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Cold extrusion and in situ formation of self-blends of UHMWPE Part 1. Processability and thermal characterization

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Abstract

The development of a novel method for the processing of nascent UHMWPE leading to high ductility and strength extrudates is described. The addition of a surface wetting agent, in this case 10 wt% mineral oil, followed by compaction and extrusion below the melting point leads to the formation of a self-blend of melted and recrystallized UHMWPE and unmelted UHMWPE powders. The presence of the self-blend, indicated by the d.s.c. results, enhances the cohesion between powder particles which leads to an extrudate with more uniform mechanical properties, as demonstrated in Part 2 of this two-part paper. This partial melting during compaction and extrusion is aided by the mineral oil, which also helps to enhance the ductility of the extrudates. The d.s.c. results also provide evidence for chain alignment. The mineral oil acts as a processing aid by allowing the blend to be processed at temperatures at least 10°C higher than are usual for the pure nascent powder. It also acts as a heat transfer agent and solvent for the UHMWPE.

Keywords: Nascent UHMWPE powder; Processing aid; Cold extrusion

1. Introduction

The processing of polyethylene into high tensile strength and modulus fibres and films has been of continuing interest for a number of years due to its high, calculated Young's modulus, abrasion and wear resistance [1–3]. Theoretical estimates of Young's modulus for a single-chain polyethylene crystal produced values in the range 182.3–340 GPa [4,5]. The highest experimental modulus value reported so far is 230–240 GPa [6]. To achieve such high Young's modulus values, polymers of high molecular weight [7–9] and chain extension [1,10] are required to provide longitudinal continuity. Ultra-high-molecular weight polyethylene (UHMWPE) fulfils the first criterion, at present, with weight average molecular weights in excess of 2×10^6 kg kmol^{-1}. Unfortunately, such high-molecular weight polyethylenes are either difficult or impossible to process in the melt due to their high melt viscosities, and much effort has been directed towards finding suitable processing methods for polyethylenes and, in particular, UHMWPE.

Zwijnenburg and Pennings [11,12] developed a technique for growing single polyethylene crystals longitudinally from flowing solutions using *p*-xylene as a solvent. They achieved growth rates of up to 31 cm min^{-1}, dependent on the polymer solution concentration and the rotor speed. Smith and Lemstra [9,13,14] developed the only commercial process, gel-spinning, with processing rates $>$ 10 m min^{-1}. This involves the dissolving of polyethylene in decalin at elevated temperatures followed by recrystallization, drawing of the resulting unentangled gel and drying. To induce orientation the fibre is subsequently hot drawn. Further developments of this are swell drawing and die-free gel spinning [15,16]. Polyethylene crystal mats have also been hot drawn using coextrusion techniques [17]. All of these processing methods involve dissolution and recrystallization steps aimed at reducing the entanglement level of the polyethylene chains prior to orientation induced by hot drawing. They all, also, involve significant quantities of solvents requiring removal and recycling. In the case of gel spinning this is ~10 kg solvent/kg polymer.

Nascent UHMWPE powders have not undergone any melting and recrystallization after polymerization and appear to have inherently low entanglement densities [18]. These nascent reactor powders may be solid state processed below their melting temperatures by compression moulding [18], coextrusion [19,20] or ram extrusion [21,22], and then hot drawn to produce highly oriented fibres and films. Solid-state extrusion can be applied to crystalline or semi-crystalline

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polymers when the processing temperature lies between the crystalline relaxation temperature and the melting temperature. Above the crystalline relaxation temperature there is a reduction in intra-crystalline forces due to a sharp increase in the thermal expansion coefficient. Ram extrusion at temperatures below the melting point, making use of this phenomenon, has been applied to, for example, polylactides [23], polytetrafluoroethylene [24], poly(ethylene oxide)/poly(methyl methacrylate) blends [25], vinyldenefluoride/vinylidene trifluoride copolymers [26] and polyethylenes with a range of molecular weights [21,22,27]. For the polyethylenes most of the ram extrusion experiments are carried out on the pure homopolymer, but there are reports of processing aids being used. Gibson and co-workers [28,29] used hydrostatic extrusion at 100°C to produce extrudates of polyethylene up to a molecular weight of 3.5×10^6 kg kmol^{-1} with castor oil as the extrusion fluid and silicone vacuum grease as a lubricant coating on the PE billets. Extrusion draws ratios (EDRs) of up to 25 were obtained with extrusion pressures in the range ~400 to ~2700 bar and extrusion speeds of up to 2 cm min^{-1} at low EDRs [28]. For the UHMWPE the highest extrusion draw ratio was 6 with an extrusion pressure of ~1000 bar. Even for EDR = 2, the extrusion pressure was 144 bar. Die swell was in the range 13.4%–17.8%. These researchers found that the silicone grease and the castor oil are stress-cracking agents for polyethylenes; the latter particularly so for low-molecular weight PE. Predecki and Statton [30] found that the use of a fluorocarbon lubricant (along with die angle) was critical to their extrusion of a low-molecular weight PE at extrusion pressures between ~6900 and 20 690 bar and temperatures between ambient and 130°C. Their extrusion rates were from 0.00254 up to 2.54 cm s^{-1}. They concluded that the lubricant was actually reducing the efficiency of molecular orientation, and that a combination of simple and elongational flow was necessary to achieve orientation and chain extension. The lubricant reduced the contribution of simple shear flow by reducing the shear stresses at the polymer–die interface.

n-Paraffins, up to a concentration of 33%, have also been used as processing aids in the solid-state extrusion of linear PE up to a temperature of 80°C [31]. However, despite the frictional coefficient decreasing with increasing *n*-paraffin content and extrusion temperature, the blended material exhibited lower orientation than the pure homopolymer, as shown by X-ray scattering experiments. In Refs. [28–31] the preparation of the polyethylene prior to ram extrusion involved melting the polymer to produce shaped billets. Reports of ram extrusion of nascent, i.e. unmelted, UHMWPE indicate that the compaction/extrusion pressures used are of the order of 1000–2000 bar [21]. In many reports of the ram extrusion of polyethylene below its melting point, the compaction preceding the extrusion takes place at a temperature above the melting point [10,22]. This is done to melt the material and eliminate any previous thermal history. It also increases the mobility of PE chains, which might increase the entanglement density on recrystallization and removes any existing chain extension or order brought about by the polymerization reaction.

In this paper, Part 1 of two, we will present the ram extrusion processing window for an UHMWPE/10 wt% mineral oil blend and the thermal characteristics of the extrudates associated with variations in the compaction/extrusion temperature, extrusion draw ratio and volumetric flow rate. The compaction preceding this extrusion was carried out at a pressure of ~9 MPa or 90 bar. Considerably lower than the compaction pressures quoted above. Both compaction and extrusion take place below the melting point of UHMWPE. Mineral oil was used, as it has been reported that it is a solvent for polyethylene [32]. It should certainly be compatible with the polymer as it is a hydrocarbon with no oxygen groups, unlike castor oil. Other solvents, e.g. decalin and xylene, are better wetting agents, but due to their hazardous nature and extraction difficulties, are not used. Part 2 will present the results of the tensile tests, X-ray scattering experiments and morphological analysis carried out on the extrudates produced by the ram extrusion described in this paper.

2. Experimental

2.1. Materials and sample preparation

The UHMWPE used in this study was supplied by Montell Polyolefins, USA (Hifax 1900 with a weight average molecular weight of 6×10^6 kg kmol^{-1} and an average particle size of approximately 200 μm). A light mineral oil, with a boiling point of 350°C and a specific gravity of 0.838, was purchased from Fisher. The mineral oil was intended to enhance the UHMWPE chain mobility as it is able to act as a solvent for PE [32].

Compacted samples of both the pure UHMWPE and a blend of 10 wt% mineral oil in 90 wt% UHMWPE were prepared using a Göttfert Rheograph 2003 capillary rheometer. This compaction ensures a uniform temperature gradient and some chain diffusion across particle boundaries prior to extrusion [33]. The blend of mineral oil and UHMWPE was prepared at ambient temperature using a 750 W Moulinex mechanical food mixer. The mixer was operated with a pulse action, 15 s mixing followed by 45 s relaxation, to minimise shear heating. This was continued until the mixture was homogeneous to the naked eye. The material for compaction, ~15 g, was fed into the barrel of the capillary rheometer which was preheated to 135°C. The barrel was blocked off at the lower end with a blank die. Feeding of the material was carried out slowly with intermittent low-level compaction to remove air pockets. The loaded barrel was left to equilibrate at 135°C for 2–3 min. The material was then compacted at a piston pressure of ~9 MPa for 15 min with the temperature maintained at 135°C. After this time the blank die was removed and

replaced with a round hole capillary die of known dimensions in preparation for extrusion and processability testing.

2.2. Processability testing

Processability testing, as well as rheological analysis, was carried out using the same Göttfert Rheograph 2003 capillary rheometer as for compaction. The barrel of the rheometer had a diameter of 12 mm and a length of 200 mm. It was equipped with a force transducer with an upper limit of 20 000 N for piston force measurement; three thermocouples to measure the temperature within the die region; and a 2000 bar pressure transducer to measure the pressure at the die entrance. Both of the transducers have a maximum operating limit of 80% of the upper limit quoted. In all the tests described here ΔP data were recorded only when a steady piston force, a steady processing pressure, or both were exhibited. Processability was assessed by considering the peak extrusion force and pressure drop across the die. Data were recorded for only one volumetric flow rate per experimental run because the equipment limitations meant there was sufficient sample in the barrel to achieve steady state for one datum only. The Bagley and Rabinowitsch corrections were neglected. The reason for this is provided in Section 3.

The initial processability tests provided data for a choice of an optimum processing temperature and were carried out at 125 and 135°C, using a round hole capillary die with a 4 mm diameter, a 7.5 length-to-diameter ratio (L/D), EDR = 9 (EDR, extrusion draw ratio) and an entrance angle of 106.6°. Both pure UHMWPE and the blended material were tested.

A second set of processability tests was carried out at 135°C using compacted samples and dies with varying diameters, but all with length 30 mm and entrance angle of 90°. The die diameters were 4, 6, 8 and 10 mm, equivalent to extrusion draw ratios (EDRs) of 9, 4, 2.25 and 1.44, respectively. EDR is defined as the ratio of barrel cross-sectional area to die cross-sectional area. The volumetric flow rate range employed was 0.01–53.01 $cm^3\,min^{-1}$. To investigate the possibility of reduction of ΔP across the die whilst retaining any improvement in material properties, a third set of tests was made using dies of 4 mm diameter (EDR = 9) and lengths of 5, 10 and 30 mm at a temperature of 135°C. Again the volumetric flow rate range employed was 0.01–53.01 $cm^3\,min^{-1}$. For the dies with $L = 5$ mm and 10 mm the extrudate exited within the die block. At the material exit point the die diameter was expanded to 20 mm with a divergence angle of 180°.

2.3. D.s.c. measurements

The thermal characteristics of the as-received and extruded pure nascent UHMWPE and the extruded mineral oil blended UHMWPE were studied using a TA Instruments 2910 TA differential scanning calorimeter with heating and cooling rates of 10°C min^{-1}. The sample weight was approximately 5 mg and indium ($T_m = 156.61$°C and $\Delta H_f = 28.4\ J\,g^{-1}$) was used for calibration purposes. The d.s.c. experiments were carried out under a nitrogen atmosphere between 30 and 180°C. The melting points quoted refer to the peak temperatures in the thermograms and are for first heatings, unless otherwise stated. Sample crystallinities were calculated from heats of fusion taken from the thermograms, assuming a purely crystalline polyethylene has a heat of fusion of 289 J g^{-1} [34]. These crystallinities are nominal as the presence of the mineral oil has not been accounted for. Therefore the blend ΔH_f values are those measured for the mixture of mineral oil and UHMWPE. The quantity of mineral oil present in the samples was not measured and could not be assumed to be the original 10 wt% as there was visual evidence that some of the oil migrated to the barrel walls during processing. Also, after extrusion, the samples were stored under vacuum at temperatures of 80–100°C, which may have further reduced the oil content. Analyses of the mineral oil content of extrudates will be carried out in the future using a technique based on supercritical fluid extraction.

Two samples were taken from each extrudate: skin and core. This was to assess any structural changes between the skin and core of the rod samples caused by compaction, extrusion or both processes. The skin and core samples were prepared by careful slicing of the extrudates at ambient temperature.

3. Results and discussion

3.1. Processability tests

A capillary rheometer may be used for assessing the processability of a material by observing the steady-state processing pressure and peak extrusion force. Some preliminary tests were conducted on blends of UHMWPE blended with 5 and 30 wt% mineral oil, as well as 10 wt%. The 5 wt% oil blend showed no appreciable differences in extrusion force and pressure from the pure polymer, and 30 wt% mineral oil proved to be an excessive amount for processing purposes.

It should be noted that the pure UHMWPE could only be extruded at EDR < 4 at 135°C, but is extrudable over a wider EDR range at 125°C. The blend material is processable at both temperatures. However, at 125°C it is not extrudable above a volumetric flow rate of 0.68 $cm^3\,min^{-1}$ at EDR = 9. This was due to the high friction force generated, which exceeded the upper limit of the force transducer (~16 000 N). Trial experiments were also performed at $T > 135$°C, e.g. 139 and 140°C, on the 10 wt% mineral oil/UHMWPE blend. At 140°C the blend exhibited flow instability, characterized by pressure oscillation and melt fracture [35]. The maximum temperature at which the blend material will flow is ~139°C. This temperature

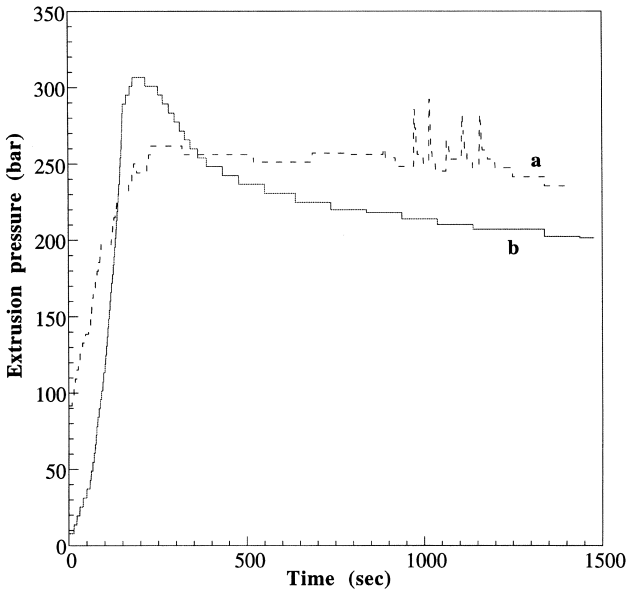

Fig. 1. Variation of extrusion pressure with time for the processing of compacted 10 wt% mineral oil/UHMWPE blend with EDR = 9, L = 30 mm, $Q = 0.68\ cm^3\ min^{-1}$ and at two temperatures: a = 125°C; b = 135°C.

window of processability is lower than that found by Waddon and Keller [22] for polyethylenes of molecular weight $< 10^6$. Their experiments were carried out on polymer that had been melted and recrystallized prior to extrusion and, therefore, did not retain any low entanglement densities. Fig. 1 shows the development of extrusion pressure with time at a volumetric flow rate of $0.68\ cm^3\ min^{-1}$ for processing temperatures of 125 and 135°C. Extrusion pressure was measured at the entrance of the die. There is a higher peak extrusion pressure at 135°C, ~310 bar, than at 125°C, ~260 bar. After ~600 s the steady-state pressures are 215 and 260 bar for 135 and 125°C, respectively. It would normally be expected that the higher processing temperature exhibits the lower extrusion pressure. There are two reasons for the higher peak extrusion pressure at a temperature of 135°C. Solid-state deformation depends on the slip between crystal planes, which is greater at lower entanglement densities. As the processing temperature increases, so does the entanglement density and the 'stickiness' of the UHMWPE portion of the blend. This leads to a decrease in flowability, shown by the higher peak extrusion pressure at the higher temperature. Once the walls of the capillary die are coated with the blend material and, most importantly in this case, with a layer of mineral oil, there is lubrication. This increases the flowability of the blend and results in the lower steady-state extrusion pressure at 135°C. The second explanation for the higher peak extrusion pressure at 135°C, is that the pressure transducer port may not have been completely full of material from the beginning of the experiment. This would have been due to the presence of solids in the blend, at the lower temperature, resulting in the transducer registering a value lower than the actual extrusion pressure. Over time the transducer port is filled and a true, real-time measurement is recorded. Thus, at 135°C the measurement is real-time because the blend material is more molten despite its 'stickiness', but at 125°C there is a time delay in obtaining an accurate value. However, considering the steady-state extrusion pressures and the high molecular weight of the UHMWPE, and comparing with the extrusion pressure values quoted in Section 1, they are a significant improvement on previously reported work.

The generation of the initial and steady-state extrusion force over time is also a good indicator of processability. The extrusion forces produced over time at temperatures of 125 and 135°C for the processing of the 10 wt% mineral oil/UHMWPE blend are shown in Fig. 2 for a volumetric flow

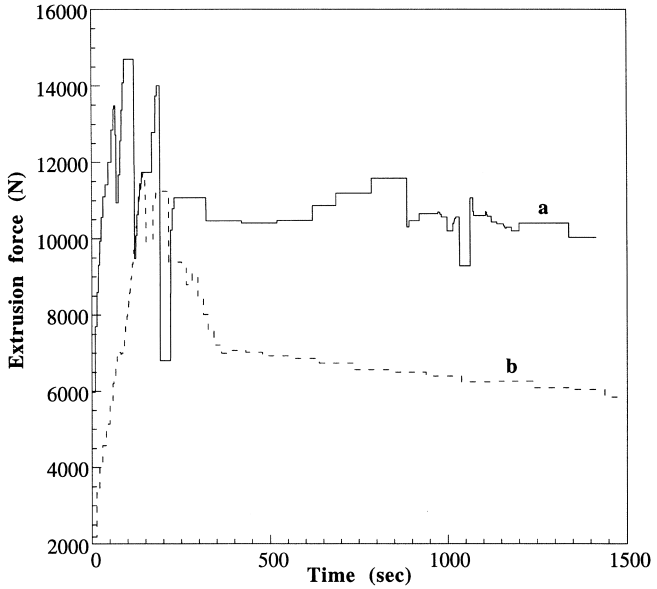

Fig. 2. Variation of extrusion force with time for the processing of compacted 10 wt% mineral oil/UHMWPE blend with EDR = 9, L = 30 mm, $Q = 0.68\ cm^3\ min^{-1}$ and at two temperatures: a = 125°C; b = 135°C.

Table 1
Peak extrusion force values for compacted 10 wt% mineral oil/UHMWPE blend and compacted UHMWPE at various volumetric flow rates and EDRs (processing temperature was 135°C)

Material	EDR	Volumetric flow ($cm^3\ min^{-1}$)		Peak extrusion force (N)	
		$\dot{\gamma}_{ap} = 0.45\ s^{-1}$	$\dot{\gamma}_{ap} = 1.8\ s^{-1}$	$\dot{\gamma}_{ap} = 0.45\ s^{-1}$	$\dot{\gamma}_{ap} = 1.8\ s^{-1}$
Blend	1.44	2.65	10.60	1950 ± 244	2480 ± 310
	2.25	1.36	5.43	1680 ± 210	2190 ± 274
	4	0.57	2.29	2185 ± 273	2430 ± 304
	9	0.17	0.68	13 150 ± 1644	12 370 ± 1546
Pure UHMWPE	2.25	1.36	5.43	2695 ± 337	3315 ± 414

rate of $0.68\ cm^3\ min^{-1}$. The peak extrusion forces are ~14 700 and ~11 350 N for 125 and 135°C, respectively. The steady-state extrusion forces are ~10 500 and ~6500 N for 125 and 135°C, respectively. This is a decrease of 38% in extrusion force for a 10°C temperature increase. A higher initial yield stress is required for the initiation of flow deformation at 125 than at 135°C. Figs 1 and 2 show that at 135°C the UHMWPE in the blend material has greater mobility and flexibility in conforming itself along the direction of flow than at 125°C. Also, at a processing temperature of 125°C the UHMWPE is mainly still a solid powder liable to block the die, especially at high processing rates ($Q > 0.68\ cm^3\ min^{-1}$). Therefore, 135°C was chosen as the processing temperature for the remaining tests. There is a reasonable processing range, $0.01\ cm^3\ min^{-1} \leq Q \leq 3.40\ cm^3\ min^{-1}$, at this temperature and flow instability is avoided. This volumetric flow rate range is for EDR = 9 and is at the lower end of industrial-scale processing rates. Although $3.40\ cm^3\ min^{-1}$ is the maximum volumetric flow rate for EDR = 9 achieved in this work due to the transducer used, it is believed that higher processing rates are possible if either the transducer limit is increased, or the capillary die length is decreased.

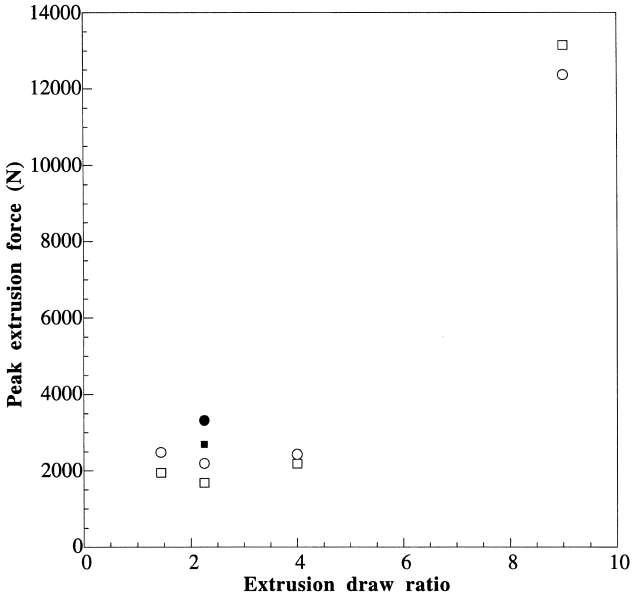

Fig. 3. Variation of peak extrusion force with EDR for compacted 10 wt% mineral oil/UHMWPE blend (open symbols) and compacted pure UHMWPE (closed symbols) processed at 135°C and two apparent shear rates: (□,■) volumetric flow rate varies between 0.17 and 2.65 $cm^3\ min^{-1}$, equivalent to $\dot{\gamma}_{ap} = 0.45\ s^{-1}$; (○,●) volumetric flow rate varies between 0.68 and 10.60 $cm^3\ min^{-1}$, equivalent to $\dot{\gamma}_{ap} = 1.8\ s^{-1}$.

A comparison of the extrusion of compacted 10 wt% mineral oil/UHMWPE blend with that of the compacted pure UHMWPE was made at a temperature of 135°C. The results are shown in Table 1 which gives the peak extrusion forces required for processing at two apparent shear rates and various EDRs for both blend and the pure material. ('Apparent shear rate' is used here for convenience; in reality the material is not a full melt and there is some slip.) These data are plotted in Fig. 3 and have a standard deviation of ± 12.5%. The peak extrusion force for the compacted blend material goes through a small minimum at EDR = 2.25. Comparison with the peak extrusion forces required to process the compacted pure UHMWPE at 135°C shows the blend requires 38% and 34% lower extrusion force than the pure UHMWPE at volumetric flow rates of 1.36 and 5.43 $cm^3\ min^{-1}$, respectively. This, when scaled-up, represents a significant energy reduction on an industrial processing plant. This is a shallow EDR (2.25) under which the blend and pure materials are both processable. Beyond this EDR only the blend is processable. The improved processability of UHMWPE when 10 wt% mineral oil is used as a processing aid to provide lubrication is further demonstrated in Fig. 4. This shows the development of pressure drop over the die with time at various volumetric flow rates. For 10 wt% mineral oil/UHMWPE blend processed at 135°C and EDR = 9, the highest ΔP was ~420 bar at $Q = 3.39\ cm^3\ min^{-1}$ and the lowest was ~210 bar at $Q = 0.08\ cm^3\ min^{-1}$. These values are significantly lower than those reported for hydrostatic extrusion [28,29], using a fluorocarbon lubricant [30] and other ram extrusions [21]. As expected, the extrusion pressure increases as the processing rate increases. This is because the molecular conformation of the polymeric material does not have sufficient time to align itself along the flow direction, creating a resistance to flow. However, the rate of change of ΔP decreases at the higher apparent shear rates.

To assess the effect of die length, L, on ΔP, experiments were carried out with dies of different lengths, 5, 10 and 30 mm, and the same diameter, 4 mm. Fig. 5 shows the results. There is a non-linear increase of ΔP with L/D, e.g.

for an increase in die length of 500% there is an increase in ΔP of more than 50%. The non-linearity increases with increasing processing rate. This is due to the greater contribution of the stretching flow in the die entrance region at higher flow rates. This non-linearity is the reason for not applying the Bagley correction, as linear plots of ΔP versus L/D are required to make this correction. Non-linear ΔP versus L/D plots have been reported before: for low-density polyethylenes [36], high-density polyethylenes [37], polystyrene [38] and polyvinylidenefluoride/polyvinylidene trifluoride copolymer [26]. Lee and Cakmak [26] attributed the non-linearity to the development of rod-like structures, observed in their copolymer, during extrusion increasing the pressure drop across the die. They based their argument on observations made on glass fibre-filled polymers (see references in Ref. [26]), and suggested that non-linearity may be the norm rather than the exception in such systems. Duvdevani and Klein's treatment [36] of their experimental results implied a compressible melt or a pressure-dependent viscosity [36]. This is felt to be unlikely; it is generally accepted that polymer melts are incompressible at normal extrusion pressures. McLuckie and Rogers [37] based their analysis on 'elastic backpressure' caused by relaxation of the polymer in the die exit leading to die swell. Given that the die swell measured for the 10 wt% mineral oil/UHMWPE blend is less than 2.5%, there is either very little relaxation of the polymer or the energy released on relaxation is absorbed by the mineral oil, resulting in the observed non-linearity and low die swell. It is obviously an advantage if the energy required for processing can be reduced by simply shortening the die. However, for most polymer processing situations the establishment of steady-state flow prior to extrusion is critical. In this case, whilst steady-state flow is important, the crucial factor is the mechanical property of the extrudate. It is important that the tensile properties of the precursors are maintained, especially if there is evidence of an improvement in these properties. This is discussed in Part 2 of this paper.

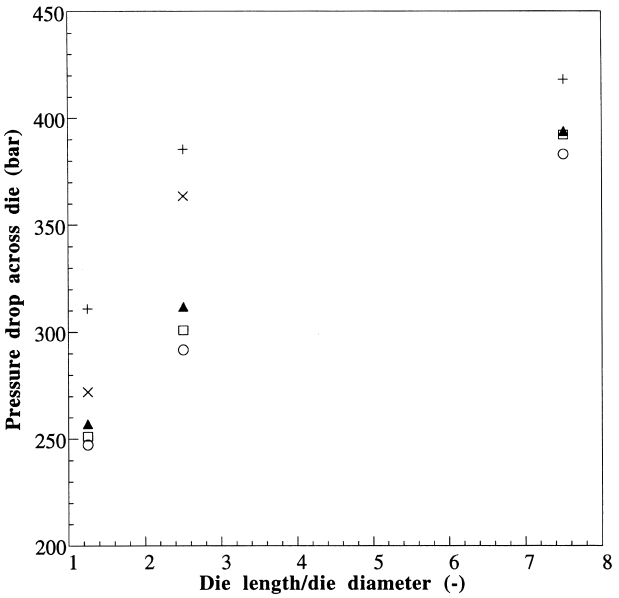

Fig. 5. Plot of pressure drop across the die versus (die length/die diameter) for 10 wt% mineral oil/UHMWPE blend extruded at 135°C, EDR = 9 and different volumetric flow rates: (○) 0.68; (□) 1.36; (▲) 2.04; (×) 2.71; and (+) 3.39 $cm^3\ min^{-1}$.

As this is solid state processing, i.e. not full melt, the generation of rheological data is extraneous. The results from the capillary rheometer may be plotted as ΔP versus

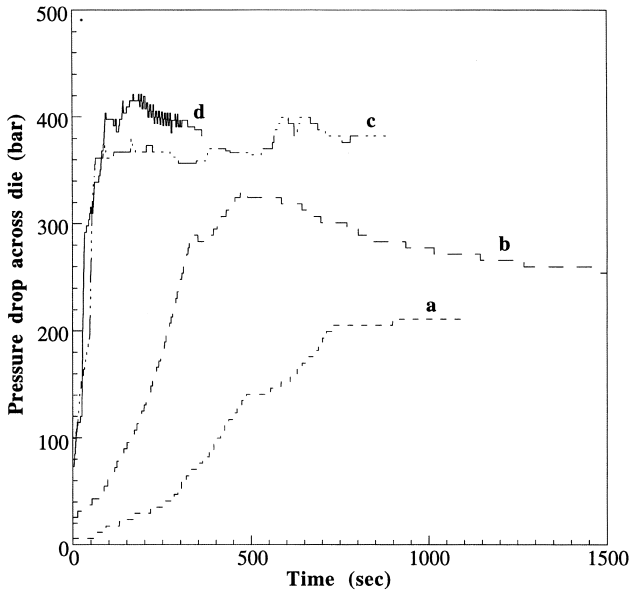

Fig. 4. Plot showing the development of ΔP over the die with time during extrusion of compacted samples of 10 wt% mineral oil/UHMWPE blend at 135°C, EDR = 9 and different volumetric flow rates: (a) 0.08; (b) 0.17; (c) 1.36; and (d) 3.39 $cm^3\ min^{-1}$.

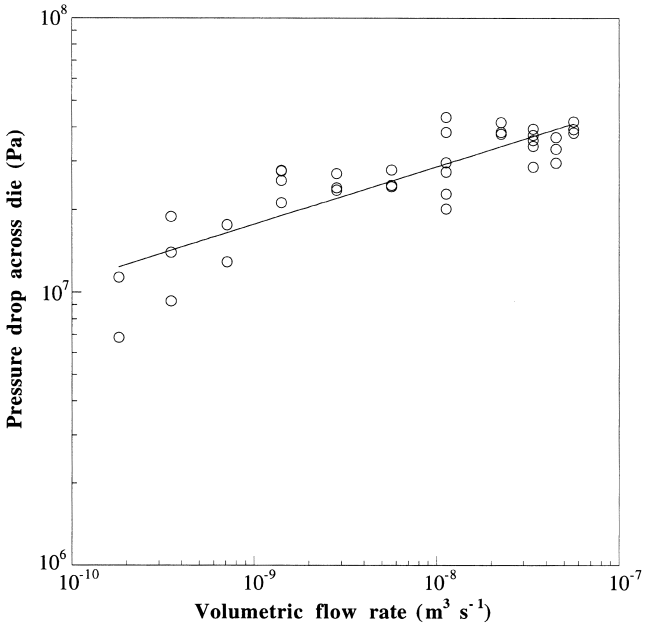

Fig. 6. Plot of pressure drop across die versus volumetric flow rate for the 10 wt% mineral oil/UHMWPE blend at 135°C, EDR = 9 and $L/D = 7.5$.

volumetric flow rate; see Fig. 6. Note that in this plot ΔP takes the units Pa and Q the units $m^3 s^{-1}$. When a power law fitting [39] is applied it yields the relationship

$$\Delta P = 1.35 \times 10^6 Q^{0.21}$$

where the power law parameters are given as

$$k = 1.35 \times 10^6 \quad n = 0.21$$

An exponent of $n = 0.21$ shows the blend material has very strong shear-thinning behaviour, similar to results reported previously for molten UHMWPE [40]. In all the extrudates produced by the processing method described in this paper the observed die swell was less than 2.5% of the die diameter. When compared with the usual 100–330% increase in diameter for molten plastics, this demonstrates the precision obtainable with the cold extrusion process. For ease of comparison some τ_w values were calculated. Melt fracture was observed at $\tau_w \sim 1000$ kPa, whereas molten polyethylene fails at $\tau_w \sim 200$ kPa [41]. This shows the semi-solid material exhibits a much higher strength before failure.

3.2. Thermal characterization

Fig. 7 shows the d.s.c. thermograms for the as-received pure UHMWPE reactor powder and pure UHMWPE extrudates processed, after compaction, at 135°C, EDR = 2.25 and volumetric flow rates of 0.17 and 0.68 $cm^3 min^{-1}$. The as-received reactor powder shows a sharp first heating melting peak at 143.0°C and a heat of fusion of 208.3 J g^{-1}. The second heating values are T_m = 136.6°C and H_f = 134.9 J g^{-1}. The degrees of crystallinity are 72.1% and 46.7% for first and second heatings, respectively; showing

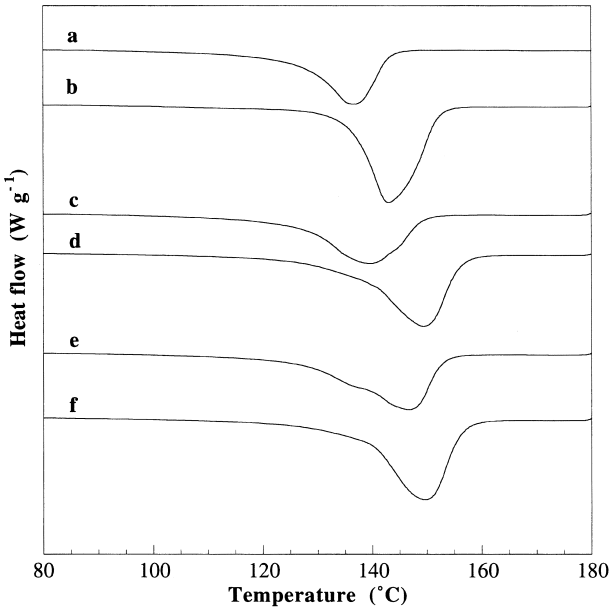

Fig. 7. D.s.c. thermograms for UHMWPE in reactor powder form ((a) 2nd heating; (b) 1st heating) and after compaction and extrusion at 135°C and EDR = 2.25: (c) skin sample and (d) core sample for $Q = 0.17$ $cm^3 min^{-1}$; (e) skin sample and (f) core sample for $Q = 0.68$ $cm^3 min^{-1}$.

the expected reduction in the amount of crystals present. The crystallinity calculated from the first heating is similar to those reported by Ottani and Porter [42] for nascent reactor powders with different synthesis temperatures and processes. The thermograms for the UHMWPE extrudates are separated into skin and core samples. The core samples have T_m = 149.4 and 149.7°C and ΔH_f = 199.8 and 207.9 J g^{-1} for volumetric flow rates of 0.17 and 0.68 $cm^3 min^{-1}$, respectively. The skin samples have T_m = 139.7 and 146.7°C and ΔH_f = 151.8 and 172.5 J g^{-1} at volumetric flow rates of 0.17 and 0.68 $cm^3 min^{-1}$, respectively. What is apparent only from the thermograms is the development of a weak shoulder or peak prior to the main UHMWPE melting peak and starting at ~134°C. This 'first peak' is very clear in the skin sample taken from extrudate processed at $Q = 0.68$ $cm^3 min^{-1}$. The degrees of crystallinity are: core 71.9% and skin 59.7% for $Q = 0.68$ $cm^3 min^{-1}$; and core 69.1% and skin 52.5% for $Q = 0.17$ $cm^3 min^{-1}$. The low-temperature endothermic shoulder has been observed before [43] and is caused by small, imperfect UHMWPE crystals becoming molten during extrusion and recrystallizing as low T_m crystals. The d.s.c. results of Lee and Cakmak [26] also show the development of an initial, second shoulder with increasing extrusion temperature which disappears beyond a critical extrusion temperature for a VF2/VF3 copolymer. The low crystallinities (<60%) for the skin samples indicate significant amounts of chain-folded structures induced by the shear heating near the barrel wall. These twin peaks are strong evidence that the extruded UHMWPE is a self-blend made up of once molten crystals and solid powders. According to the d.s.c. results of Smith and Lemstra [44], ~30% of the UHMWPE is molten during extrusion. The ΔH_f and T_m values for the skin and core samples show the presence of fewer and larger crystals in the core, with increased melting transition temperatures and decreased heats of fusion, compared with the reactor powder. The skin samples have fewer and smaller crystals than the core samples, giving rise to an ~15% crystallinity difference between skin and core samples. Thus, partial melting is taking place in the material near the barrel wall, and a little of the excess heat energy is being transferred to the core where some partial melting also takes place (see thermogram for $Q = 0.17$ $cm^3 min^{-1}$ in Fig. 7).

Figs 8 and 9 show the d.s.c. thermograms for the extrudates of UHMWPE blended with 10 wt% mineral oil, again with skin and core samples, for different EDRs at $\dot{\gamma}_{ap} = 0.45$ and 1.8 s^{-1}, respectively. Again, $\dot{\gamma}_{ap}$ here is used for convenience. Table 2 gives all the T_m and ΔH_f values extracted from the thermograms, including those for the UHMWPE extrudate. An EDR of 1 is assigned to the compacted sample with no extrusion. The thermograms show clearly melting twin peaks in both skin and core samples up to an EDR of 2.25, there is a residual first peak at an EDR of 4 and just one peak at an EDR of 9. Again, the presence of a self-blend is indicated, up to EDR = 4. The first, weak peak appears at ~134°C, corresponding to the T_m of the melt crystallized

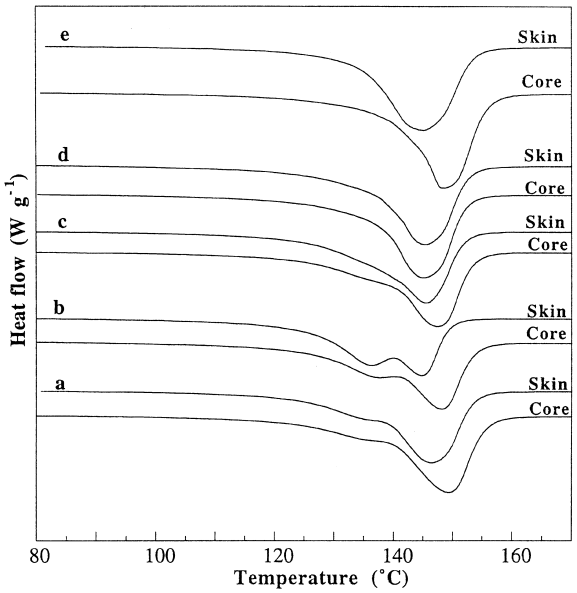

Fig. 8. D.s.c. thermograms of 10 wt% mineral oil/UHMWPE blends compacted at 135°C and ~9 MPa and extruded at 135°C, 0.17 $cm^3\ min^{-1} \leq Q \leq 2.65\ cm^3\ min^{-1}$ equivalent to $\dot{\gamma}_{ap} = 0.45\ s^{-1}$ and various EDRs: (a) EDR = 1, $Q = 0$; (b) EDR = 1.44, $Q = 2.65\ cm^3\ min^{-1}$; (c) EDR = 2.25, $Q = 1.36\ cm^3\ min^{-1}$; (d) EDR = 4, $Q = 0.57\ cm^3\ min^{-1}$; (e) EDR = 9, $Q = 0.17\ cm^3\ min^{-1}$.

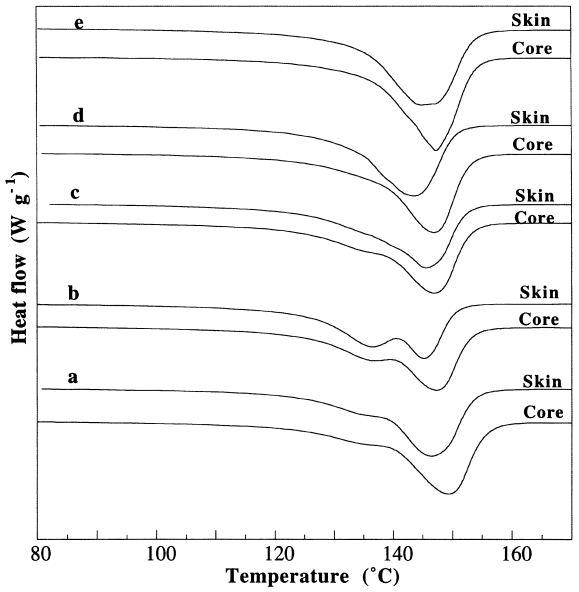

Fig. 9. D.s.c. thermograms of 10 wt% mineral oil/UHMWPE blends compacted at 135°C and ~9 MPa and extruded at 135°C, 0.68 $cm^3\ min^{-1} \leq Q \leq 10.60\ cm^3\ min^{-1}$ equivalent to $\dot{\gamma}_{ap} = 1.8\ s^{-1}$ and various EDRs: (a) EDR = 1, $Q = 0$; (b) EDR = 1.44, $Q = 10.60\ cm^3\ min^{-1}$; (c) EDR = 2.25, $Q = 5.43\ cm^3\ min^{-1}$; (d) EDR = 4, $Q = 2.29\ cm^3\ min^{-1}$; (e) EDR = 9, $Q = 0.68\ cm^3\ min^{-1}$.

UHMWPE (see Fig. 7). As with the pure material, the UHMWPE blended with 10 wt% mineral oil, when extruded below its melting point, exhibits shear-induced partial melting. At an EDR = 1, compaction but no extrusion, T_m = 149.3 and 146.4°C for core and skin samples, respectively. The ΔH_f values are 202.5 and 195.1 J g^{-1} for core and skin samples, respectively. Compaction increases the contact surface area [33] between powder particles leading to better heat conduction which is further enhanced by the presence of mineral oil. Those crystals that become molten, bridge or fuse the powder particles together when they recrystallize. This produces a more cohesive material. SEM photographs illustrating this phenomenon will be shown and discussed in Part 2. The small initial peak at ~134°C shows melting of small crystals takes place during compaction, and the d.s.c. values show an increase in the crystal size and a decrease in the amount of crystals present in comparison with the reactor powder. The compacted-only blend differs from the compacted and extruded pure UHMWPE in that the difference between the skin and core T_m and ΔH_f are less, leading to the conclusion that the mineral oil acts as a good heat-conducting agent. This would allow more even melting throughout the material and lead to more uniform and improved material properties. This aspect will be discussed in Part 2.

Using the values given in Table 2, some general trends may be observed for the higher and lower volumetric flow rates used, equivalent to apparent shear rates of 0.45 and 1.8 s^{-1}. As EDR increases the melting transition temperature decreases until EDR = 4 and then increases; and the

Table 2
Melting transition temperatures and heats of fusion for pure UHMWPE and UHMWPE/mineral oil blend extrudates (extruded at 135°C)

Material	Volumetric flow rate ($cm^3\ min^{-1}$)	EDR	Core sample		Skin sample	
			T_m (°C)	ΔH_f (J g^{-1})	T_m (°C)	ΔH_f (J g^{-1})
UHMWPE	1.36	2.25	149.4	199.8	139.7	151.8
UHMWPE	5.43	2.25	149.7	207.9	146.7	172.5
Blend	No extrusion	1	149.3	202.5	146.4	195.1
Blend	2.65	1.44	148.2	186.2	144.8	171.2
	1.36	2.25	147.3	191.8	145.5	189.3
	0.57	4	145.0	199.6	145.3	196.1
	0.17	9	148.5	213.3	145.0	211.4
Blend	10.60	1.44	147.3	191.1	145.2	174.0
	5.43	2.25	146.9	201.9	145.5	187.8
	2.29	4	146.9	205.5	143.6	193.1
	0.68	9	147.2	218.3	145.0	211.2

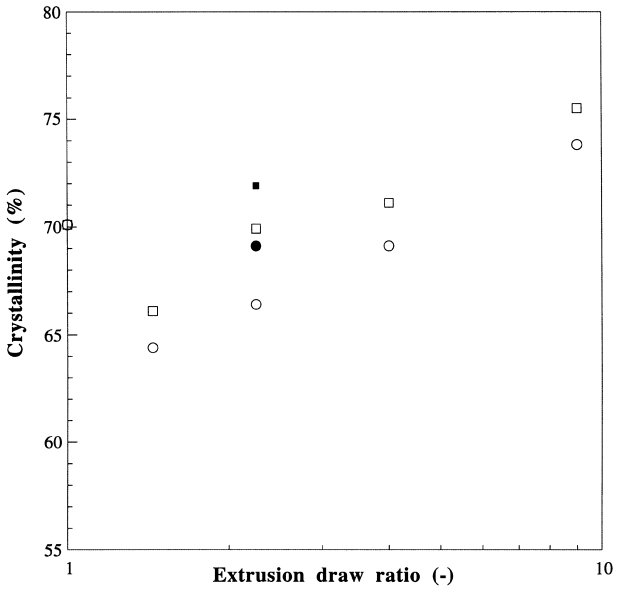

Fig. 10. Plot of crystallinity versus extrusion draw ratio for core samples of pure UHMWPE (closed symbols) and 10 wt% mineral oil/UHMWPE blend (open symbols) processed at a compaction pressure of ~9 MPa and 135°C at two sets of volumetric flow rates: (●,○) 0.17 $cm^3\,min^{-1} \leq Q \leq$ 2.65 $cm^3\,min^{-1}$ equivalent to $\dot{\gamma}_{ap} = 0.45\ s^{-1}$; (■,□) 0.68 $cm^3\,min^{-1} \leq Q \leq$ 10.60 $cm^3\,min^{-1}$ equivalent to $\dot{\gamma}_{ap} = 1.8\ s^{-1}$.

heat of fusion decreases at EDR = 1.44 and then increases. This applies to both skin and core samples, although the value for the skin T_m at $Q = 5.43\ cm^3\,min^{-1}$ and EDR = 2.25 is slightly anomalous. For the core samples, there are differences between the volumetric flow rates at the same EDR: T_m is higher for the lower volumetric flow rate values and ΔH_f is higher for the higher volumetric flow rates. There are no discernable trends or differences between the skin samples. The T_m and ΔH_f values are always higher in the core samples than in the skin samples, implying more and larger crystals present in the core. The minimum in the melting temperature when plotted against EDR was also observed by Kanamoto et al. [45] and Chuah et al. [46] at low EDRs for UHMWPE films coextruded and then hot drawn. The latter report attributes the minimum to the destruction of the initial crystals.

Figs 10 and 11 show the variation of percentage crystallinity with EDR for core and skin samples, respectively. Remember that the pure UHMWPE reactor powder has a crystallinity of 72.1%, based on the first heating, there is the expected decrease in crystallinity in the compacted and extruded pure UHMWPE samples: 69.1% and 71.9% for volumetric flow rates of 1.36 and 5.43 $cm^3\,min^{-1}$ and EDR = 2.25. The lower volumetric flow rate shows the lower crystallinity because the polymer residence time is longer, allowing more small, imperfect crystals to melt than at the higher volumetric flow rate. For the compacted alone blend sample the crystallinity is 70.1%, which compares well with a crystallinity of 69% reported for a compressed UHMWPE powder [21]. This shows that though the compaction at ~9 MPa increases the cohesion between particles it has a detrimental affect on the crystallinity. This effect may be reversed by the application of extrusion under high EDRs and volumetric flow rates. On extrusion of the compacted sample there is a decrease in the crystallinity of

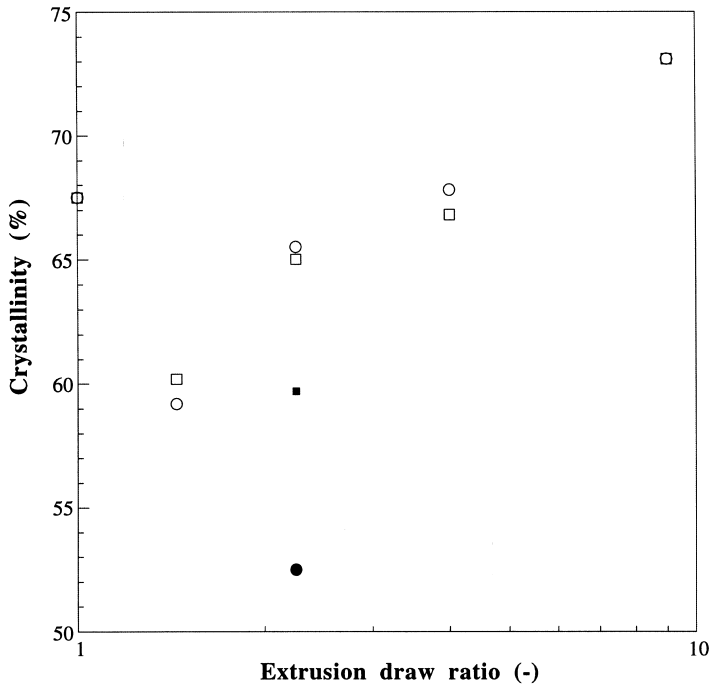

Fig. 11. Plot of crystallinity versus extrusion draw ratio for skin samples of pure UHMWPE (closed symbols) and 10 wt% mineral oil/UHMWPE blend (open symbols) processed at a compaction pressure of ~9 MPa and 135°C at two sets of volumetric flow rates: (•,○) 0.17 $cm^3\,min^{-1} \leq Q \leq 2.65\ cm^3\,min^{-1}$ equivalent to $\dot{\gamma}_{ap} = 0.45\ s^{-1}$; (■,□) 0.68 $cm^3\,min^{-1} \leq Q \leq 10.60\ cm^3\,min^{-1}$ equivalent to $\dot{\gamma}_{ap} = 1.8\ s^{-1}$.

both the skin and core at EDR = 1.44, after which the crystallinity increases. The higher volumetric flow rates for a given EDR have the higher rate of increase and higher crystallinity values due to the shorter residence time. This increase of crystallinity with increasing EDR was observed previously [21] using EDRs of 12 and 24; the minimum has also been observed before for HDPE [46] and UHMWPE [45]. This minimum is attributed to a critical EDR, beyond which the mechanisms for chain extension dominate those governing crystal destruction. Fig. 10 also shows, at EDR = 2.25, the blend to have lower crystallinity values than the processed pure UHMWPE at both volumetric flow rates. This is expected as the mineral oil is acting as a heat transfer medium which results in the core of the blend sample reaching a higher temperature and more of the crystals melting than in a pure UHMWPE sample. However, the crystallinities of the blend compacted only sample and the compacted and extruded pure UHMWPE sample are both exceeded when an EDR of 9 is used. Fig. 11 shows the same pattern for the crystallinity of the skin samples, except for two differences: (i) the crystallinity values are lower in the skin by between 2 and 5 percentage points; and (ii) in the skin there is much less difference between the crystallinities measured at different volumetric flow rates. There is an average difference between crystallinity values at the higher and lower volumetric flow rates for a given EDR in the skin of 0.6 percentage points and in the core of 2.2 percentage points. This is because the skin is in direct contact with the barrel wall and experiences the highest temperature. The skin crystallinity values of the pure UHMWPE are lower than those of the blend, again demonstrating the heat transfer qualities of the mineral oil.

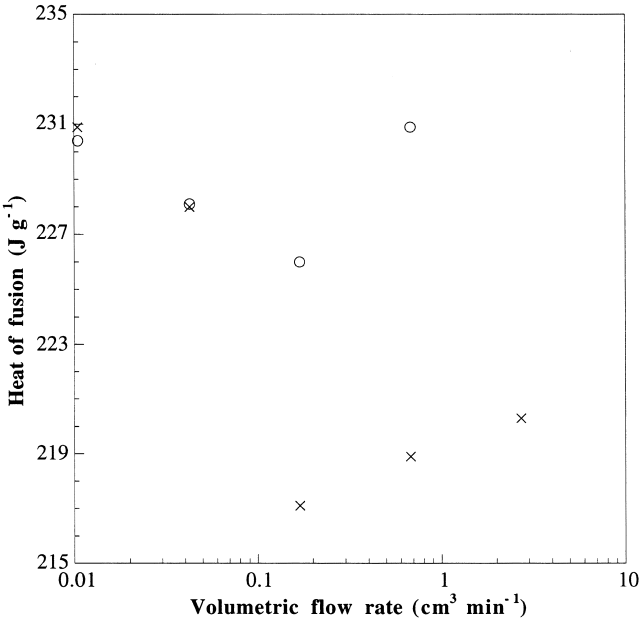

Fig. 12. Plot of heat of fusion of core samples versus volumetric flow rate for 10 wt% mineral oil/UHMWPE blend extrudates prepared with EDR = 9 and at two temperatures: (○) 125°C, (×) 135°C.

It is clear extrusion causes, by shear-induced heating, partial melting, probably of both small and large crystals. This is in addition to the partial melting taking place during compaction. Chuah et al. [46] interpreted the initial decrease in ΔH_f and T_m between EDR = 1 and 1.44 as initial distortion with subsequent destruction of crystals during extrusion. However, increasing EDR further removes the twin peaks and increases ΔH_f and, at EDR = 9, increases T_m significantly. This phenomenon may be explained by chain alignment during shear flow in the die and extension during entry into the die. Upon chain extension, any remaining small, imperfect crystals and those with the lower, compaction-induced T_m, undergo intimate packing and alignment. This would give higher crystallinity values and explain the large increase in T_m from EDR = 4 to EDR = 9. The presence of a self-blend of UHMWPE crystals with two T_m values, as evidenced by the twin peaks in the d.s.c. thermograms with EDR ≤ 4, also coincides with the low extrusion forces required for processing of the compacted blend material. There being a slight minimum at EDR = 2.25 (see Fig. 3). The large increase in crystallinity and loss of a discrete first melting peak at EDR = 9 coincides with a large increase in peak extrusion force. The relationship between the material's flowability and its crystal morphology is being investigated and will be reported at a later date.

Fig. 12 shows the variation of ΔH_f with volumetric flow rate for two extrusion temperatures, 125 and 135°C. At low volumetric flow rates, ≤ 0.04 $cm^3\ min^{-1}$, ΔH_f is almost the same for both temperatures. After this, ΔH_f continues to decrease for both temperatures, but at a higher rate for T = 135°C. Above a volumetric flow rate of 0.38 $cm^3\ min^{-1}$, the heats of fusion increase, but there is a difference of ~12 J g^{-1}, or 5.5%, between the two temperatures. Firstly, less partial melting takes place at 125 than at 135°C. Therefore, the ΔH_f values are expected to be higher as more thermally unchanged crystals remain in the material. Secondly, from Fig. 12, at low volumetric flow rates the effect of annealing time (or time spent within the die) dominates and at high volumetric flow rates, or low annealing times, the effect of temperature dominates.

4. Conclusions

The use of 10 wt% mineral oil blended with nascent UHMWPE powder improves the processability of this form of polyethylene by acting as a wetting agent, a lubricant and a heat transfer medium. The presence of the mineral oil allows the UHMWPE to be processed at higher temperatures, 135°C, and higher volumetric flow rates (also wall shear stresses, estimated at 1000 kPa) before melt fracture, after compaction at ~9 MPa for 15 min. The mineral oil helps to maintain a low entanglement density in the molten UHMWPE at 135°C.

The addition of 10 wt% mineral oil to UHMWPE reactor powder results in a more even temperature gradient through

the material during both compaction and extrusion as the mineral oil acts as a heat-conducting agent. This produces smaller differences in thermal characteristics between skin and core samples of extrudates when compared with extruded pure UHMWPE. The improved uniformity is expected to produce increased material toughness (see Part 2). Partial melting, of small and imperfect crystals, takes place during compaction to produce, on recrystallization, low T_m crystals. Further shear-induced partial melting takes place during extrusion. At EDR $\leq$ 4 the extruded material is a self-blend of once molten crystals and the original reactor powder. The molten material fuses the powder particles together, thus, increasing the cohesive strength of the final product. Also, as EDR increases, so does chain alignment and extension leading to crystallinity values higher than those of the pure material at EDR = 9.

So, the processing window for UHMWPE has been expanded in terms of temperature, volumetric flow rate and extrusion pressure by adding 10 wt% mineral oil. The d.s.c. results indicate that the tensile properties of the precursors in the transverse direction should be more nearly uniform. This should lead to the production of stronger, precision extrudates by a more effective cold extrusion method.

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