JOURNAL OF MATERIALS SCIENCE 30 (1995) 4069–4075

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

Part II *The effect of sintering temperature and time*

K. L. ALDERSON, A. P. KETTLE, P. J. NEALE, A. P. PICKLES
Department of Materials Science and Engineering, The University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

K. E. EVANS*
School of Engineering, University of Exeter, North Park Road, Exeter EX4 4QF, UK

Auxetic (negative Poisson's ratio) ultra high molecular weight polyethylene has been fabricated by a novel thermal processing route consisting of three stages–compaction, sintering and extrusion. In this paper, the sintering stage is examined in detail, the processing window investigated and the optimum conditions to produce the microporous microstructure necessary for a negative Poisson's ratio are identified. The effects of varying the processing parameters are also studied.

1. Introduction

The fabrication of a microporous form of ultra high molecular weight polyethylene (UHMWPE) which possesses a negative Poisson's ratio (ν) requires a three-stage processing route: compaction of finely divided UHMWPE powder, sintering and extrusion. The powder is compacted and sintered in a cylindrical barrel and is then extruded through a conical die. Further details of the geometry are provided in part I of a series [1, 2] which studies in detail the effects of varying the processing parameters within each stage of the fabrication route. This paper concentrates on the effects of varying the sintering conditions.

Sintering is a commonly used processing technique for UHMWPE [3–6]. In general, it occurs at temperatures just above the melting point of the polymer with the solid particles tending to coalesce. It is normally carried out for polyethylene over a range of temperatures (depending on the material used), 130–200 °C in either vacuum ovens [3] or in a nitrogen atmosphere [4, 5]. The driving force for sintering is a reduction in surface energy and this is sluggish, being opposed strongly by the viscosity of the polymer [3]. For the majority of applications, the primary function of sintering is to develop interparticle bonding which will give the material its useful mechanical properties [6]. Thus, previous research has concentrated on achieving a homogeneous microstructure with little porosity.

However, the requirements from the sintering stage to achieve auxetic microporous UHMWPE are very different and this paper examines the effects of varying only the sintering stage of the processing route on the structural integrity, microstructure and Poisson's ratio of the extrudate. The expansion of the material during sintering at different barrel positions and contraction on subsequent cooling were also investigated.

2. Experimental methods

2.1. Standard processing conditions for auxetic UHMWPE

In order to study the effects of varying the sintering stage of the fabrication route, all specimens were subjected to the same standard [1, 7] compaction and extrusion conditions that had previously been used. These are well documented and discussed [1, 2, 8] and so are only summarized in this paper. All three stages of the processing route (compaction, sintering and extrusion) were carried out in a specially designed rig with a 15-mm diameter barrel using Hoechst GUR 415 UHMWPE powder [9].

The rig was fitted with a blank die and heated to 110 °C. UHMWPE powder was added and allowed to come to equilibrium for 10 min. The compaction load was then applied, this being 7 kN (equivalent to a pressure of 0.04 GPa), at the rate of 20 mm min^{-1} using a Schenk–Trebel electro-mechanical testing machine, and was maintained for 20 min. This results in a well-formed rod.

The rods produced by this method were then sintered according to the conditions listed in Section 2.2. The standard condition previously used [1, 8] was sintering at 160 °C for 20 min, followed by immediate extrusion. For this work, extrusion took place at the same temperature as sintering (see below), at a rate of

* Author to whom correspondence should be addressed.

0022–2461

500 mm min^{-1} through a die which had an entry diameter of 15 mm, an exit diameter of 5 mm (the only non-standard condition, as standard extrusion takes place through a 7.5-mm exit diameter die), with a cone semi-angle of 30° and a capillary of length 3.4 mm. This particular die geometry was selected to encourage a large amount of fibrillation to occur to ascertain which conditions caused fibrillation to decrease or be completely absent.

2.2. Variations investigated in the sintering stage of the fabrication route.

The main processing condition examined in this study was the effect of the sintering temperature on the microstructure and resulting Poisson's ratio of the extruded specimens. Rods compacted to standard conditions were sintered in the barrel of the extrusion rig at temperatures of 100, 120, 130, 135, 140, 150, 160, 170, 180 and 190 °C for 20 min and then extruded at the sintering temperature using the extrusion conditions detailed above. The extrudates thus produced were then examined both visually and using a scanning electron microscope (SEM) and measurement of the Poisson's ratio was carried out where appropriate. As noted previously [1], the polymer does not melt at these temperatures.

For three of the temperatures investigated (140, 150 and 160 °C), the variable of sintering time was also examined. At 140 and 150 °C, three rods were sintered at each temperature; one for 10 min, one for 20 min and one for 30 min and the effect of this on the extrudates produced was examined visually and by SEM. For the temperature of 160 °C, a more comprehensive investigation was undertaken on longer specimens produced using a longer barrel and therefore larger rig of the same radial dimensions as previous work to gain more accurate results concerning the thermal expansion and contraction of the specimens. Rods were first compacted under standard conditions and then sintered by inserting them into different positions in the barrel, allowing the specimens to either expand at both ends (i.e. by placing them in the centre of the barrel's length) or to be constrained at one end (i.e. by placing the specimen at the bottom of the barrel and in contact with the die). This should indicate if specimen position in the barrel is of any significance. It should be noted that, in all cases, sintering did not take place under load. For comparison, sintering of pre-compacted rods in an oven at 160 °C was also carried out. In all cases, the axial and radial (where appropriate) expansions were measured to obtain the variation of specimen volume (in this case simply the expansions added together) with sintering times of up to 20 min.

A final variation on the sintering stage examined was to stop the processing of the UHMWPE after sintering had taken place i.e. immediately before extrusion. The sintered rods thus produced were removed from the extrusion rig and allowed to slowly air cool to room temperature. Then they were extruded at 160 °C, examined visually and their Poisson's ratios measured. To aid in the understanding of this variation in the processing conditions, the effect of slow air cooling on specimen dimensions was monitored as a function of time for samples sintered either constrained or free to expand in the barrel of the extrusion rig.

2.3. Microscopic examination of the extrudates

Samples of the extrudates were taken and prepared for SEM examination by mounting them on aluminium stubs and sputter coating them with gold. Their microstructures were then observed at magnifications of up to × 1250.

2.4. Measurement of the Poisson's ratio

For the specimens produced in this investigation, due to their small size and irregular shape, it was not possible to employ standard tensile testing methods to obtain ν. Therefore, a simple single strain compression test was carried out on sections cut from the processed samples. The sections were compressed in the radial direction and changes in the axial direction were monitored photographically (see [8] for further details).

3. Results

3.1. Effects of varying the sintering temperature

3.1.1. Structural integrity and shape of the extrudate

Varying the sintering temperature during the processing of UHMWPE to produce an auxetic material has a vary marked effect on the structural integrity and shape of the extrudate produced. At the lowest temperature investigated (i.e. 100 °C), the extrudate was in the form of aggregated clumps of powder of up to 6 mm in length. Increasing the temperature to 120 °C doubled the size of the extruded pieces of material to 12 mm but more viable sections of extrudate were not produced until 140 °C was employed as a sintering temperature. At this temperature, four pieces of extrudate were obtained, with a total length of 150 mm.

However, with the sintering temperature at 150 °C, a very different form of extrudate was produced (Fig. 1). This was characterized by cup-and-cone fractures along its 70-mm length. It should also be noted that the material had expanded on exiting the die (which had an entry diameter of 15 mm and an exit diameter of 5 mm) to a diameter of approximately 14 mm. This effect was not observed at any of the sintering temperatures prior to 150 °C.

Increasing the sintering temperature to 160 °C resulted in an extrudate of the same shape and length as a sintering temperature of 150 °C also with cup-and-cone fractures along its length, but which was slightly more radially expanded, with the width of the specimen produced being approximately 15 mm. Further increases in sintering temperature had the effect of causing the cup-and-cone fractured extrudate to resemble more closely a helix, with successive 10 °C rises in temperature causing the pitch angle between the

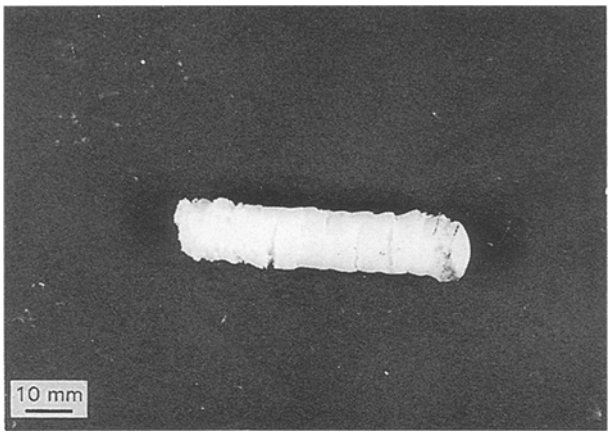

Figure 1 Photograph of an extrudate produced using a sintering temperature of 150 °C.

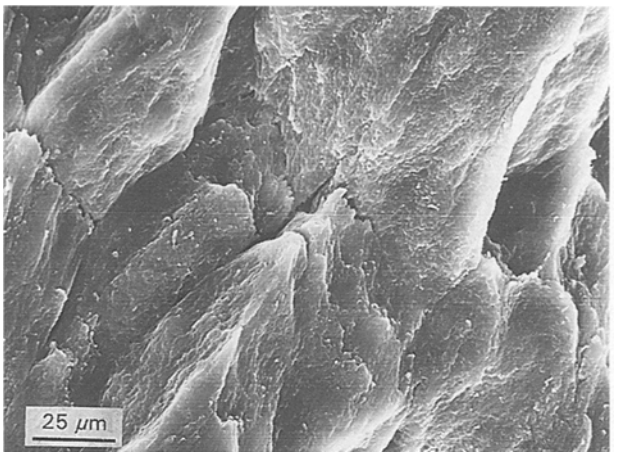

Figure 2 Micrograph of an extrudate obtained when a sintering temperature of 100 °C and a sintering time of 20 min are employed.

cup-and-cone fractures of the extrudate to increase, with the result that, at 190 °C, the extrudate had a partially uncoiled helical geometry of length 85 mm. The three highest sintering temperatures (170, 180 and 190 °C) investigated produced highly unstable extrudates which were thought to be of poor structural integrity compared with extrudates produced by sintering at temperatures of 150 and 160 °C and thus were eliminated from the next stage of the investigation i.e. microscopy studies.

It should be noted that solid unfractured rods can be produced if all other conditions remain unchanged by either using a die of exit diameter 7.5 mm [10] (in place of one with exit diameter 5 mm) or by using a barrel diameter of 10 mm (in place of one with a diameter of 15 mm) in conjunction with a die of exit diameter 5 mm [8], in other words, by reducing the ratio of entry diameter to exit diameter.

3.1.2. Microstructure of the extrudates

The characteristic feature of any auxetic, microporous polymer produced to date is a nodule–fibril microstructure [11, 12]. Therefore, samples of all extrudates produced at sintering temperatures of up to and including 160 °C were examined in an SEM. At the lower sintering temperatures (i.e. 100–130 °C), no fibrils were observed. The nodules present had deformed in the direction of extrusion and an example of this is shown in Fig. 2. It is known from previous work that this microstructure does not produce a negative ν [8].

Increasing the sintering temperature by 5 °C to 135 °C produced the first evidence of fibrillation. Here, internodule fibrillation was observed, but only at high magnifications and the fibrils were very small and few in number with the nodules. The same effect was seen at 140 °C.

At 150 °C, the microstructure is very different, with the required internodule fibrillation readily observed. However, the microstructure is very compact, with fibrils which are still very short in comparison with the spherical nodules (see Fig. 3). Increasing the sintering temperature to 160 °C has very little effect on the structural integrity of the extrudate but does cause it

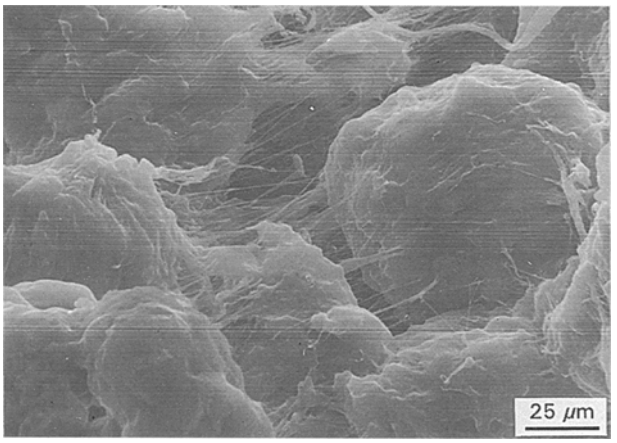

Figure 3 Micrograph of an extrudate obtained when a sintering temperature of 150 °C and a sintering time of 20 min are employed.

to expand by 1 mm more in the radial direction. Examining the microstructure of an extrudate processed with a sintering temperature of 160 °C in an SEM revealed the highest degree of fibrillation, both in number and length (see Fig. 4).

3.1.3. Measurement of Poisson's ratio

The Poisson's ratios of specimens processed as detailed above with a sintering temperature of 160 °C were measured in compression. In all cases, the value of ν was negative or zero and was highly strain dependent [10, 13] (see, for example, Table I). Specimens tested at the smallest strains had the largest negative Poisson's ratios (i.e. up to -6 at 0.9% strain in the radial direction).

3.2. Effects of varying the sintering time

3.2.1. Effects on the polymer microstructure

In all tests described above, a predetermined sintering time of 20 min was used. It was decided to see if this condition had been optimized and sintering temperatures of 140, 150 and 160 °C were selected to study the effects of varying the time allowed for sintering to occur. For the lower two temperatures, sintering times

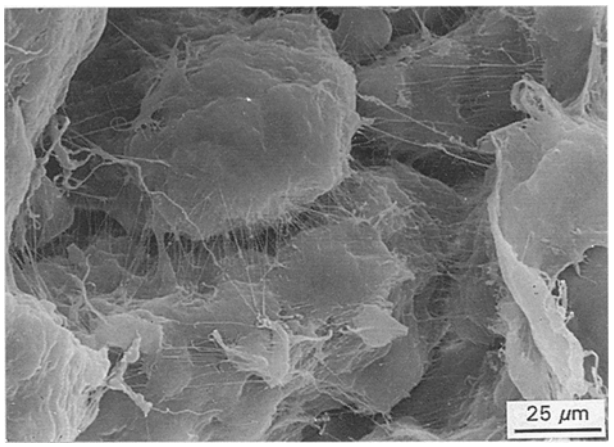

Figure 4 Micrograph of an extrudate obtained when a sintering temperature of 160 °C and a sintering time of 20 min are employed.

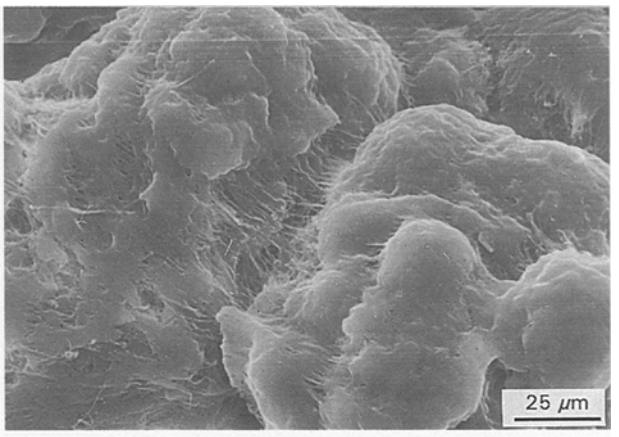

Figure 5 Micrograph of an extrudate obtained when a sintering temperature of 150 °C and a sintering time of 10 min are employed.

TABLE I Values of engineering strain and Poisson's ratio for specimens processed under standard compaction conditions, sintered at 160 °C for 20 min and then extruded at 500 mm min^{-1} through a die of exit diameter 5 mm, cone semi-angle 30° and capillary length 3.4 mm. The error in the radial Poisson's ratio is ± 0.02.

Section number	Engineering strain	Radial Poisson's ratio
1	0.009	− 6.30
2	0.009	− 5.44
3	0.019	− 1.43
4	0.019	− 1.36
5	0.019	0.00
6	0.029	0.00

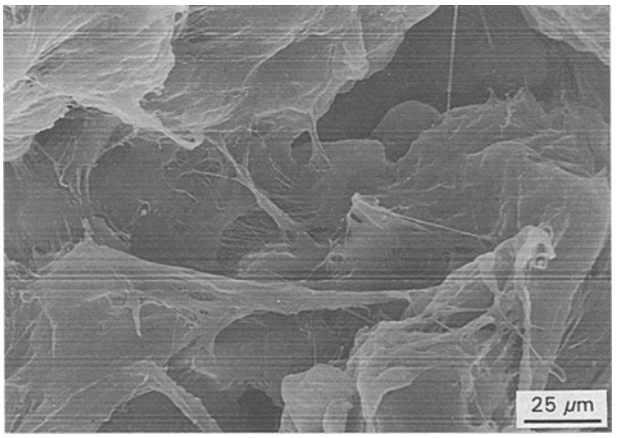

Figure 6 Micrograph of an extrudate obtained when a sintering temperature of 150 °C and a sintering time of 30 min are employed.

of 10, 20 and 30 min were employed. In all these cases, visual examination of the extrudates produced revealed no differences despite the variation in sintering time. For the extrudates sintered at 140 °C, there were also no microstructural variations. However, at a sintering temperature of 150 °C, significant differences in the microstructure were observed. These differences largely concerned the nature of the fibrils. After 10 min of sintering time, the fibrils were very short, resulting in a relatively dense extrudate (see Fig. 5). Increasing the sintering time by 10 min resulted in longer fibrils and a more microporous structure which was more likely to be able to produce the required effect (see Fig. 3). However, after 30 min, the fibrils had become both long and thick and the microstructure no longer fulfilled the criterion of nodules interconnected by multiple fibrillation (see Fig. 6). This microstructure is not ideal for producing a negative Poisson's ratio, indicating that 20 min sintering time would be the optimum for producing the required microstructure at this temperature.

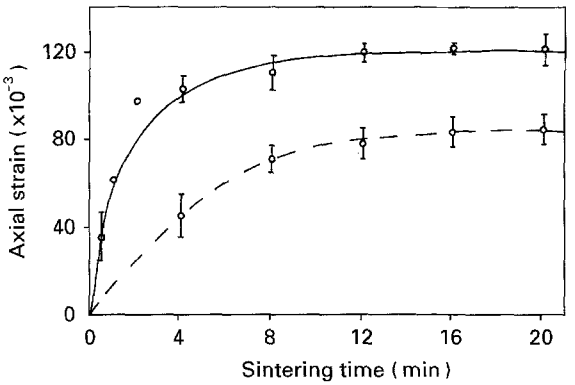

Figure 7 Graph of axial strain due to expansion against sintering time for specimens sintered in the barrel of the extrusion rig at a temperature of 160 °C. The solid line represents specimens which were free to expand and the dotted line those which were constrained at one end.

3.2.2. Effects on the polymer volume

Since fibril length and hence porosity correlate with sintering time, for a given extrusion condition, an investigation into volume changes during sintering was also conducted, at a sintering temperature of 160 °C. Fig. 7 shows the variation of specimen strain due to expansion in the axial direction with sintering times of up to 20 min for rods allowed to expand freely at both ends and those which were constrained at one end in the barrel. It can be seen that, as might be expected, the rods which were free at both ends showed a greater increase in size than those which were constrained at one end (by placing them in contact with the die at the bottom of the barrel). To see

whether this difference was due, for example, to friction with the barrel, compacted rods were sintered at a temperature of 160 °C in an oven. This resulted in both axial and radial expansion. The results are plotted in Fig. 8. The shapes of Figs 7 and 8 are very different, with the barrel-sintered samples initially expanding more rapidly before reaching a plateau dependent on their position in the barrel after around 16 min. These results suggest that fibrillation is related to the degree of expansion during sintering, with an optimum reached after 20 min. Any longer than this and fibrils coalesce into thick bundles (see Fig. 6).

3.3. Effects of allowing sintered rods to cool to room temperature before extrusion

Allowing rods sintered at 160 °C for 20 min in the barrel to cool to room temperature after expulsion from the barrel and then extruding immediately at 160 °C using extrusion conditions as detailed above had a very marked effect on the extrudates produced. Visual examination revealed that solid rods (i.e. without cup-and-cone fractures) of length 70 mm were produced but in this case, there was no radial expansion after exiting the die, with the rods having the same radial dimension as the die exit diameter i.e. 5 mm. Rods produced by this variation in processing route were then subjected to compression testing to measure their Poisson's ratios. As expected, due to the lack of radial expansion, these rods had a conventional positive Poisson's ration. So although the rods had far greater structural integrity, they were not auxetic.

In order to gain greater understanding of this effect, the response of the specimen dimensions to heating in the barrel of the processing rig and subsequent slow air cooling on removal from the barrel was measured. Figs 9 and 10 show the variation of strain with time due to expansion and contraction with sintering in the barrel followed by cooling in air. Fig. 9 represents the behaviour of samples which were allowed to expand freely by placing them in the middle of the barrel of the extrusion rig. These were then removed from the rig after 20 min and the effect of slow air cooling was studied by measuring specimen dimensions as the

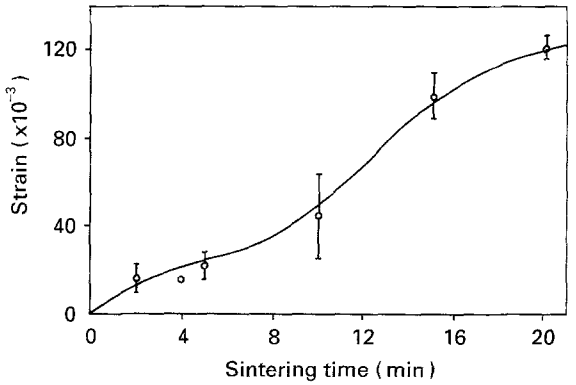

Figure 8 Graph of strain due to axial and radial expansion against sintering time for specimens sintered in an oven at a temperature of 160 °C.

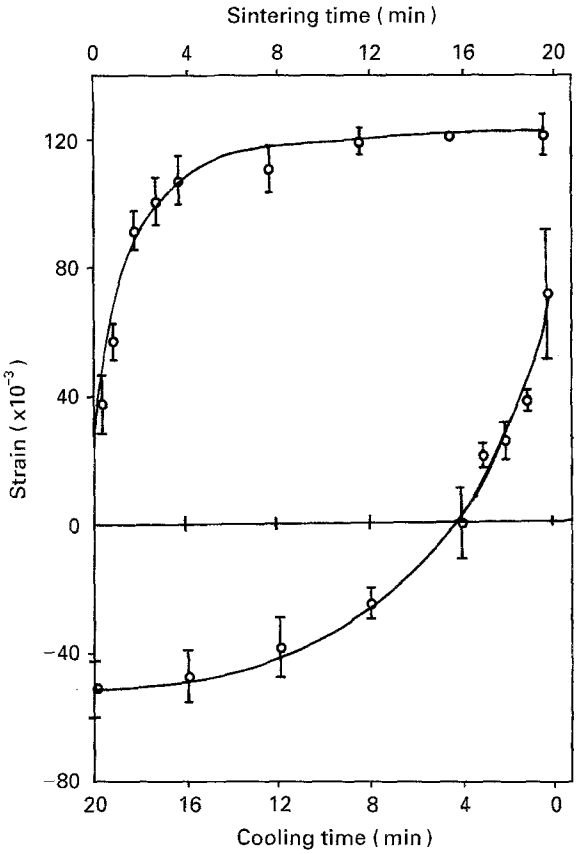

Figure 9 Graph of strain due to expansion and contraction in the axial and radial directions against sintering (upper curve) and cooling (lower curve) time for specimens initially allowed to freely expand in the barrel at a temperature of 160 °C.

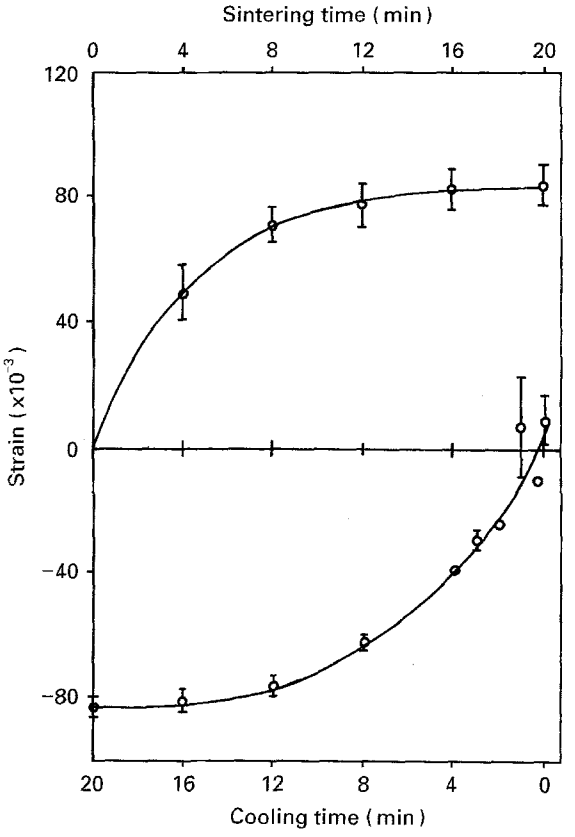

Figure 10 Graph of strain due to expansion and contraction in the axial and radial directions against sintering (upper curve) and cooling (lower curve) time for specimens initially constrained at one end in the barrel at a temperature of 160 °C.

sample cooled. Exactly the same procedure was followed to obtain Fig. 10, which represents the behaviour of samples which were constrained at one end by placing them in contact with the die at the bottom of the barrel of the extrusion rig. In both cases, the net effect was a contraction in sample dimensions compared with those of the compacted rods. It should be noted that for both conditions, contraction in the radial direction was seen along with axial contraction. The radial contraction is of great significance since in both cases, the axial contraction is not as great as the axial expansion. Thus, the large volume changes observed are caused by radial effects. It can be seen from Figs 9 and 10 that the constrained specimens contract overall to a greater degree than those allowed to expand freely in the barrel, showing large immediate contractions upon exiting into air. Hence an air-cooled specimen would require much longer at the sintering temperature to return to the same volume ready for extrusion.

4. Discussion

Halldin and Mehta [6] have stated that the pure powder used in this work has a microstructure that is not suitable for processing via sintering at any temperature because of its final porosity. If the microstructure of a rod produced using the standard sintering conditions (i.e. before extrusion) is observed (see Fig. 11), it can be seen why. The microstructure consists of nodule-like particles which are fused together at certain points and contains a large degree of porosity, resulting in a density of 852 $kg\,m^{-3}$. This is slightly less dense than the compacted rods, which tend to be less porous and have a density of around 880 $kg\,m^{-3}$ [1]. A density for the sintered rods of 852 $kg\,m^{-3}$ is not acceptable if the requirements of the sintering stage are to produce a homogeneous densified extrudate. However, this degree of porosity is essential if the target end product is a microporous form of UHMWPE with enough internal space to allow the co-operative movement of nodules and fibrils, resulting in a negative ν. The sintering conditions have an important bearing on the successful extrusion of auxetic UHMWPE, with the final extrudate density (of the order of 850 $kg\,m^{-3}$) being very close to that of the sintered material. It should be noted that conventionally moulded UHMWPE has a density of the order of 950 $kg\,m^{-3}$.

Of the variables examined in this work, the sintering temperature is the most important. It has been shown to affect the structural integrity of the extrudate from the clumps of powder produced at a sintering temperature of 100 °C to the open helices produced at 190 °C as well as the material microstructure. At temperatures below 130 °C, there is no evidence of fibrillation and the nodules have deformed. It is only when a temperature of 150 °C is used that a microstructure approaching that necessary to produce an auxetic polymer is achieved. By a combination of visual and SEM examination and measurement of ν, it has been possible to define the optimum sintering temperature for an auxetic extrudate at 160 °C. At the higher

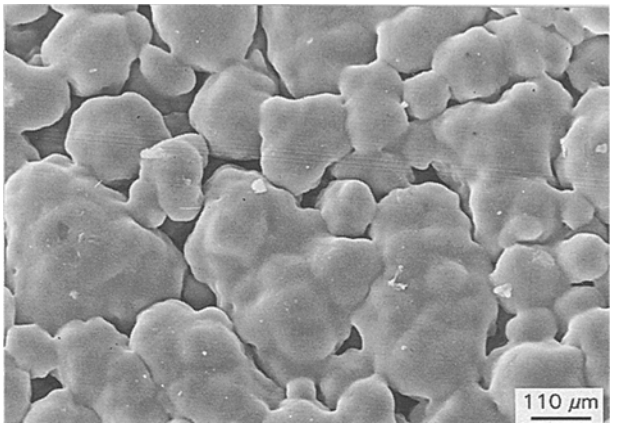

Figure 11 Micrograph of the sintered material produced under optimum sintering conditions.

temperatures, nodules no longer deform under extrusion but rather the expansion with resultant increased porosity takes place.

The property of sintering time is also of importance since it not only produces differences in the dimensions of the fibrils, but also affects the degree of expansion in the material. Investigations have shown that samples sintered within the barrel of the extrusion rig initially expand rapidly in the axial direction when compared with specimens sintered in an oven set to the same temperature, i.e. 160 °C. These investigations have also highlighted the need for specimen position within the barrel to be clearly defined. Specimens placed in the centre of the barrel are able to expand freely in both directions axially and do so to a greater extent than those which are placed in direct contact with the die at the bottom of the barrel. This has the effect of constraining the rods, which in turn reduces the amount of axial expansion seen by about a third. Thus, if the maximum amount of material expansion is required, the specimen should not be constrained at either end but should be placed in the centre of the barrel. From both SEM examinations of extrudates produced at various sintering times and studies of the variation of specimen expansion with sintering time, an optimum sintering time of 20 min has been defined. Again, as with the optimum sintering temperature of 160 °C, this condition holds for all combinations of bore diameters and barrel lengths used to date.

Currently, rods are compacted at 110 °C and then allowed to slow cool to room temperature. These rods are then reinserted into the barrel of the extrusion rig which has been allowed to attain a temperature of exactly 160 °C and sintered for 20 min before immediate extrusion occurs. There is no delay between the sintering and extrusion stages. An initial attempt to investigate carrying out each of the three processing stages separately was undertaken. Compaction and sintering were carried out according to the standard conditions but after sintering, the rod was removed from the barrel and allowed to slow cool to room temperature as at the end of the compaction stage. The sintered rods were then reintroduced into the barrel for about 3 min and extruded under standard conditions. The rods produced by this method did not

expand radially and were not auxetic i.e. they had a conventional positive Poisson's ratio. From the contraction data, heating for periods greater than 20 min would be needed to produce the same volume expansion, but would cause changes to the type of fibrillation.

The single strain measurements of Poisson's ratio indicate a large strain dependence in v. This is in agreement with a model previously developed [13] showing how the Poisson's ratio is crucially dependent on the geometry of the nodule–fibril array and that as this geometry changes, the Poisson's ratio also changes.

5. Conclusions

This investigation into the sintering stage for the fabrication of auxetic UHMWPE has revealed the narrow range of conditions for successful processing. Compacted rods which have been allowed to slow cool from their compaction temperature of 110 °C to room temperature are reinserted into the centre of the barrel of the extrusion rig and sintered at a barrel temperature of 160 °C for 20 min. The rods must not be allowed to subsequently cool to room temperature but rather must be extruded immediately. These conditions have been shown to hold for all conditions of barrel diameter and length used to date, leading to the production of auxetic UHMWPE.

Acknowledgements

The authors wish to acknowledge the financial support of ICI Chemical and Polymers (APP) and the EPSRC through the provision of a studentship (PJN) and a Research Associateship (KLA). KEE wishes to acknowledge the award of an EPSRC Advanced Fellowship during this work.

References

1. A. P. PICKLES, R. S. WEBBER, K. L. ALDERSON, P. J. NEALE and K. E. EVANS, *J. Mater. Sci.* **30** (1995).
2. P. J. NEALE, K. L. ALDERSON, A. P. PICKLES and K. E. EVANS, *J. Mater. Sci.* submitted.
3. V. KRISHNAMURTH and I. L. KAMEL, *Polym. Eng. Sci.* **29** (1989) 564.
4. K. S. HAN, J. F. WALLACE, R. W. TRUSS and P. H. GEIL, *J. Macromol. Sci. Phys.* **B19** (1981) 313.
5. R. W. TRUSS, K. S. HAN, J. F. WALLACE and P. H. GEIL, *Polym. Eng. Sci.* **20** (1980) 747
6. G. W. HALLDIN and S. D. MEHTA, in "ANTEC 83: Plastics–Engineering today for tomorrow's world" (SAMPE, Lovina, 1983) p. 238.
7. K. E. EVANS and K. L. AINSWORTH, International Patent Publication no. WO91/01210 (1991).
8. K. L. ALDERSON and K. E. EVANS, *Polymer* **33** (1992) 4435.
9. Hoechst Plastics, Hostalen GUR (PE-UHMW) datasheets, 6230 Frankfurt am Main 80, Germany.
10. P. J. NEALE, K. L. ALDERSON, A. P. PICKLES and K. E. EVANS, *J. Mater. Sci. Lett.* **12** (1993) 1532.
11. K. E. EVANS and B. D. CADDOCK, *J. Phys. D: Appl. Phys.* **22** (1989) 1883.
12. B. D. CADDOCK and K. E. EVANS, *ibid.* **22** (1989) 1877.
13. K. L. ALDERSON and K. E. EVANS, *J. Mater. Sci.* **28** (1993) 4092.

Received 22 August
and accepted 10 October 1994