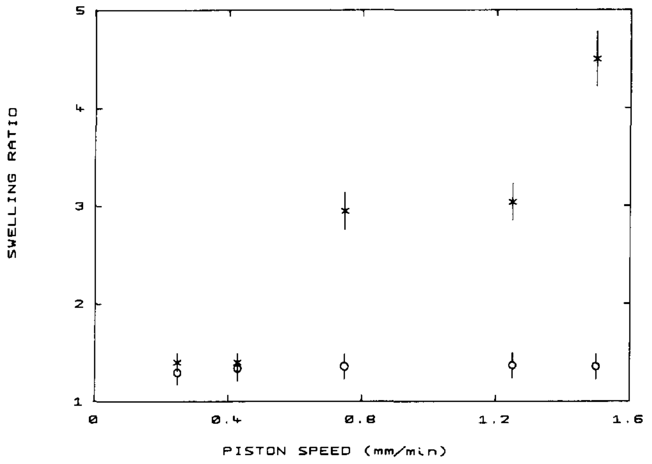

Figure 7 Plot of swellng ratio (extrudate diameter/die diameter) as a function of die wall piston speed for the same die as in *Figure 6*. ×, $T = 145$°C; ○, $T = 151$°C

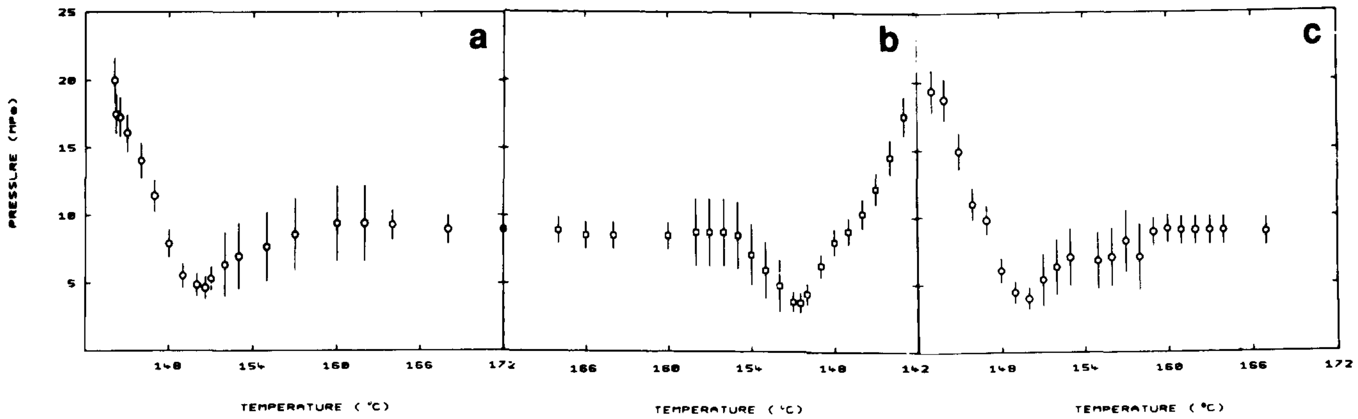

Figure 5 Examination of the hysteresis of the temperature window for HIZEX-145. (a) First run, heating followed by (b) cooling and (c) heating again. Piston speed, 0.05 cm min^{-1}; die diameter, 2 mm

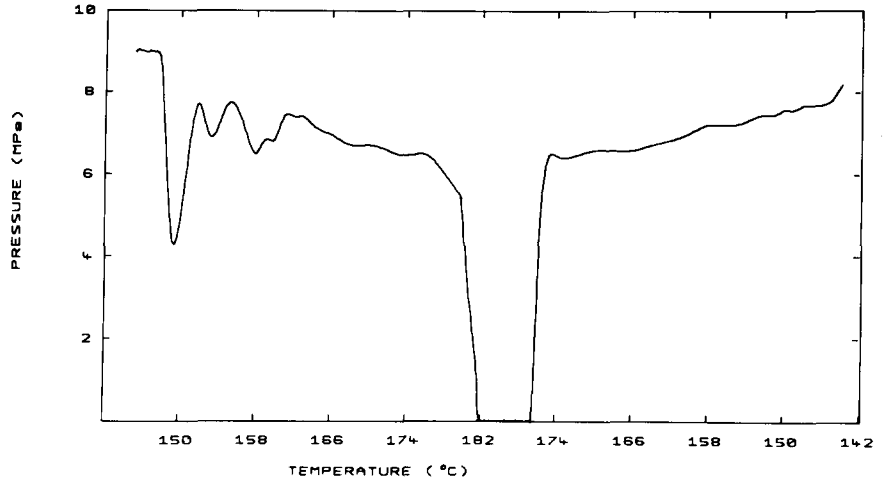

Figure 8 Memory test 1. Plot of P *versus* T for sample LAHD01. Piston motion was stopped when temperature reached 180°C and pressure was allowed to decay to zero, before resuming extrusion while simultaneously cooling the melt. Piston speed, 0.075 cm min^{-1}

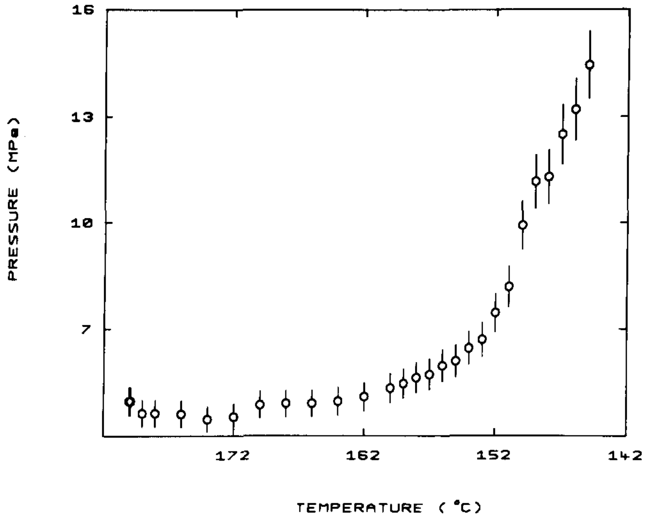

Figure 9 Memory test 2. Plot of P *versus* T for PE(R). Cooling from 180°C. Piston speed, 0.075 cm min^{-1}. See text for details

further investigation in order to ensure that the reproducibility of the results is not affected by memory effects.

In the first of the three tests (test 1) the pressure and temperature measurements were carried out as described earlier, up to 180°C. The piston motion was then stopped and the temperature maintained constant until the pressure has decayed to zero. The piston motion was then restarted at the same rate while simultaneously cooling the melt.

In the second test (test 2) the polymer, as supplied, was heated to 180°C and after 1 h holding time, it was extruded at a constant rate until the pressure reached a plateau, before cooling to around 145°C (with the piston still moving). This test is similar to that in *Figure 1b* except that in this case the melt has not previously passed through any extrusion–heating cycle.

In the third test (test 3), the heating–cooling cycle of *Figure 1* was repeated below the critical piston speed, The purpose of this test was to ensure that below the critical speed the pressure minimum effects are absent during not only the heating but also the cooling cycle.

Figures 8 and *9* are representative P *versus* T plots for tests 1 and 2. In general, the results for the repeats of the tests are rather erratic. Nonetheless, the overall trends of these results can be summarized as follows: no pressure minimum or associated effects occurred in the cooling cycle if this had not been previously observed in the heating cycle. Even when the minimum did occur in the heating cycle, this did not always occur in the following cooling cycle if the extrusion pressure was first allowed to decay to zero, as seen in *Figure 8*.

Flow visualization and pressure measurements

The experiments described above were set up as a preliminary to simultaneous flow visualization (between crossed polars) and pressure measurements. The feasibility of such combined work has now been established and one observation will be quoted. The optical arrangement for this work is similar to the set-up first used by Mackley and Keller[11] for elongational flow observation of PE melts during capillary extrusion. The preliminary results from this work, combining optical observation with pressure recording, show that the onset of the oscillations in the extrusion pressure–temperature trace coincides with the onset of some ‘pulsations’ in the flow birefringence. We are currently exploring the interpretations of this phenomenon which will form the main subject of a future publication.

DISCUSSION

The present work has consolidated and extended previous findings on the unexpected pressure minimum and associated narrow temperature window with advantageous processing features. The generality of the previous findings for PEs of different origin from $M_w \approx 3 \times 10^5$ upwards has now been established, together with its reversibility on heating and cooling (under specified circumstances, see below). Further, the much reduced die swell associated with the pressure minimum effect has been reaffirmed in a quantitatively documented manner. All these effects are consistent with and corroborate the previously proposed interpretation, namely that the effect is associated with the presence of a new phase with liquid crystal characteristics, which in the present PE is the mobile hexagonal phase.

Beyond these straightforward and mutually consistent statements, the newly recognized memory dependence of the effect in the cooling part of the cycle requires specific discussion, which leads to wider questions, still partly open.

The salient fact is that the pressure minimum only appears on cooling (even when requirements in $\dot{\gamma}$ and M_w are satisfied) when such a minimum has been first created during the preceding heating, and even then only if the pressure has not been allowed to relax completely on reversal from heating to cooling.

It can be stated, in the widest generality, that the above observation implies a structure memory. This reinforces our contention that the pressure minimum has its origin in structure changes and not in the melt rheology alone. The particulars of this structure memory, however, are not self-evident. Since fresh material is always passing through the system, structures present at an earlier stage cannot have any subsequent effect unless some residues of them are left behind. In view of the present observations, we are compelled to assume that such residues must remain, which can only be visualized as adhering to the walls of the extruder. This implies that some flow-induced extended chain crystals, in their mesomorphic hexagonal form, may persist in the melt anchored to the walls of the extruder up to at least 180°C (the highest melt temperature in our experiments) and possibly even higher. This is not as unlikely as it may appear at first sight: flow-induced extended chains are known[12] to 'superheat' and impart crystallization memory to the melt on subsequent cooling, even after exposures to temperatures as high as 180°C. The presence of such superheated structures at high temperatures has been repeatedly, if erratically, indicated by persistent birefringence and by d.s.c. endotherms[12–14]. Even more relevant to the present argument, persistence of the hexagonal crystal nature of such structures up to 180°C has been repeatedly revealed in the past through X-ray diffraction of constrained fibres containing extended chains[13–17]. In the present case two additional features are envisaged: first, the adhesion of the surviving fibrous entities to the walls of the extrusion vessel, and secondly, the nucleation of more material of the same kind through their agency when the flowing melt is subsequently cooled. It will be noted that constraints have featured prominently in past observations on the persistence of extended chain-type structures at high temperatures. Adhesion to the walls would imply such constraints making two of the factors in our argument – spatial retention and thermal survival – self-consistent.

At this stage a salient issue must be faced, namely, how to relate the observed rheological window to the thermodynamic temperature interval which, by our hypothesis, defines the stability regime of the hexagonal phase.

Let us first recall some of the conclusions in refs 1 and 2. Accordingly, orientation-induced phase transformation should set in under the prevailing elongational flow conditions satisfying the criticalities in M_w and $\dot{\gamma}$. Below a certain melt temperature, T_m (the crystal melting point, appropriately raised by the prevailing chain extension in the melt and by the enhanced pressure[2]), this gives rise to filamentous orthorhombic (*o*) crystals which are the backbones of the previously studied shish-kebabs[6]. These will raise the extrusion pressure, and if present in sufficient amount, will block the flow. However, above T_m the newly forming phase will be the mesomorphic hexagonal (*h*) phase leading to the reduced extrusion pressure creating the rheological window. While the *h* phase has not yet been diagnosed structurally *in situ* within the flowing melt itself, a highly oriented *o* component in the final solidified product has been attributed as forming within the rheologically defined temperature window, presumably in the *h* form first, transforming into the *o* form when cooled below T_m where the X-ray diffraction pattern was recorded[2]. This attribution was substantiated by the fact that no such oriented structure (in the *o* form), but only near-randomness was seen for extrusions just above the upper end (~154°C) of the rheological window. This, as concluded in ref. 2, would seem to identify the upper end of the rheological window with the upper end of the flow-induced phase regime, which at these temperatures is the *h* phase, where the corresponding 'melting' temperature would be the temperature of isotropization T_i.

Accordingly, the temperature interval T_m–T_i should define the stability range of the *h* phase. If we now place T_i close to 152–154°C, then T_m clearly cannot be far below. In fact, 150–151°C is the temperature quoted in the previous constrained fibre experiments[18]. It also features in an earlier work on high molecular weight extrudates[19]. As $T_{o \rightarrow h}$ is not expected to be significantly influenced by the state of the melt, we would not expect any significant difference in its manifestations between static and flow experiments. Indeed, the correspondence of those thermodynamic transition temperatures with the lower end of our rheological window can hardly be coincidental.

In summary, the sum total of the experiences quoted above seems to suggest a very narrow temperature regime for our orientation-induced *h* phase, which we assume to be responsible for the rheological window of low flow resistance where $T_m \sim 150$°C and $T_i \sim 152$–154°C. In other words, the sharpness of the rheological window would be a consequence of the narrowness of the *h* phase regime. At the upper end, T_i, the flow usually goes into spurt, while at the lower end, T_m, the pressure rises as the already formed *h* phase transforms into an *o* phase. If the increase in *o* crystal formation is gradual (with falling temperature), then this rising pressure region will span a comparatively wide temperature range before full solidification (blocking); if it is rapid, blocking sets in straight away, a difference reflected in the behaviour of (comparatively) low and high M_w materials[2].

We still need to reconcile the case for T_i situated close to 153°C with the presently observed memory effect up to at least 180°C. We suggest that this is a question of constraints. In static experiments on extended chain systems, T_i was found to be highly variable, in fact erratic: a value of 155°C features in published X-ray work[16] and was observed as a d.s.c. endotherm in this laboratory[20] which is hardly in excess of our present attribution of T_i. On the other hand, as quoted above, T_i may extend beyond 180°C. This variability could be due to the ill-defined and often varying constraints that need to be imposed in order to realize the *h* phase at all under static conditions. If the same held for the postulated residual entities adhering to the walls, then the persistence of the melt memory up to 180°C would follow and need not conflict with an intrinsic upper limit of ~154°C for the unconstrained *h* phase within the interior of the melt, which in turn would be the determining factor for the melt 'viscosity' anomaly. (The anomalously high melting temperatures of some solution-grown shish-kebabs was in fact found to depend sensitively on the contact with the glass slides used in microscopic viewing[12,13]. This would tie in well with our present observations and discussion.)

CONCLUSIONS

We have re-examined the extrusion pressure variation with temperature for high molecular weight PE samples from three different sources and confirm the previously reported existence of pressure minimum in a very narrow temperature window for all four materials. This includes the criticality of the extrusion speed for this phenomenon, which is the characteristic feature of elongational flow-induced chain extension. We have also established the reversibility of the effects, that is, cooling the melt while extruding above the critical piston speed produces the same effects in the same temperature window as heating, but in the reverse order. Furthermore, we have found what appears to be a structure-related memory effect on the reproducibility of the effects, that is, structures formed during heating persist for a long period and reappear during the cooling cycle. This memory effect could be explained in terms of flow-induced extended chain crystals, in their mesomorphic hexagonal phase, adhering to the walls of the extrusion vessel up to 180°C. Finally, we have established that material extruded in the pressure minimum window displays very little die swell, a requisite for the postulated liquid crystalline nature of the melt in the window.

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