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The effect of the processing parameters on the fabrication of auxetic polyethylene

Part III *The effect of extrusion conditions*

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Auxetic ultra high molecular weight polyethylene (UHMWPE) is produced via a novel thermal processing route consisting of three stages: compaction, sintering and extrusion. The latter stage, extrusion, is investigated in this paper, with particular reference to the effects of die geometry (cone semi-angle, exit diameter and capillary length) and extrusion rate on the ability of the polymer to produce an extrudate with a negative Poisson's ratio. It was found that a delicate balance must be achieved between the production of an extrudate which lacks structural integrity and one which is solid but possesses a conventional positive Poisson's ratio i.e. does not exhibit the nodule–fibril microstructure necessary for auxetic behaviour.

In conjunction with the results from the first two papers in this series, it is possible to define a set of conditions required to produce auxetic UHMWPE.

1. Introduction

Auxetic ultra high molecular weight polyethylene (UHMWPE) is fabricated by a novel thermal processing route, which consists of three stages. The first two stages – compaction of finely divided UHMWPE powder and subsequent sintering – have been discussed in two earlier papers [1, 2]. This paper continues by studying the third stage of the processing route, this being extrusion, and summarizes the whole process.

Extrusion is one of the main thermoplastic processing routes and has been extensively used for processing UHMWPE applied either to the polymer melt [3, 4] or in the solid state [5] with the main aim of previous work being to achieve very highly oriented polyethylene. Ward [6] states that both ram extrusion and hydrostatic extrusion along with other solid state engineering processes such as the novel technique of die drawing [7, 8] have achieved these ends. The effects of varying the processing parameters have been well documented, in particular with regard to the effects of die geometry [4, 5, 8] on the production of highly oriented polyethylene. For example, Hurez *et al.* [4] state that an optimum die entry angle of between 20 and 30° should be employed for melt extrusion. Perkins and Porter [5] studied varying the die entry angle from 10 to 180° in solid state extrusion and they state that the optimum extrusion angle for the production of highly oriented polyethylene is one in which extensional strains are large and extensional stresses are minimized, with shear forces also being present. The actual extrusion angle where these conditions exist will vary with the material being extruded and with extrusion conditions, with the aim being to achieve a balance between extensional and shear forces leading to an extrudate with superior physical properties due to a high degree of orientation.

In the processing route considered here, however, the aim is neither to produce a highly oriented nor a fully densified solid, but rather to achieve a particular form of nodule–fibril microstructure which has been found to lead to a negative Poisson's ratio in polymeric materials [9–12]. With the definition of optimum processing conditions for the first two stages of this processing route already achieved [1, 2], this paper studies the effects of varying the extrusion rate and die geometry on the structural integrity and ability of the extrudate to exhibit auxetic behaviour. This enables a comprehensive summary of processing conditions required to produce auxetic UHMWPE to be specified.

2. Experimental methods

2.1. Standard compaction and sintering conditions for auxetic UHMWPE

In order to study the effects of varying the extrusion stage of the fabrication route, all specimens were

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subjected to the same standard [1, 2, 11] compaction and sintering conditions. For completeness, these are summarized here; further details can be obtained elsewhere [1, 2]. All three stages were carried out in a specially designed rig with a 15-mm diameter barrel using GUR 415 UHMWPE powder [13].

The rig was fitted with a blank die and heated to a temperature of 110 °C. UHMWPE powder was added and allowed to come to equilibrium for 10 min. The powder was then compacted by applying a pressure of 0.04 GPa achieved by lowering a compaction ram attached to a Schenk–Trebel electro-mechanical testing machine at 20 mm min^{-1}. Once the compaction pressure had been reached, it was maintained for 20 min, producing a rigid rod which was expelled from the barrel and allowed to slow cool to room temperature. The constant pressure condition can either be achieved manually, by altering the displacement control or automatically, using a load control feedback loop on the tensile tester. If this latter method is used, providing a much smoother pressure control, the pressure need only be applied for 800 s to provide specimens of equivalent compaction density [14]. Sintering then took place in the barrel at 160 °C for 20 min and rods so produced were immediately extruded at 160 °C with the various conditions described below.

2.2. Variations investigated in the extrusion stage of the fabrication process

The main processing conditions examined in this study were extrusion rate and die geometry. In all cases, several specimens were produced under standard compaction and sintering conditions [1, 2] prior to extrusion in order to ensure consistency. Considering firstly extrusion rate, initial tests were carried out using a die previously found to produce auxetic material [12]. This die had an exit diameter, d, of 5 mm, a cone semi-angle, θ, of 30° and a capillary length, L, of 3.4 mm, with the bore diameter (or die entry diameter), D, being 15 mm (see Fig. 1). Four extrusion rates were considered (see Table I); 85, 234.5, 469 and 500 mm min^{-1}. A second set of tests were then carried out (also listed in Table I) using a die of entry diameter 15 mm, exit diameter 7.5 mm, cone semi-angle 30° and capillary length 3.4 mm. In this case, extrusion rates of 20, 50, 75, 200, 300, 400 and 500 mm min^{-1}, were considered.

Following this investigation, the remaining extrusions were all carried out at a rate of 500 mm min^{-1}, with the die geometry being varied as listed in Tables II–IV. There were three variables under consideration: die exit diameter, d, cone semi-angle, θ and

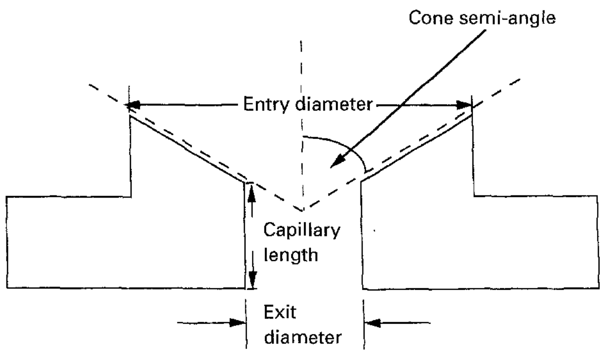

Figure 1 Schematic of a typical die, showing the variables studied in this investigation.

TABLE I Conditions used to investigate the effect of extrusion rate

Extrusion rate (mm min^{-1})	Die exit diameter d (mm)	Cone semi-angle θ (°)	Die capillary length L (mm)
85, 234.5, 469, 500	5	30	3.4
20, 50, 75, 200, 300, 400, 500	7.5	30	3.4

TABLE II Conditions used to investigate the effect of die exit diameter

Extrusion rate (mm min^{-1})	Die exit diameter d (mm)	Cone semi-angle θ (°)	Die capillary length L (mm)
500	5.0, 6.0, 7.0, 7.5, 8.0, 9.0	30	3.4
500	5.0, 6.0, 7.0, 8.0, 9.0	45	3.4
500	5.0, 6.0, 7.0, 8.0, 9.0	60	3.4

TABLE III Conditions used to investigate the effects of cone semi-angle

Extrusion rate (mm min^{-1})	Die exit diameter d (mm)	Cone semi-angle θ (°)	Die capillary length L (mm)
500	5.0	30, 45, 60	3.4
500	6.0	30, 45, 60	3.4
500	7.0	45, 60	3.4
500	7.5	30, 90	3.4
500	8.0	45, 60	3.4
500	9.0	45, 60	3.4

TABLE IV Conditions used to investigate the effects of die capillary length

Extrusion rate ($mm\,min^{-1}$)	Die exit diameter d (mm)	Cone semi-angle θ (°)	Die capillary length L (mm)
500	6.5	45, 60	0.0
500	6.75	45, 60	0.0
500	5.0	30	3.4, 50.0

die capillary length, L, as illustrated in Fig. 1. Keeping the die entry diameter, extrusion rate and die capillary length constant at 15 mm, 500 $mm\,min^{-1}$ and 3.4 mm respectively, investigations into the effect of die exit diameter were carried out at three cone semi-angles (30°, 45° and 60°). At each, at least four die exit diameters were considered, varying from 5 to 9 mm (see Table II). The second set of investigations into the effects of die geometry was carried out on cone semi-angle. As before, die entry diameter, extrusion rate and capillary length remained constant at 15 mm, 500 $mm\,min^{-1}$ and 3.4 mm respectively. In all, six die exit diameters were used, varying from 5 to 9 mm. At small die exit diameters (i.e. 5 mm and 6 mm), three cone semi-angles were considered whereas for the remaining larger die exit diameters, two cone semi-angles were used. The cone semi-angles under investigation varied from 30° to 90° (see Table III). Finally, the effect of altering the die capillary length was investigated, with zero, 3.4- and 50-mm length capillary dies used to produce extrudates (see Table IV). For the zero capillary length dies, standard compaction and sintering conditions were employed, with the die entry diameter and extrusion rate constant at 15 mm and 500 $mm\,min^{-1}$ respectively. Two die exit diameters were considered (i.e. 6.5 and 6.75 mm), each at cone semi-angles of 45° and 60°. For the 50-mm capillary length die, standard compaction conditions were used, but sintering took place at 150 °C for times of 10 and 20 min. A die entry diameter of 15 mm together with an extrusion rate of 500 $mm\,min^{-1}$ were again held constant, with the die having an exit diameter of 5 mm and a cone semi-angle of 30°.

It should be noted that each extrusion except that using the 50-mm capillary length die was carried out at the optimum sintering temperature of 160 °C as previous work [2] has shown that extrusion must take place directly after sintering. If sintering is carried out and then the sample is allowed to cool to room temperature before extrusion takes place, the extrudate obtained is an unexpanded solid with a conventional positive Poisson's ratio.

2.3. Microscopic examination of the extrudates

At least one example of each of the extrudates obtained using conditions as described above was fractured in order to study the microstructure. The fracture surfaces were mounted on aluminium stubs and sputter-coated with gold prior to examination by a scanning electron microscope (SEM) at magnifications of up to × 1250.

2.4. Measurement of the Poisson's ratio

For each sample, the Poisson's ratio was measured in one of two ways. For a simple measurement giving the value of the Poisson's ratio at a particular strain, a simple single strain compression test in conjunction with a highly magnified photographic record of the change in specimen dimensions [9] was employed. This method provides a simple one-off test of auxeticity. A more detailed measurement of Poisson's ratio was obtained using electronic resistance strain gauges [15] to provide a complete strain history of the samples. This latter test is of use in selected cases since the value of Poisson's ratio is known to be highly strain dependent [16].

2.5. Measurement of mechanical properties

In order to compare the specimens produced under different extrusion conditions, mechanical property data were obtained by performing a three-point bend test to a deflection of 7 mm on an Instron 1185 tensile testing machine. The three-point bend test was selected as a convenient means of mechanical performance to provide information on the flexural stress, flexural modulus and flexural strain at 7-mm deflection for specimens produced under different extrusion conditions.

3. Results

3.1. The effects of varying the extrusion rate

Varying the extrusion rate with all other processing variables remaining constant had a marked effect on the extrudates produced. At low extrusion rates (i.e. less than 100 $mm\,min^{-1}$), the extrudates produced resembled very closely the sintered material [2] macroscopically but did possess fibrils which were, however, very short and not widespread (see Fig. 2). The extrudates were subjected to compression testing and this revealed that the Poisson's ratio, υ, was similar to that of conventional compression moulded polyethylene i.e. a constant value of $\upsilon = +0.2$ independent of strain. At medium extrusion rates (200–300 $mm\,min^{-1}$), the extrudates also had a conventional positive υ, but their microstructure had begun to resemble that which is known to produce a negative υ in polymers i.e. nodules interconnected with fibrils. However, the exact requirement for this microstructure to achieve auxetic behaviour is more complicated, with the interconnectivity of the nodules and fibrils and the density and length of the fibrils all being of importance [9, 10]. In this case, the fibrils were too short and the fibril density too small to produce the co-operative

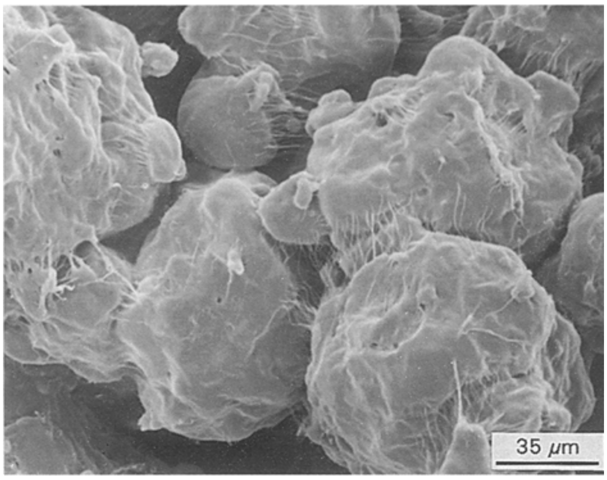

Figure 2 Micrograph of the microstructure produced at a low (i.e. 75 mm min^{-1}) extrusion rate.

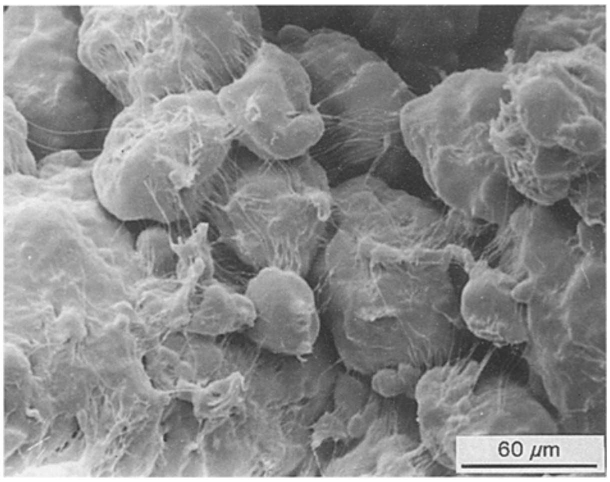

Figure 3 Micrograph of the microstructure produced at a medium (i.e. 300 mm min^{-1}) extrusion rate.

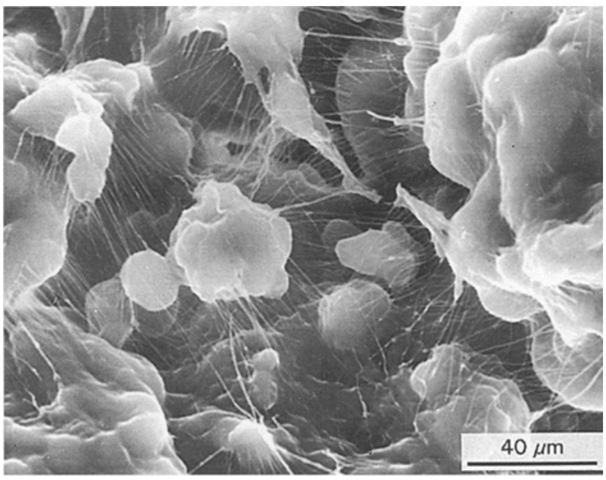

Figure 4 Micrograph of the microstructure which generates a negative Poisson's ratio in UHMWPE.

effect needed to result in auxetic behaviour (see Fig. 3).

The required nodule–fibril microstructure is produced (see Fig. 4) at high extrusion rates (i.e. greater than 400 mm min^{-1}) and the result is an extrudate which possesses a large strain dependent negative υ i.e. is auxetic (see Tables V and VI). As can be seen from Table VII, the mechanical properties of the rods using the three-point bend test were very similar for the entire range of extrusion rates considered.

TABLE V Poisson's ratio and engineering strain values obtained from single compression tests for six samples processed under standard compaction and sintering conditions with an extrusion rate of 500 mm min^{-1} employed in tandem with a die of entry diameter 15 mm, exit diameter 5 mm, cone semi-angle 30° and capillary length 3.4 mm. The error on the radial Poisson's ratio is ±0.02

Engineering strain	Radial Poisson's ratio
0.009	− 6.30
0.009	− 5.44
0.019	− 1.43
0.019	− 1.36
0.019	0.00
0.029	0.00

TABLE VI Poisson's ratio and engineering strain values obtained from single compression tests for seven samples processed under standard compaction and sintering conditions with an extrusion rate of 500 mm min^{-1} employed in tandem with a die of entry diameter 15 mm, exit diameter 7.5 mm, cone semi-angle 30° and capillary length 3.4 mm. The error on the radial Poisson's ratio is ±0.02

Engineering strain	Radial Poisson's ratio
0.020	− 0.92
0.026	− 1.03
0.026	− 0.80
0.031	− 0.88
0.040	− 0.29
0.100	− 0.20
0.296	− 0.39

TABLE VII Data obtained from three-point bend tests conducted to 7-mm deflection for rods produced under standard compaction and sintering conditions using a die of entry diameter 15 mm, exit diameter 7.5 mm, cone semi-angle 30° and capillary length 3.4 mm. Extrusion rates were allowed to vary as shown

Extrusion rate (mm min^{-1})	Flexural stress (MPa) ±0.5	Flexural modulus (MPa) ±10	Flexural strain ±0.01
20	56.6	390	0.14
50	51.5	350	0.15
75	57.0	370	0.15
200	56.0	360	0.16
300	58.4	380	0.16
400	53.4	340	0.16
500	55.6	360	0.16

3.2. The effects of varying the die geometry

The three die geometry variables investigated in this paper and summarized in Tables II–IV are considered separately below.

3.2.1. The effect of varying the die exit diameter

The conditions investigated for this processing variable are given in Table II. With die entry diameter (i.e.

15 mm), extrusion rate (i.e. 500 mm min^{-1}) and capillary length (i.e. 3.4 mm) kept constant along with standard compaction and sintering conditions, tests were carried out at three cone semi-angles, each with at least five different die exit diameters. Studying in detail the 30° cone semi-angle, the effects of varying the die exit diameter were clearly observed (see Fig. 5). At small die exit diameters (i.e. 5 mm), the extrudates produced were expanded and microporous but were not in the form of a consistent rod; having helical fractures along their lengths. If the die exit diameter is increased to 6 mm, the structural integrity of the extrudate is improved although not to an acceptable level and the fibrillation in the microstructure is reduced. At die exit diameters greater than 7 mm, homogeneous rods are produced with the microstructure necessary to achieve auxetic behaviour. However, as the die exit diameter is increased above 7.5 mm (indicating a very narrow range) a reduced amount of fibrillation is observed. This increases with increasing die exit diameter, affecting the overall behaviour of the specimen and leaving an increasingly large unfibrillated central core. It should be noted, though, that the outer layers of the extrudates do show fibrillation even after processing with a die exit diameter of 9 mm (see Fig. 6) and a negative Poisson's ratio is still obtained (see Table VIII), though this is much less negative than that obtained using a 7.5-mm exit diameter die (see Table VI).

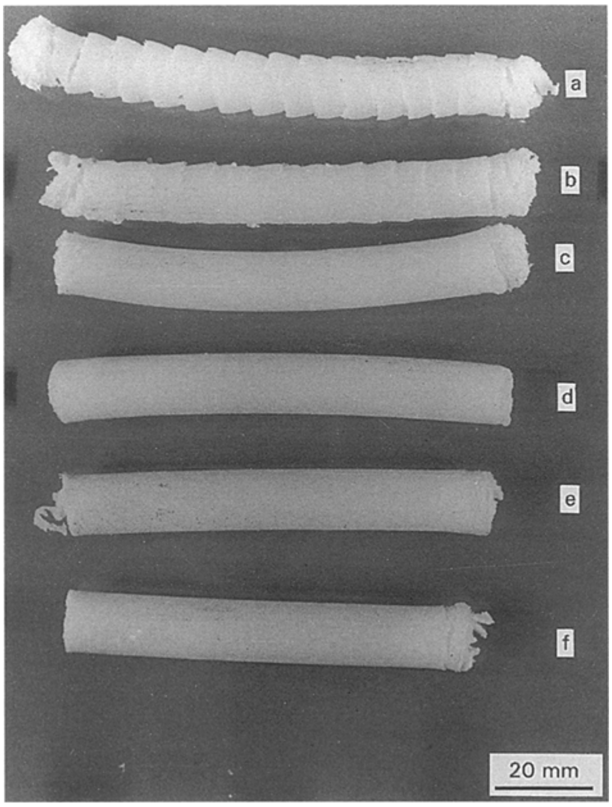

Figure 5 Extrudates produced under standard compaction and sintering conditions, with a die entry diameter of 15 mm, cone semi-angle 30°, capillary length 3.4 mm and extrusion rate 500 mm min^{-1}. Die exit diameters employed were (a) 5 mm, (b) 6 mm, (c) 7 mm, (d) 7.5 mm, (e) 8 mm and (f) 9 mm.

These findings were reinforced by using cone semi-angles of 45° and 60° in conjunction with die exit diameters of between 5 and 9 mm. In all cases, the small die exit diameters led to an expanded fibrillar structure but with poor structural integrity and surface quality. Large die exit diameters (i.e. greater than 7.5 mm) led to an increase in structural integrity but a decrease in the amount of nodule–fibril microstructure in the resulting extrudates, though this was observed in the outer layers of all the specimens. Thus a very narrow range of die exit diameters capable of producing auxetic material of high structural integrity has been defined.

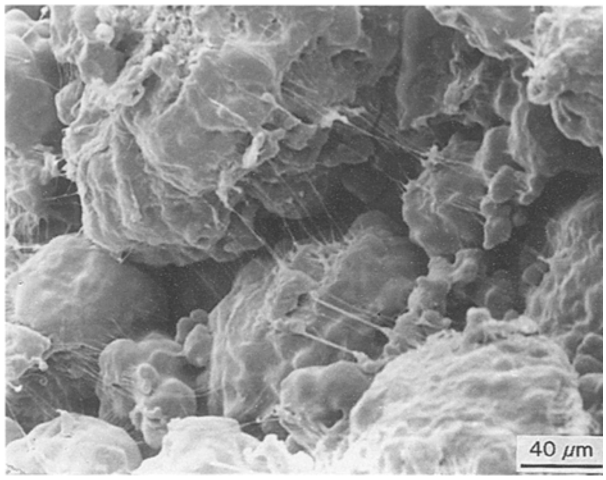

Figure 6 Micrograph of the microstructure produced using a 9-mm exit diameter die with a cone semi-angle of 60° showing the fibrillar outer region of the sample.

TABLE VIII Poisson's ratio and engineering strain values obtained from single compression tests for 22 samples processed under standard compaction and sintering conditions with an extrusion rate of 500 mm min^{-1} employed in tandem with a die of entry diameter 15 mm, exit diameter 9 mm, cone semi-angle 30° and capillary length 3.4 mm. The error on the radial Poisson's ratio is ± 0.02

Engineering strain	Radial Poisson's ratio
0.040	0.00
0.070	− 0.29
0.070	− 0.29
0.070	− 0.29
0.070	0.00
0.070	0.00
0.070	0.00
0.070	0.00
0.070	+ 0.10
0.070	+ 0.13
0.090	− 0.90
0.090	− 0.33
0.090	− 1.10
0.090	+ 0.10
0.090	+ 0.11
0.090	+ 0.22
0.100	0.00
0.110	− 0.18
0.110	− 0.18
0.110	− 0.09
0.110	− 0.09
0.110	+ 0.09

TABLE IX Data obtained from three-point bend tests conducted to 7-mm deflection for rods produced under standard compaction and sintering conditions using a die of entry diameter 15 mm, capillary length 3.4 mm and extrusion rate of 500 mm min^{-1}. Die exit diameters and cone semi-angles were allowed to vary as shown

Exit diameter (mm)	Cone semi-angle θ (°)	Flexural stress (MPa) ± 0.5	Flexural modulus (MPa) ± 10	Flexural strain ± 0.01
7	45	57.9	380	0.15
7	60	59.2	380	0.15
8	45	59.1	370	0.16
8	60	56.6	360	0.16
9	45	55.4	350	0.16
9	60	56.9	360	0.16

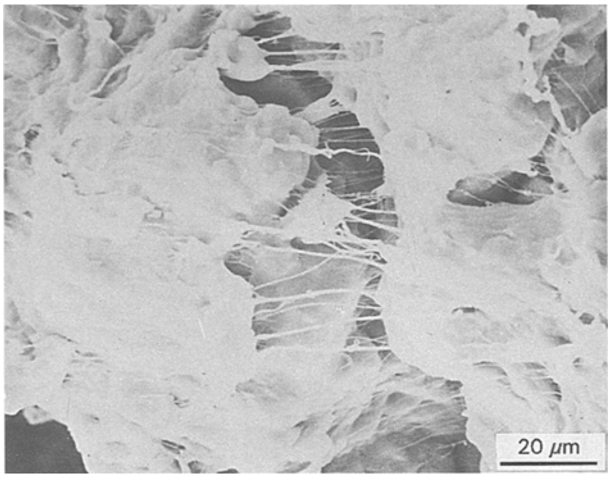

Figure 7 Micrograph of the microstructure produced using a 45° cone semi-angle die.

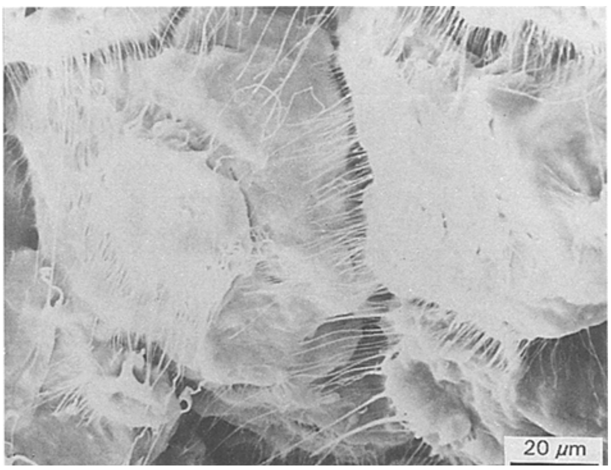

Figure 8 Micrograph of the microstructure produced using a 60° cone semi-angle die.

Despite the differences in microstructure and Poisson's ratio, it can be seen from Table IX that varying the die exit diameter has very little effect on the mechanical properties in flexure of the specimens produced. Very close agreement is seen between the flexural stress, flexural modulus and strain at 7-mm deflection as the exit diameter is increased from 7 to 9 mm for dies of capillary length 3.4 mm and cone semi-angles of 45° and 60°.

3.2.2. The effect of varying the cone semi-angle

For any specific die exit diameter, the following trends, with varying cone semi-angle, were observed. At small cone semi-angles, the extrudates produced had very good structural integrity but had a much reduced amount of fibrillation. Increasing the cone semi-angle increased the fibrillation. This is illustrated in Figs 7 and 8, which show the difference in microstructure obtained when the cone semi-angle is increased from 45° to 60° for a die exit diameter of 6 mm. Despite the changes in microstructure, the external appearance of the rods was not significantly affected by a change in cone semi-angle. If a cone semi-angle of 90° is used, the extrudate produced has a very large strain dependent negative Poisson's ratio due to a very fibrillar microstructure. However, the specimens have very little structural integrity and are often fragmentary.

From these finding a cone semi-angle of 30° appears to give the best compromise between structural integrity and auxetic behaviour.

3.2.3. The effect of varying the die capillary length

The final variation to the processing route that was investigated was the die capillary length. A definite effect on the extrudate was observed. All extrudates processed under standard compaction and sintering conditions and extruded through a zero capillary die suffered from complete lack of structural integrity, often fragmenting, regardless of the other extrusion conditions.

The extrudates produced using the die of capillary length 50 mm did possess structural integrity but they exited from the capillary with a helical fracture extended to the point of forming a zig-zag specimen geometry (see Fig. 9). It should be noted that despite the changes in macroscopic appearance, the extrudates produced using the 50-mm capillary length die did possess a nodule–fibril microstructure (see Fig. 10) but the resulting unstable specimen geometry is of little use.

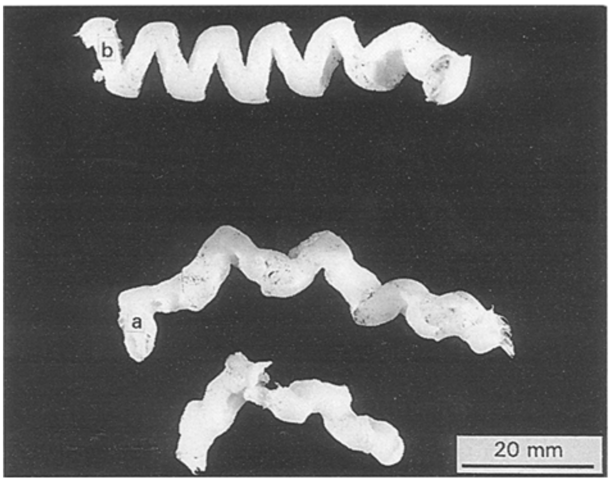

Figure 9 Extrudates produced under standard compaction with a die entry diameter of 15 mm, exit diameter 5 mm, cone semi-angle 30°, capillary length 50.0 mm and extrusion rate 500 mm min^{-1}. Sintering took place at 150 °C for (a) 10 min and (b) 20 min.

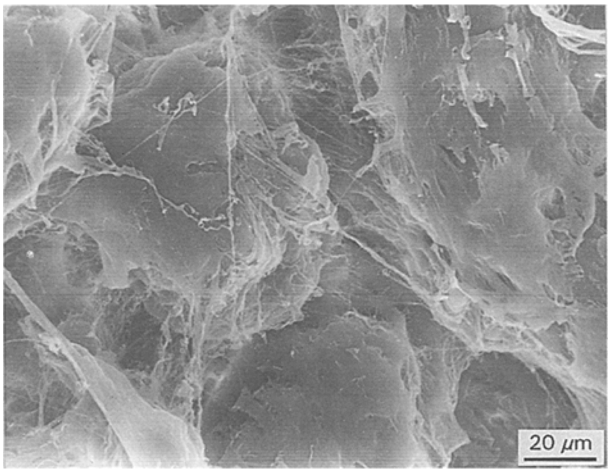

Figure 10 Micrograph of the microstructure produced using a 50-mm capillary length.

4. Discussion

The importance of the extrusion conditions in the final stage of the production of auxetic polymers has been made clear by this investigation. The processing conditions imposed on the UHMWPE are more akin to those in a solid extrusion process than in melt flow extrusion. These conditions directly affect the production of the nodule–fibril microstructure required to give auxetic behaviour, in particular the formation of fibrils of the desired length, diameter and orientation in relation to the nodules. In all of these tests, fibrils have been observed to lie more predominantly in a radial orientation. This suggests that radial compression through the die followed by expansion beyond the die is an important element of the process. Hence the importance of the relative change in diameter in passing through the die. However, shear through the die, and hence the cone semi-angle are also likely to be of importance in determining fibrillation.

Considering firstly extrusion rate, slow extrusion rates impart less shear and therefore less expansion and fibrillation is seen, resulting in shorter fibrils than are required for the desired nodule–fibril microstructure. Very fast extrusion rates give very high strain rates, and, if used in conjunction with certain die geometries, can cause helical fracture of the specimen, greatly reducing the structural integrity of the auxetic material formed. There is, therefore, a competition between the requirements of microstructural deformation, to encourage fibrillation, and macroscopic deformation causing specimen fragmentation.

It also follows that the die geometry must be selected with care. There are three variables associated with it: exit diameter, cone semi-angle and capillary length. As far as die exit diameter is concerned, auxetic material of a good structural integrity has only been obtained using a very narrow range of 7–7.5 mm for the current entry diameter of 15 mm. Below this, the material fractures on extrusion whereas with an exit diameter of above 7.5 mm, the material retains its fibrillar microstructure only in the outer regions of the specimen (see Fig. 6). The core of the material is unfibrillated.

Similar arguments can be used to explain the results seen with variations in cone semi-angle. Large cone semi-angles (i.e. approaching 90°) cause the specimens to undergo a very large amount of expansion, resulting in complete fracture of the material. As the cone semi-angle is reduced, the specimens show increased structural integrity until at 30°, they are of acceptable quality and modulus [17] whilst undergoing sufficient shear and extensional flow to produce a nodule–fibril microstructure capable of exhibiting a large strain-dependent negative Poisson's ratio. Hence, an optimum cone semi-angle of 30° has been defined provided the microstructure produced has the required connectivity.

The final die geometry variable is that of die capillary length and the need for this to be present was investigated by reducing the capillary length from 3.4 mm to zero. This produced extrudates which were fractured and fibrillar. A capillary length of 3.4 mm provides sufficient length to prevent over-expansion and fragmentation, as the material cools on leaving the die. If this constraint is applied for too long the material undergoes severe helical fracture, producing a zig-zag macrostructure.

5. Summary and conclusions

By considering the results of this paper with the first two papers in this series [1, 2], it is now possible to define the optimum processing conditions for this experimental configuration to produce auxetic UHMWPE acceptable as a structural material [17]. The processing route consists of three stages: compaction of finely divided UHMWPE powder, sintering and extrusion. The compaction stage [1] of the process exists to provide adequate bonding between particles. Investigations have shown that there exists a well defined optimum pressure of 0.04 GPa for compaction and a range of compaction temperatures of 110–125 °C. If the compaction pressure and temperature are too low, the resulting extrudate has a very low modulus whereas if the two parameters are too high, the particles are deformed. The samples are held at this temperature and pressure for between 10 and 20 min. This is not critical. The compaction conditions for successful production of auxetic UHMWPE are significantly different from those for maximum structural integrity in the compacted rod.

The sintering and extrusion conditions require, however, more precise definition. The compacted rod is reheated to 160 °C, maintained at this temperature for 20 min and then immediately extruded at a rate of 500 mm min^{-1} [2]. The die geometry used to achieve an auxetic extrudate with high structural integrity is a die entry diameter of 15 mm, a die exit diameter of between 7 and 7.5 mm, a cone semi-angle of 30° and a small (of the order of 3.4 mm) die capillary length. The resulting extrudate has been shown to demonstrate a strain dependent negative Poisson's ratio which can be successfully interpreted using a geometric model for the characteristic nodule–fibril microstructure observed in this class of auxetic materials [16].

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